

LITHIATION AND DELITHIATION MECHANISMS OF MODEL ANODES FOR LITHIUM ION BATTERIES USING THE EXAMPLE OF AU THIN FILMS:

Correlation of Electrochemical and

IN-SITU HIGH ENERGY X-RAY DIFFRACTION CHARACTERIZATION

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Dissertation

zur Erlangung des Grades *"Doktor der Naturwissenschaften"* an der Fakultät für Chemie und Biochemie der Ruhr-Universität Bochum

Düsseldorf/Bochum im Juli 2014

Gutachter: Prof. Dr. Martin Stratmann Gutachter: Prof. Dr. Frank Uwe Renner Tag der Einreichung: 09.07.2014

Tag der Disputation: 27.08.2014

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Acknowledgements

Der größte Teil der dieser Dissertation zugrunde liegenden Arbeit wurde am Max-Planck-Institut für Eisenforschung (MPIE) in Düsseldorf in der Abteilung Grenzflächenchemie und Oberflächentechnik (GO) unter der Leitung von Prof. Martin Stratmann in der Abteilung Grenzflächenstruktur und Hochtemperaturreaktionen geleitet von Dr. Frank Uwe Renner durchgeführt. Die Anfertigung der Dissertation inklusive weiterführender Datenanalyse fand am Instituut voor Materiaalonderzoek (IMO) an der Universiteit Hasselt in der Abteilung Materiaalfysica (Materialphysik) unter der Leitung von Prof. Frank Uwe Renner statt. Zunächst möchte ich Prof. Stratmann und Frank danken, dass sie mir die Gelegenheit gegeben haben meine experimentelle Arbeit in der herausragenden wissenschaftlichen Umgebung, die das MPIE bietet, durchzuführen. Prof. Startmann danke ich für die Anregungen im Rahmen des jährlichen Abteilungsseminars und der dieser Dissertation vorausgehenden Gespräche. Frank danke ich für sein Vertrauen und seine Geduld. Er hat mir bei meiner wissenschaftlichen Arbeit größtenteils freie Hand gelassen so dass ich meine eigenen Ideen verfolgen und umsetzen konnte. Er hat mir die Möglichkeit gegeben meine Arbeit auf nationalen und internationalen Tagungen zu präsentieren und mir so auch über das MPIE hinaus wissenschaftlichen Austausch ermöglicht. Zudem hat er mir mit seinem Wechsel auf eine Professorenstelle an der Universiteit Hasselt die Möglichkeit geboten dort meine Dissertation abzuschließen. Nicht zuletzt danke ich ihm, dass er mein Bestreben die Dissertation im Juli 2014 abzuschließen unterstützt hat.

Dem Center for Electrochemical Sciences (CES) an der Ruhr-Universität Bochum koordiniert von **Dr. Sabine Seisel** (danke Sabine) und der Europäischen Union danke ich für die Finanzierung in den ersten zweieinhalb Jahren meiner Arbeit.

Entscheidend zum Gelingen des Vorhabens Promotion beigetragen haben auch die Kollegen und technischen Mitarbeiter am MPIE und an der Universiteit Hasselt. In Düsseldorf war ich über all die Jahre sehr froh mich auf den Rat und die tatkräftige Unterstützung des Laborleiters des UHV-Labors **Eberhard Heinen** verlassen zu können. Seine Hilfsbereitschaft und Fachkompetenz, aber auch seine freundlich Art haben ihn mir über die Jahre meines Arbeitens am MPIE zu einem verlässlichen Ansprechpartner und Freund gemacht. Bei elektronisch-technischen Fragestellungen war ebenso kompetent und hilfsbereit auf **Herrn Schönberger** Verlass, tatkräftig unterstützt von **Herrn Wenders** und **Herrn Cohnen**. Sowohl **Eberhard** als auch **Herr Schönberger** haben durch ihren Einfallsreichtum in vielen Fällen dazu beigetragen die gerade anstehenden Probleme unkompliziert zu lösen. Wenn es um die Durchführung von Röntgenbeugungsexperimenten und Fragestellungen zu deren programm-unterstützten Auswertung ging war **Benjamin** Breitbach der Ansprechpartner der Wahl. Apropos Ansprechpartner der Wahl. Wenn es um Chemikalien ging, führte natürlich kein Weg an der netten und immer gut gelaunten Ulrike Napieralski vorbei. Danken möchte ich auch Katja Angenendt und Monika Nellessen, die nicht nur dafür gesorgt haben, dass im "Metallo-Labor" nichts drunter und drüber ging, sondern auch für EBSD und REM-Messungen kompetente Ansprechpartnerinnen waren. Beim Thema REM und EDX-Messungen kannte sich auch meine langjährige liebe Bürogenossin Else Müller-Lorentz (im Kreise der LEO-Nutzer auch unter dem Pseudonym "muelo" bekannt) bestens aus. Das LEO war eines der ersten Geräte, das ich (eingewiesen von Else) zu bedienen gelernt habe. Dirk und Alexandra Vogel möchte ich für nette Gespräche im teils gemeinsam genutzten Labor oder auf dem Gang im MPI aber auch für ihre Hilfsbereitschaft danken, Dirk besonders für seine Hilfe mit dem Grillwagen.

Ein herzlicher Dank geht an die gesamte Werkstatt des MPIE unter der Leitung von Herrn Selbach. Auch auf die Werkstatt kann das MPI stolz sein. Fast immer haben Herr Selbach und seine Mitarbeiter technisch umsetzbare Lösungen für die von den Wissenschaftlern an sie herangetragenen "Wunschvorstellungen" gefunden. Herr Baseler als Herrn Selbachs rechte Hand hat u.a. viel zur Umsetzung der in der vorliegenden Arbeit noch zur Sprache kommenden in-situ Zelle beigetragen. Außerhalb des MPI sind wissenschaftlich gesehen Uta Rütt und Olof Gutowski diejenigen, denen ich am meisten zu verdanken habe. Sie haben uns während der Synchrotron-Messzeiten zweimal herzlich bei sich im hohen Norden am DESY in Hamburg aufgenommen und durch ihren unermüdlichen (auch nächtlichen) Einsatz entscheidend zum Gelingen der Messzeiten und damit zum Zustandekommen der hier vorliegenden Arbeit beigetragen.

Wichtig für das Gelingen einer Doktorarbeit sind natürlich auch die (meist wirklich lieben) Kollegen. Zunächst möchte ich meine Arbeitsgruppenkollegen nennen: Andreas Seemayer, Julia Klemm, geborene Lengsfeld, Hubby Izzudin, Jazmin Duarte, Miriam Lange. Andreas, den ich schon von der Bonner Uni als Praktikumsassistent kannte, hat mich in den Themenbereich meiner Arbeit eingeführt und danach waren wir zwei lange Zeit die einzigen, die sich am MPIE mit Lithiumionenbatterien beschäftigt haben. Daher war der wissenschaftliche Austausch mit den anderen Kollegen meistens ein wenig limitiert. Andreas hat mich bei vielen Messungen geduldig unterstützt. Besonders denke ich da an die Synchrotron Strahlzeiten am DESY und ToF-SIMS Messungen in Eberhards Reich. Andreas, vielen Dank und alles Gute weiterhin im Ländle. Julia, die erste Erinnerung, die ich an dich habe ist, dass sich Andreas und ich einen Potentiostaten aus dem AFM-Raum ausleihen wollten, der einer gewissen Julia Lengsfeld "gehörte". Ich wünsche dir alles Gute für die Zukunft, jetzt auch mit Kind statt "nur" mit Mann. Jazmin, danke für die Initiative zu zahlreichen unterhaltsamen Gruppenaktivitäten, Miriam, danke für die Gruppengrillfeier über den Dächern Bochums und Hubby, danke für deine Hilfe mit den Prevac-Probenhaltern.

Aber auch außerhalb der Arbeitsgruppe hatte das Institut nette Kollegen zu bieten. Abdellaziz Laaboudi habe ich schon in meinem ersten Jahr am MPIE als sehr netten Kollegen kennengelernt. Nach seiner Rückkehr ans MPIE hatten wir viel Spaß zusammen am Institut und sind jetzt immer noch Freunde. Besonders danke ich dir Initiative zu einem Wochenendurlaub in Paris mit deiner Frau Souard, einer sehr netten Kollegin und Freundin (die sich bis zur namentlichen Erwähnung noch etwas gedulden muß;)) und deinem neuen Auto (schöner Wagen ;)). Ashok Vimalanandan danke ich für eine schöne Zeit als "Leidensgenossen" während der entbehrungsreichen Zeit der Promotion. Besonders in Erinnerung werden mir der Konferenzbesuch in Boston und der anschließende Aufenthalt in New York bleiben. Mit The Hai Tran lassen sich wunderbar zwar sinnfreie, aber lustige Gespräche führen, die diverse Male meine Feierabendstimmung gehoben haben. Nicht vergessen werde ich auch Xiaoxia Bai und die Diskussionen über heißen Tee (Mahlzeit-Schaumama), Sol Roselli (und den doch etwas gewöhnungsbedürftigen ;) Mate und Yizhong Luo. Den "doppelten Sergiys" Sergiy Borodin and Sergiy Merzlikin danke ich für ihre Hilfe im Laboralltag aber auch für unterhaltsame Gespräche. Ohne die KFZ-Fachkompetenz von Sergiy Borodin hätte ich jetzt nicht das Auto, das ich jetzt habe und mit dem ich (bisher) sehr zufrieden bin. Aus Karl Mayrhofers Gruppe danke ich natürlich Karl, aber auch Josef Maier, Ioannis Katsunaros und **Aleksandar Zeradjanin** für Diskussionen über elektrochemische Fragestellungen aber auch für kurzweilige Gespräche. Des Weiteren möchte ich auch Lisa Rossrucker, Claudius Laska, Jan-Philipp Grote, Claudio Baldizzone, Pascal Beese und Nicole **Fink** nennen, die des Öfteren demselben inneren Zwang wie ich folgend, den Weg in die famose Telekom-Kantine gefunden haben, mit denen ich mich aber jeweils auch an die ein oder andere heitere Situation erinnere. Als Herrscherin über die Platinelektroden wird mir Andrea Mingers in Erinnerung bleiben. Danke auch an die Truppe der Badmintonspieler am MPIE besonders an Han Zhang und Wei Guo und natürlich nicht zu vergessen die gute Seele der GO-Abteilung Cornelia Arckel.

Aber nicht nur das professionelle, auch das private Umfeld stellt einen wichtigen Teil im Leben eines Doktoranden dar. In diesem Bereich möchte ich zunächst meinen besten Freunden **Fabian Blank** und **Christian Merl** danken. Vielen Dank Jungs für die wochenendlichen Unternehmungen. Legendär bleiben das Café in Rheidt, die Fahrradtouren, vielleicht die Bärchenstube aber ganz sicher der See. **Andreas Karsch** kenne ich, wie auch Fabian noch aus Schulzeiten. Auch ihn schätze ich als Freund sehr. Angefangen hat es mit Philharmoniebesuchen in Köln. Mit **Janus Urbanek** zusammen habe ich während des Chemiestudiums die ein oder andere Hürde überwunden. Ich sage nur "Seecasino". Und was damals als Leidensgenossen begonnen hat, hat sich zu einer Freundschaft entwickelt, die mir sehr wichtig ist. Ich freue mich auch mit **Alexander Piccolin**, **Nora Kellermann**, **Manuel Eichen** und **Su Ke** befreundet zu sein.

In meiner momentanen Heimat Hasselt möchte ich mich bei meinen (internationalen) Kolleginnen und Freundinnen Farnoosh Vahidpour (Iran), Wiebke Janssen (Deutschland), Ilaria Cardinaletti (Italien), Emilie Bourgeois (Frankreich) und Elena Gjorgievska (Mazedonien) für Abwechslung vom Schreiballtag während der gemeinsamen Kantinengänge und diverse Aktivitäten in der Freizeit bedanken. Nicht vergessen möchte ich ihr männliches Pendant Pieter Robaeys (Belgien). International besetzt ist auch die immer wieder variierende Gruppe von netten Menschen, die sich in Hasselt außerhalb der Arbeitszeiten die Zeit vertreiben. Dazu zählen Giulia Maino (Italien), Rafaela Dos Reis (Portugal), Jordan Espenshade (USA, USA), Sarah Jeanloz (Schweiz), Benjamin Wenn (Deutschland), Lorenzo Grossi (Italien), Alexander Riskin (Belgien), Nikolina Pavlovic (Serbien) und noch einige mehr. Nicht vergessen möchte ich meine Klubkameraden im Schernkring Herkenrode. Auch durch euch habe ich den Fechtsport als Ausgleich zum "Bürojob" lieben gelernt, da er Körper und Geist gleichermaßen fordert und fördert.

Natürlich möchte ich auch meiner Familie ganz herzlich danken. Meiner Mutter Marita Bach, meinem Vater Heinz-Albert Bach und meinem Bruder Christoph Bach. Ich habe das Glück mich immer auf die Unterstützung meiner Eltern verlassen zu können und immer herzlich aufgenommen zu werden, wenn ich wieder mal den Weg nach Mondorf am Rhein antrete. Meinem Opa Wilhelm Bach danke ich sehr herzlich für die schöne Zeit und viele Telefongespräche vor allem während meiner Düsseldorfer Jahre. Ich hoffe du wirst mir noch viele Jahre nicht nur ein Großvater, sondern auch ein guter Freund sein. Zudem schätze ich den Zuspruch und die Hilfe, die mir meine Onkel Günter Bach und Günter Eble und meine Tanten Monika Bach und Beatrix Eble haben zuteil werden lassen. Günter Eble danke ich besonders für das Nahebringen eines Verfahrens dessen wahre Stärke ich leider viel zu spät erkannt habe, das sich aber in den letzten zwei Jahren erstaunlich gut bewährt hat.

Bevor ich zum Ende komme möchte ich noch zwei Menschen besonders erwähnen, die mein Leben in den letzten zwei Jahren positiv verändert haben: **Anna Schuppert** und **Reinhold Schilling**. **Reinhold**, ich denke du weißt worum es geht. Schade, dass ich das nicht früher erkannt habe. Mit Reinhold zusammen habe ich das Chemiestudium durchgezogen, bevor ich den konventionellen Berufsweg als Chemiker eingeschlagen habe während Reinhold (wieder einmal) erfolgreich den unkonventionellen Weg gemeistert hat. **Anna**, ich danke dir für eine Menge sehr schöner Erlebnisse miteinander. Ich bin froh dich kennengelernt zu haben. Es ist schön, dass es dich gibt!

Abstract

Lithium Ion Batteries (LIBs) are so far widely used in low power applications such as consumer electronics but they still have to be improved significantly to fulfill the growing needs for high power in fields like electromobility. As anode in classical LIBs carbonaceous material is used in which Li can be stored by intercalation between the graphene sheets. Especially promising as an alternative anode material and currently under strong research is Si which features the highest specific capacity of all elements. In Si Li is stored in the form of lithium alloys. The alloy formation is accompanied by changes in the crystal structure of the electrode material. Also Au (and other metals) alloy electrochemically with Li featuring a much higher uptake capability for Li than carbonaceous materials. In the form of growth nuclei Au is also of relevance in the context of Si nanowire anodes which are highly promising for technical application. The noble character of Au facilitates its use as model system. Model electrodes like single-crystals or thin films provide defined experimental conditions compared to real battery electrodes. The aim of this study is to get insight on the atomic level to the mechanisms during alloying (insertion of Li into the crystal structure of the electrodes) and dealloying (extraction of Li). Understanding the atomistic mechanisms of Li insertion in general is an ultimately important step on the way towards target oriented improvement of LIB anodes. A powerful method for following structural changes for example due to allow phase formation in electrode materials is the method of in-situ X-ray diffraction. This method is particularly suitable for heavy elements such as Au featuring a high interaction cross section with X-rays.

In this work in-situ X-ray diffraction (XRD) measurements at Au thin film electrode on a Cu(100) single-crystal substrate performed at the High Energy XRD beamline P07 at DESY, Hamburg are reported. In addition to the structural investigations by in-situ XRD this work presents detailed lab-based electrochemical characterization of Au thin film model electrodes. CVs, galvanostatic and potentiostatic lithiation-delithiation cycles and galvanostatic potential relaxation experiments (GITT) are described. Combining the results of electrochemical and in-situ XRD measurements a correlation between the electrochemical processing and the structural changes was achieved. The galvanostatic and the potentiostatic lithiation-delithiation cycles which cover a current range of one order of magnitude in power showed high qualitative similarity. The observed potentialtime curves point to several alloy phases involved in the lithiation-delithiation process, different reaction paths during lithiation and delithiation, and a significant stability of the involved alloy phases. During the lithiation-delithiation cycles six alloy phases were identified each showing a characteristic evolution of intensity with time. Except for the highest lithiated phase all the alloy phases showed powder-like morphology. Only the highest lithiated phase identified to be the Li-Au alloy phase Li_3Au featured high crystalline order influenced by the Cu(100) substrate and rather large crystallites. A phase evolution diagram and a phase evolution model of the Au-Li system during electrochemical lithiation-delithiation were drawn.

Zusammenfassung

Lithiumionenbatterien (LIBs) sind heutzutage im Bereich der modernen Unterhaltungselektronik schon weit verbreitet. Um aber den wachsenden Herausforderungen z.B. im Bereich der Elektromobilität gerecht zu werden, ist eine deutliche Weiterentwicklung unabdingbar. In klassischen LIBs ist das Anodenmaterial kohlenstoffbasiert. Diese Materialien können Li durch Einlagerung zwischen den Graphenschichten speichern. Ein besonderes vielversprechendes alternatives Anodenmaterial, das zur Zeit im Fokus der Forschung steht, ist Si. Si weist die höchste spezifische Kapazität aller Elemente auf. In Si lässt sich Li in Form von Legierungen speichern. Mit der Legierungsbildung gehen strukturelle Veränderungen im Anodenmaterial einher. Auch Au (und andere Metalle) lassen sich elektrochemisch mit Si legieren und weisen dabei eine deutlich höhere Aufnahmefähigkeit für Li auf als kohlenstoffbasierte Materialien. In Form von Wachstumskeimen ist Au zudem auch im Zusammenhang mit Si Nanodraht-Anoden von Bedeutung, die vielversprechend im Hinblick auf eine technische Anwendung sind. Der edle Charakter des Au begünstigt seine Verwendung als Modellsystem. Im Vergleich zu realen Batterieelektroden bieten Modellelektroden wie z.B. Einkristalle und dünne Filme definierte experimentelle Bedingungen. Diese Arbeit verfolgt das Ziel Einblick in die atomistischen Mechanismen zu gewinnen, die während der Legierungsbildung (dem Einbringen von Li in die Kristallstruktur des Elektrodenmaterials) und der Entlegierung (Entfernen von Li) ablaufen. Ein generelles Verständnis der atomistischen Mechanismen des Li-Eintrags ist ein entscheidender Schritt auf dem Weg zu zielgerichteter Weiterentwicklung von LIB-Anoden. Röntgenbeugung ist eine leistungsfähige Methode zur Untersuchung struktureller Veränderungen in Materialien beispielsweise verursacht durch Legierungsbildung. Besonders eignet sich diese Methode für schwere Elemente wie z.B. Au, die einen hohen Wechselwirkungsquerschnitt mit Röntgenstrahlung aufweisen.

Im Rahmen dieser Arbeit werden in-situ Röntgenbeugungsexperimente an Au-Dünnfilm-Modellelektroden vorgestellt, die an der Hochenergie-Röntgenbeugungs-Strahllinie P07 am DESY in Hamburg durchgeführt wurden. Zusätzlich werden in der vorliegenden Arbeit detaillierte elektrochemische Messungen an Au-Dünnfilm-Modellelektroden vorgestellt, die im Labor am MPIE durchgeführt wurden. Dazu zählen CVs, galvanostatische und potentiostatische Lithiierungs-Entlithiierungs-Zyklen und galvanostatische Potential-Relaxations-Messungen (GITT). In Zusammenschau der Ergebnisse aller vorgestellten Messmethoden konnte der Zusammenhang zwischen der elektrochemischen Behandlung und den dadurch verursachten strukturellen Veränderungen erkannt werden. Die galvanostatischen und potentiostaischen Lithiierungs-Entlithiierungs-Zyklen, die einen Strombereich von einer Zehnerpotenz umfassen, zeigten eine deutliche qualitative Ähnlichkeit. Die beobachteten Potential-Zeit-Kurven legen nahe, dass am Lithiierungs-Entlithiierungs-Prozess mehrere Legierungsphasen beteiligt sind, dass während der Lithiierung und der Entlithiierung verschiedene Reaktionswege beschritten werden und dass die beteiligten Legierungsphasen eine hohe Stabilität aufweisen. Während der Lithiierungs-Entlithiierungs-Zyklen konnten sechs Legierungsphasen unterschieden werde, die sich jeweils durch einen charakteristischen Intensitätsverlauf mit der Zeit auszeichnen. Mit Ausnahme der am höchsten legierten Phase wiesen alle Legierungsphasen pulverartige Struktur auf. Nur die am höchsten legierte Phase, die als Li-Au-Legierungsphase Li₃Au identifiziert wurde, zeichnet sich durch deutlich größere Kristallite und hohe kristalline Ordnung aus, die durch das Cu(100)-Substrat beeinflusst ist. Ein Phasenentwicklungs-Diagramm und ein Phasenentwicklungs-Modell für das Au-Li-System während der elektrochemischen Lithiierung und Entlithiierung wurden entworfen.

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1.1 Batteries

A battery in the strict interpretation of electrical engineering is a series of several galvanic elements or electric cells of the same type. However the term "battery" nowadays is used also for single electric cells. Electric cells can be divided into two groups. Cells which are only able to supply energy are called primary cells or primary elements. Their cell reaction is not reversible by charging, that is applying of an external voltage. In the case of secondary cells, however, it is possible to (nearly) reversibly restore the original state, i.e. to recharge the element. Such secondary elements can thus be discharged and charged up to typically 1000 times and are also known as accumulators or rechargeable batteries. Primary and secondary cells are used in the form of single cells/elements as well as piled up with further cells in battery "stacks" or "packs". A large variety of different battery cells is on the market delivering to various different requirements in different applications.

In daily life often primary single-cells featuring a nominal voltage of 1.5 V are encountered in different dimensions (size, capacity) for example in alarm clocks, remote controls, pocket lamps and similar applications. Most common are the micro (AAA), mignon (AA), baby (C) and mono-cell (D). Modern alkali-manganese cells have replaced the classical zinc-coal cell meanwhile. Making batteries with a multiple of the nominal voltage of a single cell is possible by series circuits of several cells. An example for this principle is the 9 V battery, a series circuit of six alkali-manganese cells. In watches on the other hand usually small coin cells as the mercury oxide-zinc cell are used. The most famous examples of secondary cells might be the nickel-metal-hydride-cells covering similar fields of application like the alkali-manganese-cells and the lead accumulators most frequently used as car batteries. In case of the latter the nominal voltage of 12 V is reached by a series of six lead-lead-oxide cells containing diluted sulfuric acid as electrolyte. In fields like the modern mobile consumer electronics lithium ion cells (or batteries) have gained a dominant position. In addition lithium ion cells offer potential for application in electric cars and large scale energy storage. To make electromobility competitive compared to combustion engines the need arises to develop batteries being on the one hand light in

weight and on the other hand capable to store and release enough energy quick enough to manage also long distance trips without time-consuming intermediate charging or annoying battery exchange. Furthermore they should be preferably small, cost efficient and safe. Batteries as stationary large scale storage systems for electrical energy are also in demand in view of the increasing use of renewable energy sources. In this field the storage systems need to absorb large amounts of energy, store the energy with only small losses, and release the stored energy on demand. Wind and solar energy are not available around the clock and seven days a week, but only, when the wind blows and the sun shines, respectively. However this is not always the case in the moment when the energy is needed. Especially for a growing use of electromobility as well as renewable energy sources the performance of today's battery technology is far from being sufficient. Research, both, on an applied level but even more on fundamental aspects is therefore highly demanded.

Electric cells are electrochemical storage systems and at the same time energy converters. During discharging the chemical energy of the active battery materials is transformed into electric energy. In case of rechargeable batteries also the inverse process, the transformation of electrical energy into chemical energy, is possible in a defined way. The nominal voltage of an electrochemical cell is determined by its active electrode materials and their position within the electrochemical series. In classical zinc-coal cells featuring zinc anodes and manganese(IV)oxide cathodes the nominal voltage is 1.5 V. Batteries featuring a multitude of the nominal voltage of the single cell are feasible by piling up of several cells. However, to yield single cells featuring highest possible cell voltage active materials are needed showing a highest possible potential difference in the electrochemical series. On the anode side elemental lithium is preferable for this, since Li features the most negative potential of all the elements. The lithium-manganese-oxide cell, for example, provides a nominal voltage of 3 V.

Lithium batteries (in general electric cells containing elemental lithium as active anode material) are, however, currently only usable as primary cells. During charging of such cells dendrite formation at the lithium electrode occurs. The reason is that it is so far technically not possible to deposit lithium as a homogeneous film from the electrolyte on a lithium electrode, since dendrite formation is favored. The dendrites may penetrate the membrane of the cell and continue growing towards the cathode leading to shortcuts and possibly to destruction of the cell.

To be able to take advantage of the outstanding nominal voltage achievable with Li based batteries also in fields depending on the application of rechargeable batteries such as the above mentioned highly actual field of electromobility and energy storage technology an urgent need for alternatives in anode material arose. The first approach in this context embedding Li into a host material was the use of carbonaceous material as anode. During charging of the battery lithium intercalates between the graphene sheets driven by the applied voltage (potentiostatic charging; compare chapter 2.1.6) or the applied current (galvanostatic charging; compare chapter 2.1.2). The maximal amount of lithium graphite-like structured carbonaceous material can take up corresponds to a composition of LiC_6 . The process of intercalation is reversible and dendrite formation does not occur. By this trick it was possible to employ lithium as active electrode material also in secondary cells. Cells based on this principle are called lithium-ion cells or lithium-ion accumulators colloquially also called lithium-ion batteries (LIBs). The development of a technique to store lithium in a host material cleared the way to make lithium based batteries rechargeable. With this the intrinsic advantage of Li featuring a very negative potential can be exploited for a wide bunch of energy consuming applications.

As cathode material in lithium-ion accumulators usually lithium-transition-metal oxides are used such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ or also other compounds like $LiFePO_4$. All this compounds are characterized by the fact, that the contained transition-metal is able to relatively easy change its oxidation number. In consequence the lithium content in all these compounds is variable. In the first commercial lithium-ion battery^{1,2} a graphite anode and a lithium cobalt oxide ($LiCoO_2$) cathode were used. In this case the reaction equation for discharging and charging of the battery reads:

$$nC + XLi^+ + Xe^- \longleftrightarrow Li_XC_n$$

$$LiCo(III)O_2 \longleftrightarrow Li_{(1-x)}Co(II)_xCo(III)_{(1-x)}O_2 + XLi^+ + Xe^-$$

But already in modern consumer electronics even classical LIBs reach their limits considering the necessity to recharge a smart phone every day under extensive use. And yet LIBs are facing even much higher challenges. They are foreseen to form the fundament of electromobility and large-scale energy storage.

The main obstacle in establishing electric cars as automobile standard are still the batteries. They are still to big, too heavy and too expensive and their performance is not sufficient to make driving electric cars comfortable. The cruising radius is too small and charging of the batteries takes too long to replace established combustion engines. But for several niche markets, such as golf carts, short-distance commuting, or electric bicycles, the technology became interesting..

In respect of sustainable energy generation using renewable energy sources such as wind, sun or water the problem exists as mentioned already above that the energy production cannot be controlled according to the needs. Energy is produced when the wind is blowing and the sun is shining independent of the actual needs. In consequence energy has to be stored intermediately in energy storage devices capable to uptake and release high energy

amounts in short time.

Especially for these applications besides the nominal voltage some other parameters are crucial:

- The capacity denotes the amount of electric charge an electric cell can store. Its physical dimension is the ampere-second (As). In battery technology usually the dimension milliampere-hour (mAh) is used.
- Even more meaningful than the capacity is the specific capacity. In context of specific capacity the volumetric specific capacity, the capacity per volume-entity has to be distinguished from the gravimetric specific capacity, the capacity per mass-entity. The usually used dimension is milliampere-hour per gram or cubic centimeter (mAh/g respectively mAh/cm³)
- The electric power is the electric work extractable from the cell per time entity. Its dimension is Watt (W). The power is the product of the discharging voltage U and the discharging current I.

The pressing aim is to develop batteries featuring high power, high (reversible) capacity, high energy density, long cycle life and quick charging and discharging. To meet these requirements LIBs have to be improved much further. Improvement of the battery means improvement of the components of the battery such as electrodes, electrolyte and separator as well as of their interplay.

The present work dedicates to fundamental research of the atomic processes occurring at the anode during charging and discharging of LIBs to get to an better understanding of these processes opening the door for targeted improvement of anodes for LIBs.

1.2 Anode Materials for Lithium-Ion Batteries

As already mentioned, in case of graphite the specific capacity is only $372 \text{ mAh/g} (\text{Li}_2 \text{C}_{11})$,^{3,4} since the uptake capability for lithium is limited to only one lithium atom per six carbon atoms.⁵ The need for a significant improvement of the specific capacity of lithium-ion batteries (LIBs) to cope with the upcoming challenges in the fields of electromobility and energy storage technology also requires the search for anode materials featuring significantly higher specific capacity. Hereto different approaches were followed. Several researches concentrated on the further development of carbonaceous materials such as carbon nanotubes^{6,7} others realized metals or alloys thereof to be promising, seeking for high-performance anode materials.^{8–11} In fact also combinations of both approaches were tested.^{12, 13} Some metals, but also silicon, are able to store lithium. On depositing

lithium on electrodes consisting of these materials no successive growth of a lithium layer is observed on the surface. Rather lithium penetrates into the crystal structure of these materials by diffusion. The occurring process is called insertion or lithiation. In result alloys are formed. In some cases lithium occupies only interstitial sites within the atomic arrangement of the host metal. In other cases new phases are formed featuring crystal structures partially strongly deviating from the crystal structure of the host material.⁵

In some cases – for example in the case of aluminum – only one single alloy phase is formed by electrochemically forced lithium insertion.¹⁴ In other cases – for example in the case of gold – several alloy phases are involved (see chapter 6.5). In addition the alloy phases can be crystalline as in the case of $aluminum^{14}$ and $gold^{15,16}$, or as in the case of silicon mainly amorphous.^{9,17,18} Lots of materials feature a higher specific capacity than graphite^{5,9} and are consequently apriori of interest to replace the classical graphite electrodes. Silicon features with 4200 mAh/g the highest theoretical capacity of all the available LIB anode materials; 4,19 ten times higher than that of existing commercial graphite (372 mAh/g).^{3,4} But a material featuring high specific capacity is not necessarily a good anode material. The more lithium the materials can take up the more they expand in volume. The volume expansion can amount to ca. 400% of the original volume for example in the case of silicon.⁴ The repeated volume expansion and volume shrinkage during several charge-discharge cycles results in many cases in cracking and pulverization of the electrode material^{4,12,19-21} causing mechanical and electrical contact loss to the current collector and associated capacity fading.^{8,22-26} The result is a massive capacity loss, up to destruction of the electrode. Approaches to solve the problems associated to the volume expansion are for example the use of anode materials as thin $films^{16,27-29}$ or in nano-structured form,^{12,30-41} for example Si nanowires, porous materials³ or the use of composite materials being composed of different materials featuring different expansion behavior during lithiation.⁴²

In the present work lithium insertion and extraction at Au anodes were investigated. Also Au shows electrochemical lithium insertion at higher specific capacity (451 mAh for $\text{Li}_{15}\text{Au}_4$)^{3,16} than graphite. Au has the advantage of high interaction cross section with X-rays and is therefore perfectly suited for fundamental research in the field of lithiation mechanisms at anode materials for lithium-ion batteries. Despite the apparently high price is has been used in thin film batteries where the price of the Au electrode is in fact not the limiting contribution to the total cost.^{3,16} Technically metal thin films can be easily prepared by RF sputtering.

Another benefit of Au as anode material are the very low potentials (close to 0 V vs. Li/Li^+) Li insertion into Au occurs at. Li insertion potentials much higher than 0 V vs.

 $\rm Li/Li^+$ leads to reduced cell voltage and lower energy density of the batteries.^{16,43} In case of Au Li insertion occurs roughly below 200 mV (see chapter 5). For comparison in case of the technically promising Si and also largely investigated Sn the Li insertion already starts at 300 mV (Si)⁴⁴ or even 800 mV (Sn).¹⁶

The lithiation-delithiation behavior of Au was so far investigated by several researchers. In 2002 Taillades et al. reported about some galvanostatic lithiation-delithiation measurements and basic ex-situ XRD measurements.¹⁶ They identified two lithiation and delithiation plateaus in the galvanostatic potential time curves. From their ex-situ XRD measurements at these plateaus they concluded the Au to be transformed in another phase during lithiation and to be recovered during delithiation. From their experiments they proposed two Li-Au alloy phases to occur both at the limit of the Au-Li solid solution range (Au₆₀Li₄₀).

In 2008 Yuan et al. performed galvanostatic lithiation-delithiation experiments at mesoporous Au sponges identifying two lithiation and two delithiation plateaus.³

Renner et al. reported in 2008 about in-situ XRD investigations on the electrochemically driven alloying and dealloying of Au substrates with Li-ions from organic electrolytes.¹⁵ During their potentiostatic measurements they found the reversible formation of two distinct sets of peaks at -0.1 V and 0.1 V assigned to unidentified nanosized Li-Au alloy phases. Also they observed the occurrence of the α -Li-Au solid solution phase.

In 2012 Misra et al. reported investigating silicon nanowire anodes by in-situ XRD about a finding not directly related to the lithiation of Si.⁴ They observed their Au catalyst layer employed for nanowire growth to form on its part alloys with the inserting lithium. During the lithiation cycle they observed the successive formation of two different Li-Au alloy phases at low potential vs. Li/Li⁺. The occurrence of the two Li-Au phases was found to depend on the magnitude of the galvanostatic current, the way of nanowire growth and the details of electrochemical treatment. A separate experiment testing pure Au film and Au nanoparticles revealed the formation of the two phases only in the case of the nanocrystalline Au and not in the case of thin films. They found correspondences between the XRD peaks of their phases and the peaks observed by Taillades et al.¹⁶ and Renner et al.,¹⁵ but not a complete correlation.

Thakur et al. reported about the beneficial effect of Au coatings on the performance of silicon materials as anodes for LIBs in terms of capacity and cycle life⁴⁵ as it was previously shown for the case of Ag coatings⁴⁶ and Fullerene coatings.⁴⁷ All of them attributed the beneficial effect of the thin coating layer to its ability to host a stable SEI-film. The Au coating was assumed to hinder the structural degradation in the porous silicon as it undergoes volume expansion during lithiation.⁴⁵

As just mentioned the lithiation-delithiation behavior of Au is not only interesting with regard to pure Au anodes. Also in the case of different Si based anodes (see above) Au is of interest. Thus it has influence on the performance of this electrode material promising for future application as standard anode material for LIBs.⁴

1.3 Electrolytes for Lithium-Ion Batteries

In classical electric cells usually aqueous solutions are used as electrolyte. In lead accumulators diluted sulfuric acid is used. However, in the field of lithium-ion batteries (LIBs) the use of aqueous solutions for electrolyte is not possible, since water is not stable close to the lithium equilibrium potential. The so called electrochemical window of water – the potential range a solvent is electrochemically stable in – is not appropriate to allow the operation of a LIB. For this reason another solvent with appropriately located electrochemical window is needed.

Technically usually special organic carbonates are used for this purpose. The charge of these carbonates is not compensated by metal cations as in a classical salt. Rather these carbonates carry at two of their three oxygen atoms organic substituents. Instead of ionic bonding as between metal cation and carbonate anion in a salt crystal here covalent C-O-bonds are present. Organic carbonates are electrochemically stable within the potential range lithium reduction occurs in and at the same time they are polar enough to dissolve the lithium necessary for the operation of the battery in form of a lithium salt. The lithium salts usually feature bulky anions with only small charge density as for example PF_6 . The bulkiness and small charge density of the anions reduces the lattice energy of the salts and favors their dissolution in the organic carbonate solvents. Organic carbonates do not feature any polar element-hydrogen bond allowing hydrogen evolution. Organic carbonates frequently used as electrolyte in LIBs are for example Dimethylcarbonate (DMC), Ethylmethylcarbonate (EMC), Diethylcarbonate (DEC), Ethylenecarbonate (EC) or Vinylidenecarbonate (VC). Often also mixtures of different carbonates are used. Moreover diverse additives are added to the electrolyte to ameliorate the electrolyte's properties²⁰ for example with respect to the solid-electrolyte interphase (SEI) film formed by partial decomposition of the electrolyte (see also chapter 1.4). In practice organic electrolytes feature a severe disadvantage. They are easily inflammable impairing the operational safety of the LIBs operated using them.

An alternative for electrolytes for LIBs are ionic liquids. Ionic liquids are are organic salts which are liquid at room temperature. Ionic liquids exhibit high ionic conductivity, high chemical, electrochemical and thermal stability and are at the same time not volatile

and inflammable.^{48,49} Their special features arise from the ions they consist of as any other salt. The anions as well as the cations of the ionic liquids are big organic ions. This is the reason for their low melting point compared to inorganic salts such as for example NaCl melting at 801°C. As effect of the size of the ions the lattice energy is low enough due to steric reasons as well as due to the small charge density to yield a liquid at room temperature.

Due to their above mentioned characteristics ionic liquids have attracted wide attention for use as solvents for catalysis, chemical synthesis and separations. They are used as heat carriers in solar thermal energy generators and in the field of electrolyte applications as electro-deposition of electropositive materials, light emitting electrochemical cells, photo-electrochemical cells, electrochemical capacitors, fuel cells and batteries. For use as electrolyte in batteries ionic liquid with imidazolium based cations have received high attention due to their high ionic conductivity. Since the imidazolium based cations feature an acidic proton their use in combination with elementary Li as in LIBs is unfavorable. Ionic liquids consisting of N-alkyl-N-methylpyrrolidinium cations (PYR_{1R}⁺) (R indicates the number of carbons in the alkyl group) and bis(trifluoromethanesulfonyl)imide anions (TFSI⁻) do not feature an acidic proton and for example PYR₁₃TFSI and Pyr₁₄TFSI^{48,50} show high room temperature ionic conductivity. With this PYR₁₃TFSI and Pyr₁₄TFSI are highly favorable for use as electrolyte in LIBs. Pyr₁₄TFSI was used in the present work due to its higher conductivity.

As already mentioned ionic liquids feature a very low vapor pressure. Even at high vacuum conditions (10⁻⁶ mbar) there is no considerable gas phase. That is why they are much safer with respect to heat evolution inside the batteries and inflammability than organic carbonates. Similar to organic carbonates ionic liquids are capable to dissolve the lithium necessary for the operation of the battery in form of its salts. In the case of ionic liquids as well as organic carbonates as electrolyte solvent lithium salts featuring large, weakly Lewis basic anions (big ions carrying only small charge and consequently of low charge density) are used to ameliorate the solubility of the salts. Moreover the low vapor pressure of ionic liquids enables their use under vacuum conditions being of interest in fundamental research with regard to preferably defined and undistorted conditions.

1.4 The Solid-Electrolyte Interphase (SEI)

The term "Solid-Electrolyte Interphase" (SEI) denotes the interface layer between electrode and electrolyte resulting from the partial decomposition of the battery electrolyte in presence of lithium. The SEI is so far only little understood and it is still uncertain if this



Figure 1.1: Sketch of the Solid-Electrolyte Interphase (SEI) formed at a graphite anode using organic carbonate based electrolyte.⁵⁸

SEI, which passivates the surface of the anode material, is crucial for the safe operation of lithium-ion batteries or if it slows down reaction kinetics.⁵¹ In case of graphite anode and organic carbonates as electrolyte the SEI is imagined to be built up as shown in Fig. 1.1. Its thickness is typically 30-50 nm and it consists of lithium-oxide (Li₂O), lithium-fluoride (Li_F), lithium-carbonate (Li₂CO₃), semi-carbonates and polyolefines.

Most research in field of SEI has so far been conducted at carbon based anode materials in combination with organic electrolytes. The type of electrolyte and the presence of additives turned out to have great influence on structure and performance of the SEI.^{26,52–56} So far only little work has been conducted regarding SEI formation and behavior on other anode materials. Among these also materials regarded to be most promising for technically relevant advanced anode materials such as silicon.⁵⁷ To the best of my knowledge no research on SEI formation on Au electrodes was reported even less in combination with ionic liquid based electrolytes.

1.5 Motivation and Prospect of this Work

As pointed out there is a strong need to improve the performance of lithium ion batteries (LIBs) with regard to electromobility and energy storage technology. The electrodes of LIBs offer much space for improvement to tackle this challenge. On the anode side one promising approach is to replace the still dominating carbonaceous materials by metals capable to form lithium alloys upon charging of the batteries.

Both, the negative and positive electrodes of real batteries (in the sense of ubiquitous commercial batteries) often consist of powder electrode material mixed with a binder, blended to yield a slurry and applied on a current collector. The electrolyte usually

contains additives to ameliorate the properties of the battery. Such real systems are hardly adapted for the investigation of lithiation mechanisms, since they contain too many factors disturbing detailed understanding. For this reason within the scope of the present work thin film model electrodes were used. Model electrodes feature a defined surface and, in case of thin films, also a defined volume. The limited volume in case of the thin films in comparison to bulk materials is completely accessible for lithiation. Also highly lithiated alloy phases can be expected to occur. Another benefit of thin films is their higher tolerance towards volume expansion.

As discussed above the insertion of Li into the crystal structure of metals is usually accompanied by changes of the crystal structure of the electrode material. The formed metal-lithium alloys feature different crystal structure compared to the pristine metal. Changes in crystal structure can be nicely addressed by the method of X-ray diffraction (XRD).

In-situ measurements are most promising to get access to a detailed understanding of the structural changes in the crystal structure during Li-insertion and extraction. Insitu measurements are measurements conducted directly during the processes (here the electrochemical lithiation and delithiation).

Here, the aim of in-situ XRD measurements is to observe and follow the structural changes due to alloy phase formation initialized by the electrochemical treatment just during the electrochemical treatment is proceeding by the structure sensitive method of X-ray diffraction. We employed high-energy synchrotron based in-situ X-ray diffraction and focused for this on gold which is a very suitable model system for this technique. In some cases of LIB anode materials it is crucial to perform in-situ experiments when metastable phases are involved. When metastable phases are involved the structures during the electrochemical processes can differ significantly from what can be found after switching off the potential, dismounting the sample, cleaning it and transferring it to measuring devices to perform ex-situ measurements. In-situ XRD measurements allow to directly correlate the electrochemical measurements with the phase formation in the electrode.

Misra et al.⁴ (among others) pointed out the necessity of in-situ measurements in the case of silicon. In the present work the need for in-situ measurements will become evident in the case of Au electrodes. In contrast there are also materials such as Al where in-situ and ex-situ experiments show the same results concerning the formed alloy phase.¹⁴

As discussed in more detail in section 1.2 this work focuses on Au anodes because of first, its relevance in several kinds of nano-structured Si based anode materials (see above) and second, its very good cross section with X-rays.

For the measurements planned it was necessary to use High-Energy-XRD (HEXRD) in combination with high beam intensity. The beam energy had to be high enough to on the one hand in general allow penetration of the electrolyte and the walls of the electrochemical in-situ cell and on the other hand effect the angles, at which diffracted intensity can be expected, to be small enough (according to Bragg's law; eq. 2.2) to be able to cover large parts of the reciprocal space with one diffraction pattern acquired using an flat panel detector which allows a sufficient time resolution of the in-situ experiments (compare section 2.2). High beam intensity is also a prerequisite for obtaining a diffraction pattern in short time allowing high time resolution. For the electrochemical treatment a ionic liquid based electrolyte was used.

2 Techniques

2.1 Electrochemical Techniques

Electrochemical measurements investigate an electrode in reaction to an external electrochemical force. This force can be an applied potential (potentiostatic measurements) or current (galvanostatic measurements) or also changes in ionic strength or pH-value, for example. In more complex cases this external potential or current is changed continuously or discontinuously, successively or abrupt between set limits. The observed reaction of the system reveals insights in the mechanisms of the electrochemical process.

2.1.1 Cyclic Voltammetry (CVs)

In the case of cyclic voltammetry the electrochemical force imposed to the system is a voltage periodically changed between an upper and a lower limit at constant rate. During applying the potential the current response of the system to this force is monitored to yield cyclic current-potential curves, so called cyclic voltammograms.

In practice cyclic voltammetry is conducted by changing the potential applied to the sample starting from a specific value in positive or negative direction at constant rate. When a set reverse potential is reached the direction of potential feed is reversed until the starting potential is reached again. During this procedure the current provoked by the applied potential is monitored. This procedure is repeated several times yielding in several cyclic current-potential curves.

CVs provide an overview at which potentials within the preset potential range electrochemical processes take place. At the respective potentials the current-potential curve shows variations of current for example peaks. In this work CVs are also nicely suited to explore the electrochemical window of the electrolyte used. Peaks during the period of lowering the potential indicate reduction reactions. For this reason the period of lowering the potential is called cathodic branch of the CV. Analogously the period of raising potential where oxidation reactions take place is called the anodic branch. If a specific electrochemical reaction is reversible associated current peaks due to the reductive and the oxidative process occur in the cathodic branch and in the anodic branch of the CV. An irreversible electrochemical process is announced by single current peaks in the cathodic or the anodic branch.

2.1.2 Galvanostatic lithiation/delithiation

In the case of galvanostatic measurements a specific current is applied to the system and the evolution of the potential is monitored with time.

Galvanostatic charge-discharge curves served for characterization of the model electrodes. For battery charging and discharging galvanostatic charge-discharge cycles are conducted by first applying a constant negative current. A negative current corresponds to charging of the battery accompanied by a reduction process at the model electrode. In lithium-ion batteries (LIBs) Li-ions are shuffled from the cathode material towards the anode during charging the battery. At the anode they are reduced to atoms inserting into the electrode material to effect alloying. Tendentially thereby the potential decreases with time, since the crystal structure of the model electrode fills with lithium resulting in a growing force (more negative potential) necessary to insert further lithium into the electrode material. In dependency of the electrode material plateaus in the potential evolution with time appear during which the potential keeps more or less constant. Plateaus in the potential-time evolution are hints for two phase regions, during which, from the starting material, an alloy phase is formed or an already formed alloy phase transforms into another phase featuring higher lithium content. After reaching a defined potential (typically the lithium deposition potential or a slightly higher one) the charging of the battery is finished and the applied current is abruptly switched in sign. The now positive current effects an oxidation at the model electrode. Lithium deposited during the charging process gets reduced to Li ions passing over into the electrolyte. Lithium inserted into the crystal structure of the metal during charging is extracted now from the crystal structure accompanied by dissolution of the metal-lithium alloy phases. Consequently the positive current effects a discharging of the model cell. This is accompanied by tendentially increasing potential since it gets more difficult to dissolve further lithium from the alloy phases. During the potential increase potential plateaus occur in dependency of the electrode material as already observed during charging the cell. These plateaus again denote two phase regions. Galvanostatic lithium insertion and extraction are used as standard for electrochemical characterization of electrode materials for LIBs since they reflect the conditions during normal cell operation.

2.1.3 Differential charge curves

The differential charge corresponds to the derivative of the converted charge (applied current times lithiation time) with respect to the potential measured over time during the galvanostatic treatment. To yield differential charge curves this differential charge is plotted against the corresponding potential. While in the galvanostatic charge-discharge curves the potential evolution can be followed and features therein, such as plateaus, can be recognized, the differential charge curves give a more detailed insight at which potentials phase transformations occur. Peaks in the differential charge curve correspond to plateaus in the galvanostatic charge-discharge curves. The peak positions in the differential charge curves give the exact plateau potential. From the height of the peaks it can be seen if a plateau is at constant potential or if the plateau is sloped and the width of the peaks reflects if a plateau is a straight line or if it is bended. The differential charge curves shown are calculated from the lithiation-delithiation curves by means of difference quotients.

2.1.4 Nominal Lithium Content (NLC)

The nominal Li content is the calculational Li content assuming the entire current flown during the electrochemical lithiation or delithiation is converted in Li-ion reduction. Any possible side reactions are not considered. By integrating the total current flown in a certain time range the converted charge results. By dividing the resulted charge by the elementary charge the number of Li-ions results which could have been reduced by this amount of charge. This number of theoretically (nominally) reduced Li-ions is set in relation to the number of Au atoms present in the thin film. The quotient gives the stoichiometric factor x in the formula Li_xAu which can be called nominal Li content (NLC).

In short the nominal Li content (NLC) is to be understood as the theoretical number of Li^+ ions possible to reduce by the current flown in a certain time range usually starting at the beginning of lithiation, if the entire current is used to reduce Li^+ ions, normalized to the total number of Au atoms available for lithiation in the Au film sample. The NLC corresponds to the stoichiometric factor x in the specification of composition Li_xAu).

2.1.5 Galvanostatic Intermittent Titration Technique (GITT)

Galvanostatic intermittent titration technique (GITT) measurements in contrast to the simple galvanostatic measurements include some intermediate potential relaxation times. For this reason GITT measurements can be described as galvanostatic potential relaxation

2 Techniques

measurements. First the sample is galvanostatically lithiated at a specific current for a specific time to insert/extract lithium. Then the electrochemical circuit is opened (ocp conditions) and the potential evolution is monitored. After a specific preset time the cell is switched to galvanostatic treatment again. The described switching between galvanostatic lithiation/delithiation and hereinafter monitoring of the open cell potential (ocp) is kept up over the complete lithiation/delithiation cycle. During the galvanostatic periods lithium is inserted/extracted and during the ocp periods the potential relaxes towards the momentary equilibrium. Directly after switching to ocp the potential increases (in the lithiation half-cycle) or decreases (in the delithiation half-cycle) very quickly due to the omission of the overpotential related to the ohmic resistance and the electron transfer resistance through the electrode surface. Subsequently, the potential continues relaxing on longer time-scales due to balancing of concentration gradients and self discharging of the electrochemical double layer capacitor. After anew switching on the current the overpotential due to ohmic and electron transition resistance is established again marked by a steep initial potential decrease (in the lithiation half-cycle) or increase (in the delithiation half-cycle). The charging of the double layer capacitor by ionic transport and the evolution of concentration gradients takes longer and leads to a further slower decrease/increase. During the period of reestablishing concentration gradients and the double layer capacitor also lithiation/delithiation starts again.^{59,60}

From the potential-time curves acquired during GITT measurements important information to calculate diffusion coefficients and thermodynamic and kinetic parameters can be obtained.⁶¹

2.1.6 Potentiostatic lithiation-delithiation measurements

Alternatively to the galvanostatic lithiation-delithiation experiments potentiostatic lithiationdelithiation experiments can be employed. In the latter method a potential is set and the resulting current is recorded as a function of time. From the current response information about the electrochemical processes taking place at the set potential can be obtained. To distinguish several electrochemical processes taking place in a potential range of interest it is advantageous to change the set potential step by step. For potentiostatic lithiation-delithiation experiments the termination criterion is, in contrast to the galvanostatic experiments, bases on the current provoked by the applied potential. Applying a potential the current in most cases decreases starting from an initial value. As soon as the current undercuts a set value the potential is changed. When no additional electrochemical reaction takes place at a specific potential the current decreases quickly. In this case the shape of the current time curve is similar to an exponential decay curve. When an additional electrochemical process takes place at a specific potential the current consumed by this process gets superimposed to the double layer charging current. In result the decrease of current is characteristically changed.

An advantage of the potentiostatic method is that by keeping the potential constant a proceeding of the occurring processes in thermodynamic equilibrium is more probable than in galvanostatic measurements. However, the galvanostatic charge-discharge cycles can be used for orientation with respect to choosing proper potential values for potentiostatic measurements.

2.2 X-Ray Diffraction (XRD)

X-rays are electromagnetic radiation in the frequency range between $3 \cdot 10^{16} s^{-1}$ and $6 \cdot 10^{19} s^{-1}$ corresponding to an energy range of 100 eV - 250 keV ($\lambda = 1 nm - 10 pm$). The energy range of X-radiation overlaps in wide range with the energy range of γ -radiation. Classically X-radiation and γ -radiation were classified by their origin. While X-radiation origins from high energetic electron processes, γ -radiation origins from processes in the atomic nucleus.

Classically X-rays are produced for imaging, spectroscopy, or diffraction in various applications such as medical diagnostics and treatments or material's characterization by so called X-ray tubes. In these tubes electrons accelerated in an electric field are collided onto metal targets. This process results in two types of X-radiation: so called Bremsstrahlung and so called characteristic X-radiation. The term Bremsstrahlung denotes the continuous spectrum of X-radiation due to the abrupt deceleration of the electrons hitting the target material. Characteristic X-radiation occurs when the accelerated electrons colliding onto the target feature sufficient energy to excite electrons from the inner shells of the target atoms. The energy relaxation of electrons from higher shells to replace the removed electrons is accompanied by the emission of electromagnetic radiation at the lower end of the frequency range of X-rays.

To yield X-rays of higher energy and intensity necessary for the presented in-situ X-ray diffraction experiments (see below) another way of producing X-rays is favored. As the occurrence of Bremsstrahlung in X-ray tubes, this alternative way of producing X-rays also bases a on the general effect that accelerated charged particles emit electromagnetic radiation.

When relativistic charged particles such as electrons (kinetic energy about 1 GeV) are forced on a circular orbit for example by magnets they get continuously transversely accel-

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Figure 2.1: Constructive and destructive interference at a double slit.

erated accompanied by continuous tangential emission of electromagnetic radiation in the X-ray range. X-rays produced in this way are called synchrotron radiation. Synchrotron radiation can be produced featuring much higher energy and intensity than the usual energy and intensity of X-rays produced in X-ray tubes.

Diffraction is the deflection of waves (for example electromagnetic waves) at a barrier. When electromagnetic waves (and also other kinds of waves) pass a slit the slit is the origin of cylindrical waves. When (electromagnetic) waves pass a double-slit the two resulting cylindrical waves interfere behind the slits resulting in an interference pattern. Fig. 2.1 shows the extremal cases of totally constructive interference (Fig. 2.1 (a)) and destructive interference (Fig. 2.1 (b)). Totally constructive interference is observed if the difference in path between the two electromagnetic waves is a multitude of the wavelength. The intensities of the single (electromagnetic) waves sum up. Destructive interference occurs when the difference in path length is an odd multitude of a half of a wavelength. The intensities of the single (electromagnetic) waves extinguish each other. Due to the phenomenon of interference a periodical variation of intensity is observed behind the slits. This so called interference pattern gains in intensity and sharpness, when more equidistant slits are added to yield a lattice. The interference pattern is especially nicely developed when the wavelength of the radiation is in the order of the periodicity of the lattice.

As it is the case for all (electromagnetic) radiation also for X-radiation the phenomenon of diffraction at periodical arrangements such as lattices is observed. The phenomenon of diffraction can be used to gather information about the crystal lattice of solids. By irradiating solids by light featuring a wavelength in the dimension of the atomic lattice distance of the solids diffraction and interference occurs at the crystal lattice of the solids yielding in a interference pattern, colloquially also called diffraction pattern. From the diffraction pattern information about the crystal lattice giving rise to the pattern can be gathered.


Figure 2.2: Unit cell and lattice planes

Dependent on its crystal system to every crystal a so called unit cell can be assigned. The unit cell is the (in due consideration of the crystal's atomistic symmetry) smallest parallelepiped capable to describe the whole crystal just by translation of this unit cell. The unit cell is associated with a local coordinate system featuring the periodicity of the crystal as unit vectors denoted as a, b and c in the respective x-, y- and z-direction (not necessarily ortho-normal). The whole crystal can be described only by translation of the unit cell by multiples of the unit vector along the coordinate axes.

In a crystal different so called lattice planes can be defined determined by the Miller indices⁶² of the type (hkl). Based on the local coordinate system every so called lattice plane in the crystal can be specified by giving the reciprocal value of the intersection point of the plane with the coordinate axes in units of the unit vectors. The Miller index (120) for example denotes a plane intersecting the x-axis at a, the y-axis at b/2 and the c-axis at infinity $(1/\infty = 0)$. Hence the (120) plane is parallel to the z-axis. The Miller index (120) does not only denote a single plane but the family of all planes parallel to that. Fig. 2.2 shows a unit cell of a face centered cubic crystal. The orientation of the (100), (110) and (111) lattice plane is marked within the unit cell. In addition projections perpendicular to the respective lattice planes are shown to visualize the different atom arrangement characterizing different lattice planes.

From the Miller indices the distance between the parallel (120) planes can be calculated. In case of a cubic crystal system (a=b=c; $\alpha=\beta=\gamma=90^{\circ}$) formula 2.1 holds:

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Figure 2.3: Graphical derivation of Bragg's law

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{2.1}$$

The angles at which maxima of diffracted intensity occur - 2ϑ - is correlated with the wavelength of the incident X-ray beam λ , the inter-planar distance of the respective family of planes d and the number of the diffraction maximum n, the so-called order, by Bragg's law (formula 2.2).^{62,63}

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta) \tag{2.2}$$

Equation 2.2 is graphically visualized in Fig. 2.3. The term $n \cdot \lambda$ denotes the difference in way between the two rays reflected at different atomic planes.

Rearrangement of eq. 2.2 yields in formula 2.3:

$$2\theta = 2 \cdot \arcsin(\frac{n \cdot \lambda}{2 \cdot d}) \tag{2.3}$$

With formula 2.3 the angles (with respect to the direction of incoming beam) can be calculated at which interference maxima are observable. The X-ray beam can be diffracted at all the different families of atomic planes (hkl) each forming a periodic lattice at which diffraction can occur.

For powder-like samples consisting of millions of randomly oriented nanosized crystallites formula 2.3 is sufficient. At the 2θ -angles predicted by formula 2.3 diffraction rings will occur.

Using single-crystals no diffraction rings will be observable but distinct reflections since within a single crystallite the different families of planes are arranged in specific defined directions.

To discuss X-ray diffraction in more detail it is of advantage to introduce the reciprocal space.⁶⁴ In reciprocal space all the families of planes within a crystal are represented by



Figure 2.4: 2-D representation of the Ewald-sphere

a lattice point of the reciprocal lattice. In case of cubic crystals the reciprocal lattice is also cubic. The q-vector is the vector pointing from the center of the reciprocal space (000) to the lattice points, for example (120). The lattice point (120) represents the (120) family of planes in real space. Its distance q(120) from the origin of reciprocal space is connected to the d-value of the family of planes in real space by formula 2.4:

$$q = \frac{2 \cdot \pi}{d} \tag{2.4}$$

The axis of reciprocal space are defined in a way that q(120) is perpendicular to the family of (120) planes. That way the (120) family is represented by its normal and the length of the normal is reversely proportional to the plane distance d.

According to an established convention the writing (120) denotes one specific point in reciprocal space while also all the symmetry equivalent points represented by all possible permutations of h, k, and l are meant by writing $\{120\}$; hence (102), (210), (201), (012), (021), (-120), (-102), (-210), (-201), (0-12), (0-21) and all inverted (hkl)-triples.

Another approach to predict diffraction patterns is the concept of the "Ewald-sphere".⁶⁵ The Ewald-sphere (see Fig. 2.4) is a sphere (in 3D) or a circle (in 2D) of the radius $|q_i| = |q_d| = 2\pi/\lambda$. The center of the Ewald-sphere coincides with the zero point of the

real crystal's coordinate system. The zero point of the reciprocal coordinate system is located on the surface of the Ewald-sphere (the circle line in 2-D). The zero point of the real and the reciprocal space are connected by the reciprocal vector q_i . When turning the crystal on the diffractometer around a point in the region of interest in the sample accompanied by turning the real coordinate system of the crystal around its origin (the origin of the microscopic coordinate system of the crystal (corner of a unit cell, center of the Ewald-sphere) can be defined to be everywhere inside the crystal, especially at the center of rotation of the crystal) then also the reciprocal coordinate system is turned around its origin (at the surface of the Ewald-sphere). A specific reflection (for example (120)) is observable during rotation of the sample when the respective reciprocal lattice point intersects the Ewald-sphere. In this case the reflection-condition for this reflection is said to be fulfilled. The direction in space the reflection can be observed in, in relation to the incoming beam, represented by the vector q_d , is geometrically determined by the position the respective lattice point of the reciprocal lattice intersects the Ewald-sphere. From Fig. 2.4 it is geometrically obvious that not all lattice points of the reciprocal lattice can penetrate the Ewald-sphere. Only the lattice points within the big circle in Fig. 2.4 of double the radius of the Ewald-sphere. From this consideration it is clear that the larger the wavelength of the electromagnetic radiation is (the smaller in consequence the Ewald-sphere is $(|q_i| = |q_d| = 2\pi/\lambda$, see above)) the less reflections can be observed and the smaller regions of the reciprocal space can be addressed.

The presented X-ray diffraction experiments targeted to image large parts of the reciprocal space with high time resolution using an flat panel detector. For this it is advantageous to work with a high energy X-ray beam. Explained with the simple model based alone on Bragg's law 2.2 the consequence of high beam energy are small diffraction angles:

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\theta) \tag{2.5}$$

with

$$E = h \cdot \nu = h \cdot \frac{c}{\lambda} \tag{2.6}$$

follows

$$n \cdot \frac{h \cdot c}{E} = 2 \cdot d \cdot \sin(\theta) \tag{2.7}$$

and from this

$$\Rightarrow \frac{1}{E} \sim \sin(\theta) \tag{2.8}$$

If the energy is high enough the diffraction angles assigned to the atomic families of planes with large inter-planar distances (Miller indices between about (100)-(800) in our case) are small enough to catch the beams diffracted at these planes with a flat panel



Figure 2.5: Influence of the energy of the X-ray beam correlated with the size of the Ewald-sphere on the reflections observable.

detector of about 40 cm edge length in a distance of ca 140 cm from the sample (explicit values from the measurements presented within this work).

In the more sophisticated approach of the Ewald-sphere a reflection can be observed when its associated reciprocal lattice point intersects the Ewald-sphere (see Fig. 2.5). In ideal case of a perfectly ordered single-crystal and a perfectly monochromatic X-ray beam the the reciprocal lattice points are mathematical points and the Ewald-sphere is of infinitesimal thickness. In real case the lattice points have specific extension and the Ewald-sphere shows specific thickness. Consequently in real case it is more probable thus to fulfill reflexion conditions meaning overlapping of the Ewald-sphere and the lattice points for several reflections at the same time. If the radius of the Ewald-sphere is large (high beam energy, low wavelength, large radius of the Ewald-sphere according to equation 2.9) various lattice points of the same lattice plane can overlap with the Ewald-sphere at the same time to yield reflections (B in fig. 2.5). If the Ewald-sphere is small only few or even only one lattice point of a specific lattice plane fulfill reflection conditions (C in fig. 2.5). If the radius of the Ewald-sphere would be infinitesimal complete lattice planes could fulfill reflection conditions at the same time and the whole lattice plane could be imaged at the detector at the same time (A in fig. 2.5).

$$R_E = \frac{2 \cdot \pi}{\lambda} \tag{2.9}$$

According to these considerations for the XRD-measurements presented here high beam

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Figure 2.6: Relevance of periodic meshes representing reciprocal lattice planes for interpretation of diffraction patterns

energy was chosen to image preferentially only one lattice plane at a time. Due to the actual finite beam energy in the diffraction patterns usually also reflections originating from other lattice planes are present or reflections from a specific lattice plane are only visible on one side of the pattern.

In the upper half of an acquired diffraction image the X-rays diffracted under reflection are represented, in the lower half the X-rays diffracted under transmission. On the vertical axes through the center in the upper half the X-rays reflected at the atomic plane parallel to the surface of the sample are represented, in the lower half the X-rays transmitted through the same plane. On the vertical axes.the X-rays reflected/transmitted to the left or the right of an atomic plane perpendicular to the surface can be seen. All the other positions on the detectors can be reached by reflection/transmission at any atomic planes tilted around the beam direction. But only planes containing the beam direction can contribute to the diffraction image since for all the other planes the vector q will not coincide with the Ewald-sphere (approximated as a plane within a small enough range of angle).

The previously discussed will also clarify that all the reflections visible on the detector and stemming from the same crystal(ite) have to coincide with a specific periodic mesh (see Fig. 2.6).



Figure 2.7: Mismatch between bended Ewald-sphere and flat detector. Because of the mismatch between the bended Ewald-sphere and the planar reciprocal lattice planes especially at high 2θ values some reflections are only present at the left or the right hand side of the pattern.

When the reciprocal lattice is rotated around a specific axis successively different lattice planes of the reciprocal lattice coincide with the Ewald-sphere. The result is an changing arrangement of reflections showing the symmetry of the respective lattice plane. For example for a cubic crystal turned around one of the plane normals (for example z) a quadratic diffraction pattern results when the x-y-plane coincides with the Ewald-sphere. Reversely, if not all the reflections observed in an diffraction pattern coincide with a single mesh most probably more than one crystallite is involved (compare Fig. 2.6 and section 6.7.

Since the Ewald-sphere features at a finite primary beam energy of 80 keV (beam energy used for the presented experiments) a finite radius there are several diffraction patterns showing specific reflections at high diffraction angles only on the right or left hand side of the pattern, visible for example in Fig. 2.7. For the marked reflections there is no intensity at the centro-symmetric position. As mentioned above this is a result of the mismatch between the bended Ewald-sphere and planar reciprocal space planes which also leads to the reflections in Fig. 2.6 not coinciding with the drawn meshes, since these reflections origin from other lattice planes.

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It has to be mentioned that for the cubic crystal system as for most of the other crystal systems not all thinkable reflections can be observed. There are some rules for systematic extinction of reflections^{66,67} dependent on the crystal system, the Bravais lattice,⁶⁶ and also on symmetry elements present or absent in the respective space group. For example in the cubic space-group Fm3m, Au and Cu crystallize in, the first five reflections are $\{111\}, \{200\}, \{220\}, \{311\}$ and $\{222\}$. There are for example no $\{100\}, \{110\}, \{210\}, \{300\}$ reflections.

Apart from the so far discussed border cases of a three dimensional powder-like sample consisting of millions of nano-crystallites statistically oriented leading to spherical distribution of diffracted intensity (including also rotation of the sample around an arbitrary axes) and a single crystal leading to three dimensional discrete reflections there are more options of crystalline order in a sample.

In a 2-D powder the grains are arranged pointing with a specific atomic plane vector all in the same direction, but having random orientation regarding the rotation around this vector. The effect is a high density of reciprocal lattice points on circular orbits in reciprocal space within the reciprocal lattice plane perpendicular to the direction of uniform order. When this circular orbits in reciprocal space intersect the Ewald sphere there are usually two intersection points. At the corresponding angles diffraction spots are visible. If the Ewald sphere is large enough possibly also complete circular orbits of high reciprocal lattice point density can coincide with the Ewald sphere if the sample is oriented properly.

When the statistical rotational orientation in a 2-D powder is transformed into a uniform orientation also perpendicular to the plane of order the rings of intensity start to show non-uniform intensity distribution until reaching perfect 3-D order only discrete reflections as observed for a single crystal remain. In this case the crystallites are said to show a perfect texture.⁶⁸⁻⁷⁰ Usually perfect texture of many very small crystallites is not observed. Smaller or larger deviations in one or the other direction are usually present leading to an extension of the reflection sizes in the associated direction. In fact all the transition states between perfect single crystals and perfect powders exist.

3 Technical Equipment

3.1 Sputter Deposition Facility

The sputter deposition facility used for the preparation of the thin film was a high frequency magnetron sputter deposition facility custom-made at the MPIE. It consists of two chambers, an introduction chamber for loading and unloading of substrates and the main chamber in which the sputter deposition was performed. For vacuum generation a combination of a sliding vane rotary pump and two turbomolecular pumps was used. The rotary pump delivered the pre-vacuum for both chambers while each chamber featured an own turbo pump. The two chambers were separated by a plate valve. The intro chamber consisted of a load-lock and a transfer rod featuring a sample transfer mechanism (PRE-VAC SP. Z O.O., Poland). This enabled the transport of samples prepared by sputter deposition into a glove box without contact to air. The main chamber contains a rotatable substrate holder, a separate holder for a quartz micro balance, inlets for working gas and reaction gas, if necessary, and two magnetrons for plasma generation coverable by a shutter each. The magnetrons are RF-magnetrons. Consequently the plasma is generated within a high frequency (in the range of radio frequency (RF)) alternating electric field which is superimposed by a magnetic field. The magnetic field is generated by permanent magnets mounted beneath the targets inside the target holders. A hinged window of the size CF 200 mounted at the front of the facility enables the access of the interior of the facility for cleaning and maintenance work.

The sputtering process was controlled by an INFICON IC6 deposition controller.

3.2 Electrochemical Cells - Ex-Situ Cell

The electrochemical cell employed for the electrochemical measurements in the laboratory at MPIE is shown in Fig. 3.1. At the bottom there is a base plate made from Teflon serving for better handling and electric isolation. On top of the Teflon plate a brass plate serving as sample support is screwed. At the same time the sample can be contacted via this brass support as working electrode. A ring of copper presses a Teflon hat on the

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Figure 3.1: Electrochemical cell used for the lab-based experiments presented in this work. The cell was custom-made in the MPIE workshop.

sample from above. Screws are used to connect the copper ring with the brass plate. An O-ring covered by Teflon serves for sealing between the sample and the Teflon hat to avoid the electrolyte from flowing out. The area exposed to the electrolyte inside the cell has a diameter of 4 mm. Two Li sheets contacted via special brackets serve as the reference and counter electrode.

3.3 Electrochemical Cells - In-Situ Cell

To be able to use Li as reference and counter electrode also during in-situ measurements a specially designed in-situ cell¹⁴ was used. This in-situ cell shown in Fig. 3.2 was a custom-made design developed in consultation with the workshop at the MPIE. Since this cell features for technical reasons a relatively thick Teflon wall (1 mm) it can only be used employing high energy X-rays of high intensity. The cell consists of a Teflon corpus allowing the insertion of the Teflon sample holder containing the sample from below. An O-ring seals between the corpus and the sample holder. The cell is filled with electrolyte (about 0.3 ml to yield an about 1 cm high electrolyte volume above the sample) and two Li sheets are hanged into the electrolyte serving as reference and counter electrode. The contacting of the working electrode is managed via the base plate of the cell and the reference and counter electrode are contacted via banana plugs through the cover of the cell. A further O ring seals between corpus and cover. In addition to the holes for feed-through of the contacts the cover features two additional holes to allow a purging of the cell with inert gas. It is possible to mount the cell readily in a glove box before the cell is brought to the diffractometer for measurements.



Figure 3.2: Electrochemical cell used for the in-situ XRD experiments presented in this work. The cell was custom-made in the MPIE workshop.

The design of the cell was on the one hand guided by the need to have a sufficient amount of electrolyte in contact with the sample to ensure proper electrochemical conditions avoiding running into a Li shortcoming by concentration gradients. Then the material of the cell had to be chosen adequately to be stable at the operation conditions of the cell and at the same time to show low absorption for X-rays. This issue lead to the preference of Teflon over glass. On the other hand the wall thickness of the cell at the position it will be penetrated by the X-rays was supposed to be as thin as possible. This lead to the narrow necking in the middle of the cell to make the X-ray beam pass as less material as possible in addition to the sample. All additional material in the pathway of the beam including the electrolyte reduces the intensity of the (diffracted) beam and leads to additional undesired intensities in the XRD patterns. Accordingly, to be able to penetrate the whole cell the X-ray beam had to be of high intensity.

3.4 Glovebox

The electrochemical measurements in the laboratory at MPIE were performed inside a argon filled glovebox (SYLATECH GmbH, Germany). The glovebox is equipped with to introduction chambers (a small one an a big one). In addition it features a High Vacuum (HV) attachment (PREVAC SP. Z O.O., Poland) equipped with an HV transport vessel to transfer samples from the Ultra High Vacuum (UHV) or HV facilities at MPIE (for example the sputter deposition facility (see chapter 3.1) into the glovebox or from the glovebox into the UHV/HV facilities under HV conditions or under inert gas.

The glovebox features two independent gas cleaning tracts to remove oxygen and water.

The setup of the glovebox allowed to reduce the oxygen content in the glovebox atmosphere to below 0.5 ppm and the dew point to about -120 °C.

3.5 Potentiostat

For the electrochemical measurements an Ivium Compact Stat potentiostat (IVIUM Technologies B.V., Netherlands) was employed featuring a measuring ranges reaching from -4 to +4 volts in terms of potential and from -40 mA to +40 mA in terms of current.

3.6 Synchrotron Radiation Facility

The synchrotron radiation source used for the XRD experiments was the PETRA III electron storage ring at the Deutsches Elektronen SYnchrotron - DESY - in Hamburg, Germany. PETRA III is a high brilliance 3rd Generation Synchrotron Radiation Source. It is the biggest and most brilliant storage ring light source in the world featuring a circumference of 2.3 km.

The experiments were performed at the High Energy Materials Science - HEMS - beamline P07 at Petra III. Fig. 3.3 (a) shows an aerial picture of the DESY campus with the electron storage ring PETRA III and the beamline P07 marked. The HEMS beamline P07 consists mainly of three optical-hutches to manipulate the X-ray beam decoupled from the electron storage ring and four experimental-hutches. The beamline is jointly operated by the Helmholtz-Zentrum Geesthacht and DESY. The HEMS beamline satisfies high-energy X-ray diffraction and imaging techniques. It is tunable in energy in the range from 30 keV to 200 keV and optimized for micrometer focusing. Its brilliance is 10^{18} photons per second and its energy resolution 5-250 eV at 80 keV.

The diffractometer available in experimental-hutch 2 at the HEMS beamline is a HU-BER General Purpose Diffractometer (HUBER Diffraktionstechnik GmbH & Co. KG, Germany) with theta swing tilt shown in Fig. 3.4. The diffractometer is used for the characterization of surfaces and interfaces.[?],?

The detector used for the XRD experiments was a PERKIN ELMER XRD 1621 Flat Panel 2D-detector. At an area of 41 cm x 41 cm it bears 2048 x 2048 pixels featuring a pixel size of 200 μ m x 200 μ m. The intensity saturation is reached at 65 kcts/pixel. Due to the very short readout time of 66 ms very high time resolution is achievable.

More detailed information about DESY and PETRA 3 in general and the HEMS beamline in particular can be found on the DESY-website.



Figure 3.3: Aerial picture of the DESY campus with PETRA III and P07 marked (a) and design study of the high energy materials scene beamline (HEMS) (b).

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Figure 3.4: HUBER General Purpose Diffractometer

4 Experimental

4.1 Sample Preparation

4.1.1 Substrates for Thin Film Samples

Cu served as substrate for the thin film samples since Cu does not show any electrochemical lithium insertion. Consequently it does not influence investigations at the applied Au films. For the electrochemical measurements performed in an Ar-filled glovebox (oxygen content below 0.5 ppm, dew point ca. -120° , see chapter 3.4) to avoid contact to air and moisture poly-crystalline Cu discs were used. while for the in-situ XRD measurements Cu(100) single-crystals were used. The Cu disks were ground using grinding paper of grain sizes 1000 and 2500 and polished afterwards using silica particles of 50 nm grain size in form of a basic aqueous suspension. The Cu(100) single-crystals (MATECK GmbH, Germany) were prepared under Ultra High Vacuum (UHV) conditions by sputtering and annealing.

4.1.2 Preparation of Thin Film Samples

To produce the thin films samples sputter deposition using a radio frequency magnetron sputter deposition facility (see chapter 3.1) was used. The sputtering procedure was carried out in Ar atmosphere at approximately $3.3 \cdot 10^{-3}$ mbar. The procedure was controlled by an INFICON IC6 deposition controller and carried out at room temperature. The deposition rate was 0.1 nm/s.

4.1.3 Reference and Counter Electrodes

In both cells – the ex-situ cell as well as the in-situ cell – thin Li sheets served as reference and counter electrodes. The Li needed was supplied partially by GOODFELLOW LTD., UK and partially by KISCO LTD., Japan. GOODFELLOW supplied Li straps of 99.9% purity in two different dimensions (thickness/width/length): 0.38 mm/25 mm/100 mm

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and 0.20 mm/38 mm/200 mm. The Li purchased from KISCO was delivered with dimensions of 0.4 mm/25 mm/35 m. From the Li straps the electrodes were cut by scissors. As electrodes served Li strips of the respective thickness of the Li sheets and of 2.5 to 3 cm length. To remove soiling attached to the Li strips and thin nitride and oxide layers the strips were cleaned before usage. For this purpose the Li was ground using whetstones (knife whetstones; LANSKI Ltd., USA) of grain sizes 600 (grinding material Al_2O_3) and 1000 (grinding material alumina based ceramics). The lubricant was hexane. During the grinding the Li strips were fixed from the bottom by a sapphire nail file. After cleaning in hexane the Li strips were ready to use as electrodes.

4.1.4 Electrolyte

The electrolyte employed for the electrochemical treatments of the samples within the context of the present work is based on an ionic liquid. Ionic liquids are organic salts featuring sufficiently low lattice energy to yield a melting point near room temperature. The reason for this behavior are steric effects and the high volume to charge ratio of the underlying ions. For the experiments presented here 1-Butyl-1-Methylpyrrolidinium-bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI) was employed due to its high room temperature ionic conductivity^{48–50} (see section 1.3). It consists of pyrrolidinium cations, substituted at the nitrogen atom by a methyl and a butyl group, and amide anions carrying two trifluoromethanesulfonyl groups each.

A lithium salt (lithium-bis(trifluoromethanesulfonyl)imid (LiTFSI)) was dissolved in the ionic liquid. The lithium salt supplies the lithium necessary for the operation of the LIB. The anion of the Li salt and the anion of the ionic liquid are identical. The concentration of the lithium salt was 0.3 mol per liter of ionic liquid. After mixing the components the salt was dissolved completely first by stirring, before the electrolyte was cleaned from dissolved gases such as oxygen or nitrogen and water by heating in high vacuum $(2 \cdot 10^{-6} \text{ mbar})$ for twelve hours. It is necessary to remove traces of water and air from the electrolyte since Li reacts easily with both of them (even with nitrogen!). The electrochemical treatment is in addition impaired by traces of water since water would be decomposed under hydrogen evolution at potentials above the Li-ion-reduction potential. For this reason the ionic liquid, the Li salt and the readily prepared electrolyte after heating were stored inside an argon filled glove box (see chapter 3.4).



Figure 4.1: The electrolyte used for the all the presented electrochemical treatments is based on the ionic liquid $Pyr_{14}TFSI$. Apart from the measurements presented in chapter 5.1 where only the pure ionic liquid was used in all other measurements a 0.3 M solution of the Li salt LiTFSI in the ionic liquid $Pyr_{14}TFSI$ was employed as electrolyte.

4.2 Electrochemical measurements

All the electrochemical measurements were acquired using a Ivium Compact Stat potentiostat (IVIUM Technologies B.V., Netherlands). The construction of the electrochemical cells each allowed the electrolyte to cover a spot of 4 mm in diameter of the electrode's surface.

4.2.1 Cyclic Voltammograms (CV)

The cyclic voltammograms acquired at the different model electrodes covered a potential range of 0-1 V or 0-1.5 V vs. Li/Li^+ -reference electrode. The lower potential limit of 0 V was given by the beginning of lithium deposition at the model electrode. At the upper potential limit of 1 V or 1.5 V the delithiation was considered to be completed. The rate of potential feed was 1 mV/s or 5 mV/s, respectively

4.2.2 Galvanostatic Lithiation-Delithiation

Galvanostatic lithiation-delithiation experiments were performed at currents of 16.6 μ A (1.7 C) and 1.66 μ A (0.17 C) in case of the measurements performed in laboratory at MPIE (lab-based measurements) and at 22.7 μ A, 16.6 μ A and 9.9 μ A in case of galvanostatic experiments during in-situ XRD measurements at DESY (in-situ measurements). During lithiation the currents featured negative sign and during delithiation positive sign. The lower potential limit was at 0 mV or 5 mV, respectively and the upper potential limit was

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1 V or 1.5 V, respectively.

To yield the differential charge curves from the galvanostatic measurements performed in laboratory at MPIE the difference quotient was calculated including 200 data points each for the measurement at 16.6 μ A (1.7 C) and including 2000 data points each for the measurement at 1.66 μ A (0.17 C) (compare Figs 5.11 and 5.14).

4.2.3 Galvanostatic Intermittent Titration Technique (GITT): Galvanostatic Insertion with Intermediate Potential Relaxation Periods

GITT measurements were conducted at 1.66 μ A (0.17 C). The galvanostatic periods took 1000 s and the ocp periods took 2000 s. The lower potential limit was 5 mV and the upper potential limit was 1.5 V

4.2.4 Potentiostatic Insertion

Potentiostatic lithiation-delithiation experiments were carried out employing current limits of 5 μ A and 1 μ A, respectively. Employing a current limit of 5 μ A the potential steps were 100 mV between 1.5 V and 300 mV during lithiation and between 500 mV and 1.5 V during delithiation. In the potential range below the potential steps were 20 mV. At a current limit of 1 μ A the potential steps were 100 mV between 1.5 V and 300 mV during lithiation. In the potential steps were 100 mV between 1.5 V and 300 mV during lithiation and between 500 mV and 1.5 V during delithiation. In the potential steps were 100 mV between 1.5 V and 300 mV during lithiation and between 500 mV and 1.5 V during delithiation. In the potential range below the potential steps were 100 mV between 1.5 V and 300 mV during lithiation and between 500 mV and 1.5 V during delithiation. In the potential range below the potential steps were 10 mV.

4.3 In-Situ XRD measurements

In-situ XRD measurements at P07 HEMS beamline (see chapter 3.6) at DESY were performed at a beam energy of 80 keV, corresponding to a wavelength of 0.0155 nm, at a grazing incidence angle of 0.02° in transmission mode. The angle was optimized to yield as much signal from the Au film as possible. The X-ray beam featured a width of 30-40 µm and a height of 2-3 µm. The Au sample was kept at constant position/rotation during the measurements. Only after the first lithiation the sample was moved by 0.5 mm to the right and subsequently back again and rotated in original position around the ω_s axis of the diffractometer (perpendicular to the Huber tower, see Fig. 3.4). For data acquisition a 2D detector (PERKINS XRD 1621 (see chapter 3.6)) was used. For justification of the sample a common point detector was used.



Figure 4.2: Electrochemical cell for in-situ XRD measurements mounted on the diffractometer and connected to potentiostat and argon supply.

The communication with the hardware was managed by Tango servers providing a standardized interface for a custom made client called "online". The image acquisition and radial intensity integration to yield 1-D diffractograms from the 2-D diffraction patterns was executed by the QXRD software.⁷¹

5 Electrochemical Characterization of an Au Thin Film Model Anode

This work focuses on the evaluation of structural changes associated with alloying and dealloying processes during lithiation-delithiation cycling of Au thin film model electrodes. First lab-based electrochemical characterization of a Au film model electrode will be presented in the present chapter. In chapter 6 the in-situ XRD measurements during galvanostatic treatment of a Au film will be described.

Lab-based electrochemical characterization of a Au film model electrode were performed in addition to the in-situ electrochemical treatment to characterize the model system electrochemically in more detail. Important conclusions also substantiating the correlation between electrochemistry and structural changes in the electrode material will be drawn from the lab-based electrochemical characterization.

First CVs of the sample in contact with pure ionic liquid ($Pyr_{14}TFSI$) were acquired to test out the electrochemical window of the ionic liquid.

In a second step the pure ionic liquid was replaced by a 0.3 M solution of the Li salt LiTFSI in the ionic liquid $Pyr_{14}TFSI$ to examine the lithiation-delithiation cycling behavior of the Au thin film anode.

For a more detailed characterization of the Au film as anode in LIBs purely galvanostatic measurements, galvanostatic measurements with intermediate relaxation time (Galvanostatic Intermittent Titration Technique, GITT) and potentiostatic measurements were performed.

5.1 Cyclic Voltammograms in Absence of Li-Salt

Figure 5.1 shows a CV of an Au thin film on a Cu substrate. The ionic liquid $Pyr_{14}TFSI$ was utilized as electrolyte without addition of the Li salt LiTFSI (which will be added later to perform lithiation experiments). The potential scan rate was 1 mV/s and the potential range tested reached from 0 V to 4 V versus Li/Li⁺. Lowering the potential starting from 2 V the measured current remained at almost zero micro ampere in the



Figure 5.1: Cyclic Voltammogram of the Au-thin-film-electrode in the ionic liquid $Pyr_{14}TFSI$ without the presence of the Li salt LiTFSI. The scan rate was 1 mV/s. At 0.45 V in cathodic direction the current increases (range A). The electrolyte starts decomposing, the limit of the electrochemical window of $Pyr_{14}TFSI$ is reached. In anodic direction there are no considerable electrochemical processes between 0.45 V and 3 V (range B). At higher potential (range C) there is a current peak at 3.50 V assignable to Cu oxidation (Cu $\rightarrow Cu^{2+}$) (peak C1) and another one assignable to electrolyte decomposition (peak C2). After returning to cathodic current direction at 3.30 V there is a current peak (peak C1') due to Cu ion reduction. In conclusion $Pyr_{14}TFSI$ offers a large electrochemical window of about 3.1 V (0.45 V to 3.55 V), but the electrochemical window of the pure ionic liquid does not reach to the potential range Li insertion in Au is expected to occur in (0.25 V to 0 V).

range between 2 V and 0.5 V (range B in Fig. 5.1). At 0.45 V a cathodic current arose and stayed sharply increasing until the reversal potential (0 V) was reached (range B in Fig. 5.1).

After reversing the direction of potential sweep the current decreased again without considerable hysteresis. The current peak very close to the Li/Li⁺ potential resulting from this behavior is assigned to electrochemical decomposition of the electrolyte $Pyr_{14}TFSI$. During subsequent current evolution while changing the potential in anodic direction no further electrochemical processes could be detected between 0.45 V and 3 V vs. Li/Li⁺ (range B in Fig. 5.1). No current peaks were observed in the CV in this potential range. Only when a potential of 3.4 V was reached the current started to rise (range C in Fig. 5.1). With increasing cycle number a sharp peak gained in intensity at 3.5 V (peak C1). This potential is close to the potential of Cu oxidation at 3.3852 V vs. Li/Li⁺. At 3,6 V the current starts increasing again resulting in another current peak at 3.8 V (peak C2). After some cycles the maximum intensity of the peak at 3.5 V gets smaller again. Instead the broader peak at 3.8 V gains in intensity.

Starting from the eighth cycle the ratio of integral peak current and the peak shape stays constant for both peaks. At 4 V the potential is switched to cathodic direction again. It becomes directly evident from the shape of the current evolution at the beginning of the cathodic branch that the peak at 3.8 V is assigned to an irreversible process, maybe to some decomposition of the electrolyte. No negative current peak attributable to a corresponding reduction process can be found. At 3.3 V there is a peak (peak C1') identifiable to be caused by the reverse reaction to the reaction provoking the peak at 3.5 V in the anodic branch. The mean of the peak positions in anodic and cathodic branch is 3.4 V which is quite close to the potential of $Cu \leftrightarrow Cu^{2+}$ transition (3.3852 V vs. Li/Li⁺). From this it can be concluded that the two associated peaks at 3.5 V and 3.3 V origin from reversible Cu oxidation and Cu^{2+} reduction. Obviously the Au film on the Cu substrate is not completely closed.

The relative large distance of 200 mV between the two associated peaks is striking to note. The simple case where the current in the CV is determined by the coupling of diffusion of reactive species to the electrode surface and an electron transfer process at the surface is assumed. If the electron transfer step would be fast, the distance between oxidation and reduction peak would supposed to be 57/n mV.[?] In the present case it is with 200 mV obviously much larger. This observation points to slow electron transfer. The Matsuda's number could be found to be 0.206 by interpolation of experimental data.[?] According to this finding the velocity of electron transfer is in the intermediate regime.

There is no further current peak in the cathodic branch until the decomposition of the

electrolyte starts again at 0.45 V ⁺(range B in Fig. 5.1). According to the observations made from Fig. 5.1 and presented in this paragraph the electrochemical window of the pure $Pyr_{14}TFSI$ ionic liquid electrolytes can be determined to reach from 0.45 V until 3.6 V comprising a voltage range of about 3.1 V. However it does not reach to the potential range Li insertion in Au is expected to occur in (0.25 V to 0 V, see below).

5.2 Cyclic Voltammograms in Presence of Li-Salt

After the pristine Au film was evaluated by CV the pure $Pyr_{14}TFSI$ ionic liquid electrolyte was replaced by an 0.3 M solution of the lithium salt LiTFSI in $Pyr_{14}TFSI$. The presence of Li-ions also in the electrolyte will promote the Li insertion into the Au-film, since it assures Li-ions to be present in direct vicinity to the Au-surface. Utilizing the Licontaining electrolyte the CV measurements (as described in chapter 5.1) were repeated limiting the scanned potential range to 0 V to 1.5 V.

Single Reduction Current Peak - Increase of Current at Reversal Potential

Figure 5.2 displays cyclic voltammograms within a potential range between 0 V and 1.5 V versus Li/Li⁺ acquired at a potential scan rate of 1 mV/s. Starting from 1.5 V in cathodic direction the current remains negligible until around 200 mV (Only very small capacitive currents prevail.). When lowering the potential further (range A in Fig. 5.2) a steep increase in cathodic current is observable enduring until the lower reversal potential is reached. The absolute value of current flowing at the lower reversal potential (0 V) increases significantly from the first to the eighth cycle. The largest difference in current flowing at the lower reversal potential (0 V) is between the first (27.4 μ A) and the second (47.5 μ A) cycle. In the cycles subsequent to the eighth cycle the absolute value of current stays roughly at the value of the eighth cycle.

Single Reduction Current Peak - Change from Positive to Negative Hysteresis

Furthermore within the first three cycles a change in hysteresis behavior can be distinguished from "positive" to "negative". In the first cycle (peak A1) a pronounced positive hysteresis can be observed. After reversing the scan direction the measured current continues increasing until at 32 mV in anodic direction a maximum of -30 μ A is reached. During the second cycle in contrast to the first cycle in range A the current is almost



Figure 5.2: Cyclic Voltammogram (CV) of the Au-thin-film-electrode in the ionic liquid Pyr₁₄TFSI in presence of the Li salt LiTFSI. The scan rate was 1 mV/s. Starting from 1.5 V in cathodic direction the current remains negligibly until around 0.2 V. Lowering the potential even more a steep increase in cathodic current is observable (range A). When the reverse potential of 0 V is reached a high cathodic current is established. Driving the potential in anodic direction three positive current peaks occur at 0.26 V, 0.41 V and 0.58 V (peak B1, B2, B3). So in contrast to 5.1 there are anodic processes observed in the low voltage region (range B). It is assigned to Li dissolution from Li alloys formed during the cathodic branch of the CV. Above 0.8 V there are no significant electrochemical processes observed (range C). Interestingly the ionic liquid clearly does not start to decompose at 0.45 V in the cathodic branch. Hence obviously the addition of the Li salt widens the electrochemical window of Pyr₁₄TFSI to cover the potential range of Li insertion and enables thereby its use as electrolyte for LIBs.

identical in behavior in cathodic and anodic scan direction - no hysteresis is observed. The third cycle already shows a negative hysteresis. In anodic direction the current is lower than in cathodic direction at the same potential. The negative hysteresis gets more pronounced until the eighth cycle and remains for the subsequent twelve cycles measured.

Three Oxidation Current Peaks - Shift in Peak Potential

In the anodic branch there are three peaks in the current potential curve (range B in Fig. 5.2). One at 0.268 V (peak B1), another one at 0.412 V (peak B2) and the third one at 0.584 V (peak B3). The three peaks occur due to three different oxidation processes. Three different mechanisms of Li-Au dealloying can be concluded from this, for example the dissolution of three different Li-Au alloy phases. Also for the three oxidation peaks there is an increase in peak current with cycle number similar to the behavior observed in the cathodic branch near the lower reversal potential. At the same time the peak positions shifts slightly to more positive potentials. Raising the applied potential to more positive values no further peak occurs in the anodic branch (range C in Fig. 5.2).

General Conclusions

The CV measurements showed one a single reduction peak suggesting only one phase transformation to be involved in the alloy formation. Three oxidation peaks occurred in the CV pointing to three different phase transformations involved during dealloying. All the current peaks present in the CV are attributed to the lithiation and delithiation of the Au thin film. In consequence the CV measurements point to different mechanisms of lithiation and delithiation.

In comparison with the CV measurements without addition of the Li salt LiTFSI the addition of LiTFSI turned out to widen the electrochemical window of the ionic liquid $Pyr_{14}TFSI$ enabling the process of Li-Au alloy formation. In the CV there is no decomposition of the electrolyte starting at 0.45 V in cathodic direction detectable anymore. Instead the electrochemical stability window extends to the region in which Li insertion is expected (0.25 V to 0 V).

The observations from Fig. 5.2 will be discussed in more detail in section 5.3.



Figure 5.3: Hysteresis upon Li insertion (alloy formation) into the Au thin film. Fig. 5.3 (a) shows the potential region around the lower potential limit of the CV (0 V) from Figure 5.2 in more detail. Note that the x-axis is scaled differently than the x-axis in Fig. 5.2. The direction of potential sweep is marked by the arrow. For the sake of clarity the potential scale is adapted. The deviation from ideal behavior (symmetrical current evolution with respect to lower reversal potential (0 V)) and the transition from positive to negative hysteresis becomes clear. Fig.5.3 (b) shows the same curves than Fig. 5.3 (a) but normalized to 1 a.u. at the lower reversal potential. Note that absolute values of current are given. The uniform evolution of current in the cathodic branch points to an independancy of the limitation behavior on the current.

5.3 Discussion: Cyclic Voltammograms in Presence of Li-Salt

In Fig. 5.3 (a) the region of the CV of the Au film around the lower reversal potential (range A in Fig. 5.5) is plotted for the cathodic branch (from 0.3 V to 0 V vs. Li/Li^+ on the left part of the plot) and the anodic branch separately (0 V to 0.3 V on the right part). Fig. 5.3 (b) shows the same excerpt as Fig. 5.3 (a), but the current at the reversal potential of 0 V is normalized to 1 (in arbitrary units (a.u.)) for each CV. Note the different scaling of the axes in comparison to Fig. 5.5.

Difference in Onset-Potential of Reductive Current Peak in the First and the Second CV

From Fig. 5.3 the significant difference in curve shape between the first and the subsequent CVs becomes apparent. In the first CV the reductive current starts increasing considerably at about 100 mV while in the subsequent cycles the increase of reductive current occurs from roughly 200 mV.

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To explain this behavior two possible reasons are considered.

One reason refers to SEI-film formation. At the beginning of the first CV there is not any SEI-film present. It is formed during the first cathodic branch of the CV for the first time. Several researchers reported about the capability of the SEI-film to enhance the Li insertion into the electrode material by lowering the lithiation potential. Hence before the Li insertion can start to a high extend the SEI-film has to be formed. If the SEI-film formation would start only around 100 mV also enhanced Li insertion could only be observed below this potential threshold. In contrast to the first CV in the second CV the SEI-film is already present and Li insertion can start already at higher potential.

Another possible reason for the different starting potential of the cathodic current increase could be associated to the observation from the XRD-experiments presented in chapter 6.5 that in the first cycle Au is the starting material for lithiation while after delithiation no Au is recovered anymore. Hence in the subsequent cycles another material probably a Li-poor alloy phase is the starting material for lithiation possibly enabling Li insertion already at higher potentials.

Based on the fact known from the XRD-measurements, that the material present at the beginning of the first and the second cycle are not identical the second reason is favored. Nevertheless the first reason may also contribute to some extend to the observed difference in onset-potential for the reductive current peak in the first and the second cycle.

Significant Increase of Current at the Lower Reversal Potential during the First Eight CVs

From Fig. 5.3 (a) also the above mentioned significant increase of current at the lower reversal potential during the first eight CVs becomes apparent. This phenomenon could be attributed to crack formation during cycling as observed at different anode materials and geometries before.^{4,12,19–21} Crack formation in the electrode material of LIBs is assigned to mechanical stress applied to the electrode material during the lithiation-delithiation process, since the lithiation process is accompanied by large volume expansion of the host material. The problem of crack formation by volume expansion is most prominent in the case of Si which undergoes a very high volume expansion of about 400%⁴ to reach the final composition of Li₁₅Si₄. Also in the case of Au the volume expansion due to Li insertion is considerable. Assuming a final composition of Li₃Au (a₀= 0.6302 nm⁷²) (compare section 6.7) the unit cell of Au (a₀= 0.40784 nm) has to widen by 369%. The stresses occurring during this huge expansion will presumably also result in crack formation in the case of the Au film. Crack formation increases the Au surface in contact with the electrolyte. During the first cycle the increase of surface area due to crack formation can be assumed



Figure 5.4: Efficiency of alloying/dealloying during CVs. The curve "lithiation" denotes the integral of the current flown during Li alloying in the CVs of Figure 5.2. The curve "delithiation" represents the integral of the current flown during Li dealloying in the CVs of Figure 5.2. The curve "efficiency" gives the alloying-dealloying efficiency (charge converted during delithiation divided by the charge converted during lithiation) for each cycle. The charge converted during lithiation and delithiation increases pronouncedly within the first five cycles and continues to increase slowly until the 20th cycle. The efficiency increases largely during the first eight cycles.

to be the largest, since an relatively homogeneous and dense Au film has to be penetrated by the Li atoms. During the following cycles the surface area newly formed by further crack formation will decrease until the surface area in contact with electrolyte will be nearly constant.

The above discussed effect of crack formation in the electrode material accompanied by increasing surface in contact with the electrolyte can be used to explain the observed behavior of increasingly larger reductive current in general and increasingly larger absolute values of current at the lower reversal potential limit in particular during the first eight CVs.

Lithiation-Delithiation Efficiency

Fig. 5.4 shows the integrals of the lithiation and delithiation currents from the CVs (Fig. 5.2) in dependance of the cycle number. It corresponds to the charge turned over during lithiation and delithiation.

The amount of charge turned over in the lithiation process (curve "Lithiation" in Fig. 5.4), increased within the first three cycles almost to the double amount. Hereinafter it keeps increasing, but only very slightly at least until the 20th cycle. The amount of

charge turned over in the delithiation process (curve "delithiation" in Fig. 5.4) is in the first cycle $(1.72 \ \mu\text{C})$ only about one third of the charge turned over in the alloying process $(6.62 \ \mu\text{C})$, suggesting a very bad coulombic efficiency (curve "efficiency" in Fig. 5.4) of the lithiation-delithiation reactions (27%). Much more charge is converted in the alloying than in the dealloying process. Within the first five cycles the charge turned over in the dealloying process increases to around the five fold value of the first cycle (9.23 μ C). It keeps increasing and from the 11th cycle it increases almost parallel to the charge turned over in the alloying process.

As mentioned above in the first cycle the coulombic lithiation-delithiation efficiency curve "delithiation" in Fig. 5.4) is only 27%. The efficiency becomes apparently significantly better during the first eight cycles. Until the 20th cycle it still improves slightly to yield an efficiency of 97.4% in the 20th cycle. Nevertheless it should be noted here that an accepted requirement for an anode material of technological relevance should be an alloying-dealloying efficiency of 99.5-99.9%.

The total alloying-dealloying efficiency during the first 20 cycles is only 83%. If the charge turned over would be completely associated to lithiation and delithiation a total alloying-dealloying efficiency of 83% would mean a Li accumulation of two equivalents of Li during the presented 20 CV cycles. An accumulation of two equivalents of Li would mean to "cycle" the Au film between the compositions Li_2Au and Li_3Au in the last cycles.

This scenario is, however, not realistic. On the one hand the CV cycles look qualitatively very similar from the third to the 20th cycle. In the anodic branch clearly the same peaks occur. Hence also the dealloying processes occurring are supposed to stay the same during all 20 cycles. On the other hand the subsequently measured galvanostatic lithiation-delithiation current-time curve (see chapter 5.4) is very similar to the current-time curve of an unlithiated sample. With this (almost) all the Li inserted in the respective cathodic branches of the CVs is supposed to get extracted during the anodic branch. Consequently the reason for the low lithiation-delithiation coulombic efficiency especially in the first cycles is of another origin.

Here a phenomenon extensively discussed but not understood so far in detail for all electrode/electrolyte interfaces especially not for the electrode/electrolyte interfaces under discussion here comes into consideration. The Solid Electrolyte Interphase (SEI) (see chapter 1.4).

SEI Formation

The SEI is an interface layer between the electrode surface and the electrolyte formed by partial decomposition of battery electrolyte in presence of Li.⁵¹ Numerous studies focused on SEI layers for different electrode materials and electrolytes, mainly classical LIB electrolytes (mixtures of organic carbonates with addition of Li salt and different additives).^{51,73} Zhang et al. reported about their investigations on SEI film formation on graphite electrodes and observed the SEI-film formation taking place in two mayor stages. The first stage takes place before lithiation actually starts. The result is a loose, highly resistive film. The second stage occurs in the potential range where lithiation takes place. The two processes occur simultaneously. In the second state a stable, compact and highly conductive SEI film is produced.²⁶

The first stage of SEI-film formation is represented in Fig. 5.5. Fig. 5.5 shows a zoomin from Fig. 5.2. A small peak in the CV at 550 mV in cathodic direction (compare¹⁸) becomes apparent most pronouncedly in the first cycle, but it is detectable also in the subsequent cycles. Obviously the SEI-film formation process is not limited to the first cycle. Also in the subsequent cycles SEI-film formation occurs, but to a smaller extend.

More difficult to separate is the second part of the SEI-film formation process, since it is superimposed by the lithiation processes. But the second part of SEI-film formation can be used to explain the observed bad alloying/dealloying efficiency in the first cycles and the difference between the apparently remaining two equivalents of Li in the anode material after the CVs suggested by the above presented efficiency calculations and the Li content of approximately zero concluded from the shape of the successive first galvanostatic currenttime curve.

Taking into account the necessity of SEI-film formation, the observed high irreversible capacity can be attributed to SEI-film formation.

Continuation Lithiation-Delithiation Efficiency

In the first cycle the SEI-film formation obviously claims the highest fraction of the cathodic current. It is not surprising to find the fraction for SEI-film formation the highest in the first cycle since before the first cycle there is no SEI-film present at all and the SEI-film has to be established newly. Consequently the irreversible capacity is the highest. Further SEI-film formation in the second and subsequent cycles is also expectable considering assumed crack formation during Li insertion. Crack formation during Li insertion was observed at a lot of electrode materials during lithiation / delithiation.^{4,12,19-21} Due to crack formation (compare above) new surface area can be expected to be created which has to be covered by SEI-film newly formed in the second and subsequent cycles. The shrinking of amount of surface area newly formed by crack formation explains the decreasing current consumed for SEI-film formation in the subsequent cycles. In consequence the lithiation-delithiation efficiency increases. After about eight cycles the surface



Figure 5.5: Zoom-in to the CVs presented in Fig. 5.2. At about 560 mV a small peak is observable in the cathodic branch. In accordance with the works of Zhang et al.²⁶ and Chan et al.¹⁸ this peak is attributed to the first stage of SEI-film formation.

is in a almost stable state. Only very few new cracks are formed, only very little new surface is exposed to the electrolyte and the delithiation efficiency reaches 97.4% in the 20th cycle.

Concluding the above discussed considerations with respect to the fact that the lithiationdelithiation efficiency was found to start at very low level in the first cycle and ameliorate significantly within the first eight cycles, the just described behavior is probably explainable by the formation and maintenance of the Solid-Electrolyte Interphase (SEI).

Three Different Delithiation Processes in the Anodic Branch

As shown in Fig. 5.6 (a) in the anodic branch three peaks show up at different potentials and different intensities. The first peak at 0.268 V (peak B1 in Fig. 5.6) features the smallest intensity, the second peak at 0.412 V (peak B2) medium intensity and the third peak at 0.584 V (peak B3) the highest intensity. The simultaneous increase of the integral peak current for all three peaks within the first eighth cycles can be attributed in analogy to the increase of cathodic current at the reversal potential to an increase of electrode surface in contact with the electrolyte due to crack formation (see above).

The number of peaks visible points to three different states of delithiation maybe assignable to three different alloy phases passed through during delithiation, each of them related to a specific potential. The phase transition at the highest potential consumes the highest amount of charge since the integral of the corresponding peak is the largest.



Figure 5.6: The three oxidation peaks in the CVs (see Fig. 5.6 (a)) show an increasing amount of charge converted in the underlying oxidation processes within the first eight cycles. The integral of the curves and the peak current increases. At the same time there is a shift in peak potential within the first eight cycles observable. Plotting the peak current in dependance of the peak potential for the first five cycles (quadratic spots (CV) in Fig. 5.6 (b)) yields for every oxidation peak a linear dependance. For the first peak there are less data points since the first peaks comes out clearly only from the third cycle on. The circular spots represent the current-potential couples from the differential charges curves (DC) assigned to the delithiation plateaus of the galvanostatic lithiation-delithiation measurements (see Figs.5.10 and 5.12). They almost coincide with the regression lines through the data points extracted from the CV. This finding underlines a good correlatability between the two types of measurements. Probably in both measurements the same alloy phases are dissolved.



Figure 5.7: Fig. 5.7 (a) shows the potential region around the lower potential limit of the CV (0 V) from Figure 5.2 normalized to a current of 1 a.u. at the lower potential limit known from Fig. 5.3 (b). During the increase of reductive current three regions (1, 2, 3) characterized by different slopes can be distinguished maybe attributable to three different processes of alloy formation. Fig. 5.7 (b) shows the plot known from Fig. 5.3 (a), but with all current-potential curves normalized to the same rising point of current.

Accordingly a large amount of material undergoes this phase transformation since a large amount the starting material for this phase transformation is obviously present. In contrast the phase transformation at the lowest potential consumes the lowest amount of charge because probably only a little of the starting material for this phase transformation is present. For the middle peak the argumentation is analogous. From the previous consideration the three alloy dissolution peaks may be concluded to origin from dealloying of different alloy phases with different Li content.

Three Different Lithiation Processes in the Cathodic Branch

Hints to the occurrence of three different alloy phases are also observable in the cathodic branch of the lithiation region. Fig. 5.3 (b) and Fig. 5.7 (a) show the same data as Fig. 5.3 (a) but normalized to a current of 1 a.u. at the reversal potential of 0 V. From the third cycle on all the cathodic branches of the normalized current-potential curves equal each other. The almost identical curve evolutions suggest the lithiation process in the cathodic branch to proceed in the same way starting from the third cycle despite the considerably different absolute value of currents (see Fig. 5.3 (a). This is understandable attributing the increasing current to increasing surface due to progressing crack formation (see above).

However, the cathodic increase in current is not linear with increasing potential as it could be expected for a simple deposition process of Li on the Au surface. Rather during

5.3 Discussion: Cyclic Voltammograms in Presence of Li-Salt



Figure 5.8: Scheme of the proposed process of lithiation during CVs. As result of increasing Li diffusion resistance of the three involved alloy phases and the forced potential feed not the complete sample is lithiated, but only the surface-near region. This lithiated surface-near region contains probably the three alloy phases of different Li content in a layered arrangement.

the cathodic increase in current three regions featuring different slopes are distinguishable. These regions are marked in Fig. 5.7. Interestingly the rate slows down approaching the lower potential limit of 0 V. (see Fig. 5.7). In the beginning of the cathodic increase in current the current increases linearly as expected. The tangent is at constant high slope during a potential range of approximately 80 mV. Then there is a transition to a potential regime where the slope is again constant, but at smaller value than before. Before the potential reaches 0 V another change in slope of the tangent is observable.

The observation of the three potential ranges featuring different constant slopes is obviously independent on the total current flowing, since the normalized current evolution with potential (Fig. 5.3 (b) is identical from the third to the eight and even to the 20th cycle. From this the reason for the behavior observed can be assumed to origin from the sample itself and not from diffusion phenomena in the electrolyte. Perhaps during alloy formation the uptake rate of Li decreases due to alloy phase formation. If the alloy phases show Li diffusion properties different from Au (here in particular smaller than Au) a behavior as the observed one could be explained. At the electrode's surface at different potentials different alloy phases are formed showing different Li diffusion properties. In the present case the Li diffusion would have to be the smaller the higher the Li content of the respective alloy phase is.

It has to be noted that in the first cycle there are no different regions characterized by different slopes. The increase seems to be just linear. Maybe in the first cycle starting from pure Au and featuring only low amount of inserted Li according to Fig. 5.4 only one phase transformation is involved in the lithiation process.

Taking into account results from the XRD-measurements presented in chapter 6.3 and 6.5 proving that during CVs only a small volume of the Au thin film was lithiated and considering additionally the above discussed observation that during the three delithiation peaks different amounts of charge are converted the following scheme of the lithiation process during the third to 20th CV is proposed:

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When the potential undercuts the potential for the formation of the lowest lithiated alloy phase this phase is formed starting at the surface and proceeding into the Au-film. However, before the complete film is converted into the lowest lithiated alloy phase the potential has been lowered due to the set constant potential feed of 1 mV/s to a potential the formation of the medium lithiated alloy phase is enabled. In consequence at the surface the Li content gets higher, but the lithiation front of the first phase slows down proceeding into the film. The smaller slope in region 2 in Fig. 5.7 points to higher resistance for Li diffusion in the newly formed medium lithiated alloy phase moderating the insertion of further Li. During the medium lithiated alloy phase proceeds growing into the film the potential is lowered further and reaches the potential the highest lithiated alloy phase can start to grow at also beginning from the surface. Fig. 5.7 (a) suggests the highest lithiated alloy phase to have a even higher resistance for Li diffusion, since region 3 is characterized by an even smaller slope of the current-potential curve.

In Fig. 5.8 a scheme of the process of lithiation during CVs is proposed. According to Fig. 5.8 the result of the proposed process is a lithiation only in the surface near region of the Au film. The lithiated region consists of subsequent layers of the three different alloy phases.

Continuation: Three Different Delithiation Processes in the Anodic Branch

According to the proposed scheme for lithiation during the CV not the complete electrode material is in the highest state of lithiation. During delithiation the transition from the highest state of lithiation to a medium state of lithiation is thus underrepresented. The highest state of lithiation transforms during the first delithiation peak probably into the medium state of lithiation. Together with the amount of material already in the medium state of lithiation (see Fig. 5.8 there is more starting material for the second phase transformation than for the first phase transformation and the peak is accordingly larger. The argumentation for the second peak can be extended to the third peak resulting in an even bigger charge turned over in the third peak.

Concluding this paragraph the delithiation process can be assumed to occur reversing the steps involved in the lithiation process.

From Fig. 5.6 (a) moreover, a shifting of the peak positions of all the three oxidation peaks to higher potentials is observable during the first eight cycles. The shift goes along with a gain in peak current. Taking into account also the results of the discussion of Figure 5.15 (see section 5.6) there seems to be a linear dependency of the peak potential on the current flowing at the respective peak potential marked out in Figure 5.6. Hence
the peak potential in Figure 5.2 and the insertion or extraction potential in Figure 5.15 are dependent of the current flowing.

This finding reminds to the general current-potential diagram for electrolysis. The potential deviates from equilibrium potential while current is flowing but after the overpotentials are overcome there is a approximately linear correlation between current and potential. When plotting the plateau potentials installing during galvanostatic lithiation/delithiation at lithiation currents of 1.68 C and 0.168 C, respectively, into Figure 5.6 they occur to lay on straight lines parallel to the ones obtained from the CV; only a little shifted to lower potentials.

Aspects of SEI-film formation

Discussing Fig. 5.3 (a) and Fig. 5.6 (a) the increasing current at the lower reversal potential limit and the increasing integral oxidation-current during the first eight cycles was assumed to be caused by crack formation and accompanied gain in electrode surface in contact with the electrolyte. Interpreting the evolution of coulombic lithiation-delithiation efficiency by means of Fig. 5.4 SEI-film formations was assumed to be present in the potential range of Li insertion leading to the observed small coulombic efficiency in the first cycles.

Discussing the cathodic branches of Figs. 5.3 and 5.7 the alloy phase formation during lithiation was concluded to proceed in the same way during all the CV cycles from the third cycle on, since the normalized current-potential curves coincide. In consequence so far no concrete difference in the reductive current-potential curves (Figs. 5.3 and 5.7) attributable to considerably different contribution of SEI formation within the first eight cycles has been specified.

During the anodic branch of the CV, however, the reductive current potential curves in Fig. 5.9 (a) and 5.3 (b) differ significantly within the first eight cycles. From the third to the eighth cycle there is a successive decrease of charge turned over during the anodic branch of the CV apparent. Since the difference during the anodic branch of lithiation is the only difference between the current potential curves in Fig. 5.3 (b), starting from the third cycle, the anodic branch is the only regime where differences in SEI-film formation could be concluded to occur. To quantify the differences the curves in Fig. 5.3 (b) were integrated and the integrals were normalized to the integral of cycle 9, since at cycle 9 the coulombic efficiency has reached a almost constant level. Table 5.1 shows the results of integrating and normalizing.

In the second cycle for example 1.35 times the amount of current is converted during lithiation in comparison with the 9^{th} cycle. Assuming the normalized amount of charge



Figure 5.9: Aspects of SEI formation. Fig. 5.9 (a) shows the same plot as Fig. 5.3 (b).
Fig. 5.9 (b) is similar to Fig. 5.4. The curves "lithiation" and "delithiation" are known from Fig. 5.4 and represent the amount of charge converted in the reductive peak in CV (lithiation) and the oxidative peak (delithiation). The normalized curves in Fig. 5.9 (a) differ only in the anodic branch. This difference is assigned to SEI formation. According to the argumentation in the text it is possible taking this SEI-film formation into account to approach the "lithiation" curve in Fig. 5.9 (b) starting from the "delithiation" curve.

anodic branch (see text and Figs. 5.3 (b) and 5.7) assigned to the different in integral of the curves in Fig. 5.3 table 5.1 gives the ratio of the integral of the current potential curve of cycle n to the one of cycle 9. Cycle 9 taken as reference since from the 9th cycle the ratio between the integral of reduction peak and the oxidation peaks is almost constant at about 92%.	Table 5.1: SEI-film formation. Assuming the SEI-film formation only occurring within the
in integral of the curves in Fig. 5.3 table 5.1 gives the ratio of the integ of the current potential curve of cycle n to the one of cycle 9. Cycle 9 taken as reference since from the 9th cycle the ratio between the integral of reduction peak and the oxidation peaks is almost constant at about 92%.	anodic branch (see text and Figs. 5.3 (b) and 5.7) assigned to the difference
of the current potential curve of cycle n to the one of cycle 9. Cycle 9 taken as reference since from the 9th cycle the ratio between the integral of reduction peak and the oxidation peaks is almost constant at about 92% .	in integral of the curves in Fig. 5.3 table 5.1 gives the ratio of the integral
taken as reference since from the 9th cycle the ratio between the integral of reduction peak and the oxidation peaks is almost constant at about 92% .	of the current potential curve of cycle n to the one of cycle 9 . Cycle 9 is
reduction peak and the oxidation peaks is almost constant at about 92% .	taken as reference since from the 9th cycle the ratio between the integral of the
1 1	reduction peak and the oxidation peaks is almost constant at about 92% .

cycl. no.	1	2	3	4	5	6	7	8	9	10
area ratio		1,350	1.293	1.209	1.333	1.078	1.039	1.007	1.000	1.006
cycl. no.	11	12	13	14	15	16	17	18	19	20
area ratio	1.020	1.029	1.032	1.034	1.035	1.036	1.034	1.032	1.030	1.027

used for Li reduction is considered to be constant, in the second cycle 35% of it is additionally consumed for SEI-film formation. The percentage of current used for SEI-film formation can be analogously read out from table 5.1 for the other cycles.

Even at higher cycle numbers the coulombic efficiency is not 100% according to Fig. 5.4. For example in the 9th cycle it is 92%. For this reason generally a difference between the amount of charge converted during lithiation and delithiation, has to be taken into account. The difference is assumed to occur due to "maintenance" of the SEI-film (see above). In this approach this difference is assumed to be expressed by a fixed ratio approximated by the ratio between the charge converted during lithiation and delithiation in the 9th cycle. Consequently this assumption allows to estimate from the total amount of charge converted during lithiation (curve "delithiation" in Fig. 5.4) the "quasi ideal" total amount of charge converted during lithiation (without contributions of emergent of SEI-film) by multiplication of the total amount of charge converted during delithiation in each cycle by this factor. The result is graphically displayed in Fig. 5.4 (b) (curve "quasi ideal lithiation"). Multiplication of this "quasi ideal" total amount of charge converted during lithiation is obtained represented by the curve "quasi real" total amount of charge converted during lithiation is obtained represented by the curve "quasi real" total amount of charge converted during lithiation is obtained represented by the curve "quasi real" in Fig. 5.4 (b).

The curve "quasi real" is at higher cycle number similar to the curve "lithiation" representing the measured amount of converted charge. Only in the first three cycles there is a still a significant discrepancy (the blue curve could not be calculated for the first cycle, since in the first cycle the current potential curve is significantly different from the curve in the 9th cycle, the other current potential curves were normalized to). This observation may suggest other processes than SEI-film formation taking place during the first three cycles. For example reactions between Li and the cell material are of relevance at the beginning of the experiment expressed by an observed turning brownish black of the cell walls. Also shortcomings in the assumptions made for the presented estimation can have effect here.

Conclusions

Concluding the previous chapter the CV measurements suggested a different starting material for lithiation in the first and the subsequent cycles by a shift in onset-potential of the cathodic current. Expressed by the observed increase of absolute value of reductive current at the reversal potential and the increase of total reductive current crack formation accompanied by an increase of electrode surface is probably of importance in the case of the Au thin film electrode. SEI formation occurring in two different steps^{26,57} probably

also proceeds in the system investigated influencing the lithiation-delithiation efficiency calculated from total reductive and oxidative current. Interestingly the measured CVs gave rise to the assumption that the second step of SEI formation only occurs in the anodic branch of the CVs. Mechanistically clearly the presence of three different phase transformation during delithiation could be observed. During lithiation three analogue phase transformation could be anticipated.

5.4 Conventional Galvanostatic Lithiation-Delithiation Cycles I

After getting an overview where electrochemical processes occur in the tested potential range by CV measurements (see section 5.2) the Li insertion into the Au thin film (100 nm) electrode material (lithiation) and extraction of Li from the formed Li alloy(s) (delithiation) were investigated in more detail by galvanostatic lithiation-delithiation cycle experiments (see chapter 2.1.2 for an introduction to the technique). Therefore a constant current was applied by adjusting the potential of the working electrode with respect to the potential of the reference electrode in a way keeping the flowing current constant at the set value. During the so called lithiation half-cycle the current is negative. At the anode reduction occurs. After reaching the lower potential limit the delithiation half-cycle begins characterized by positive current. At the anode oxidation occurs.

First a higher current of 1.7 C (16.6 μ A) was chosen for the galvanostatic lithiationdelithiation cycle experiments. The C-rate refers to a final alloy composition of Li₃Au after complete loading. Li₃Au was taken as reference because Li₃Au was found to be the highest lithiated phase observed in the in-situ XRD investigation of Li insertion into an Au thin film model electrode presented below. (see chapters 6.5 and 6.7).

Fig. 5.10 shows the potential evolution with time during the first five galvanostatic lithiation-delithiation cycles measured at a 100 nm thin Au film on a Cu substrate. The time scale was converted into a scale of nominal Li content (NLC, see chapter 2.1.4). The NLC corresponds to the x in the specification of composition Li_xAu). The first cycle is displayed twice. Once as measured and once shifted along the x-axes.

From the original potential-time curves measured also differential charge curves were calculated (compare section 2.1.3 for an introduction to differential charge curves) shown in Figure 5.11.

In the following a detailed description of the potential-time curves obtained during galvanostatic lithiation-delithiation cycle experiments at 1.7 C using the examples of the first and the second cycle is given. A short summary can be found at the end of the



Figure 5.10: Galvanostatic Li insertion-extraction cycles acquired at the Au thin film sample at a current of 1.7 C $(-/+ 16.6\mu A)$. Fig. 5.10 (a) shows all the cycles measured, Fig.5.10 (b) only the first and the second cycle described in detail in the text. The very first lithiation-delithiation cycle of the Au thin film electrode differs before the second discharging plateau significantly from the subsequent cycles. Among other features the plateau potential of the first plateau is lower than in the subsequent cycles. From the second plateau on all the cycles are highly similar. To visualize this finding the 1st cycle is displayed on the one hand as measured and on the other hand shifted along the x-axes to coincide the beginning of the second lithiation plateau of the first and the subsequent cycles. In all the curves there are two pronounced voltage plateaus during discharging (A1, A2) and three plateaus during charging (B1, B2, B3). In addition two "intermediate-plateaus" (IA1, IB1; see text) occur.

chapter.

For sake of practicability the description of Fig. 5.10 is started with the second cycle. At the beginning of the second cycle the potential drops very quickly to 154 mV at a NLC of 0.067. In the following it increases again slightly to form the beginning of a first potential plateau at 184 mV (NLC: 0.283). The consequence is a dip in the potential-time curve at a NLC of 0.067 (D1 in Fig. 5.10 (b)). Towards a NLC of 0.8 the potential has slowly decreased to 161 mV forming the first lithiation potential plateau (A1). In the differential charge curve (Fig. 5.11) this plateau reflects in a peak at 184 mV. Subsequently the decrease of potential-time curve is reached. The following anew slight potential increase leads into a second potential plateau (A2) starting at 57 mV (NLC:1.17). The second plateau lasts until at a NLC of 2.15 a potential of 49 mV is reached. This second lithiation plateau expresses in the differential charge curve by a peak at 57 mV. Afterwards the potential decay accelerates again to reach the lower boundary potential of 5 mV at a NLC of 2.40. At 5 mV the direction of galvanostatic current was switched in sign to force extraction of Li from the electrode.

The switch of the direction of galvanostatic current results in a steep increase of potential mitigating already after short time to lead into a potential plateau (B1) between NLCs of 2.28 (194 mV) and 1.28 (227 mV). This plateau is on the cathodic side relatively clear defined but fades on the anodic side. This reflects in the steep increase of the differential charge curve on the cathodic side to form a peak at 197 mV and the transition to only slow decrease on the anodic side (see Fig. 5.11). Subsequently the potential increase in the potential-NLC curve accelerates again leading into a second delithiation potential plateau (B2) between NLCs of 1.05 (370 mV) and 0.94 (394 mV). This second delithiation potential plateau is considerably shorter than the first delithiation plateau and also much shorter than the lithiation plateaus. In the differential charge curve this second delithiation plateau is expressed by a relatively small peak at 384 mV. After an anew pronounced increase in potential after the second delithiation potential plateau follows a third delithiation potential plateau (B3) between NLCs of 0.83 (479mV) and 0.40 (520mV). This third delithiation potential plateau is considerably wider again than the second delithiation plateau. But it is as the first delithiation plateau not very clearly defined on the anodic side, resulting in an unsymmetric broad peak in the differential charge curve showing a maximum at 492 mV. On the cathodic side the peak shows a steep slope and on the anodic side the slope is considerably smaller. Afterwards, the potential increase accelerates for the last time. At a NLC of 0.15 the upper potential limit of 1 V is reached.

Considering the shifted curve in Fig. 5.10 it becomes clear from Fig.5.10 that the first lithiation-delithiation cycle is very similar to the second cycle previously described from the beginning of the second lithiation potential plateau on. To yield the shifted curve the potential-NLC curve of the first cycle (black curve) was shifted along the axis of NLC to coincide the points where the dips introducing the second lithiation plateaus occur. Fig. 5.10 shows the differences between the first and the second lithiation-delithiation cycle to be of importance only before the second lithiation plateau starts.

In the first lithiation-delithiation cycle the initial decrease of potential is less pronounced than in the second lithiation-delithiation cycle. Moreover there is an inflection point visible (IP) during the initial potential decrease. As in the second cycle in the first cycle the initial potential decrease is followed by a dip (D1'), but this dip is considerably broader than the first dip (D1) in the first cycle and the bottom of the first dip is located at lower potential in the first cycle (66 mV instead of 156 mV). The time needed to reach the bottom of the first dip is significantly longer in the first cycle (0.216 units of NLC) than in the second cycle (0.075 units of NLC). The potential maximum successive to the first dip is located at 158 mV in the first cycle and consequently at considerably lower potential than in the second cycle (184 mV). Moreover the potential difference between the bottom of the first dip and the subsequent potential maximum at the beginning of the first lithiation plateau is larger in the first cycle (92 mV) than in the second (28 mV) and the time difference between the bottom of the dip and the potential maximum is also larger in the first cycle (0.400 units of NLC) than in the second cycle (0.250 units of)NLC). In the first cycle the first lithiation potential plateau takes more time (0.750 units)of NLC) than in the second cycle (0.520 units of NLC) and the potential decrease to reach the second lithiation potential plateau is slower.

The third until 20th lithiation-delithiation cycle were found to be very similar to the second cycle. No considerable changes could be found.

Apart from the five obvious potential plateaus in the second cycle (A1, A2, B1, B2, B3) some smaller features are worth mentioning. Between the first and the second lithiation plateau as well as between the first and the second delithiation plateau there are inflection points in the potential time curve detectable resulting in something what could be called "intermediate plateau" (IA1 and IB1). The term "intermediate plateau" will be used in the following to denote features during a significant potential increase/decrease characterized by an inflections point in the potential-NLC curve. The described features suggest the presence of only very narrow plateaus. But since they are nestled in regions of pronounced potential increase/decrease they feature themselves pronounced slope reflecting in only small peaks in the diff. charge curve. The corresponding peaks in the differential charge

curves (Figure 5.11) assigned to the intermediate plateaus IA1 and IB1 can be found at 89 mV (intermediate lithiation plateau) and at 290 mV (intermediate delithiation plateau).

The maximum NLC of 2.40 reached during the second lithiation half-cycle differs from the maximum NLC of 2.25 reached during the second delithiation half-cycle. This observation reproduced in all the other lithiation-delithiation cycles creates the impression that more Li is inserted than extracted. According to a NLC during lithiation of 2.40 and 2.25 during delithiation the coulombic efficiency is 94 %.

It is striking to note that the lithiation plateaus feature dips while the delithiation plateaus do not.

In conclusion, from the second lithiation plateau of the first cycle on the potentialtime/NLC curves during the galvanostatic lithiation-delithiation cycles of the 100 nm Au-film feature three pronounced delithiation plateaus at 200 mV (B1 in Fig. 5.10), 380 mV (B2) and 490 mV (B3). In addition there is an intermediate delithiation plateau at 290 mV (IB1) recognizable. During lithiation there are two main plateaus at 183 mV (A1) and 57 mV (A2) observable and an additional intermediate lithiation plateau at 89 m V (IA1).

5.5 Conventional Galvanostatic Lithiation-Delithiation Cycles II

In addition to the galvanostatic measurements at 1.7 C also similar measurements at 0.17 C (1.66 μ A), thus at a tenth of the rate were conducted. Figs. 5.12, 5.13, and 5.14 show the galvanostatic lithiation/delithiation curves and the corresponding differential charge curves.

At 0.17 C no lithiation-delithiation cycle with pristine Au as starting material is available since the measurements at the lower rate were conducted succeeding the measurements at higher rate using the same sample.

In the following a detailed description of the potential-time curves obtained during galvanostatic lithiation-delithiation cycle experiments at 0.17 C using the example of the third cycle is given. A short summary can be found at the end of the chapter.

In the third cycle, representative for all cycles measured at 0.17 C (Figs. 5.12 and 5.13), after switching on the current the potential rapidly drops until at 234 mV (NLC: 0.11) the bottom of a potential dip (D1.1) is reached. The dip resembles the dips observed during the measurements at 1.7 C but here the dip does not lead directly into a lithiation plateau. In fact it follows another dip at 229 mV (NLC: 0.19) (D1.2) which is broader than the initial dip. After that second dip the first lithiation plateau (A1) follows. It



Figure 5.11: Differential charge curves obtained from the galvanostatic lithiationdelithiation curves in Figure 5.10 by differentiating the flown charge with respect to the potential and plotting this differential charge versus the potential (see chapter 2.1.3). Fig. 5.11 (a) shows the differential charge curves assigned to all the lithiation-delithiation cycles measured, Fig. 5.11 (b) only the differential charge curves assigned to the first and the second cycle described in detail in the text. The Figures show that Au-Li alloy formation and dissolution occurs in the second cycle at potentials of 184 mV (A1) and 57 mV (A2) (lithiation) and 197 mV (B1), 384 mV (B2) and 492 mV (B3) (delithiation). Intermediate plateaus are found at 89 mV (IA1) and and 290 mV (IB1). At these potential values there are peaks in the differential charge curves. The dips in the galvanostatic potential-time curves express by the features at 66 mV (D1', 156 mV (D1) and 43 mV (D2) leading to the positive peaks symmetric to A1, A1' and A2. The occurrence of positive and negative peaks for the lithiation plateaus is assigned to the occurrence of potential maxima subsequent to the dips.



Figure 5.12: Galvanostatic lithiation-delithiation cycles measured at a Au thin film at a current of 0.17 C (-/+ 1.66 μA). Fig. 5.12 (a) shows all the cycles measured, Fig. 5.12 (b) only the third cycle described in detail in the text. As also observed at the higher C-rate in all cycles the potential evolutions curves feature two voltage plateaus during lithiation (A1 and A2) and three during delithiation (B1, B2, and B3). In addition four "intermediate-plateaus" (IA1, IA2, IB1, and IB2; see above) occur. All the measured lithiation-delithiation cycles feature a very similar potential-time/potential-NLC behavior. The origin of the difference between the first cycle and the subsequent cycles will be discussed in chapter 5.10

reaches from 232 mV (NLC: 0.23) to 211 mV (NLC: 1.10). The corresponding peak in the differential charge curve is located at 232 mV showing high intensity. Then the current starts decreasing much quicker. During the subsequent potential decrease leading into the second lithiation plateau an intermediate plateau occurs at 126 mV (NLC: 1.22) (IA1) analogue to the measurements at 1.7 C. The following large plateau is preceded by a potential dip at 100 mV (NLC: 1.21) (D2). The second lithiation plateau (A2) extends subsequently from 112 mV (NLC: 1.33) to 98 mV (NLC: 2.67). In the differential charge curve the second lithiation plateau is represented by a intense peak at 114 mV. After the second lithiation plateau a steep decay starts enduring until the lower boundary potential of 5 mV is reached at a NLC of 2.99. Within this decay another intermediate plateau can be found at 47 mV (NLC: 2.91) (IA2).

After switching the direction of galvanostatic current the potential increases very quickly before it flows into a long and flat plateau reaching from 162 mV (NLC:2.84) to 178 mV (NLC: 1.86) (B1). This first delithiation plateau expressed in the corresponding differential charge curve (Fig. 5.14) by a peak at 164 mV which is sharply defined at the cathodic side and fades considerably more slowly at the anodic side. After the first dissolution plateau the potential increases strongly until a pronounced plateau, significantly narrower than the first one, is reached at 333 mV (NLC: 1.56) (B2). It lasts until a po-



Figure 5.13: Galvanostatic Li insertion into/extraction from the Au thin film at a current of 0.17 C (-/+ 1.66 µA). Fig. 5.13 shows excerpts from Fig. 5.12.

tential of 345 mV (NLC: 1.46) is reached and is represented by a peak at 335 mV in the differential charge curve also showing a steep increase on the cathodic side and a relatively slow decay on the anodic side. During the potential increase between the first and the second delithiation plateau an intermediate plateau occurs at 0.237 V (NLC:1.64) (IB1). In the further course of the potential-NLC curve after an anew potential increase a third delithiation plateau establishes ranging from 428 mV (NLC: 1.36) to 467 mV (NLC: 0.84) (B3). The corresponding peak in the differential charge curve is located at 425 mV. Subsequent to this third delithiation plateau the potential starts increasing again pronouncedly until the upper boundary voltage is reached. Within this final potential increase at an additional intermediate plateau is distinguishable at 917 mV (NLC: 0.58) (IB2) which is most pronounced in the first cycle. In the differential charge curve it expresses by a very small and broad peak (inset Fig.5.14 (b)) . .

As also observed in the measurements at 1.7 C the delithiation plateaus at 0.17 C are not initiated by a dip in contrast to the lithiation plateaus.

Furthermore also in the measurements at 0.17 C a considerable difference between the maximum NLC reached during lithiation (2,99) and the maximum NLC reached during delithiation (2.54) is apparent. This phenomenon also observed by Yuan et al.³ will be discussed in section 5.7. According to a NLC during lithiation of 2.99 and 2.54 during delithiation the coulombic efficiency is 85 %.

In conclusion, the potential-time evolution during galvanostatic lithiation-delithiation cycles of the 100 nm Au-film model electrode features three pronounced delithiation plateaus at 164 mV, 335 mV and 425 mV. In addition there are intermediate plateaus at 237 mV and 917 mV recognizable. During lithiation there are two main plateaus at 232 mV and 114 mV observable and intermediate plateaus at 126 mV and 47 mV.



Figure 5.14: Differential charge curves obtained from the galvanostatic lithiationdelithiation curves in Figs. 5.12 and 5.13 by differentiating the charge with respect to the potential and plotting this differential charge versus the potential (see chapter 2.1.3). Fig. 5.11 (a) shows the differential charge curves assigned to all the lithiation-delithiation cycles measured, Fig. 5.11 (b) only the differential charge curves assigned to the third cycle described in detail in the text. The Figures show that Au Li alloy formation and dissolution occurs in the second cycle at potentials of 232 mV (A1) and 114 mV (A2) (lithiation) and 164 mV (B1), 335 mV (B2) and 425 mV (B3) (delithiation). At these potential values there are peaks in the differential charge curves. Also features announcing the intermediate plateaus and the dips in front of the lithiation plateaus are recognizable. As example the small peak assigned to the second intermediate delithiation plateau IB2 is shown in the inset of Fig. 5.14 (a). The occurrence of positive and negative peaks at the potentials of the lithiation plateaus is assigned to the occurrence of potential maxima subsequent to the dips.



Figure 5.15: Comparison of the voltage curves obtained during galvanostatic lithiation-delithiation (Fig. 5.15 (a)) and differential charge curves (5.15 (b)) obtained from galvanostatic lithiation-delithiation cycle experiments at 1.7 C and 0.17 C. Displayed is the respective fourth cycle each from Figure 5.11 (1.7 C) and Figure 5.14 (0.17 C). The shape of the voltage curves and also the differential charge curves for both lithiation currents is very similar. Plateaus in the voltage curves and peaks in the diff. charge curves are comparable. Hence the underlying alloying mechanisms are supposed to be the same. Nevertheless differences in deposition potentials are obvious. At the lower C-rate (0.17 C) during lithiation the deposition potentials are higher whereas they are lower during delithiation.

5.6 Comparison: Conventional Galvanostatic Lithiation-Delithiation Cycles I/II

In Figures 5.15 (a) and (b) the above presented voltage-NLC curves recorded during the galvanostatic lithiation-delithiation cycles at currents of 1.7 C and 0.17 C and the corresponding differential charge curves calculated are compiled. On the first view they show high similarity.

General Shape of Potential-Time Curves, Plateaus

As the measurements at 1.7 C also the measurements at 0.17 C show two main potential plateaus during lithiation and three during delithiation. The intermediate plateaus between the first and the second lithiation plateau and the first and the second delithiation plateau are more pronounced at the lower current. At the lower current additional intermediate plateaus between the second lithiation plateau and the lower potential limit and between the third delithiation plateau and the upper potential limit become apparent. Also beyond these particular features the two potential-time curves show high qualitative similarity in shape.

Table 5.2: Overview over the plateau potentials during galvanostatic lithiationdelithiation cycle experiments employing different currents. At the lower current (0.17 C / 1.66 μ A) the potential plateaus are located at higher potentials during lithiation and at lower potentials during delithiation than at the higher current (1.7 C / 16.6 μ A).

lithiation potentials	1.7 C / 16.6 µA	0.17 C / 1.66 µA
1 st lithiation potential	184 mV - 161 mV	232 mV - 211 mV
1 st intermediate lith. plateau	89 mV	126 mV
2 nd lithiation potential	57 mV - 49 mV	112 mV - 98 mV
2 nd intermediate lith. plateau	—	47 mV
1 st delithiation potential	194 mV - 227 mV	164 mV - 178 mV
1 st intermediate delith. plateau	290 mV	237 mV
2 nd delithiation potential	370 mV - 394 mV	333 mV - 345 mV
3 rd delithiation potential	479 mV - 520 mV	428 mV - 467 mV
2 nd intermediate delith. plateau	—	917 mV

Table 5.3: Comparison of the lithiation-delithiation data of the galvanostatic lithiation/delithiation experiments at 1.7 C / 16.6 μ A and 0.17 C / 1.66 μ A. At the lower current (0.17 C / 1.66 μ A) the NLC is higher during lithiation as well as during delithiation. But the discrepancy between the NLC during lithiation and delithiation is smaller at the higher current.

appl current	durat	ion / s	charg	ge/μC	NLC/ equivalents		
	lith.	delith.	lith.	delith.	lithiation	delithiation	
1.7 C / 16.6 µA	1710	1630	28390	27060	2.40	2.25	
0.17 C / 1.66 µA	21485	18181	35665	30180	2.99	2.54	

Dependency of Plateau Potentials on Current

Quantitatively significant differences in the plateau potentials become immediately clear from the potential-NLC curves and the differential capacity curves. During lithiation the plateau potentials are higher at lower current, during delithiation they are lower at lower current. In the differential capacity curves this phenomenon expresses in distinct peak positions of the lithiation and delithiation peaks at both currents. An overview over the plateau potentials at both lithiation currents is given in table 5.2.

Difference in NLC during Lithiation/Delithiation

Fig 5.15 and 5.3 also show the maximum NLC during lithiation with 2.99 to be higher at 0.17 C than the maximum NLC at 1.7 C (2.40). Also the NLC extracted during delithiation is higher at 0.17 C (2.54) than at 1.7 C (2.25)). In consequence the discrepancy between the NLC inserted and extracted, respectively, is higher at 0.17 C. Consequently, the coulombic efficiency calculated based on the previous values is higher at 1.7 C (94%) than at 0.17 C (85%).

Miscellaneous

At 0.17 C the initial potential decrease is slower than at the higher rate.

At both lithiation rates the lithiation plateaus are introduced by dips in the potential-NLC curve while the delithiation plateaus are not.

When plotting the peak potentials observed at the two different currents as pairs of values into Fig. 5.6 these pairs of values almost coincide with the regression lines connecting the potential-current pairs extracted from the three reductive peaks in the CVs.

5.7 Discussion: Conventional Galvanostatic Lithiation-Delithiation Cycles

General Shape of Potential-Time Curves, Plateaus

Theoretically potential plateaus during galvanostatic lithiation-delithiation cycles are assigned to two phase regions in the Au-Li phase diagram. Since the involved alloy phases are not recognized just from the galvanostatic lithiation-delithiation experiments and their thermodynamic stability is not proven the term "alloy phase evolution diagram" will be used in the following instead of the term "phase diagram". The transition regions between the plateaus and between plateaus and potential limits signify single phase regions in the "alloy phase evolution diagram".

In the galvanostatic lithiation-delithiation cycles at 1.7 C (Fig. 5.10) and 0.17 C (5.12) presented above consequently obviously several two-phase regions in the alloy phase evolution diagram of the Li-Au system are crossed. Two two-phase regions are supposed to be crossed during lithiation and three two-phase regions during delithiation. The width of the plateaus should correlate with the difference in Li content of the phases forming the actual two-phase region. Staying in this image during the two (broad) lithiation plateaus a large difference in Li content is probably overcome while for the two phases separated by the second delithiation plateau a very similar Li content is likely. The different intermediate plateaus possibly represent two-phase regions between phases even much closer in Li content.

Since electrochemical Li-metal alloy phase formation is known to occur at potentials above the actual Li deposition potential (0V vs. Li/Li+) the observed plateaus are assumed to origin from several steps of Li-Au alloy phase formation and dissolution.

Taillades et al.¹⁶ reported a galvanostatic lithiation-delithiation cycle of a 200 nm Au thin-film electrode in a 1 M solution of LiPF_6 in a mixture of Ethylenecarbonat (EC), Propylenecarbonat (PC), and Dimethylcarbonate (DMC) as electrolyte. They applied a current of 0.63 C. Their potential-time curve shows high qualitative similarity to the potential-time curves presented here. Two lithiation potential plateaus (at 150 mV and 100 mV) and three delithiation plateaus featuring comparable ratio of duration and comparable plateau potential. However they distinguished only two delithiation plateaus (at 180 mV and 400 mV) instead of three distinguished here (two pronounced plateaus and one narrow).

Also Yuan et al.³ performed galvanostatic lithiation-delithiation cycles at a 100 nm thin Au-film. They used 1 M LiPF₆ in a 1:1 mixture of EC and DMC as electrolyte at a C-rate of 0.39. The corresponding potential-time curve also showed high qualitative similarity to the here presented measurements featuring two lithiation plateaus (at 230 mV and 110 mV) and two pronounced delithiation plateaus at 150 mV and 400 mV. The small second delithiation plateau is only very weakly developed in their measurements. However, in their potential-time curve features reminding to the second lithiation intermediate plateau and the first delithiation intermediate plateau are observable, but were not discussed in detail in their work.

Mechanistic Comparison

Since the potential-time curves measured at 1.7 C and 0.17 C compared in Fig. 5.15 not only feature the same number of lithiation and delithiation plateaus but also highly similar quantitative behavior the lithiation/delithiation can be assumed to proceed following very similar or identical reaction paths fir both C-rates including similar or identical phase transitions. The fact that at 0.17 C two additional intermediate plateaus get apparent could possibly either point to very small actual differences in the lithiation-delithiation pathways or at 1.7 V just the current is too high to resolve these intermediate plateaus.

Thermodynamic/Kinetic Stability of the Alloy Phases

The fact that the same phase transitions occur within the relatively large current range tested proves at least kinetic stability of the involved phases within this current range comprising one decimal power and points to possibly also thermodynamic stability. Since there are different numbers of plateaus during lithiation and delithiation the lithiation and the delithiation processes are supposed to occur along different paths. This insight is, however, not compatible with the before considered thermodynamic stability of the anticipated Li-Au alloy phases and rather suggests only kinetic stability.

Dependency of Plateau Potentials on Current

Comparing the galvanostatic lithiation-delithiation cycles at 1.7 C and 0.17 C shown in Fig. 5.15 the correlating potential plateaus turned out to shift using higher current to lower values during lithiation and higher values during delithiation. A behavior like this is expectable and can be attributed principally to the ohmic resistance of the cell and and electron transfer resistance through the electrode's surface leading at higher current to higher overpotential ($U = R \cdot I$). Mainly at the higher current also diffusion overpotential may come into effect.

Characteristic Peak-Shape in Differential Charge Curves

Most of the potential plateaus are represented in the differential charge curve (Fig. 5.15 (b)) by unsymmetric peaks. The ascending flank of the peaks is relatively steep while the descending flank is considerably less steep. Obviously most of the electrochemical processes occurring during the lithiation-delithiation cycle set in at a relatively defined potential (probably the potential of the actual process). But the end of the processes is less defined. Possibly towards the end of the plateaus it gets successively more difficult

to convert the remaining electrode material into the respective new phase - maybe due to suboptimal electrical contact or due to diffusion limitation.

In the following some further outstanding features getting apparent comparing the first and the subsequent lithiation-delithiation cycles as well as the lithiation-delithiation cycles acquired at the different currents will be discussed.

SEI Formation

By regarding Fig. 5.10 and Fig. 5.11 the first galvanostatic lithiation-delithiation cycle turns out to feature special characteristics not observable in the subsequent cycles.

In the first cycle the initial potential drop is slower than in the following cycles but it continues to lower potential values. Fig. 5.16 shows a zoom-in into Fig. 5.10 at the very beginning of the first lithiation-delithiation cycle. After starting the lithiation the potential drops quickly as it is also observed for the subsequent cycles. At around 680 mV, however, the dropping rate reduces. A linear slope is formed. At around 470 mV the dropping rate increases again. Some time later the lithiation potential ends up in the dip in front of the first lithiation plateau introduced in chapter 5.4. The intermediate linear slope during the initial potential drop observed in the potential-time curve expresses itself also in the differential charge curve5.16. At 560 mV in the first lithiation half-cycle there is a small peak which is not observable in the subsequent cycles any more.

The described feature is considered to origin from SEI-film formation. As explained in more detail in section 1.4 the SEI is the interface layer between electrode and electrolyte resulting from the partial decomposition of the battery electrolyte in presence of lithium.

Zhang et al. reported about their investigations on SEI film formation on graphite electrodes and observed the SEI-film formation taking place in two mayor stages.²⁶ The first stage takes place in a potential range before lithiation actually starts. The result is a loose, highly resistive film. The second stage occurs in the potential range where lithiation actually takes place. In this potential range alloy phase formation and SEI-film formation occur simultaneously. In this second state a stable, compact and highly conductive SEI film is produced. Also in the case of Si nanowire anodes SEI-film formation in a voltage range above the Li insertion potential into Au was reported by Chan et al.¹⁸ They also observed an inflection point in the galvanostatic potential time curve and an associated small peak in the corresponding differential capacity curve at 620 mV. Priorly Graetz et al. were able to assign features in their measurements at nano-structured silicon between 500 mV and 700 mV to SEI-film formation.⁷⁴

Taking the above compiled citations into account the reason for the phenomena pointed out in Fig. 5.16 is in all probability attributed to the first step of SEI-film formation²⁶



Figure 5.16: Excerpt from the galvanostatic lithiation-delithiation curve of the first cycle at 1.7 C (Fig. 5.10 (a)) and excerpt from the corresponding differential charge curve in comparable potential region (Fig. 5.11 (b)). At the beginning of the first lithiation half-cycle there is a conspicuity in the potential-time evolution unique for the first lithiation/delithiation cycle (Fig. 5.16 (a)). The dropping rate of potential varies to yield an inflection point conveying the impression of an "intermediate plateau". This phenomenon also expresses in the differential charge curve by a small peak (Fig. 5.16 (b)). According to the literature^{18, 26, 74} SEI-film formation at the electrode-electrolyte interface is probably the reason for the observed phenomena.

occurring in a potential range above the range of Li insertion.

Occurrence of Potential Dips

At the beginning of the two lithiation plateaus during the galvanostatic lithiation-delithiation cycles at both currents dips in the potential-time/NLC curve were observed (see Fig. 5.10 and 5.12). Two different effects are considered to be the origin of these dips:

One possible explanation for the occurrence of the dips could be the formation of the solid electrolyte interphase (SEI). Several researchers reported on the enhancing influence of the SEI-film on the Li insertion. At the beginning of the first cycle there is no SEI-film present at all. Hence SEI-film has to be established at the beginning of the first cycle as already assumed to be the reason for the inflection point in the potential-time curve in the first cycle and the associated retarded potential decrease in comparison to all subsequent cycles (see above). When (as reported in literature (see above)) SEI-film formation also endures parallel with Li insertion and the formed SEI-film has an enhancing influence in terms of lowering the voltage necessary to start Li insertion, the Li insertion potential can be expected to shift during SEI-film formation to a lower potential resulting in a dip in the potential-time curve. The occurrence of another dip at the beginning of the second lithiation plateau may then occur due to a similar process where restructuring or new

formation of SEI-film at the lower potentials is accompanied by a reduction of voltage necessary for the second step of lithiation. But also in the second (and all the subsequent cycles) cycles potential dips at the beginning of the lithiation plateaus are present. This could be explained by partial dissolution or disordering of the SEI-film during the lithium extraction process resulting in the need to reform or reorder the SEI-film during the subsequent lithiation half-cycle.

Hence possibly the dips at the beginnings of the galvanostatic lithiation potential plateaus are attributed to the second region of SEI-film formation located within the potential range of Li insertion as described by²⁶ (compare above). At the beginnings of the delithiation plateaus no potential dips are observable since SEI-film may not be actively dissolved influencing the delithiation potentials.

If SEI-film formation is the actual reason for the occurrence of the dips the observed potential evolution at the beginning of the first cycles can be attributed to the first step of SEI-film formation in the present system while the second step of SEI-film formation is causal for the observed dips. Takamura et al.⁷⁵ showed that thin evaporated metal films enhanced the lithiation/delithiation rates of graphite anodes. They proposed that metals such as Au and Ag form a Li alloy and allow Li movement through the metal while providing a stable SEI-film between the carbon and the electrolyte.⁴⁵

Another possible explanation for the occurrence of the potential dips at the beginning of the lithiation plateaus could be the interplay between nucleation of the Li-Au alloy phases and the subsequent growth of the nuclei. If the nucleation would start at only lower potentials than nucleus growth would be possible to proceed at a potential-time behavior as the observed could be expected. First the potential has to be decreased to start nucleation. After nuclei are present nucleus growth can continue at higher potentials resulting in a dip in potential-time curve.

The aggravated nucleus formation in comparison with nucleus growth, accompanied by a lower potential needed to initialize nucleation, would be able independently of the influence of the SEI-film to explain qualitatively the presence of potential dips at the beginning of the lithiation plateaus. The absence of potential dips at the beginning of the delithiation plateaus in this image would either speak for still remaining nuclei of the lower lithiated phases in the electrode material or for facilitated nucleation during decreasing the Li content of the electrode material.

The SEI-film formation would only be able to explain the observed potential time behavior if the presence of the SEI-film would facilitate Li insertion by lowering the potential necessary for Li insertion and if SEI-film formation would occur in the same potential range as alloy formation. If the SEI-film formation would occur at higher or lower potentials than Li insertion the potential-time behavior expectable would be different, especially not showing dips. Also SEI-film formation occurring during Li insertion but without the presence of any influence of the SEI-film on the lithiation process cannot explain the potential dips.

Since nucleus formation does not affect the NLC while SEI-film formation increases the NLC by consuming current not available for actual lithiation (see below) and since during delithiation no dips are observable, SEI-film formation might be favored in searching for the reason for the observed potential dips. This insight would highlight the importance of the SEI for the performance of the anode material also in the case of the here presented Au thin-film electrode in combination with the used ionic liquid based electrolyte.

Also in the galvanostatic potential-time curves reported by Taillades et al.¹⁶ there is a small potential dip at the beginning of the first lithiation potential plateau. Although they did not discuss its origin it occurs most probably due to the same phenomenon as the here reported dips. The small markedness of the dip in the curve of Taillades may be attributed to the small current or to the different electrolyte showing different SEIfilm formation. Taillades neither mentioned the occurrence of the dip nor discussed the influence of SEI formation on the potential-time curve.

Examining a 100 nm Ag thin film in contact with an organic liquid electrolyte (1 M LiPF_6 in EC-PC-DMC) Taillades et al. observed in the galvanostatic lithiation-delithiation potential time curve at a current of 0.63 C a much more pronounced dip before the beginning of the first lithiation plateau. They attributed it to lithium diffusion effects giving rise to polarization/depolarization phenomena.

In conclusion of the here presented discussion the reason for the occurrence of the potential dips at the beginning of the lithiation plateaus could be on the one hand SEIfilm formation parallel to lithiation processes or on the other hand the interplay between nucleation and nucleus growth or even a superimposition of both phenomena. However the particular reason in the present case cannot be definitively stated.

Difference in NLC during Lithiation/Delithiation

Another finding probably correlated to SEI-film formation or also to charging of the electrochemical double layer capacitor is the seemingly remaining Li after the end of Li extraction even in the higher cycles. The lithiation half-cycle in the galvanostatic potentialtime/NLC curve is found to take longer (with respect to time as well as NLC) than the delithiation half-cycle at both currents tested (Figs. 5.10, 5.12 and 5.15). A higher NLC was achieved during lithiation than consumed during delithiation. This observation was also reported previously by Taillades et al.⁴⁵ and Yuan et al.³ without giving a substantiated explanation or discussion. Taillades reported a lithiation-delithiation efficiency of only 57% and Yuan even much less (31.5%, 2nd cycle) while in the here presented measurements the efficiency is 85% at 0.17 C (third cycle) and even 94% at 1.7 C (2nd cycle). Yuan considered a relative inefficiency of the alloying process to be causal for his bad efficiency.

The most obvious reason for such behavior could be Li remaining in the electrode material during the lithiation-delithiation cycle. But the potential-time curves are almost identical during the 20 cycles examined speaking against this theory. Adding up the seemingly Li overshoot over the 20 cycles measured a Li accumulation in the electrode material of four equivalents would result. This can be excluded, however, by the reproducibility of the galvanostatic lithiation-delithiation cycles.

More probably the observed difference in NLC between the lithiation and the delithiation branch is attributable to SEI-film reordering and anew formation as considered to be the reason for the potential dips at the beginnings of the lithiation plateaus. Consequently the total Li content of the sample can be best estimated from the delithiation branch. Considering the Li dissolution to be quasi complete the maximum NLC at 1.7 C (2.25) is about 10% smaller than at 0.17 C (2.54). Hence, apparently at the higher current less Li could be inserted. Possibly the reason for this observation is limited accessibility of some regions in the sample at the higher lithiation current.

The discrepancy between the maximum NLC during lithiation and delithiation is considerably higher at 0.17 C than at 1.7 C. Assigning this discrepancy to SEI-film formation would mean that SEI-film formation at the lower rate takes a higher fraction of the current converted, possibly since the SEI-film has more time to properly structure at lower rates. This possible scenario could also explain the slower initial decrease of the potential-time curves measured at 0.17 C compared to the initial decrease of the potential-time curves measured at 1.7 C. This finding points to differences on SEI-film formation and SEI structure at the different currents.

Considering results from the already mentioned in-situ XRD measurement where the highest lithiated alloy phase was found to be Li_3Au (see chapter 6.7.1), however, at both currents the lithiation seems to be incomplete. Probably not all the Au is available for lithiation anymore due to crack formation and consequent possible contact loss of parts of the Au. Another explanation could be incomplete delithiation already in the first delithiation cycle resulting in a specific amount of Li remaining in the sample. This could on the one hand limit the lithiation capacity in all the subsequent cycles and on the other hand explain the observed large potential difference between the first lithiation potential plateaus in the first and the second cycle.

Difference between first and subsequent cycles

For Si-based anode materials several studies reported about the amorphization of Si during lithiation and observed a significant difference between the first and subsequent lithiation-delithiation cycles of a originally crystalline Si sample.^{8,9,17,18,31,76} They proved the observed difference to be assigned to the difference in lithiation of the pristine, crystalline Si sample and of amorphous Si identified to remain after the first Li extraction. Substantiated by in-situ XRD results of the electrochemical lithiation-delithiation of Au thin films presented in chapter 6, the observed difference between the first and the second lithiation cycle in the case of Au can be attributed to a similar phenomenon. Also Au is not recovered crystalline after delithiation. The reason for the missing recovery of crystalline Au could be the above considered Li remaining inside the electrode material.

5.8 Conclusion: Conventional Galvanostatic Lithiation-Delithiation Cycles

To conclude the chapter the main findings from the galvanostatic lithiation-delithiation measurements at 1.7 C and 0.17 C, respectively are summarized as follows:

At both lithiation rates the qualitative potential-time behavior is very similar. There are two large lithiation plateaus and two large and a considerably shorter delithiation plateaus. Also intermediate plateaus between the first and second lithiation plateau and the first and second delithiation plateau are present at both lithiation currents. At 0.17 C additional intermediate plateaus get clear between the second lithiation plateau and the lower potential limit and between the third delithiation plateau and the upper potential limit. But maybe also at 1.7 C the processes assigned to these additional plateaus occur only leaving weaker traces in the potential-time curves. Hence obviously the process of lithiation/delithiation proceeds at both rates (which are separated by a factor 10!) along an at least very similar reaction path.

From the previously stated it can therefore be concluded that there are no significant differences on the atomic level between lithiation/delithiation at the two lithiation rates tested. The rather small differences in peak potentials for the two different lithiation rates (1.7 C and 0.17 C) can be attributed to current dependent ohmic and electron transfer overpotential. The dependence of the plateau potential on the lithiation/delithiation current fits nicely to what could be extracted from the CVs (see discussion of the CVs, chapter 5.3, Figure 5.6 (b)). This finding underlines the correlatability of the presented electrochemical CV and lithiation-delithiation measurements. Since a linear dependency

of the current on the potential was found in Fig. 5.6 (b) probably diffusion overpotentials not yet play a role at the used currents at least during delithiation.

5.9 Galvanostatic Cycles with Intermediate Potential Relaxation Periods

In addition to the simple galvanostatic measurements also so called galvanostatic measurements with intermediate potential relaxation periods were conducted. This type of electrochemical measurements is also known as galvanostatic intermittent titration technique (GITT).

Following the typical procedure of this type of measurements, first the sample was lithiated galvanostatically at a specific current (here: 0.17 C) for a specific time (here: 1000 s). Then the electrochemical cell was switched to open circuit potential (ocp) measurements: The electric circuit was opened and the potential evolution was monitored. After a set time (here: 2000 s) the cell was switched to galvanostatic treatment again (see Fig. 5.17 (c)). The described switching between galvanostatic lithiation/delithiation and potential tracing of the hereinafter opened cell was kept up over the complete lithiation/delithiation cycle.

The resulting potential-time and potential-NLC curves, are reproduced in Fig. 5.17 (a) to (d).

In Fig. 5.17 (a) the potential evolution is plotted over time, in Fig. 5.17 (b) over Li content. Fig. 5.17 (c) shows a zoom-in into Fig. 5.17 (a) to illustrate the measuring principle explained above (and in chapter 2.1.5). In Fig. 5.17 (d) the potential-NLC curve of the second GITT cycle is exemplified together with the nomenclature of plateaus and other features in the curve introduced in chapter 5.4. It is important here to have the comparison between potential-time and potential-NLC curves, because the lithiation in the presented experiment does not go straightforward with time due to the intermediate ocp periods. From both plots the similarity of the relaxation measurements to the purely galvanostatic measurements becomes clear on the first view. Although Fig. 5.17 (a) is dominated by relaxation periods the two lithiation plateaus known from the purely galvanostatic measurements are clearly distinguishable at around 227 mV (A1 in Fig. 5.17 (a)) and 111 mV (A2). From the above described delithiation plateaus only the two large plateaus are clearly obvious at around 168 mV (B1) and 440 mV (B3). The narrow delithiation plateau can be anticipated at 336 mV (B2). Details as intermediate plateaus observed in the purely galvanostatic measurements are not distinguishable.

As it becomes clear from Fig. 5.17 (a) during the 2000 s lasting ocp periods the po-



Figure 5.17: Galvanostatic lithiation-delithiation cycles at the Au thin film model electrode at a current of 0.17 C (-/+ 1.66µA) with intermediate potential relaxation periods. This method is known as Galvanostatic Intermittent Titration Technique (GITT). In Fig. 5.17 (a) the acquired potential time curves are plotted over time and in Fig. 5.17 (b) over the nominal Li content (NLC). Fig. 5.17 (c) shows a zoom-in into Fig. 5.17 (a) with the periods of galvanostatic lithiation (L) and ocp marked. In Fig. 5.17 (d) the potential-NLC curve of the second lithiation-delithiation cycle is exemplarily shown. The nomenclature of the plateaus and other features is analogue to chapter 5.4. After every 1000 s of lithiation/delithiation the system was switched to ocp for 2000 s while the evolution of potential was continued to follow. Also with intermediate potential relaxation periods the evolution of potential has strong similarities to the one observed during purely galvanostatic lithiation-delithiation cycles (Figures 5.10, 5.12). The shift between the first cycle and the subsequent cycles will be discussed in chapter 5.10

tential relaxes to higher values during lithiation and to lower values during delithiation as expectable just assuming disappearing overpotentials. During galvanostatically ruled periods it drops quickly to the actual lithiation potential. After 1000 s the next relaxation step starts (see Fig. 5.17 (c).

In the plot against nominal Li content (NLC) (Fig. 5.17 (b, d)) the ocp regions have vanished since during ocp there is no lithiation taking place. What remains are the gal-vanostatic periods. Due to the time needed to return each time from the relaxed potential to the deposition potential after each relaxation step the curve shows discontinuities. In comparison to Fig. 5.17 (a) in Fig. 5.17 (b) the similarity to the purely galvanostatic measurements becomes more obvious. There the lithiation (A1, A2) and delithiation plateaus (B1, B3) get apparent more clearly. The short second dissolution plateau (B2) is unambiguously visible and also the initial dips at the beginning of the lithiation plateaus (D1, D2) as well as the intermediate plateaus (IA1, IA2, IB1, IB2) get apparent.

The Figure suggests a higher Li content to be achieved by the galvanostatic relaxation measurements than by the purely galvanostatic experiments. This finding will be addressed in the following discussion.

5.10 Discussion: Galvanostatic Cycles with Intermediate Potential Relaxation Periods

Comparison Galvanostatic Lithiation-Delithiation Cycles with and without Intermediate Potential Relaxation Periods

In Fig. 5.18(a) a comparison is given between galvanostatic lithiation-delithiation cycles at 0.17 C without (curve 1) and with (curve 2, GITT) intermediate relaxation under open cell conditions. The potential evolutions are plotted over the nominal Li content (NLC). (As mentioned in chapter 5.4 the nominal Li content is calculated from the overall charge flown assuming the charge completely converted in lithiation.) This leads automatically to the disappearing of the relaxation periods (compare Fig 5.17), since during the relaxation periods no external current flows. Curve 3 is obtained by additional manually removing the regions where the potential returns to the respective lithiation/delithiation potential after switching on the current again. The method is illustrated in Fig. 5.18 (b).

Regarding Fig. 5.18(a) first of all it is striking to note that the purely galvanostatic measurement (curve 1) as well as the GITT measurements (curve 2) clearly show the same lithiation/delithiation potentials and very similar potential evolutions. From this identical lithiation mechanism are obvious. However, a difference in final Li content achieved using



Figure 5.18: Fig. 5.18 (a) illustrates a comparison between the galvanostatic lithiationdelithiation cycles at 0.17 C with (curve 2) and without (curve 1) intermediate relaxation periods at open cell conditions plotted over the nominal lithium content (NLC). To yield curve 3 from the curve 2 the periods of potential decrease towards the respective lithiation potential were manually removed according to Fig. 5.18 (b). by means of Fig. 5.18 (a) the high similarity between galvanostatic lithiation-delithiation cycles with (GITT) and without (purely galvanostatic) intermediate relaxation periods will be discussed.

the two different treatments is suggested. While under purely galvanostatic conditions (curve 1) about three equivalents of Li are inserted per Au atom before the set lower potential limit of 5 mV is reached, under "relaxation conditions" (curve 2) there seems to be higher Li loading possible (3.4 Li per Au atom).

Curve 3 shows a maximum nominal Li content lower than curve 2 due to the process obtaining curve 3 from the curve 2 by skipping the regions, where the potential returns to its initial value after the end of the relaxation periods.

There is a high similarity between the curve 1 and curve 3. But the maximum nominal Li content of the curve 3 is even lower than the maximum NLC of the purely galvanostatic experiment (curve 1). To explain the difference the following has to be considered. Probably the current flown after the end of the relaxation regions until the potential reaches the actual lithiation/delithiation potential again ("skipped periods" in Fig. 5.18 (b) is not entirely attributed to the build-up of concentration gradients and the electrochemical double layer and SEI-film formation. Rather a part of this current is already used for further lithiation/delithiation.^{59,60} Hence, not all the current flowing in the "skipped periods" must be neglected in calculating the nominal Li content. However it cannot be stated here to what percentage the current has to be taken into account. But it is likely to not yield only lower NLC in the measurements with and without relaxation time.

Characteristic Shape of Potential-Time Curves during OCP

The first cycle of GITT-measurements (Fig. 5.17 (a)) starts at lower potential (410 mV) than the subsequent cycles and seems therefore a bit shifted with respect to the other cycles. The reason is that the cell was at ocp conditions after the previous measurement over night and meanwhile the potential relaxed towards equilibrium as in the GITT measurements. The observed potential of 410 mV after a 36 h relaxation period corresponds to the equilibrium potential value measured at the end of the third delithiation plateau in the GITT measurements. In analogy to the just discussed shift between the first and second cycle of GITT measurements also the shift observed between the first and the subsequent cycles in the purely galvanostatic measurements (Fig. 5.12) and the potentiostatic measurements employing a current limit of 1 μ A (Fig. 5.22) can be assigned to potential relaxation during a previous ocp period while the cell was not in operation over night..

Fig. 5.19 (a) reproduces the second cycle of the GITT measurements (5.17 (d)) plotted over time. Fig. 5.19 (b) shows representative potential-time evolutions during the potential relaxation periods marked in Fig. 5.19 (a) at the different (de)lithiation plateaus



Figure 5.19: Comparison of potential-time evolutions typical for the ocp periods at the different lithiation (A1, A2) and delithiation (B1, B2, B3) plateaus during the galvanostatic lithiation-delithiation cycles with intermediate relaxation time (GITT). Fig. 5.19 (a) shows the whole second GITT lithiation-delithiation cycle. Fig. 5.19 compares the particular ocp-periods marked in Fig. 5.19 (a). For better comparability the ocp-periods during delithiation are plotted mirrored at a horizontal line. In addition all the ocp-curves are shifted along the potential axis to coincide all the staring points of potential relaxation. The phase transformations associated with the different potential plateaus is found to occur in different distance from the equilibrium potential.

(A1, A2, B1, B2, B3 in Fig. 5.19). For better comparability they are shifted and turned to start at the same position and increase with time. At the very beginning of the ocp curves there is a region of quick almost linear increase of potential due to disappearance of the overpotential related to ohmic and electron transfer resistance (region "overpotential relax" in Fig. 5.19; first stage of potential relaxation; compare section 2.1.5). Subsequently the potential increase slows down while diffusion gradients are leveled and the electrochemical double layer condenser discharges (region "diffusion relax" in Fig. 5.19; second stage of potential relaxation).

Obviously the potential evolution with time is significantly different during the relaxation periods at the different (de)lithiation plateaus concerning both the first and the second stage of potential relaxation. During the first delithiation plateau (B1 in Fig. 5.19) there is only a small linear increase. Only small overpotentials prevail. In the second stage there is hardly any further potential increase. Consequently there are only very small concentration gradients to level. During the second lithiation plateau (A2) the prevailing overpotential is significantly higher. Moreover there is a significant potential increase in the second stage. In consequence during the second lithiation plateau considerable concentration gradients can be assumed. During the first lithiation plateau (A1) in the first as well as in the second stage there are even considerably larger increases of potential registrable. The associated alloying process occurs at higher deviation from equilibrium conditions than the processes occurring at the other plateaus. The highest deviation from equilibrium can be registered during the third delithiation plateau (B3). In the first stage of potential relaxation as well as in the second stage the increase of potential is the highest. In conclusion the first dealloying process occurring during the first delithiation plateau is closest to equilibrium conditions while the third dealloying process is most away from equilibrium conditions.

Fig. 5.20 provides an overview over all the relaxation periods during the entire lithiationdelithiation cycle (see Fig. 5.19). Obviously during the second lithiation plateau and the first delithiation plateau not only the potential relaxation is only small compared to the potential relaxation occurring during the first lithiation plateau and the third delithiation plateau (see above). Moreover the equilibrium potential is almost constant for the second lithiation plateau and the first delithiation plateau while it shifts significantly during the first lithiation plateau and the third delithiation plateau.

Taking in account Fig. 5.19 (a) again it becomes apparent that during the first lithiation plateau the plateau potential is quite constant while the equilibrium potential reduces. This speaks against a definite reversible transition of one phase into another and rather matches the imagination of more phases involved. Similar could also be assumed for the third delithiation plateau where the equilibrium potential as well as the plateau potential increase with time. This may suggest a solid solution of Li to be present in which the lithium content increases with time leading to a successive change of the chemical potential of this solid solution resulting in changing potential. Another option would be a more complex mixture of phases present at the same time. Moreover the potential difference between the plateau potential and the equilibrium potential is significantly larger at the first lithiation plateau and third delithiation plateau than during the first delithiation plateau. In the image of the solid solution this could mean significant concentration gradients building up due to initial unequal distribution of Li leveling out during the relaxation periods. In the image of the complex mixture there could be diffusion processes dominant after switching to ocp because the phases formed during lithiation may be only of kinetic stability and reorder during the relaxation periods. But since the curve 3 in Fig. 5.18 (a) is very similar to the curve 1 either these changes are reversible after switching on the current again or they are not severe.

A definite reversible transition of one phase into another can rather be assumed for the second lithiation plateau and the first delithiation plateau where plateau potential and equilibrium potential are constant. The phases involved can be assumed to be of the same chemical potential resulting in the same free enthalpy and therefore the same



Figure 5.20: Periods of potential relaxation under ocp conditions. Fig. 5.20 shows the potential evolution with time during ocp periods during lithiation of the sample (Fig. 5.20 (a)) and delithiation of the sample (Fig. 5.20 (b)). During the different (de)lithiation plateaus characteristic behavior of the potential-time curves is observed. During the second lithiation plateau and the first delithiation plateau the potential-time curves are highly similar and the potential relaxes rather little. During the first lithiation plateau and the third delithiation plateau the potential-time curves do not coincide and show more pronounced potential relaxation. Obviously the (de)lithiation processes at low potential, possibly forth and back-reaction of the same alloying process, occur closer to equilibrium conditions than the (de)lithiation processes at higher potential.

equilibrium electrochemical potential. Moreover the equilibrium potential associated with the first delithiation plateau (154 mV) is found to be very close to the equilibrium potential associated with the second lithiation potential (146 mV). This finding substantiates the assumption of analogous phase transitions forth and back. But as mentioned above the forward reaction occurs further away from the equilibrium potential. Hence during the forward reaction higher overpotentials (due to electron transition or diffusion maybe through the phase newly formed) and concentration gradients are probably involved.

5.11 Potentiostatic Lithiation-Delithiation Cycles I

To compare with the galvanostatic lithiation-delithiation cycle measurements also potentiostatic lithiation-delithiation cycle measurements were carried out (see Fig. 5.21 and 5.22). In contrast to the galvanostatic measurements thereby the deposition potential is controlled and the current response is recorded. While performing galvanostatic experiments the external current, a quantity not related to the mechanisms on the atomic scale (e. g. phase formation) is kept constant independent on the adjusting potential, in potentiostatic experiments it is better possible to take account of these mechanisms on the atomic scale by controlling the potential. Since each phase transformation occurs at a specific potential the individual phase transformations can be triggered by setting the potential adequately. However it has to be taken into consideration that setting the potential already at the beginning of the lithiation process to the Li/Li⁺ potential all the alloy formation steps could occur simultaneously (compare discussion of the CVs, chapter 5.3).

To let the different steps of alloy phase formation occur one after the other and to avoid large currents the potential was reduced stepwise during the lithiation half-cycle starting from 1.5 V, first in 100 mV steps until 0.3 V. Then the potential steps were reduced to 20 mV to have higher potential resolution in the potential range of alloy formation. After reaching the lower potential limit (5 mV) the potential was raised again during the delithiation half-cycle in 20 mV steps in the dealloying potential range (up to 500 mV. Hereafter, the step-size was increased again to 100 mV until the upper potential limit of 1.5 V was reached.

In contrast to the galvanostatic experiments where the end of the charging process of the model anode is reached, when the potential decreases below a set value, in the potentiostatic experiments the current has to be used as criterion for the end of charging. A specific potential is held as long as the provoked current had decreased below a set value. This criterion has to be applied to every single potential step. The results presented below were obtained using the procedure just described.

In the following a detailed description of the potential-time curves and current-time curves obtained during potentiostatic lithiation-delithiation cycle experiments employing a potential limit of 5 μ A and using the example of the third cycle is given. A short summary can be found at the end of the chapter.

Fig. 5.21 shows current and potential evolutions on time and nominal Li content obtained using a current limit of 5 μ A. This means in the lithiation branch the potential was reduced as soon as the current got more positive than -5 μ A and in the delithiation branch the potential was raised as soon as the current got more negative than +5 μ A.

In the lithiation half-cycle the potential is reduced step by step starting at 1.5 V. At 1.5 V occurs hardly any cathodic current at all. Hence the potential is lowered to 1.4 V. Here, there is only a very low cathodic current yielded which is however more positive than -5 μ A and the potential is lowered further. Lowering the potential step by step a growing current is yielded at the beginning of the respective step and the potential has to be held increasingly longer to wait for the current to decrease below the set current limit. At 400 mV it still takes not more than 20 s to reach the set current limit of 5 μ A.



Figure 5.21: Potentiostatic lithiation-delithiation cycles acquired at the Au thin film sample. During lithiation the potential was decreased in small steps starting from 1.5 V. Reaching the lower potential limit of 5 mV the potential was risen again stepwise to 1.5 V. Every potential step was held until the provoked current decreased below the current limit of 5 µA. The received potential-time / potential-NLC curves show characteristic potential plateau where the current can be held above the current limit for a long period. Fig. 5.21 (a) shows a plot of the potential-time curves during the potentiostatic measurements together with the current-time curves measured. In Figs. 5.21 (c) and (d) exemplarily exemplified at the third cycle selected excerpts from Fig. 5.21 (a) are presented to highlight the difference in current time curves recorded at actual potential plateaus and during periods of pronounced potential decay. In Figure 5.21 (b) the potential evolution is plotted against the nominal Li content (NLC).

the potential decay at the beginning is relatively steep. So far the current-time curves observed at the different potentials all showed similar behavior. The current decreases in a concave shape featuring a high slope at the beginning which gets smaller with time. This shape will be referred to as "standard shape" in the following (see Fig. 5.21 (d)).

At 200 mV, however, a faradaic electrochemical process comes into effect. The potential value can be held considerably longer than the previous potential value (about 1000 s) without the current dropping under the limit. In addition, the current shows a behavior deviating from the standard shape ("non standard shape" in Fig. 5.21 (c): After about 30 s of decreasing quickly (similar to the standard shape) it passes a minimum and starts increasing again. The increase is significantly slower than the previous decrease, but after 320 s the even value of current from the beginning of the potential step is recovered. After passing a maximum at just this current the current decreases again, but considerably slower than at the beginning of the potential step. The decrease of current is only interrupted by a time limit for the potential step, set in addition to the current limit due to practical reasons. Lowering the potential to 180 mV the current initially increases again and starts dropping down quickly. But as at the previous potential level after a short time of steep decay a faradaic electrochemical process comes into effect. Current is turned over in this electrochemical process and the quick decay of current is stopped. Unlike at the previous potential level it does not start to increase again, but it goes down rather slowly. The electrochemical processes dominating the potential steps at 200 mV and 180 mV are supposed to be identical since only the time limit forced a premature potential reduction to 190 mV. With this the potential steps at 200 mV and 180 mV form a first lithiation potential plateau (A1).

Reaching the subsequent potential step at 160 mV the situation has changed back again. There is no significant faradaic electrochemical process consuming the current any more and consequently the current drops down again quickly showing standard shape. The same holds also for the next potential steps until at 60 mV the situation turns again. Another considerable faradaic electrochemical reaction becomes apparently into effect. Again the current first starts dropping down, gets curbed then, passes a minimum and increases again, similar to what happened at 200 mV. At 60 mV the following maximum is even more pronounced than at 200 mV. Since at 60 mV the time limitation came into effect again the potential was reduced to 40 mV before the current limit of 5 μ A was reached. Consequently the potential step at 40 mV is prolonged by finishing the electrochemical process starting to occur at 60 mV. With this the potential steps at 60 mV and 40 mV form a second lithiation potential plateau (A2). At the subsequent potential steps until the potential limit of 5 mV no pronounced electrochemical reaction takes place any more,

and so the potential steps consume only little time.

Having a closer look to the lengths of the potential steps occurring during the transition between the first and the second potential plateau it gets apparent that the potential step at 100 mV is slightly wider than the surrounding steps (IA1). This reminds to the intermediate plateaus found in the galvanostatic measurements.

Concluding the previous paragraphs during the potentiostatic lithiation half-cycle two potential plateaus (A1, A2) showing characteristic current responses deviating from the standard shape (see Figs 5.22 (c) and (d)) can be detected reminding to the potential plateaus known from the galvanostatic measurements. During the potentiostatic lithiation half-cycle a correspondence to the intermediate plateaus found in the galvanostatic measurements is detectable (IA1). Within the potential decrease between the first and the second lithiation potential plateau the potential step at 100 mV is slightly wider than the surrounding steps.

Then the potential is started to be increased again step by step in the delithiation halfcycle. Until 100 mV the potential steps are very short, then they start to broaden. At 180 mV an significant faradaic electrochemical process comes into effect. The potential step is again very broad as it was the case at the potential plateaus during stepwise lowering of the potential. But the current response is different from the response observed at the potential plateaus in the lithiation half-cycle. Unlike at the lithiation potential plateaus the current does not start to increase again after an initial drop. Instead in the beginning the decay is less pronounced and after some time there is a kink in the currenttime-curve whereupon the current decreases slower than before. Also at this potential plateau the time limitation comes into effect and the potential is raised to 200 mV without the current having been dropped to the lower current limit of 5 μ A. The current response to this shows different behavior then the response to the previous raising of potential to 180 mV. After only a very short pronounced decay the current turns to decrease only very slowly. With time the decay gets increasingly steeper again. In consequence, there is a inflection point in the current-time curve. The characteristic current-time evolution previously described for the potential step at 200 mV is observable also at the next potential step at 220 mV being still a relatively broad one, but considerably narrower than the previous step at 200 mV. Together the potential steps at 180 mV, 200 mV and 220 mV form a first delithiation potential plateau (B1).

During the following rather narrow potential steps the current-time-curve returns to its "standard shape" until at 360 mV the potential step width suddenly increases to yield a relatively broad step again forming a second delithiation potential plateau (B2). The current-time-curve at 360 mV reminds to what was observed at the lithiation potential plateaus: First the current drops quickly, but only a bit before it reaches a minimum. After, it increases again and reaches after short time a maximum before it decreases slowly, but accelerating at the end. The subsequent potential steps are narrower again and the current-time-curve regains their standard shape.

At 460 mV, 480 mV and 500 mV the last "reactive" potential region (B3) is reached represented by broad steps. At 460 mV the current drop is of standard shape, but considerably slower than between the reactive regions. At 480 mV the current-time-curve of different shape: A very short steep decay is followed by a much less steep almost linear one. At 500 mV the situation is similar to 480 mV, but the potential step is narrower. The described last potential plateau in the delithiation half-cycle (B3) is followed by a steep increase in potential. The associated narrow potential steps feature current responses in standard shape until the upper voltage limit of 1.5 V is reached and the next cycle starts.

Having a closer look to the lengths of the potential steps occurring during the transition between the first and the second delithiation potential plateau it gets apparent that the potential step at 260 mV is conspicuously broad (IB1). This observation reminds to the intermediate plateaus found in the galvanostatic measurements.

Concluding the previous paragraphs during the delithiation half-cycle three potential plateaus (B1, B2, B3) showing characteristic current responses deviating from the standard shape (see Figs 5.21 (a) and (b) can be detected reminding to the delithiation potential plateaus known from the galvanostatic measurements. Also during the potentiostatic delithiation half-cycle a correspondence to the intermediate plateaus found in the galvanostatic measurements is detectable (IB1). Within the potential increase between the first and the second delithiation potential plateau the potential step at 260 mV is conspicuously broad.

In Figure 5.21 (b) the potentiostatic lithiation-delithiation cycles from Fig. 5.21 (a) are plotted versus the nominal Li content. The nominal Li content (NLC) reached in the above described potentiostatic lithiation-delithiation cycle measurements is 2.72 Li atoms per Au atom during the lithiation half-cycle and 2.53 Li atoms per Au atom during the delithiation half-cycle. Hence more Li seems to be inserted than extracted. According to a NLC during lithiation of 2.72 and 2.53 during delithiation the coulombic efficiency is 93 %.

Concluding chapter 5.11 during potentiostatic lithiation-delithiation cycles of the 100 nm Au-film employing a potential limit of 5 μ A the potential-time curve features three pronounced delithiation plateau potentials at 180 mV, 360 mV and 480 mV. In addition there is an intermediate plateaus at 260 mV recognizable. During the delithiation half-cycle there are two main potential plateaus at 200 mV and 60 mV and one intermediate
plateau at 100 mV observable.

5.12 Potentiostatic Lithiation-Delithiation Cycles II

Fig. 5.22 shows current and potential evolutions with time (Fig. 5.22 (a)) and NLC (Fig. 5.22(b)) during potentiostatic lithiation-delithiation cycle measurements performed employing a current limit of 1 μ A (instead of the above 5 μ A). This means in the lithiation branch the potential was reduced as soon as the current got more positive than -1 μ A and in the delithiation branch the potential was raised as soon as the current got more negative than +1 μ A.

The potential steps were chosen more densely for this experiment. During lithiation 0.1 V steps were chosen between 1.5 V and 300 mV, a potential range where not yet any lithiation reaction was expected to occur. Between 300 mV and the lower potential limit of 5 mV the potential was lowered in this experiment in steps of 10 mV (compared to 20 mV in the measurement employing a current limit of 5 mV). During delithiation the 10 mV potential step distance was kept until 550 mV. Between 600 mV and 1.5 V again 100 mV steps were sufficient.

In the following a detailed description of the potential-time curves and current-time curves obtained during potentiostatic lithiation-delithiation cycle experiments employing a current limit of 1 μ A and using the example of the second cycle is given. A short summary can be found at the end of the chapter.

From the potentiostatic experiment with a current limit of 5 μ A the current at potentials above 0.5 V is already known to be very low, and hence it is expectable to see the potential stepping down quite quickly at the beginning of the lithiation half-cycle. Despite the smaller current limit the potential decreased in 45 s, starting from 1.5 V, to 0.5 V to keep the current above 1 μ A (using the 5 μ A current limit it took 35 s). At smaller potentials some current arises and the potential has not to be reduced that quickly any more.

After 680 s a potential of 230 mV is reached and can be kept for about 500 s. This voltage level is the first level the current-time-curve deviates from the standard shape (see Fig. 5.22 (d)), also found in the measurements using the higher current limit of 5 μ A (compare above). The current-time curve is not a fast decay characterized by a concave shape any more. Similar to the first "stable" voltage level at the measurement using the higher current limit of 5 μ A (Fig. 5.21) the current first drops well pronounced. After a short time the decay is hindered. The current stays at constant level for a while before it again starts decreasing, but much slower than at the beginning. In contrast to the measurement using the 5 μ A current limit (Fig. 5.21) it does not turn to increase after the



Figure 5.22: Potentiostatic lithiation-delithiation cycles acquired at the Au thin film sample. During lithiation the potential was decreased in small steps starting from 1.5 V. Reaching the lower potential limit of 5 mV the potential was risen again stepwise to 1.5 V. Every potential step was held until the provoked current had decreased below the current limit of 1 µA. The received potential-time / potential-NLC curves show characteristic plateau potentials where the current can be held above the current limit for a long period. Fig. 5.22 (a) shows a plot of the potential-time curves during the potentiostatic measurements together with the current-time evolutions measured. In Figs. 5.21 (c) and (d) exemplarily by means of the second cycle selected excerpts from Fig. 5.22 (a) are presented to highlight the difference in current-time curves recorded at actual potential plateaus and during periods of pronounced potential decay. In Fig. 5.22 (b) the potential curve is plotted against the nominal Li content (NLC). The technique of measuring is the same as in Figure 5.21. Only the current limit is 1 µA instead of 5 µA.

initial decay but only forms a plateau. The next potential step, 220 mV, is held ten times longer (about 5000 s) signifying the faradaic electrochemical process causative for the first lithiation potential plateau coming into effect actually only at 220 mV. The associated current-time-curve is similar to the curve at the previous potential step featuring, however, a maximum of current after the initial decay. The subsequent voltage plateau (210 mV) takes only 2000 s, hence the first lithiation potential plateau (A1 in Fig. 5.22 (b) comes to an end. The current-time-curve reminds to the curve obtained at 230 mV showing only a plateau and no maximum after the initial decay. The subsequent voltage steps get successively shorter and the current-time curves return to the standard shape from step to step. After a few steps there is one step at 120 mV of about double the width of the previous steps (IA1). The associated current-time-curve slightly differs from the standard shape. This reminds to the intermediate plateaus found in the galvanostatic measurements.

After this broader step the steps are of similar width as before it again. Meanwhile the potentials has lowered to 100 mV. At 90 mV another significant faradaic electrochemical process starts (see Fig. 5.22 (c)). At the beginning of the potential step the current-time curve resembles the one at 100 mV showing just a steep concave decay. When the current has dropped to 1.5 μ A there is a sudden change. The current runs into a minimum and starts increasing very pronouncedly afterwards. After passing a maximum at three third of the initial current value of this step, the current decreases only very slowly in a slightly concave shape taking as much as 6500 s to reach the current limit of 1 μ A. The next potential steps are also rather broad. They take 1600 s, 700 s and 400 s. Together the potential steps between 90 mV and 60 mV form the second lithiation potential plateau (A2). The associated current-timen curves feature qualitatively similar behavior showing a shape deviating from the standard shape, but featuring no minimum. The following steps are smaller until the lower potential limit is reached: Their current-time curves show standard shape.

Concluding the previous paragraphs during the potentiostatic lithiation half-cycle two potential plateaus (A1, A2) reminding to the potential plateaus known from the galvanostatic measurements can be detected. They show characteristic current responses deviating from the standard shape (see Figs. 5.22 (c) and (d). Also an analogon to the intermediate plateau observed in the galvanostatic measurements between the two lithiation potential plateaus is apparent.

The first potential steps during the delithiation half-cycle are very narrow. Accordingly the current drops very steeply during these potential steps. After only 500 s 160 mV is reached. The potential steps become broader again. The subsequent three potential

steps at 170 mV, 180 mV and 190 mV are with 1500 s, 3000 s and 1000 s are very broad accompanied by a non standard current-time curve. The quick drop of current is hindered at about three third of the initial current and transforms into a slower decay its shape is different for the three respective cycles. The first delithiation potential plateau is thus located around 180 mV (B1 in Fig. 5.21 (b))). Thereafter the potential steps get smaller resulting in pronouncing increase in potential. Subsequently two relatively broad steps occur at 340 mV and 350 mV featuring specific non standard current-timecurves. The second delithiation potential is reached (B2). Directly thereafter the steps get narrower and the potential increase steeper again. A last region of broad potential steps is established between 440 mV and 480 mV. During this third delithiation potential region (B3) the current drops quickly to half the initial value and turns abruptly then to a slow slightly concave decay. After the last delithiation plateau is finished, the potential rises in short time to the upper potential limit.

Concluding the previous paragraph during the potentiostatic delithiation half-cycle three potential plateaus showing characteristic current responses can be detected (B1, B2, B3) reminding to the potential plateaus known from the galvanostatic measurements (Figs. 5.10 and 5.12). Also during the delithiation half-cycle a correspondence to the intermediate plateaus found in the galvanostatic measurements is detectable (IB1). Within the potential increase between the first and the second delithiation potential plateau the potential steps at 240 mV and 250 mV are wider than the surrounding steps.

In Figure 5.22 (b) the potentiostatic lithiation-delithiation cycles from Fig. 5.22 (a) are plotted versus NLC. The nominal Li content (NLC) reached in the above described potentiostatic lithiation-delithiation cycle measurements is 2.88 Li atoms per Au atom during the lithiation half-cycle and 2.56 Li atoms per Au atom during the delithiation half-cycle. Hence more Li seems to be inserted than extracted. According to a NLC during lithiation of 2.88 and 2.56 during delithiation the coulombic efficiency is 89 %.

Concluding chapter 5.12 during potentiostatic lithiation-delithiation cycles of the 100 nm Au-film employing a potential limit of 1 μ A the potential-time curve features three pronounced delithiation plateaus at 180 mV (B1), 350 mV (B2) and 450 mV (B3). In addition there is an intermediate plateau at 240 mV/250 mV (IB1) recognizable. During lithiation there are two main plateaus at 220 mV (A1) and 90 mV (A2) and one intermediate plateau at 120 mV (IA1) observable.

5.13 Comparison: Potentiostatic Lithiation-Delithiation Cycles I/II

In Figure 5.23 (a) and (b) the voltage-NLC curves during lithiation and delithiation yielded employing potential limits of 5 μ A and 1 μ A are compiled. On the first view they show many similarities.

General Shape of Potential-Time Curves, Plateaus

Like the measurements employing a potential limit of 5 μ A the measurements employing a potential limit of 1 μ A show two main plateau potentials during lithiation and three main plateau potentials during delithiation. Intermediate plateau potentials in analogy to the intermediate plateaus observed in the galvanostatic measurements between the first and the second lithiation plateau and the first and the second delithiation plateau are announced by slightly broader potential steps and associated current-time curves deviating from the standard shape. Also beyond these particular features the potentialtime curves acquired employing potential limits of 5 μ A and 1 μ A show high qualitative similarity in shape.

Dependency of Plateau Potentials on Current

Quantitatively a significant difference in the plateau potential becomes immediately clear from the potential-NLC curves. During lithiation the plateau potentials are higher at a potential limit of 1 μ A, during delithiation they are lower at at a potential limit of 1 μ A. An overview over the plateau potentials at both lithiation rates is given in table 5.4.

Difference in NLC during Lithiation/Delithiation

Figure 5.23 and table 5.5 also shows the maximal NLC during lithiation with 2.88 equivalents to be higher at a current limit of 1 μ A than the maximum NLC during lithiation at 5 μ A (2.72). Also the maximum NLC extracted during delithiation is a little higher at the 1 μ A current limit (2.56) than at 1 μ A (2.53)). The discrepancy between the NLC inserted and extracted, respectively, is higher at a potential limit of 1 μ A. The coulombic efficiency calculated based on the previous values is higher at 1.7 C (93%) than at 0.17 C (89%).



- Figure 5.23: Comparison of the voltage-NLC curves obtained during potentiostatic lithiation-delithiation measurements employing current limits of 5 μ A and 1 μ A, respectively. Displayed are the third cycle from Figure 5.21 (current limit 5 μ A) and the second cycle from Figure 5.22 (current limit 1 μ A). The shape of the voltage curves for both current limits is relatively similar. The positions of the potential plateaus are qualitatively comparable. Hence the underlying alloying mechanisms are the same. Nevertheless quantitatively differences in absolute value of the potential plateaus are obvious. Employing the lower current limit (1 μ A) during lithiation the deposition potentials are higher. During delithiation the potential plateaus are located at lower potential employing the lower current limit. The previously described observation can be explained by higher ohmic and electron transfer resistance at higher current.
- Table 5.4: Overview over the positions of potential plateaus during potentiostatic lithiation-delithiation cycle experiments employing different current limits. At the lower current limit (1 μA) the potential plateaus are located at higher potentials during lithiation and at lower potentials during delithiation than at the higher current limit (5 μA).

lithiation potentials	current limit 5 µA	current limit 1 µA
1 st lithiation potential	200 mV/180 mV	$230 \ {\rm mV}/220 \ {\rm mV}/210 \ {\rm mV}/200 \ {\rm mV}$
1 st intermed. lith. plateau	100 mV	120 mV
2 nd lithiation potential	60 mV/40 mV	$90~\mathrm{mV}/80~\mathrm{mV}/70~\mathrm{mV}$
1 st delithiation potential	180 mV/200 mV	$170 \ { m mV}/180 \ { m mV}/190 \ { m mV}$
1^{st} intermed. delith. plateau	260 mV	$240~\mathrm{mV}/250~\mathrm{mV}$
2 nd delithiation potential	360 mV	$340~\mathrm{mV}/350~\mathrm{mV}$
3 rd delithiation potential	460 mV / 480 mV	$450 \ { m mV}/460 \ { m mV}/470 \ { m mV}$

Table 5.5: Comparison of the lithiation-delithiation data of the potentiostatic lithiation/delithiation experiments employing current limits of 5 μ A and 1 μ A. Employing the lower current limit (1 μ A) the NLC is higher during lithiation as well as during delithiation. But the discrepancy between the NLC during lithiation and delithiation is smaller at the higher current limit.

current limit	duration /s		charge $/\mu C$		NLC /eq.	
	lith.	delith.	lith.	delith.	lith.	delith.
5 μA	3165	3662	32338	30298	2.72	2.53
1 µA	17803	15795	34265	30345	2.88	2.56

5.14 Discussion: Potentiostatic Lithiation-Delithiation Cycles I/II

Presence of Potential Plateaus

From Fig. 5.21 and 5.22 at the first view the different width of the different potential steps is obvious (see Figs. 5.21 (a, b) and 5.22 (a, b)). Not every installed potential is kept up for the same time span since not at every potential a considerable faradaic current is provoked. A significant faradaic current can be provoked, if at the applied potential a significant electrochemical reaction takes place. If no considerable electrochemical reactions occurs the current at the respective potential plateau decreases quickly under the set current limit and the potential is consequently changed to the subsequent potential step.

Consequently the potential plateaus observed in the potentiostatic lithiation-delithiation cycle measurements (A1, A2, B1, B2, B3 in Figs. 5.21 (b) and 5.22 (b)) signify electrochemical transformation of one phase into another, in analogy to the plateaus in the potential time curves of the galvanostatic lithiation-delithiation measurements (A1, A2, B1, B2, B3 in Figs. 5.10 (b) and 5.12 (b)). At the observed potential plateaus phase transformations between different phases occur. The phases in equilibrium at the respective potential plateau are supposed to feature apart from the same electrochemical potential consequently also same Gibbs enthalpy and same chemical potential.

Characteristic Shape of Potential-Time Curves Next to the Potential Plateaus

During every potential step the provoked current decreases tendentially with time and vanishes when the respective electrochemical process is completed. At potential steps a significant electrochemical reaction for example a phase transformation occurs the decrease of current to reach the set current limit takes significantly longer than at the potential steps where only non-faradaic currents are prevail. In the above presented potentiostatic lithiation-delithiation cycle measurements (see Figs. 5.21 (a, c) and 5.22 (a, c)) not only at two specific potentials during lithiation and three specific potentials during delithiation the width of the potential steps was found to be significantly higher than at the other potentials. Admittedly the potential plateaus are found to occur rather abrupt while changing the potential. There is only a slight widening of the potential steps observable before the actual plateau potential. But the potential steps after the actual potential plateaus show a significantly less pronounced narrowing. This means that at the end of the electrochemical transformation a higher overpotential is necessary to complete the transformation. This finding reminds to the peaks in the differential charge curves showing a tailed shape (see Figs. 5.11, 5.14). As in the discussion of this tailed shape in section 5.7 also the phenomenon discussed here can be most probably attributed to regions in the sample more difficult to access for the Li atoms associated with (higher) (diffusion) overpotential.

Characteristic Widths of Potential Plateaus

The width of the potential plateau should correlate with the difference in Li content of the phases transforming at the respective potential plateau. Staying in this image during the two (broad) potential plateaus during lithiation (A1, A2) a large difference in Li content is probably overcome while during the second delithiation plateau (B2) only a small difference in Li content is overcome. The analogs to the intermediate plateaus detected in the galvanostatic measurements (IA1, IB1) observed in the potentiostatic measurements (see Figs. 5.21 (b, c, d) and 5.22 (b, c) which are characterized by slightly widened potential step widths are supposed to represent electrochemical phase transformations between phases very close in Li content. Since electrochemical Li-metal alloy phase formation is known to occur at potentials above the actual Li deposition potential (0 V vs. Li/Li+). In summary, the observed plateaus are assumed to origin from several steps of Li-Au alloy phase formation and dissolution.

Mechanistic Comparison / Thermodynamic/Kinetic Stability of the Alloy Phases

Since the potential-time curves measured employing a current limit of 5 μ A (Fig. 5.21) and 1 μ A (5.22) not only feature the same number of lithiation and delithiation plateaus but also highly similar quantitative behavior the lithiation and delithiation can be assumed to proceed following very similar or identical reaction paths. The fact that the same

phase transitions occur in both measurements associated with mean currents of 8 μ A (current limit 5 μ A) and 2 μ A (current limit 1 μ A) proves their kinetic stability within this current range and points to possibly also thermodynamic stability. Since there are different numbers of plateaus during lithiation and delithiation the lithiation and the delithiation processes are supposed to occur along different paths. This insight is, however, not compatible with the before considered thermodynamic stability of the anticipated Li-Au alloy phases and rather suggests only kinetic stability.

Dependency of Plateau Potentials on Current

Comparing the potentiostatic lithiation-delithiation cycles employing a current limit of 5 μ A and 1 μ A (see Fig. 5.23) the correlating potential plateaus turned out to shift at higher current limit to lower values during lithiation and higher values during delithiation. Since a higher current limit implicates higher mean current (8 μ A mean current for the current limit of 5 μ A, 2 μ A mean current for the current limit of 1 μ A)) a behavior like this is expectable and can be attributed principally to the ohmic resistance of the cell and and electron transfer resistance through the electrode's surface leading at higher current to higher overpotential ($U = R \cdot I$). Mainly at the higher current also diffusion overpotential may come into effect.

Difference in NLC during Lithiation/Delithiation

The lithiation half-cycle in the galvanostatic potential-time/NLC curve is found to take longer (with respect to time as well as to NLC) than the delithiation half-cycle at both current limits employed (Fig. 5.21 (b) and 5.22 (b)). A higher NLC was achieved during lithiation than consumed during delithiation.

The most obvious reason for such behavior, Li remaining in the electrode material during the lithiation-delithiation cycle, can be excluded regarding the reproducibility of the potentiostatic potential-time curves over several cycle in analogue argumentation as in the context of the galvanostatic measurements.

More probably the observed difference in NLC between the lithiation and the delithiation branch is attributable to SEI-film reordering and anew formation as considered to be the reason for the current dips at the beginnings of the lithiation plateaus and the analogue potential dips in the galvanostatic potential-time curves. Consequently the total Li content of the sample can also in the potentiostatic case be best estimated from the delithiation branch. Considering the Li dissolution to be quasi complete the maximum NLC employing a current limit of 1 μ A (2.56) is almost identical to the maximum NLC employing a current limit of 5 μ A (2.53). Hence employing both current limits the same amount of Li could be inserted.

The discrepancy between the maximum NLC during lithiation and delithiation is considerably higher employing a current limit of 1 μ A than a current limit of 5 μ A. Assigning this discrepancy to SEI-film formation would mean that SEI-film formation employing the lower current limit takes a higher fraction of the current converted , possibly since the SEI-film has more time to properly structure and order at lower current.

Characteristic Shape of Current-Time Curves

In the measurements employing both current limits the shape of the current-time-curve (see Figs. 5.21 (a, c, d) and 5.22 (a, c, d)) is meaningful. In Fig. 5.24 (a) the current-time-curves, assigned to the potential steps before, during and after the second delithiation plateau, normalized to unity potential step width, are shown. When no significant electrochemical reaction takes place the shape of the current-time curve is like shown in Fig. 5.24 at 320 mV, 330 mV and 390 mV. This shape was called the "standard shape" in chapter 5.11. It is characterized by a quick nonlinear monotonous decrease of the current on time. The current flowing during the decay time is composed of two contributions.

The first contribution to the current flowing, dominant at the beginning, is the charging of the electrochemical double layer. The current used for charging of an electrochemical double layer is proportional to the change of electrode potential with time. The proportionality constant is the capacitance of the electrochemical double layer C_d (eq. 5.1).

$$I = C_d \cdot \frac{dE}{dt} \tag{5.1}$$

The potential is specified as a step function. The potential change from one step value to the next is almost instantaneous. The current cannot react immediately. So most of the current needed to recharge the electrochemical double layer flows when the potential has already reached its new value. Since the rate of potential change is relatively high the current is high as well. It dominates the current-time-curve at the beginning of every new potential step.

The second contribution to the current flowing is the current due to lithiation of the Au film. This current is smaller in amplitude, but endures longer than the current for recharging the electrochemical double layer.

Fig. 5.24 (a) shows the current-time curves observed at subsequent potential steps comprising exemplarily the second delithiation potential plateau (B2 in Fig. 5.22 (b)) normalized to unity potential step width. When the potential draws closer to the plateau



Figure 5.24: Current-time-curves observed at selected potential steps during the delithiation half-cycle of the potentiostatic lithiation-delithiation experiments employing a current limit of 1 µA. The width of the potential steps is normalized to 1 a.u. (arbitrary unit). At potential steps before and after the actual plateau potential the current-time-curves show standard shape. As exemplified in Fig. 5.24 (a) for the case of the second delithiation potential plateau (B2 in Fig. 5.22 (b)) at the actual plateau potential larger total currents are observed. Comparing the current-time-curves at the different potential plateaus they turned out to differ (Fig. 5.24 (b)). Different delithiation kinetics for delithiation of the different alloy phases can be assumed from this.

value at which the significant electrochemical reaction proceeds the shape of the currenttime-curves starts to change to pronounced extend. The contribution of the lithiation or delithiation current gets higher. At the actual plateau potential value the contribution of the lithiation or delithiation current is the highest. In the presented example of the second delithiation plateau (Fig. 5.24 (a)) this is the case at 350 mV/360 mV. At the end of the potential plateau follows a transition of the current-time-curve back to standard shape. The contribution of the previously dominating electrochemical reaction gets smaller again.

Fig. 5.24 (b) compiles the current-time curves assigned to the actual plateau potentials of the three delithiation steps (B1, B2, B3 in Fig. 5.22 (b)) normalized to unity potential step width. The current-time curves at the actual potential plateaus are found to differ from plateau to plateau. Every potential plateau shows a characteristic shape of the associated current-time curve (Fig. 5.24(b)). From the different shapes of the currenttime curves at different potential plateaus differences in lithiation/delithiation kinetics between the respective lithiation/delithiation steps (expressed by the different potential plateaus) can be concluded.

Also during lithiation characteristic shapes or changes in shape of the current-timecurves can be found. In Fig. 5.25 (a) the current-time-curves before, during and after



Figure 5.25: Fig. 5.25 (a) shows the current-time curves observed at selected potential steps around the second lithiation plateau (A2 in Fig. 5.22 (b)) of the second cycle of the potentiostatic lithiation-delithiation experiments employing a current limit of 1 μA (Fig. 5.22). The width of the potential steps is normalized to 1 a.u. (arbitrary unit). At potential steps before and after the actual plateau potential the current-time-curve shows the standard shape. At the actual plateau potential the shape of the normalized current-time curves differs significantly from the standard shape due to the actual dominating electrochemical process superimposing to the current due to charging of the electrochemical double layer capacitor and SEI-film formation giving rise to the standard shape. Fig. 5.25 (b) represents an excerpt from Fig. 5.22 (a) providing an overview in real time over the current evolutions plotted in Fig. 5.25 (a) normalized to 1 a.u. .

the second lithiation plateau (A2 in Fig. 5.22 (b)), normalized to unity potential step width, are arranged. Fig. 5.25 (b) shows for orientation the current-time curves from Fig. 5.25 (a) together with the associated potential-time curves in the chronicle order (compare Fig. 5.22 (a). The first five curves (160 mV-100 mV) belong to potential steps before the actual lithiation potential. Except the curve at 120 mV they all show similar evolution. The individual current decay curves are similar in shape. The different extend of bending is due to differences in real potential step length. The curve at 120 mV however has a remarkably different shape. It intersects some of the before mentioned curves. It belongs to a potential step being considerably wider than the surrounding steps. 120 mV is the potential at which in the galvanostatic measurement at 0.17 C (Fig.5.12) an intermediate plateau was found to occur (IA1). Hence the phase transition occurring at the intermediate plateau in the galvanostatic measurement can also be assumed to occur in the potentiostatic measurements (see above).

At 90 mV the lithiation potential plateau (A2) starts. The corresponding current-timecurve features a shape considerably different from the shapes of the current-time curves observed at higher potentials. In Fig. 5.25 (b) (showing the current-time-curves shown in Fig. 5.25 without normalization in chronicle order (compare Fig. 5.22 (a))) the currenttime curve at 90 mV can be observed to be akin to the current-time curves at 100 mV or 110 mV at the very beginning of the potential step. The current just drops down quickly. At 90 mV, however, short before reaching the current limit the decay turns into a increase of current. Hence, a significant faradaic electrochemical process has arisen. Remarkably the significant faradaic electrochemical process does not arise immediately when the potential is lowered to 90 mV, but obviously needs some time of lingering at the potential step. But after is has been initiated it continues for a long time avoiding the current to drop to the set limit for 5450 s. The electrochemical process taking place during the resulting potential plateau (A2) is another step of alloy formation. The alloy phase present before the beginning of the voltage plateau is converted into another alloy phase.

The result of superimposition of the two previously discussed current contributions is a dip in the current-time curve measured during the lithiation potential plateau recalling the dips observed in the potential time curves at the beginning of the lithiation plateaus of the galvanostatic measurements (Fig. 5.12).

As already discussed for the dips in galvanostatic potential-time curves (see chapter 5.7) also the dips in the potentiostatic current-time curve could origin either from SEI-film formation occurring parallel to lithiation and at the same time lowering the lithiation potential or from the interplay between nucleation and nucleus growth assuming the

nucleation to occur at lower potentials than nucleus growth.

If SEI-film formation is the process decisive for the occurrence of the current dips, lowering the potential during potentiostatic measurements to keep the current above the current limit would at some point yield in the installation of a potential the SEI-film can grow at. While SEI-film grows the lithiation potential would shift above the installed potential resulting in a retarded current increase at the installed potential.

If nucleation is the decisive process, lowering the potential during potentiostatic measurements to keep the current above the current limit would at some point yield in the installation of a potential nucleation can occur at. The subsequent nucleus growth requiring only lower potential than the installed potential would give rise to a retarded current increase at the installed potential.

As discussed in context with the galvanostatic measurements (see chapter 5.7) the explanation assuming SEI-film formation might be favored, since the dips in the current-time curves are only present in the current-time curves during the two lithiation potential plateaus (apart from very tiny dips in the current-time curves during the second delithiation potential plateau) and the NLC also in the potentiostatic measurements is higher during lithiation.

Concluding the previous discussion concerning the origin of the dips in the potentiostatic current-time curves at the lithiation plateau potentials, analogue to the case of the galvanostatic measurements, the reason for the observed current dips can be related either with the SEI-film formation or with the interplay between nucleation and nucleus growth or to a superimposition of both phenomena. A definitive distinction is not possible here.

Reaching the subsequent potential step at 80 mV the current-time-curve differs again. Although the potential step at 80 mV is still broad and the formation of the Li richer alloy phase started at 90 mV is supposed to continue the current-time curve differs significantly from the curve observed at 90 mV. No dip is found at the beginning of the current-time curve anymore. The explanation for this can be found either considering the nuclei for the new alloy phase already to be formed or assuming the SEI-film already to be present (compare above). The same argumentation holds for the next potential steps at 70 mV and 60 mV still belonging to the second lithiation potential plateau (A2).

At 40 mV and 20 mV the phase conversion process taking place during the previous potential plateau is finished. The shapes of the current-time-curves (Fig. 5.25) differ from the curves observed at 90 mV,80 mV, 70 mV and 60 mV. The shape at 40 mV and 20 mV reminds to the shape observed at the potential steps (at 100 mV or 110 mV) before the phase transformation. But the shape of the current-time-curves at 40 mV and 20 mV is not identical with the shape of the current-time-curves at 100 mV or 110 mV. However it

is also meant by the expression of "standard shape". Hence obviously "standard shapes" before and after the phase transformation differ.

This observation is, however, expectable, since the composition of the surface of the sample in contact with the electrolyte changed during the phase transformation. Hence, the charging of the electrochemical double layer can be expected to show different behavior, because the double layer capacity at the new surface may be different than before and also the further lithiation inside the composition range of the new phase follows other mechanisms than the lithiation of the lower lithiated phase before the phase transition. Hence, the "standard shape" of the current-time-curve in the lower potential range ruled by charging of the double layer, SEI-film formation, and further lithiation is expected to be different from the the "standard shape" of the current-time-curve in the higher potential range.

Analogous argumentation holds for the first lithiation potential plateau. The following argumentation is exemplified for the case of nucleation being the reason for the occurrence of the current dips. But in the case of SEI-film formation being the reason for the occurrence of the current dips the argumentation would be analogue.

At the beginning of the first potential step contributing to the potential plateau (220 mV) the current-time-curve also shows an initial drop which is then turned into an intermediate increase. So also for the underlying phase transformation there is first a need for nuclei to form which can after their relatively long formation time grow relatively quickly. The subsequent potential steps of the potential plateau do not feature a dip in the current-time-curve any more. The new phase has already nucleated and crystallites just have to grow. The time consumed until the respective newly formed phase can grow is with 60 s each about the same at the first lithiation potential plateau (A1) and the second lithiation potential plateau (A2). Consequently, nuclei able to grow further are formed in the same time. But in case of the second phase transformation the nuclei grow quicker than for the first. At the second phase transformation the current increases after the dip much steeper and reaches more than double the maximum value than at the first one. In consequence phase growth is faster for the second phase transition.

Concluding the previous paragraphs it can be stated that the nucleation of the respective newly formed alloy phase for both phase transformations observed during lithiation is considerably slower than the nucleus growth.

During the first and the third delithiation potential plateau (B1 and B3) there is no dip observed at the beginning of the current-time-curve associated with the respective first contributing voltage step. The growth of the respective new lower lithiated alloy phase starts directly at the beginning of the respective potential step showing the respective characteristic current-time-curve shown in Fig. 5.24 (b). Hence, either there are still nuclei of the phases left in the sample (from the lithiation process) or the nucleation is very quick. If the latter explanation would be accurate the nucleation of the newly formed allow phases can be assumed to be considerably quicker than the nucleus growth.

At the beginning of both potential steps of the second delithiation potential plateau there is a very small and narrow dip. Consequently in the associated phase transformation nucleation is a limiting step. But as mentioned it does not take long time until there are enough nuclei to grow further in the sample. The dip occurs only 0.6 s after the potential was increased. Hence, in contrast to the other phase transformations discussed before for the second delithiation phase transformation the rate of nucleation can be assumed to be of the same order as the rate of nucleus growth. At both potential steps occurs nucleation as well as nucleus growth.

5.15 Overview: Galvanostatic and Potentiostatic Lithiation-Delithiation Cycles I/II

Fig. 5.26 (a) shows a comparison between the potential-time curves measured galvanostatically at 1.7 C (16.6 μ A) and 0.17 C (1.66 μ A) and potentiostatically employing current limits of 5 μ A (mean current: 8 μ A) and 1 μ A (mean current 2 μ A). Fig. 5.26 (b) represents a zoom-in into Fig. 5.26 (a).

Potential Plateaus and Intermediate Plateaus

In the potentiostatic measurements the potential evolution known from the galvanostatic experiment is reproduced very well. The two main potential plateaus during lithiation (A1, A2) and the three potential plateaus during delithiation (B1, B2, B3) are clearly recognizable.

The intermediate plateaus observed in the galvanostatic measurements are also detectable in the potentiostatic measurements. However in contrast to the galvanostatic measurements in the potentiostatic measurements only the respective first intermediate plateaus in the lithiation (IA1) and delithiation half-cycle (IB1) get apparent. Analogue to the galvanostatic measurements where the intermediate plateaus are more obvious at lower current in the potentiostatic measurements the intermediate potential plateaus are more obvious in the measurements employing the smaller current limit. They are announced in the potentiostatic measurements by slightly wider potential steps within the pronounced potential decay between the actual potential plateaus.



Figure 5.26: Comparison of the potential-NLC curves obtained by performing galvanostatic lithiation-delithiation cycles at 1.7 C (16.6 μ A) and 0.17 C (1.66 μ A) and potentiostatic lithiation-delithiation cycles employing current limits of 5 μ A (mean current: 8 μ A) and 1 μ A (mean current: 2 μ A) presented above (compare Figs. 5.10, 5.12, 5.21, 5.22). All the potential-NLC curves show two lithiation potential plateaus and three delithiation potential plateaus and high qualitative similarity. Quantitatively the plateau potentials shift in dependance of the absolute value of current flowing. The observed high similarity of the potential-NLC curves suggest very similar or even identical reaction paths of electrochemical alloying and dealloying of the investigated Au thin film sample. Fig. 5.26 (b) shows a zoom-in into Fig. 5.26 (a).

Shift of Plateau Potential with Current

The exact plateau potentials during the lithiation and delithiation half-cycle are in the galvanostatic measurements as well as in the potentiostatic measurements dependent on the absolute value of current flowing. The higher the current the more the plateau potentials during the lithiation half-cycle are shifted to lower potentials and the more the plateau potentials during the delithiation half-cycle are shifted to higher potentials.

As can be seen from Fig. 5.26 the potential plateaus of the potentiostatic measurement with a potential limit of 1 μ A (mean current 2 μ A) are at similar potential values as the potential plateaus observed in the galvanostatic measurement at 0.17 C (1.66 μ A). And the potential plateaus of the potentiostatic measurement with a potential limit of 5 μ A (mean current 8 μ A) are at similar potential values as the potential plateaus observed in the galvanostatic measurement at 1.7 C (16.6 μ A).

Occurrence of Dips in Potential-Time and Current-Time Curves

The dips at the beginning of the lithiation plateaus in the galvanostatic measurements (D1, D2) do not find their analogy in the potential-time curves of the potentiostatic measurements, since in the potentiostatic measurements the potential can only be reduced during lithiation and raised during delithiation. But the underlying phenomenon expresses in the potentiostatic current-time curves by a retarded upcoming of the current attributed to the phase transformation at the first potential step of the potential plateaus. As discussed in chapter 5.14 the result of this phenomenon is an initial pronounced decay of the current followed by a stabilization, an intermediate increase and subsequent only slow further decrease of the current. The behavior in question was found to occur to a pronounced extend at the beginning of both potential plateaus during the lithiation halfcycle and to a small extend during the second potential plateau during the delithiation half-cycle. Also in the galvanostatic measurements the dips in the potential-time curves are present at the beginning of the lithiation plateaus. The second delithiation plateau shows in the galvanostatic measurements an outstanding abrupt begin in contrast to the other delithiation plateaus. Probably this feature in the galvanostatic measurements can be correlated with special shape of the current time curves during the potential steps contributing to the second delithiation plateau in the potentiostatic measurements. As discussed in chapters 5.7 and 5.14 the equivalent phenomenon of dip occurrence in the galvanostatic potential-time and potentiostatic current-time curves can be explained by SEI-film formation or by nucleation or a combination of both.

Common Features and Differences in NLC

As discussed during the discussion of the galvanostatic lithiation-delithiation cycles (see chapter 5.7) the maximum NLC during delithiation is probably a better estimation for real Li content the sample has been lithiated to than the maximum NLC during lithiation. During lithiation simultaneously occurring SEI-film formation leads to an increased NLC most pronouncedly at lower current. Also in the potentiostatic measurements employing a current limit of 1 μ A (mean current: 2 μ A) the maximum NLC during lithiation was found to be higher as in the measurements employing a current limit of 5 μ A (mean current: 8 μ A). Also taking galvanostatic and potentiostatic measurements together still the following statement holds: The lower the lithiation current is the larger is the maximum NLC during lithiation. As discussed in chapters 5.7 and 5.14 the reason for the observed behavior could be differences in SEI formation and in accessibility of the sample for Li at the different currents.

Interestingly during delithiation the maximum NLC in both potentiostatic measurements was found to be almost identical (2.56 employing a current limit of 1 μ A and 2.53 employing a current limit of 5 μ A). Hence employing both current limits the maximum NLC during delithiation is in principle identical. Just from this observation in the discussion of the potentiostatic measurements was anticipated, that a NLC around 2.55 could be the maximum possible. Considering that the maximum NLC during galvanostatic delithiation at 0.17 C was found to be 2.54 it is very probable that the maximum possible NLC is indeed in this region.

Together with the knowledge from in-situ XRD measurements that Li_3Au is the highest lithiated phase observed the assumption arises that the electrode was in all three cases fully lithiated to Li_3Au . The "missing" Li could be explained considering contact loss of parts of the initial Au film probably already in the first lithiation-delithiation cycle. In this case 15% of the initial electrode material is not accessible anymore for lithiation probably due to the consequences of volume expansion and shrinkage.

Another possible explanation could be that Li after the first delithiation remains inside the electrode material. This approach would be capable to provide a reason for the difference between the first and the subsequent lithiation half-cycles and could moreover explain the finding from the XRD measurements that no crystalline Au is recovered after delithiation of the electrode.

Finally there is still the observation of a maximum NLC of only 2.25 during the delithiation half-cycle in the galvanostatic measurements at 1.7 C to classify. Obviously in this measurement the maximum NLC is different from all the others. Possibly during this measurement featuring the highest mean current an additional limitation probably

5 Electrochemical Characterization of an Au Thin Film Model Anode



Figure 5.27: Scheme of the proposed process of alloy formation/dissolution during galvanostatic and potentiostatic lithiation-delithiation experiments.

related to diffusion phenomena in the electrode material came into effect.

Conclusion

The very good qualitative and quantitative correspondence of the galvanostatic and potentiostatic lithiation-delithiation cycle experiments in particular with respect to the number of lithiation and delithiation potential plateaus and intermediate plateaus, the plateau potential and its dependance on current, the final degree of lithiation, the occurrence of potential/current dips and the difference between NLC inserted and extracted suggest strongly the same reaction path to be followed during lithiation and delithiation in both types of measurements at least within the covered lithiation-delithiation current range of one decimal power. In particular the appearance of the same alloy phases and the presence of the same phase transformations can be assumed. This result speaks for a considerable stability of the involved phases.

Based on the results of the galvanostatic and potentiostatic lithiation-delithiation cycle experiments a model of the lithiation-delithiation mechanism is proposed:

Fig. 5.27 shows a sketch of the proposed mechanistic model. The results of the galvanostatic and potentiostatic lithiation-delithiation cycle experiments suggested in contrast to the results of the CV measurements (see Fig. 5.8) that the complete pristine Au material is transformed during the first lithiation potential plateau of the first cycle (A1' in fig. 5.10) into an Li-Au alloy phase (lithiation state 1'). This alloy phase is during the second lithiation plateau of the first cycle (A2 in figs. 5.10, 5.12, 5.21, and5.22) entirely converted into another Li-Au alloy phase (lithiation state 2) representing the highest lithiated state observed in the presented measurements. During the first delithiation potential plateau (B1) the entire phase (lithiation state 2) is transformed into a less lithiated state (delithiation state 1). In the course of the second delithiation potential (B2) plateau the

	Li content X in Li_xAu	Li content X in Li_xAu				
	remaining Li	contact loss				
phase $1/3$	1.49 - 1.65	1.15-1.32				
phase 2	3.00	3.00				
phase 4	1.49	1.15				
phase 5	0.71	0.22				
phase 6	0.58	0.075				

Table 5.6: Li-Au alloy phases 1-6

Li-content is further reduced to yield delithiation state 2. During the third delithiation plateau (B3), however a material different from Au is recovered (delithiation state 3) even after raising the potential back to the starting value.

The second lithiation-delithiation cycle has a different starting material, hence, and also the first lithiation state in the second cycle (lithiation state 1) is different from the first lithiation state in the first cycle (lithiation state 1'). The first lithiation state in the second cycle (lithiation state 1) probably transforms during the first lithiation intermediate potential plateau (IA1) into the lithiation state 1'. From this point on the lithiation-delithiation cycles are reproducible comprising lithiation state 1, lithiation state 1', lithiation state 2, delithiation state 1, delithiation state 2 and delithiation state 3.

Alloy Phase Evolution Diagram

Moreover. based on the conclusions drawn from the lithiation-delithiation experiments an "alloy phase evolution diagram" of the Au-Li system during the electrochemical lithiationdelithiation cycles will be proposed in the following. Fig. 5.28 shows this "alloy phase evolution diagram". The nomenclature of the occurring alloy phases refers to the desciption of the results of the in-situ XRD experiments (chapter 6.5) where the nomenclature will be inductively introduced (see fig. 6.22).

In table 5.6 the assumed alloy phases together with their Li content calculated from the galvanostatic measurement at 0.17 C assuming the maximum NLC during delithiation to reflect the actual Li content of the sample. Depending on which of the above (chapter 5.15) discussed reasons for only 2.55 equivalents of Li being extracted during delithiation applies two different Li contents can be calculated. If a specific amount of Li remains inside the sample after the first delithiation the percentages are higher (second column) than if less electrode material is accessible after the first delithiation due to contact loss during the first cycle (third column).

The adoption of this nomenclature to the phenomenological development of the alloy phase evolution diagram presented here will simplify to recognize the similarity in the image of alloy phase evolution derived from electrochemistry and from the XRD-experiments.

The first lithiation plateau (after the SEI-film formation) in the first lithiation halfcycle at 158 mV described in section 5.4 is assigned to a two phase region between Au and a Li-Au alloy phase, (called phase 1/3). Then follows a region of decreasing potential indicative for a single phase region. Here only phase 1/3 is present. The following plateau at 57 mV represents a two phase region between phase 1/3 and another Li-Au alloy phase called phase 2. At the end of lithiation only phase 2 is present as can be seen from the decreasing potential. After switching the direction of galvanostatic current still only phase 2 is present. The potential increases then. It follows the first delithiation plateau at 195 mV, a two phase region between phase 2 and (again) phase 1/3. After the subsequent increase of potential (single phase region of phase 1/3) the small second pronounced delithiation plateau at 380 mV is reached where phase 1/3 transforms into phase 4. During the single phase region of phase 4 the potential increases to reach the last delithiation plateau at 480 mV where phase 4 and phase 5 coexist. The XRD results suggest to correlate the intermediate plateau observed within the final potential increase to another phase transformation leading to phase 6. The results from galvanostatic measurements (as well as the XRD results) suggest that phase 6 is not again crystalline Au as discussed above by means of the different plateau potential of the first lithiation plateau in first and second cycle. However it probably a Li-poor phase since it is the ending-phase of delithiation and no pure (lithium free) Au is recovered.

During subsequent Li loading phase 6 instead of Au forms a two phase region with a Li-Au alloy phase, similar to the first cycle. The single phase region of the phase 6 is followed by a plateau, which is however at a different potential than the first lithiation plateau in the first cycle. And another feature is new in the second cycle. In the slope following the first lithiation plateau leading to the second plateau another intermediate plateau is present, announcing an additional phase transformation. The phase next to the second plateau is supposed to be phase 1/3 as in the first cycle. This is supported by the fact of identical potential values for the second plateau in first and second cycle. Hence the phase at the end of the first plateau was not yet present in the lithiation process of the first cycle. As it will turn out in chapter 6.5 this "new" phase has already appeared in the first cycle, but during delithiation as phase 4.

In conclusion an alloy phase evolution diagram for the lithiation-delithiation of the Au film could be established showing five different Li-Au-alloy phases (phase 1-5 (phase 1/3 are in fact two phases: phase 1 and phase 3 (see chapter 6.5)) and an Li-poor boundary phase (phase 6).



Figure 5.28: Alloy phase evolution diagram for electrochemical alloying of an Au thinfilm with Li. Based on the knowledge acquired during discussion of the galvanostatic lithiation-delithiation cycle experiments an alloy phase evolution diagram can be set up containing, apart from Au, five different Li-Au alloy phases (phases 1-5, phase1/3 are in fact two different phases) and a Li poor boundary phase (phase 6). The occurrence and transition of the alloy phases can be correlated with the measured galvanostatic potential-time curves (compare Figs. 5.10 and 5.12). Also the difference between the first and the subsequent potential-time curves can be taken into account.

5.16 Comparison: CVs / Lithiation-Delithiation Cycles

In the CV measurements (Fig. 5.2) three oxidation peaks (B1, B2, B3) are obvious. In the lithiation-delithiation cycle experiments (Figs. 5.10, 5.17, 5.17, 5.21, 5.22) also three delithiation plateaus were observed. As visualized in Fig. 5.6 there is in addition a very good correlation between the peak potentials of the oxidation peaks in the CVs and the plateau potentials in the galvanostatic lithiation-delithiation cycle experiments in dependance on the current. Consequently the underlying electrochemical transition is probably identical.

While in the CV measurements there was only one reductive current peak creating the impression of three involved reduction processes by the presence of three regimes of different slope at the ascending flank of the reductive current peak, the lithiationdelithiation experiments revealed two lithiation potential plateaus. Since the currents during lithiation were higher in the CVs than in the lithiation-delithiation experiments a different lithiation mechanism in CVs than in lithiation-delithiation experiments could be considered. Because, however, the delithiation was found to be most probably identical in CVs and lithiation-delithiation experiments (see above and considering Fig. 5.6), it is improbable that during CV (at higher currents) the identical phase transformations forth and back are involved in lithiation and delithiation of the sample as assumed in the discussion of the CVs (chapter 5.3) while during lithiation-delithiation experiment different phase transformations for lithiation and delithiation are involved. And because the assumption of three phase transformations during lithiation in the CV measurements was mainly made guided by the obvious presence of three phase transformations during delithiation the results from the lithiation-delithiation experiment are considered to be more reliable.

In consequence after weighting the results of all the measurements available two lithiation processes and three delithiation processes are assumed for all the measurements including CVs. With this the range of prevalence of the observed mechanism of lithiationdelithiation can be extended to even higher currents than 16.6 µA substantiating a pronounced at least kinetic stability of the involved phases. From the occurrence of different phase transformations during lithiation and delithiation different reaction paths during lithiation and delithiation can be proven to be treated.

While the involved alloy phase transformations during CV and lithiation-delithiation experiments are according to the previous discussion considered to be identical significant differences in SEI formation between CV and lithiation-delithiation experiments were assumed in the discussions of the respective experiments. While the CV measurements suggested the SEI to be formed only in the anodic branch, in the lithiation-delithiation experiments the SEI seemed to be formed already before lithiation started.

The lithiation-delithiation cycle experiments suggest the complete lithiation of the model electrode to the highest lithiated phase which was identified based on the XRD experiments presented below to be Li₃Au. In the CV measurements only one equivalent of Li was found to be inserted and extracted reproducibly in stable operation (after the 8th cycle). In the CV measurements the potential was only for 400 s below 200 mV that is in the range where Li-Au alloy formation is expectable. Due to the quick decrease of the potential (after 150 s the potential was already at 50 mV where the second lithiation plateau was observed at a current of 16.6 μ A) high currents occurred and the second lithiation process can be assumed to having started already before the first lithiation process was accomplished. Therefore the lithium content at the surface was supposed to increase while the lower parts of the sample below were not at all lithiated. This is proved by the fact that pristine Au is still present in large amount after CVs (compare in-situ XRD) results) at the beginning of the first galvanostatic lithiation-delithiation cycle experiment. Hence a very thin surface layer was obviously lithiated quickly to even the highest lithiated phase (Li_3Au) (see Fig. 5.8). In the CV measurements the lithiation rate during the ascending flank of the reduction peak was observed to decrease in dependence of the potential (not the current). The explanation could be a decreasing Li diffusion velocity with increasing Li content of the electrode material. The upcoming diffusion resistance in the electrode material led to the decrease of slope in the ascending flank of the reduction peak with decreasing potential.

The galvanostatic lithiation-delithiation experiment at 1.7 C delivered hints for upcoming diffusion limitations at least during lithiation avoiding a complete lithiation at 16.6 μ A. Together from the CV measurements and the lithiation-delithiation cycle experiments hints for diffusion limitation through the electrode material at high currents at least during lithiation can be concluded which influence the cycling behavior of the electrode material. At small currents the model electrode is lithiated completely up to the highest lithiated phase (Li₃Au) and at very high currents only a thin highly lithiated surface layer is formed avoiding further lithiation. According to Fig. 5.6 showing linear current-potential correlation for the delithiation potentials no hint could be found to diffusion limitation during delithiation. The reason may be the higher difficulty to expand the electrode material during lithiation compared to the volume shrinkage during delithiation.

In conclusion of the electrochemical measurements the phase transformations during

lithiation and delithiation were found to be the same in galvanostatic and potentiostatic lithiation-delithiation experiments involving two phase transformations during lithiation and three during delithiation. According to the above discussion the same phase transformations can be assumed for the CV measurements.

While during CV measurements pointed to a lithiation of an only small surface-near volume of the sample (see Fig. 5.8) in the lithiation-delithiation experiments the whole sample was found to be lithiated (see Fig.6.11). The reason for this different behavior is supposed to be the difference in potential reduction rate.

The in-situ XRD measurements presented in the following chapter will lead a step further towards the aim of establishing a mechanistic model of the lithiation and delithiation processes during electrochemical alloying of Au with Li.

6 In-Situ XRD Investigation of an Au Thin Film Model Electrode

This work focuses on the use of synchrotron-based high-energy XRD for characterization of alloy phase formation and dissolution processes during lithiation-delithiation cycling of Au thin film model anodes. After characterizing the model system electrochemically in detail by lab-based electrochemical treatment presented in chapter 5 in this chapter the in-situ diffraction results of the Au thin films are reported. Au offers a number of unknown metastable intermediate phases and strongly scatters X-rays. Therefore Au was chosen as an interesting test case which nevertheless has practical implications, for instance in thin film batteries or as seed particles in relation to Si nanowire growth for battery applications..

6.1 Electrochemistry: Galvanostatic Lithiation-Delithiation of a Gold Thin Film

In-situ XRD investigations using synchrotron radiation (compare chapters 2.2, 3.6, and 4.3 for theoretical background and experimental methods) were performed during electrochemical (galvanostatic) lithiation-delithiation cycling of a 100 nm thin gold thin-film at different currents. For practical reasons discussed in chapter 3.3 the electrochemical cell used for these in-situ XRD investigations performed at the synchrotron radiation facility DESY (Hamburg) (see chapter 3.3) differed from the electrochemical cell employed for the purely electrochemical measurements performed in the lab at MPIE (see chapter 3.2). The measurements performed in the lab at MPIE will be referred to as "lab-based measurements" in the following. In contrast the experiments performed at the synchrotron radiation facility DESY (Hamburg) will be referred to as "in-situ measurements".

Since the electrochemical cells employed for the in-situ measurements differed from the lab-based cell in which the measurements presented in chapter 5 were performed, first the electrochemical behavior of the in-situ cell during the XRD measurements is described in this chapter.



Figure 6.1: Galvanostatic lithiation-delithiation cycle experiments at a 100 nm Au film on a Cu(100) singlecrystal during in-situ XRD measurements. Galvanostatic potential-time/NLC curves were measured at currents of 22.7 μ A, 16.6 μ A and 9.9 μ A. In Fig. 6.1 (a) the potential evolution with time is displayed. Fig. 6.1 (b) shows the same curves plotted against the nominal Li content (NLC). As also observed in the measurements presented in section 5.4 the first cycle differs from the second cycle (both acquired at $22.7 \,\mu\text{A}$). The lithiation plateaus (A1, A2) observed in Fig. 5.10 and 5.12 can best be recognized in the fourth cycle (9.9 μ A). Even though at the other currents the plateaus are not that pronounced as at 9.9 μ A, they are recognizable, however. During delithiation the three voltage plateaus (B1, B2, B3) known from Figs. 5.10 and 5.12 are anticipatable in all the lithiation-delithiation curves. The plateaus make apparent at which potentials phase transformations due to Li insertion into the Au thin film and extraction from the formed alloys occurs. The delithiation half-cycles are much more similar in the potential-NLC curve than the lithiation half-cycles.

It is of high importance to analyze the electrochemical measurements performed in the in-situ cell and compare the results with the measurements performed in the ex-situ cell discussed in detail in chapter 5 to be able to correlate the detailed electrochemical measurements performed in the ex-situ cell with the limited number of measurements performed in the in-situ cell. In particular it is important to be able to transfer the insights into the structural changes in the model electrode obtained during the in-situ measurements to the microscopically processes involved during the ex-situ measurements.

Fig. 6.1 shows the potential evolutions with time (6.1 (a)) and NLC (6.1 (b)) during the galvanostatic lithiation-delithiation cycles performed during the in-situ XRD measurements. (The nominal Li content is the calculational Li content assuming the entire current flown during the electrochemical lithiation or delithiation is converted in Li-ion reduction, see chapter 2.1.4) In Fig. 6.1 (a) the potential evolutions obtained at different currents (22.7 μ A (2.3 C), 16.6 μ A (1.7 C) and 9.9 μ A (1.0 C)) are plotted over time, in Fig. 6.1 (b) over the nominal Li content. Analogue to the lab-based lithiation-delithiation cycles for "in-situ lithiation" of the model electrode a negative current was applied until the installing potential dropped below a lower current limit of 5 mV. Then the current was switched is sign. The positive current to force delithiation was kept up until an upper potential limit of 1.0 V was reached.

During lithiation in principle in all the "in-situ lithiation-delithiation curves" two potential plateaus (A1, A2 in Fig. 6.1) are recognizable as also observed during the experiments performed in the glovebox in the laboratory at MPIE (compare Fig. 5.10 and 5.12). The two lithiation plateaus (A1, A2) get most apparent in the potential-time curve obtained at 9.9 μ A featuring potential plateaus at 200 mV and 70 mV, strongly reminding of the two lithiation potential plateaus occurring in potential-time curves measured in the labbased electrochemical cell which are displayed in Figs. 5.10 and 5.12. For comparison: The lab-based experiments revealed potential plateaus at 193 mV and 59 mV applying a current of 16.6 μ A and 231 mV and 113 mV using a current of 1.66 μ A.

The potential-time curves obtained at the higher currents (22.7 μ A, 16.6 μ A) are not as clearly developed as the potential time curve acquired at 9.9 μ A, but still two (main) plateaus are obvious.

Comparing the in-situ measurements at the different currents during lithiation the plateau-potentials are found to be the lower the higher the current is (Fig. 6.1). As discussed in section 5.4 the decrease in plateau-potentials with increasing current during lithiation and also the increase in plateau-potentials with increasing current during delithiation observable during delithiation in Fig. 6.1 can be explained by increasing overpotential due to ohmic and electron transfer resistance according to Ohm's law ($U = R \cdot I$).

As also already observed and discussed in chapter 5.4 presenting the lab-based galvanostatic lithiation-delithiation experiments in the galvanostatic in-situ-measurements a significant difference in shape of potential-time curves between the very first lithiationdelithiation cycle and the subsequent cycles gets apparent. Since the first two cycles shown in Fig. 6.1 were measured at the same current the comparison is without any doubt justified. In case of the in-situ measurements in the first cycle the potential plateaus are located at 160 mV (A1') and 50 mV (A2), in the second cycle at 180 mV (A1) and 30 mV (A2). As it will come out in chapter 6.5 the reason for this is most probably the difference in lithiating pristine Au in the first cycle and a different probably Li-poor phase in the subsequent cycles, since pure Au is not recovered after the first lithiation-delithiation cycle. In addition SEI-film formation could contribute to the observed difference in currenttime/NLC curve of the first and the subsequent cycles (see discussion of the lab-based measurements chapter 5.7).



Figure 6.2: Galvanostatic lithiation-delithiation cycle experiments at 16.6 µA (1.7 C) measured at a 100 nm Au film on a Cu(100) singlecrystal in the lab at MPIE (lab-based) and during in-situ XRD measurements (in-situ). In Fig. 6.2 (a) the potential evolution with time is displayed. Fig. 6.2 (b) shows the same curves plotted against the nominal Li content (NLC). According to Figs. 6.2 (a) and (b) the lithiation-delithiation cycle takes more time in the in-situ cell. However the lithiation halfcycle takes more-time and the delithiation half-cycle takes less time than in the lab-based measurements. In general in the lab-based measurements the potential plateaus A1 and A2 during lithiation and B1, B2 and B3 during delithiation are more precisly defined than in the in-situ measurements.

In addition lithiation (until the lower potential limit is undercut) takes more than double the time in the first cycle than in the second cycle in case of the in-situ measurements. As discussed for the lab-based experiments the difference between the first and the subsequent cycles is assumed to occur due to SEI-film formation and due to a change of the electrode material during the first lithiation-delithiation cycle (compare section 6.5). In contrast to the in-situ-measurements in the lab-based measurements the first lithiation half-cycle takes only 15% more time than the second one. The observed difference between in-situmeasurements and lab-based measurements could be explained by the assumption, that after only four CV cycles (see Fig. 6.3 below) in the case of the in-situ measurements the SEI-film is not that largely developed as in the lab-based experiments where 20 CV cycles were conducted before starting galvanostatic treatment (see chapter 5.2, Fig. 5.2). For this reason a larger amount of the SEI-film could still have to be build up during the first lithiation half-cycle of the in-situ-measurements. But also the assumed presence of leak currents in case of the in-situ-experiments (discussed below) is assumed to have some effect here.

During the delithiation half-cycles three plateaus are distinguishable most probably corresponding to the three delithiation plateaus observed in the lab-based measurements (see chapter 5.4, Figs. 5.10 and 5.12). In general the potential plateaus occurring during the delithiation half-cycles appear to be less pronouncedly developed in case of the in-situmeasurements than in case of the lab-based measurements. This comes most clear directly comparing the lithiation-delithiation cycles at 16.6 μ A each from both measurements (Fig. 6.2). Fig. 6.2 shows a comparison between the galvanostatic lithiation delithiation cycles at a current of 16.6 μ A (1.7 C) obtained from the lab-based measurements performed in the ex-situ cell (see chapter 3.2) and the in-situ experiments conducted in the in-situ cell (see chapter 3.2) and the in-situ experiments conducted in the in-situ much narrower and feature a more pronounced slope. While the duration of lithiation and delithiation half-cycle is comparable in the lab-based measurements in the in-situ measurements the delithiation half-cycles generally consume significantly less time than the lithiation half-cycles.

Surprisingly in all the in-situ delithiation half-cycles only about 1.2 Li equivalents are dissolved while significantly different amounts of Li seem to be inserted at the different currents (Fig. 6.1 (b)). Also in the delithiation half-cycles the above mentioned dependency of plateau potentials on the current flowing becomes manifest in analogy to the lab-based measurements.

In addition a dependency of the maximum NLC on the absolute value of galvanostatic current can be extracted from Fig. 6.1 also in analogy to the lab-based measurements.

As already mentioned comparing the lithiation-delithiation experiments at 16.6 µA from the lab-based measurements and the in-situ-measurements (Fig. 6.2) the lithiation takes significantly longer in the in-situ measurements, while the results of the XRD-measurements presented below do not suggest do not suggest a higher degree of lithiation in the in-situ measurements. Rather, also deduced from the observed differences in duration of the lithiation and delithiation half-cycles between the galvanostatic measurements at 16.6 µA in both cells (see Fig. 6.2) and the less precisely defined lithiation and delithiation plateaus in the in-situ current-time curve , leak currents in the electrochemical cell used for in-situ measurements are assumed to be responsible for the measured difference of charge converted during lithiation and delithiation. According to a closer observation of the behavior these leak currents are dependent on the applied current and the potential installed and in particular of different magnitude during lithiation and delithiation. The correction of the leak currents is discussed in more detail in the following paragraphs.

Assuming the same final degree of lithiation in the lab-based measurement and the insitu measurement the lithiation half-cycle should last the same time in both measurements at the same current (for example 16.6 μ A). This is , however, not the case. The in-situ lithiation at 16.6 μ A takes 2683 s while the lithiation in the lab took 1720 s. With this the in-situ-lithiation takes 953 s longer corresponding to a charge additionally converted of $1,59*10^{-2}$ C. To consume this absolute value of charge a current of 5.96 µA is necessary during the 2683 s of lithiation. Consequently the estimate made suggests a leak current of 5.96 µA.

As it is already obvious comparing the lithiation time at 16.6 μ A and 1.66 μ A in the lab cell, there is no rigid inverse proportionality between the current applied and the lithiation time. The product of lithiation time and current applied gets larger with decreasing current. This suggests the degree of lithiation to get higher applying smaller current (compare to similar observations in the lab-based measurements (sec. 5.7) attributed, depending on the applied absolute value of galvanostatic current, to more current consumed in SEI formation (decisive at low currents) or to incomplete lithiation due to diffusion limitations (decisive at high currents)). The behavior just described complicates to get access to the leak currents at other lithiation currents than 16.6 μ A where not both, in-situ measurements as well as lab-based measurements, are available. To come to an rough estimation rigid inverse proportionality between applied current and lithiation time is assumed. In this case holds

$$Q_1 = Q_2 \Longleftrightarrow I_1 \cdot t_1 = I_2 \cdot t_2 \tag{6.1}$$

where Q is the charge, I the current and t the time.

Taking the pair of values from the lab-based measurement at 16.6 μ A (lithiation time: 1720 s) as reference it holds:

$$16.6\mu \mathbf{A} \cdot 1720s = I_2 \cdot t_2 \tag{6.2}$$

Applying equation 6.2 to all the different lithiation cycles a theoretical time span t_2 dependent on the respective current applied can be calculated to compare with the observed duration of the lithiation half-cycle. In table 6.1 an overview is given over the calculations to estimate the leak current. In the three left columns the lithiation current and the measured lithiation time is listed for the different lithiation experiments. The fourth column gives the results for the "theoretical" lithiation time according to eq. 6.2, column five the ratio between measured and calculated (theoretical) lithiation time and column six the time difference. The charge in column seven is calculated by multiplying the time difference by the current applied and the leak current is calculated by dividing the charge by the time measured for the duration of the lithiation half-cycle. For the lab-based measurement at 1.66 µA as comparison a "leak current" of 0.31 µA could be calculated. However for this measurement the difference between the charge converted in

	lab	lab	in-situ	in-situ	in-situ
$\fbox{ current applied/ \mu A }$	16.6	1.66	16.6	9.9	22.7
time measured/ s	1720	21200	2683	7132	1310
time calc. acc. to eq. $6.2/s$	1720	17200	1720	2884	1257
ratio	1	1,23	1,56	2,47	1,04
time difference/ s		4000	963	4248	53
$ m charge/~\mu C$		6640	15986	42055	1203
$\fbox{leak current/ \muA}$		0.31	5.96	5,.90	0,.92

Table 6.1: Approach to estimate the leak currents during in-situ galvanostatic lithiationdelithiation experiments. This table applies to the lithiation half-cycle. Assuming the same degree of lithiation reached in the lab-based measurements and the in-situ-measurements the time measured for the lithiation half-cycle at 16.6 μ A each should be the same. The observed time difference can be converted into an nominal leak current. To estimate the leak currents at 9.9 μ A and 22.7 μ A rigid inverse proportionality was assumed, although rigid inverse proportionality obviously does not hold comparing the lab-based experiments at 16.6 μ A and 1.66 μ A. The resulting leak currents of are about 6 μ A.

the lithiation and delithiation half-cycles is considered to occur due to SEI-film formation and charging of the electrochemical double layer capacitor. (compare section 5.7).

For the in-situ measurements at 16.6 μ A and 9.9 μ A almost identical leak currents of almost 6 μ A are calculated. At 22.7 μ A the leak calculated current is considerably smaller, maybe due to shortcomings in the approach or due to dependence of the leak current on the lithiation current .

To get an estimation of the prevailing leak currents during delithiation an analogous approach is followed comparing the time needed for delithiation in the lab-based measurements and the in-situ measurements at 16.6 μ A. As already mentioned the charge converted during the Li extraction half-cycles is quite similar at all different currents tested. It is with around 1.2 equivalents of Li about half the NLC found in the lab-based measurements to correspond to complete lithiation assuming partial contact loss of the initial electrode material or Li remaining in the material (about 2.55 equivalents of Li). For this reason it is expectable to yield leak currents of around the magnitude of the respective delithiation current.

6.2 Electrochemistry: CVs of a Gold Thin film model electrode

Also at the sample the in-situ XRD measurements were performed at cyclic voltammograms were measured before the galvanostatic lithiation-delithiation cycle experiments.

	lab	lab	in-situ	in-situ	in-situ
current applied/ μA	16.6	1.66	16.6	9.9	22.7
time measured/ s	1650	18425	996	1695	629
time calc. acc. to eq. $6.2/$ s	1650	16500	1650	2767	1206
ratio	1	1,11	0.60	0.61	0.52
time difference/ s		1975	654	1072	577
${ m charge}/~{ m \mu C}$		3278	10856.4	10612.8	13097
$ \text{leak current/ } \mu \text{A}$		0.18	10.9	6.26	20.82

6 In-Situ XRD Investigation of an Au Thin Film Model Electrode

Table 6.2: Approach to estimate the leak currents during in-situ galvanostatic lithiationdelithiation experiments. This table applies to the delithiation half-cycle. Assuming the same degree of lithiation reached in the lab-based measurements and the in-situ-measurements the time measured for the delithiation half-cycle at 16.6 μ A each should be the same. The observed time difference can be converted into an nominal leak current. To estimate the leak currents at 9.9 μ A and 22.7 μ A rigid inverse proportionality was assumed, although rigid antiproportionality obviously does not hold comparing the lab-based experiments at 16.6 μ A and 1.66 μ A. The resulting leak currents are of about the dimension of the applied current.

Fig. 6.3 shows the current-potential curves obtained. On the first view the "baseline" is observed to be tilted against the horizontal indicating considerable ohmic resistance in the electrochemical cell. Starting from 1.0 V the voltage was reduced at a rate of 5 mV/s. In the cathodic branch between 0.7 V and 0.32 V (range B in Fig. 6.3) a very broad peak featuring very small intensity occurs. Around 90 mV (range A in Fig. 6.3) the current starts to increase significantly and keeps rising until the lower potential limit of 0 V is reached at a current of -29.7 μ A (peak A1,1). After switching to the anodic branch a small further increase of the current occurs resulting in a maximum in current at -30.3 μ A/20 mV. Consequently in the in-situ measurements a positive hysteresis is observed in the first CV cycle as also in the lab-based measurements. In further progress of potential sweep (range B in Fig. 6.3) two oxidative current peaks can be distinguished. The two oxidative peaks occur at 364 mV (peak B1) and 504 mV (peak B2). After the last oxidation peak there is no further feature in the anodic branch.

In the second cycle the broad peak observed in the first cycle between between 0.7 V and 0.32 V (range B in Fig. 6.3) is not present any more and the reductive current starts increasing already at 130 mV. The absolute value of current reached at 0 V is considerably higher in the second cycle (-44 μ A) than in the first cycle. In the following anodic branch there is still positive hysteresis, no negative as in the lab-based experiments. In the anodic branch the oxidation peaks gain in height (increasing peak current) accompanied by a shift to higher potential. In the third and the fourth cycle the reductive current at 0 V gets still higher and the oxidation peak keeps gaining in peak current and shifting.

The very broad peak between 0.7 V and 0.32 V is assumed to occur due to SEI-film formation, in analogy to the discussion of the lab-based experiment. Also the difference in potential of current increase for the reduction peak between the first and second cycle can be recognized in the in-situ experiment and is also here attributed to either the facilitation of insertion in presence of SEI-film which is not present at the beginning of the first cycle or the difference between lithiation of Au and what remains after delithiation. In the proceeding of the present chapter it will be proven that Au is not recovered after delithiation and instead another phase remains.

The two oxidation peaks found in the in-situ experiment at 364 mV and 504 mV occur at similar potentials than the second and the third peak in the lab-based measurement (356 mV, 484 mV). Therefore the two reductive peaks observed in the in-situ measurements are assumed to correlate with the second and third reduction peak in the lab-based measurements. Same phase transitions are assumed to occur in both measurements. For comparison it has to be noted that the exact peak position turned out to be dependent on the current flowing.

The increase of reductive (peak A1) and oxidative (peak B1, B2) peak current with increasing cycle number could be explained as above by ongoing crack formation, increasing electrode surface area and ameliorating accessibility for Li.

The first oxidation peak from the lab-based measurements cannot be found in the in-situ measurements. In addition the in-situ measurements do not show negative hysteresis after the first (second) cycle. These two observations may origin from the same phenomenon. As assumed during discussion of the in-situ galvanostatic experiment leak currents are assumed to be of relevance in the in-situ cell. The leaks current may lead to (preferred) dissolution of the highest lithiated phase. This highest lithiated phase also assumed from the discussion of the lab-based measurements (section 5.3) to feature lowest Li conductivity was assumed to be the reason of growing difficulties to insert further Li. When this phase gets (preferentially) dissolved, further Li can diffuse into the electrode material still at higher rate also in the anodic branch to form lower lithiated alloy phases and there will be no oxidation peak in the anodic branch due to forced dissolution of the highest.

6.3 X-ray Diffraction: Characterization of a Gold Thin Film Model Electrode

To investigate the structural changes within the Au thin-film electrode during the previously described galvanostatic lithiation-delithiation cycles in-situ X-ray diffraction (in-situ



Figure 6.3: Cyclic Voltammogram of the Au-thin-film-electrode used for in-situ XRD measurements in the ionic liquid $Pyr_{14}TFSI$ in presence of the Li salt LiTFSI. The scan rate was 5 mV/s. The cathodic branch only features one peak assigned to Li insertion. In the anodic branch there are two peaks similar to the second and the third delithiation peak found in the lab-based measurements (Fig. 5.2). The first delithiation peak found in the lab-based measurements is not present here. Possible reason for the discrepancy are the leak currents in the cell discussed above.

XRD) measurements were performed. The experiments were carried out using hard Xrays of a wavelength of 0.155 Å (0.0155 nm corresponding to a beam energy of 80 keV). As discussed in more detail in chapter 2.2 the high energy allows to image large parts of individual reciprocal lattice planes by means of of a flat panel detector. In principle the flat panel detector used for the measurements presented here (PERKIN ELMER XRD 1621, see chapter 3.6) allowed a time resolution of up to 66 ms. For the present measurements every six seconds an diffraction image was acquired. By radial intensity integration of the obtained 2-D diffraction patterns 1-D diffractograms were yielded.

To characterize the starting state of the sample in the following an diffraction image acquired before the beginning of the galvanostatic treatment will be discussed by reference to Figs. 6.4 and 6.6.

Fig. 6.4 (a) and (b) show the corresponding 1-D diffractogram. Clearly distinguishable are the (111), (200), (220), (311) and (222) peaks of Au and the (200), (220), (311) peaks of Cu. In case of Cu the (200) and (311) peaks are of similar height while the (220) peak is only very weak. Higher indexed diffraction peaks of both the metals are beyond the range of angle shown. Interestingly there is no trace of the Cu(111) peak. The reason for the absence of the Cu(111) peak will be discussed in the context of description of Fig.


Figure 6.4: Starting state of the Au thin film model electrode. Figs 6.4(a) and (b) show the diffractogram of the Au thin film sample before the start of Li insertion. The (111), (200), (220), (311) and (222) peaks of Au are clearly distinguishable. Moreover some peaks assigned to the Cu substrate ((200), (220), (311)) and a bunch of peaks originating from Teflon from the electrochemical in-situ cell.

6 In-Situ XRD Investigation of an Au Thin Film Model Electrode



Figure 6.5: Starting state of the Au thin film model electrode. Fig. 6.5 shows the diffraction pattern of an Au thin film on a Cu(100) single-crystal substrate before the start of Li insertion corresponding to the diffractogram presented in Figs. 6.4 (a) and (b). The diffraction pattern is dominated by distinct diffraction spots originating from the Cu substrate as well as the Au thin-film. Obviously the Au film is not polycrystalline.

6.6.

Apart from the Cu substrate and the Au sample there are some additional peaks. Most of them - including a very dominant peak at 1.805° origin from the Teflon wall of the cell which the beam had to penetrate in addition to the sample. Some peaks in Figure 6.4 (a) at low diffraction angles not assignable to Au, Cu or Teflon are marked by a star. It will be referred to these peaks in chapter 6.4. The Au peaks are stronger in intensity than the Cu peaks although the Au layer only features a thickness of 100 nm. The most important reason for this is that the sample was rotated around its vertical axis to optimize its orientation with respect to the beam in order to maximize the Au intensity and avoid Cu intensity. Further factors could be on the one hand by the higher interaction cross section of Au with X-rays than Cu and on the other hand by the positioning of the 2-3 µm high X-ray beam to cover the entire Au layer and partially pass above the sample.

In Fig. 6.5 (a) the diffraction pattern corresponding to the diffractogram shown in Fig. 6.4 (a) is displayed. The presence of distinct diffraction spots gets immediately apparent. The spots origin from Cu and Au respectively. In the case of Cu diffraction spots are clearly expected because the substrate was bought as a single-crystal. In the following the diffraction pattern will be evaluated in more detail to prove the orientation of the Cu single-crystal substrate and Figure out the arrangement of the Au film on top of the Cu

substrate.

Fig. 6.6 (a) shows the diffraction patterns known from Fig. 6.5 together with superimposed meshes for Cu and Au representing specific 3-D orientations of the crystallites contributing to the diffraction pattern. In Figs. 6.6 (b) and (c) the reflections of Cu and Au are indexed with help of these meshes.

The most prominent Cu reflections in the diffraction pattern (Fig. 6.6) are the Cu(200)reflection on the vertical axis and two Cu(311)-type reflections arranged symmetrically to the horizontal axes, but only present on the left half of the pattern. They are located at azimuthal angles of 72.5° and 107.5° from the vertical axis. Also in the 1-D diffractogram (Fig. 6.4 (a)) the Cu(200)-peak and the Cu(311)-peak are of approximately the same intensity. Moreover there is an additional Cu(311)-type reflection at 25.24° azimuthal angle from the vertical axis and a Cu(220)-type reflection at 45°. But they are both of only small intensity. The Cu(220)-peak in the 1-D diffractogram is accordingly small. The spots can be used to confirm the orientation of the surface of the crystal to in fact be Cu(200). This is apparent from the Cu(200) diffraction spot being located on the vertical axes.

Together with the beam center the most intense Cu reflections, the Cu(200) reflection on the vertical axis and the (311)-type reflection on the left hand side symmetrical to the horizontal line span a mesh (see Fig. 6.6 (a) and (b)). Such a mesh is characteristic for a specific 3-D crystal-orientation. Hence all the intense reflections of Cu are assignable to a single 3-D crystal-orientation represented by the mesh like it is expected for a singlecrystal. The 3D crystal-orientation found also explains the absence of the Cu(111) peak in the diffractogram mentioned describing Fig. 6.4 in chapter 6.3. The mesh representing the discussed dominating 3-D crystal orientation does not coincide with any point on the theoretical (111) diffraction ring because the normal vector of no {111} plane lies in the diffraction plane. For more detailed analysis of the origin of the weak Cu-reflections it will be referred to chapter 6.4.

According to Figure 6.6 (a) also the Au film shows distinct reflections rather than diffraction rings. Moreover, these reflections are only few and of high intensity. Hence also the Au-film RF-sputtered on the Cu(200) singlecrystal substrate features high crystallographic order. On the vertical axes the Au(111) diffraction spot is located signifying that the Au atoms arrange densely packed on the Cu surface featuring Au(111)-type lattice planes parallel to the surface. In addition to the Au(111)-spot on the vertical axes there are two more spots at Au(111)-distance from the center in the upper half of the pattern, each at 70.5° to both sides from the vertical axes. This observation is not in line with the assumption of only one crystal orientation (in case of a single crystal). Instead



Figure 6.6: Starting state of the Au thin film model electrode. Figs 6.6 (a) to (c) show the diffraction pattern of a Au thin film on a Cu(100) single-crystal substrate before the start of Li insertion corresponding to the diffractogram presented in Figs. 6.4 (a) and (b). The three most intense Cu reflections coincide with a mesh denoted "Cu mesh" and origin from a single crystallite showing (200) orientation parallel to the surface of the sample. The most intense reflections of the Au film coincide with two meshes ("Au mesh 1" and "Au mesh 2") denoting two different crystal orientations. In both crystal orientations the (111) atomic plane is parallel to the Cu(200) surface. In Fig. 6.6 (b) and (c) the "Cu mesh" and the "Au mesh 1" are superimposed to the indexed diffraction pattern. In addition to the intense reflections the patterns contain also weak reflections originating from Cu (circles in Fig. 6.6 (a)) and Au (squares in Fig. 6.6 (a)).

a pattern as the one observed can only occur, when at least two crystal orientations are present. These two crystal orientations can be transformed into each other by 180° rotation around the vertical axes. The two crystal orientations related by 180° rotation can also be considered as different stacking orders of Au.

The fact that not all the reflections observed origin from the same crystal orientation can be visualized by the meshes in Fig. 6.6 (a). Not all the Au reflections visible coincide with one single mesh. Two mirror-inverted meshes are necessary (Au mesh 1 and Au mesh 2 in Fig. 6.6 (a)) signifying the two different stacking orders (or crystal orientations). Since for example the two (111)-type spots located at 70.5° (see Fig. 6.6 (a)) from the vertical axes are of similar intensity, the two orientations are supposed to be approximately equal amounts of Au arranged in ABC stacking order and ACB stacking order, respectively. In addition to the (111)-type reflections on the vertical axes and at 70.5° azimuthal angle to both sides of the vertical axes there are two (200)-type reflections at 54.7° from the vertical axes each. Each of the (200)-type reflections stems from one of the two stacking orders present. Moreover to each of the stacking orders belongs one of the (220) reflections at 35.3° azimuthal angle and two of the four (311) reflections. There are two more intense (311) reflections at 29.5° and two less intense ones at 79.98°. One stacking order provokes the reflection at 29.5° and at 79.98° on the right hand side of the pattern and the stacking order provokes the reflection at 29.5° and at 79.98° on the right hand side. The (222) reflections are found at double distance of the (111) spots from the center, each. In Fig. 6.6 (c) the reflections coinciding with the mesh "Au mesh 1" are indexed and the included angles are given.

All the Au reflections mentioned so far coincide with one of two grids mirror symmetrical to the vertical axis (see Fig. 6.6 (a)). The grid width is in all cases equal to the (111)-distance and the smaller angle in each mesh is 70.5°. The bigger angle is 109.5°, consequently. These angles are the angles geometrically possible to occur between two different (111)-directions. Since all the reflections mentioned above coincide with the two meshes minimum two crystal orientations can be assumed. For more detailed analysis of the origin of the weak Cu-reflections it will be referred to chapter 6.4.

6.4 Discussion X-ray Diffraction: Characterization of the Gold Thin Film Model Electrode

As presented in section 6.5 the diffraction pattern of the Au thin film sample before the start of the galvanostatic treatment shows Cu and Au reflections (Figs. 6.5 and 6.7 (a)). The intense reflections of Cu are explainable by one single crystal orientation while in the

case of Au the prevalence of two crystal orientations is obvious. However in the case of Cu as well as in the case of Au the diffraction patterns shows further (weak) reflections not coinciding with the so far assumed crystal orientations represented by the meshes in Fig. 6.6 (a-c). In the following chapter will be shown that these weak reflections represent additional crystal orientations possibly related to imperfections of the Cu(100) single-crystal. For an introduction to the following discussion please refer to chapter 2.2.

Fig. 6.7 shows the diffraction pattern known from Fig. 6.5 without (a) and with (b-d) meshes to explain the unexpectedly occurring weak (311)-type and (220)-type reflections. In Fig. 6.7 (a) in addition to the intense (200) and (311)-type reflections there are two considerably less intense reflections in the diffraction image. One also at the (311) distance from the beam center and the other one at the (220) distance. There are two possible explanations for this phenomenon.

The first possibility is as follows. Including the two weak reflections and the beam center, a new mesh could be spanned also matching the intense (311)-type reflection in the upper left quadrant of the image (compare Fig.6.7 (b)). This means an additional crystal orientation is assumed to be present within the Cu crystal. The presence of an additional crystal orientation would implicate that the Cu crystal is not a perfect single-crystal, but shows some deviations. In addition the mesh associated with this additional crystal orientation would not include the (200) reflection. Hence the corresponding crystallite would not even show the same (200)-orientation parallel to the surface like the main crystallite. The reason for the strong deviation of the orientation of the additional crystallite from the orientation of the main crystallite could be deformations due to stresses applied to the outer regions of the Cu crystal during mounting of the Cu crystal into the cell.

The other explanation assumes the two additional reflections of low intensity to be independent. In this case two additional meshes representing two additional crystal orientations could be spanned each of them including one of the weak reflections and the (200) reflection (see Fig. 6.7 (c),(d)). Assuming this second explanation all the reflections would stem from grains oriented with the (200) plane parallel to the sample's surface. The weak reflections should origin from crystallites rotated around the surface normal in comparison to the main crystal. The (220)-type reflection should origin from a crystallite rotated by 10° around the surface normal in one direction with respect to the main crystal and the (311)-type reflection should origin from a crystallite rotated by 15° in the opposite direction.

However, rotations of 10° in one direction and 15° in the opposite direction are much too high to explain the appearance of the spots under discussion in the diffraction pattern (see fig. 6.7) by non-idealities of the crystal, a not absolutely monochromatic X-ray beam



Figure 6.7: Diffraction pattern of the starting state of the Au film model electrode on Cu(200) single-crystal without (a) and with (b-d) grids to explain the unexpectedly concurring weak (220) and (311) reflections of Cu. The first possibility of explanation is sketched in Fig. (b). It is possible to construct a mesh containing both reflections. But this would not be compatible with single-crystallinity. In the alternative possibility of explanation both reflections can be explained by a respective mesh also matching the intense Cu(200) reflection (c), (d). Hence also the weak (220) and (311) reflections may origin from a crystal showing (200)-orientation at its surface.

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Figure 6.8: Diffraction pattern of the starting state of the Au film model electrode on a Cu(200) single-crystal together with a grid to explain the unexpectedly occurring (220) reflections of Au. The most obvious mesh matching the (220) reflections is shown. It also covers the Au(111) reflection. Hence the underlying crystallite shows also (111) orientation parallel to the surface. Assuming this, two possibilities are imaginable. Either the (220) reflections represent another crystallite rotated around the surface normal or they stem from the same crystal as the other reflections. The first case probably applies.

and the deviation between the bended Ewald-sphere and the planar lattice planes (see section 2.2). This can be easily seen by the fact, that the intense Cu(311)-type reflections do not show corresponding reflections point-symmetric with respect to the beam center.

Consequently some deviations from ideal single-crystallinity are present in the Cu(100) substrate possibly emerged during the mounting of the crystal into the in-situ electrochemical cell. If the effected regions of the crystal are only rotated with respect to the main crystallite (compare fig. 6.7 (c) and (d)) or if there is even 3-D disorder (fig. 6.7 (b)) is not distinguishable based on the present data.

As already mentioned during the description of Fig. 6.6 also in the case of the diffraction pattern of the Au thin-film there are weak reflections assignable to Au present in the pattern which do not coincide with the so far drawn meshes ("Au mesh 1" and "Au mesh 2"). Fig. 6.8 marks out the occurrance of weak (200)-type and (311)-type reflections and an additional mesh covering all the so far not assigned reflections. In addition this mesh

drawn in Fig. 6.8 also covers the Au(111) reflection on the vertical axis. Consequently also the crystal orientation associated with the new mesh features a Au(111) atomic plane parallel to the surface of the sample. As in the case of the two independent new meshes covering the (200) reflection of Cu (see above) there are also here two possibilities. Either the weak reflections stem from a different crystallite showing different rotational crystal orientation with respect to the vertical axis or they origin from the same crystallite as the other reflections. In fact the diffraction plane containing the (111) as well as the (-220) and (2-20) reflection is at 24° rotation around the vertical axes with respect to the plane the more intense reflections lay in and in addition there are theoretically two other crystal orientations (diffraction planes) between the diffraction plane which the intense reflections belong to and the diffraction plane the weak reflections belong to. They are located at 13° and 19° rotation around the vertical axis with respect to the orientation of the diffraction plane which the intense reflections belong to. Considering these findigs, even taking into account the non-ideality of the Au crystallites (no point-like reflections but reflections showing certain extension), a not absolutely monochromatic X-ray beam (no infinitesimal thin Ewald-sphere) and the deviation between the bended Ewald-sphere and the planar lattice planes (see section 2.2) the weaker (220)-type reflections on the horizontal axes will not origin from the same crystallites as the intense reflections.

Consequently also in the case of the Au layer deviations from a perfect orientation are found. Possibly this observation is correlated with the regions of the Cu-crystal deviating from the orientation of the main Cu crystallite. It can be considered here, that the (111)-Orientation of Au-film also in the "distorted part" substanciates, that the distorted parts of the Cu-crystal show (100) orientation parallel to the surface (compare figs. 6.7 (c) and (d)). Possibly only the Au film on top of these misoriented parts of the substrate deviates in orientation from the rest of the Au-film arranged on the Cu main crystallite and on top of the main crystallite only the two main orientations of Au prevail. In the following only the main crystallite of Cu will be discussed.

From the diffraction pattern in Fig. 6.6, however, the crystallite size cannot be determined. Even if there are only two crystal orientations of Au present on the main crystallite of Cu the number of crystallites can be still between two and a very high number, depending on if all the (sub)grains featuring the same crystal orientation are adjacent or if there is a statistical distributions of (sub)grains featuring ABC and ACB stacking order. Hence the Au film on top of the main crystallite of Cu is either bi-crystalline or poly-crystalline showing a strong texture.

Assuming a bi-crystal the observed preferred orientation of Au on the Cu surface is not necessarily affected by interactions between Au and Cu. Assuming a strongly textured polycrystal uniform orientation of all the Au crystallites on Cu could only be expected if Au would orient at the crystal structure of Cu. A reason for preferred orientation of metal on another metal are directions of coincidence between the two atomic lattices.

Above the Cu substrate was shown to show deviations from an ideal Cu(100) singlecrystal. The Au film RF sputter deposited thereon shows (111) orientation parallel to the Cu single-crystal's surface. Both possible stacking orders for the Au film (ABC and ACB) were found to occur (see chapter 6.3).

In the following will be shown that the crystallites forming the Au-film feature also uniform orientation perpendicular to the Cu single-crystal's surface and are not present in statistical rotational orientation perpendicular to the surface (2D-powder, in-plane powder). According to this result there is still the possibility of the Au thin film to represent a Au bi-crystal. If the orientation of the Au-crystallites would be statistical the possibility of facing a bi-crystal could be excluded. In contrast a statistical orientation would be very improbable if a preferred orientation would be enabled by the specific interface between the Cu(100) lattice plane forming the surface of the Cu single-crystal substrate and the Au(111) lattice plane.

To test if the rotational orientation of the Au-crystallite, represented by the Au reflections visible in Figs. 6.5 and 6.7 (a), with respect to the orientation of the Cu-crystal, represented by the Cu reflections visible in Figs. 6.6 (a) and 6.7 (a), leads to some coincidence of the Cu(100) and Au(111) lattice the rotational orientation between Cu and Au is determined first.

To be able to use the Cu crystal as a reference system for the orientation of the Au film by bringing the orientations of the Cu(100) singlecrystal and the Au film into relation the orientations will be individually determined with respect to a known orientation, referred to as "reference orientation" in the following.

In Figs. 6.9 (a, b) and 6.10 (a,b) on the right hand side a cubical excerpt from the reciprocal lattice of Cu or Au (reflecting also the cubical symmetry of the unit cells) arranged in respective reference orientation described in the following is shown.

In reference orientation in the case of Cu the cubical excerpt from the reciprocal lattice of Cu is oriented with the normals of cube faces coinciding with the x- ,y- and z-axes of a Cartesian coordinate system (Fig. 6.9 (a) (right hand side)). In reference orientation in the case of Au the cubical excerpt from the reciprocal lattice of Au is oriented to coincide one space diagonal with the z-axis. A further space diagonal coincides with the x-z-plane (Fig 6.10 (a) (right hand side)).

The green spots in Figs. 6.9 and 6.10 (right hand side) denote reciprocal lattice points. The bigger red spots highlight the reciprocal lattice points in the actual orientation of



Figure 6.9: Determination of the orientation of the Cu singlecrystal with respect to a defined reference orientation. On the right hand side of Fig. 6.9 (a) and (b) a cubical excerpt from the reciprocal lattice of Cu is shown. The green spots denote reciprocal lattice points. The bigger red spots highlight the reciprocal lattice points coinciding with the paper plane representing (assuming large enough Ewald sphere (see chapter2.2)) the back-side of the Ewald sphere if the X-ray beam incides perpendicular to the paper plane. On the left hand side the resulting diffraction pattern with consistent indexing is shown. In Fig. 6.9 (a) (right hand side) the reference orientation for the Cu crystal is displayed. In this reference orientation the normals of cube faces of the cubical excerpt from the reciprocal lattice coincide with the coordinate axes. To obtain the diffraction pattern of the (100)-oriented Cu singlecrystal observed in Fig. 6.6 the cubical excerpt from the reciprocal lattice has to be rotated by 18.5° around the z-axes with respect to its reference orientation (6.9 (b)). Other equivalent orientations are given in table 6.3.

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Figure 6.10: Determination of the orientation of the Au thin film with respect to a defined reference orientation. On the right hand side of Fig. 6.10 (a) and (b) an excerpt from the reciprocal lattice of Au is shown. The green spots denote reciprocal lattice points. The bigger red spots highlight the reciprocal lattice points coinciding with the paper plane representing (assuming large enough Ewald sphere (see chapter2.2)) the back-side of the Ewald sphere if the Xray beam incides perpendicular to the paper plane. On the left hand side the resulting diffraction pattern with indexing is shown. In Fig. 6.10 (a) (right hand side) the reference orientation for the Au film is displayed. In this reference orientation the cubical excerpt from the reciprocal lattice of Cu is oriented to coincide one space diagonal with the z-axes. A further space diagonal coincides with the x-z-plane. To obtain the diffraction pattern of the (111)-oriented Au thin film observed in Fig. 6.6 the cubical excerpt from the reciprocal lattice has to be rotated by 30° around the z-axes with respect to its reference orientation (Fig. 6.10 (b)). Other equivalent orientations are given in table 6.3.

a)	Cu	18.5°	108.5°	198.5°	288.5°	b)	Au	30°	150°	270°
	Cu	71.5°	161.5°	251.5°	341.5°	D)	Au	90°	210°	330°

Table 6.3: Table 6.3 (a) lists the symmetrically equivalent orientations with respect to the reference orientation described in the text and in Fig. 6.9 found for the Cu(100) singlecrystal at which the calculated diffraction pattern matches the experimentally observed diffraction pattern (Fig. 6.5). Table 6.3 (b) lists the symmetrically equivalent orientations with respect to the reference orientation described in the text and in Fig. 6.10 found for the Au(111) thin-film at which the calculated diffraction pattern matches the experimentally observed diffraction pattern (Fig. 6.5).

Table 6.4: By bringing the angles received for the quadratic and the hexagonal lattice in correlation the orientation of the Au film on the Cu substrate can be yielded (table 6.3 (c)).

possible angles between $Cu(100)$ lattice and $Au(111)$ lattice									
angle	11.5°	48.5°	101.5°	138.5°	191.5°	228.5°	281.5°	318.5°	
angle adapted	41.5°	78.5°	131.5°	168.5°	221.5°	258.5°	311.5°	348.5°	
$\operatorname{coordinates}$	(3/1)	(-3/1)	(-1/3)	(1/3)	(3/1)	(-3/1)	(-1/3)	(1/3)	

the crystals coinciding with the paper plane representing (assuming large enough Ewald sphere (see chapter2.2)) the back-side of the Ewald sphere if the X-ray beam incides perpendicular to the paper plane. On the left hand side of Figs.6.9 and 6.10 the resulting diffraction pattern with indexing is shown each. By turning the reciprocal lattice (right hand side of Figs. 6.9 (a) and 6.10 (a)) (and with this also the real lattice and the real unit cell) around the z-axes the angles (with respect to the reference orientations) could be figured out at which the calculated diffraction patterns coincide with the diffraction patterns observed in Figs. 6.5 (a) and 6.7 (a) for the Cu crystal and the Au crystal each. The corresponding orientation of the excerpts from the reciprocal lattice are displayed for Cu in Fig. 6.9 (b) and for Au in Fig. 6.10 (b). In Figs 6.9 (b) and 6.10 (b) only one example is given for an angle of rotation around the z-axis with respect to the respective reference orientation at which the diffraction patterns observed in Figs. 6.5 (a) and 6.7 (b). In Figs 6.9 (c) and 6.10 (c) only one example is given for an angle of rotation around the z-axis with respect to the respective reference orientation at which the diffraction patterns observed in Figs. 6.5 (a) and 6.7 (b). The figs 6.5 (c) and 6.7 (c) is yielded. Table 6.3 lists also the symmetrically equivalent angles.

Since in the cubic crystal system the z-axis of the reciprocal space coincides with the z-axis of the real space and in particular with the c-axis of the unit cell, the discussion of the angles at which the diffraction pattern known from Fig. 6.4 occurs (according to the above presented approach) can be continued in real space.

Table 6.3 (a) lists the angles the diffraction pattern shown in Fig. 6.4 occurs at in case of the Cu(100) singlecrystal. The diffraction pattern occurs at 18.5°, 108.5°, 198.5°, 288.5° and at 71.5°, 161.5°, 251.5°, 341.5°. The angles of the first group are separated

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Figure 6.11: Diffraction patterns of Cu (a) and Au (b) known from Fig. 6.4 with indexing

by 90° each and the angles of the second group as well. This refers to the symmetry of the (100)-plane. The angles between the respective first angles of each group is 53°. The angle of 53° can be explained as follows. The diffraction pattern of Cu observed in Fig. 6.4can be indexed as shown in Fig. 6.11 (a) taking the angles observed between the reflections into account. According to the chosen indexing the diffraction plane is an (0-62)-plane. The other (0-62)-type plane also perpendicular to the (200) plane giving rise to the same diffraction pattern is the (0-26)-plane at an angle of 53.1° around the sample's normal with respect to the (0-62)-plane. This finding explains the angle distance observed between the two groups.

Table 6.3 (a) lists the angles the diffraction shown in Fig. 6.4 occurs at in case of the Au(111) thin film. The known diffraction pattern occurs at 30°, 150°, 270° and at 90°, 210°, 330°. The angles of the first group are separated by 120° each and the angles of the second group as well. This refers to the symmetry of the (111)-plane. The angles between the respective first angles of each group is 60°. The angle of 60° can be explained as follows. The diffraction pattern of Au observed in Fig. 6.4can be indexed as shown in Fig. 6.11 (b) taking the angles observed between the reflections into account. According to the chosen indexing the diffraction plane is an (0-22)-plane. The other (0-22)-type planes also perpendicular to the (200) plane giving rise to the same diffraction pattern are located at an angle of 60° and 120° around the sample's normal with respect to the (0-22)-plane. This finding explains the angle distance of 60° observed between the two groups of angles.

6.4 Discussion X-ray Diffraction: Characterization of the Gold Thin Film Model Electrode



Figure 6.12: In Fig. 6.12 the quadratic Cu(100) lattice and the hexagonal Au(111) lattice are superimposed one the one hand in the orientations defined by the reference orientations introduced in Figs. 6.9 and 6.10 (Fig. 6.12 (a)) and on the other hand in an orientation to coincide one unit vector of each lattice (Fig. 6.12 (a)). The two orientations shown can be transferred into each other by 30° rotation of the Au(111) lattice.

After determining the angles (with respect to the respective reference orientation) which the observed diffraction patterns occur at one of the symmetrically equivalent angles yielded in the case of the Cu crystal (for example 18.5°) can be defined as the reference orientation for the the orientation the Au-film on the Cu substrate. In the first row of table 6.4 the rotation angles with respect to this Cu based reference system are listed at which the Au diffraction pattern shown in Figs. 6.6 (a) and 6.7 (a) can be observed.

Based on the above determined relative orientation of the Au(111) thin film with respect to the Cu(100) substrate in the following a sketch of the arrangement of the Au atoms on top of the substrate will be presented. The Cu(100)-surface is represented by a quadratic lattice, the Au(111)-layer by a hexagonal lattice. In Fig. 6.3 the Cu(100) lattice and the Au(111) lattice are superimposed coinciding at one specific lattice point (big red dot). In Fig. 6.12 (a) the lattices are drawn in the specific rotational relation defined by the reference orientations in Figs. 6.9 (a) and 6.10 (a). On the x-axis the unit vectors of the hexagonal lattice are rotated by 30° with respect to the unit cell vectors of the quadratic lattice. In Fig. 6.12 (b) on the x-axis the unit cell vectors were brought to coincidence in direction by rotating the hexagonal lattice by -30°. To measure the angles of torsion between the two lattices referring to the arrangement shown in Fig. 6.12 (b) the angles between Cu(100) lattice and Au(111) lattice (6.4, 1st row) have to be adapted by addition of 30° (6.4, 2nd row). At these angles relative to the orientation in Fig. 6.12 (b) the unit vector of the hexagonal Au(111) lattice was found to be oriented with respect to the Cu(100) substrate according to the above described procedure.

Fig. 6.3 shows the quadratic Cu(100) surface and the hexagonal Au(111) lattice rotated



Figure 6.13: Orientation of the sputtered Au thin film on the Cu singlecrystal substrate. In Fig. 6.12 the quadratic Cu(100) lattice and the hexagonal Au(111) lattice are superimposed in an orientation yielded by Combining the described orientations a sketch of the arrangement of the Au atoms on top of the Cu(100) single-crystal substrate results. The Cu(100) lattice is colored in black, the Au(111) lattice in red. The two atom grids are commensurate in one of the three equivalent directions of the Au(111) lattice. The fourth lattice point along one of the three equivalent directions of the Au(111) lattice (point (4/0)) coincides with point (3/1) of the Cu(100) lattice. by 41.5° with respect to each other. The (4/0) lattice point of the hexagonal Au(111) lattice coincides with the (3/1) lattice point of the Cu lattice. Also at the other angles listed in table 6.4 the (4/0)-type lattice points of the hexagonal Au(111) lattice coincide with the (3/1)-type lattice points of the Cu lattice. A precise correlation is given in table 6.4.

The observed preferential orientation of the Au-film on the Cu-substrate proves that the crystallization of the sputter deposited Au atoms is ruled by the interaction between the Cu substrate and the deposited Au atoms.

Concluding the previous discussion the Au film was found to be arranged with (111)type lattice planes parallel to the surface of the Cu(100) single crystal. Also a rotational preferred orientation of the Au film on the Cu(100) substrate could be found: the (4/0)type lattice points of the hexagonal Au(111) lattice coincide with the (3/1)-type lattice points of the Cu lattice.

Also Renner et al.¹⁵ observed at their thin Au films on mica and at their sputter deposited Au particles on HOPG a preferential (111) orientation of the Au parallel to the surface of the mica crystal. But perpendicular to the surface rotational disorder prevailed. This points to the conclusion that Au(111) interfaces are generally preferred to minimize the interface energy of Au. In the case of the Cu(100) substrate described above obviously additional uniform rotational order is attributed to the $\sqrt{10}R41.5$ superstructure allowed by the lattice parameters of Au and Cu.

To further determine the structural order in the Au film and discuss the interplay between nucleation and nucleus growth an analysis of the grain size would be inevitable. If the grain-size would be found to be very large possibly a bi-crystal featuring two large grains each featuring one of the two observed stacking orders would be present resulting from only very slow nucleation and rather quick nucleus growth. If the grain-size would be found to be small the possibility of the presence of a statistical arrangement of small crystallites featuring either ABC or ACB stacking order could be considered resulting from very quick nucleation and rather slow nucleus growth. However since in the diffraction patterns a limitation in resolution of the detector caused by the pixel size gets apparent, a grain size analysis cannot conducted here. Nevertheless, the highly uniform rotational orientation of the Au film on the Cu substrate although there is only coincidence in one direction between the Cu(100) and the Au(111) lattice may point to the presence of only small Au grains. Anyway, it can be stated that the film formation of Au on Cu by RF sputter deposition is ruled by interactions between the Cu substrate and the deposited Au.

6.5 X-ray diffraction: Alloy Phase Formation-Dissolution

After the Li insertion changes in the diffractogram are obvious. In Fig. 6.14 the diffractogram of the lithiated state (after the first lithiation half-cycle) is plotted together with the diffractogram of the unlithiated state. As it is clearly visible there are various additional diffraction peaks pointing to Li-Au alloy phase(s) newly formed during galvanostatic lithiation. Furthermore the absence of the Au peaks signifys the complete conversion of Au into Li-Au alloy(s).

(Please note: The most intense additional peak at 2.40° superimposes to the most left peak of the four small "unidentified" peaks marked by a big star in Figs. 6.4 (b) and 6.14 (b). Also after delithiation the small peak becomes not detectable any more. However it will become important again in the discussion of Fig. 6.19.)

Fig. 6.15 shows the complete diffraction pattern of the lithiated sample (a) and a series of excerpts from the diffraction patterns of the unlithiated state (6.15 (b), compare Fig 6.5), the fully lithiated state (Fig. 6.15 (c), compare Fig. 6.15 (a)) and the subsequent delithiated state (Fig. 6.15 (d)). The absence of Au intensities already observed in Fig. 6.14 is also visible in the diffraction pattern of the lithiated state (Fig. 6.15 (a) and (c)). During lithiation obviously the gold reflections have vanished and various diffraction rings have appeared. The diffraction rings signify clearly the presence of at least one powder-like alloy phase.

Also Renner et al.¹⁵ observed during the lithiation of a Au single-crystal the formation of powder-like alloy phases due to a break-up of the homogeneous single-crystal lattice into nanometer-scale grains. In contrast the independent Au nanoparticles also investigated did not fracture and keep their size and orientation.

Furthermore, also distinct spots have appeared during the lithiation period (Fig. 6.15 (a) and (c). Probably, this is a sign for a newly formed non-powder-like crystalline alloy phase featuring either large crystallites or strong preferential orientation (texture). More specifically a 2-D powder may be considered from this single diffraction pattern. In a 2-D powder the grains are arranged pointing with a specific atomic plane vector all in the same direction, but having random orientation regarding the rotation around this vector (see chapter 2.2). The effect is a high density of reciprocal lattice points on circular orbits in reciprocal space within the reciprocal lattice plane perpendicular to the direction of uniform order. As a result of the respective Ewald-sphere cutting this circle vertically two spots symmetric with respect to the beam center are then visible on the detector. Another possibility would be just a limited number of rather big grains randomly oriented. In order



Figure 6.14: Comparison between unlithiated and lithiated Au thin film sample. Figure 6.14(a) and (b) show the diffractogram of the fully lithiated Au thin film sample together with the diffractogram of the starting state known from Figure 6.4 (a) and (b). The peaks of Au have disappeared. Instead a number of other peaks appeared attributed to Li-Au alloy phases.



Figure 6.15: Fully lithiated state of the Au thin film model electrode. Fig. 6.15 (a) shows a diffraction pattern of the fully lithiated state. During lithiation various new diffraction rings arose due to the formation of Li-Au alloy phases. Moreover new diffraction spots arose announcing a non powder-like alloy phase. In Figure 6.15 (b)-(d) the main changes during a complete lithiation/delithiation cycle are arranged. In the unlithiated state (Fig. 6.15 (b)) there are only spots from Cu single crystal and the Au film. In the lithiated state (Fig. 6.15 (c)) the Cu spots are left but the Au spots are gone. Instead various diffraction rings and spots assigned to Li Au alloy phases are present. After subsequent delithiation the alloy phases are widely dissolved. But there are neither spots nor rings originating from reformed Au. Hence no crystalline Au lost is recovered after lithiation-delithiation cycling.

to be able to distinguish between the two proposed scenarios the sample was rotated around its normal. The detailed analysis of the crystallinity of the phase responsible for the spots is further described in chapter6.5.

In summary in Fig. 6.15 (a) to (d) a selection of detector images compiles the main findings during the first lithiation/delithiation cycle. Before lithiation (6.15 (b)) there is a highly ordered Au layer arranged with a (111) surface parallel to the surface of the Cu(100) single crystal substrate. On lithiation Au reflections disappear and Li-Au alloy phases grow resulting in diffraction rings and even diffraction spots (Fig. 6.15 (c)). During delithiation the alloy phases disappear. But no respective Au-rings are visible, i.e. crystalline Au is not recovered. Neither the spots known from the starting state nor diffraction rings at the 2 Theta angles of Au are visible (Fig. 6.15 (c)).

The disappearance of crystalline Au is displayed in Figs. 6.16 and 6.19 (a) in more detail. Fig. 6.16 (a) shows the intensity of the Au(111) peak first decreasing and then vanishing with time starting from the beginning of the first lithiation of the sample. The rate of decreasing of the intensity increases with time. Even significantly before the lithiation half-cycle is finished there is no intensity of Au left. Obviously at this point there is no (crystalline Au remaining in the sample any more probably as consequence of the Li insertion accompanied by Li-Au alloy formation.

The inset in Fig. 6.16 shows the Au(111) peak at different subsequent equidistant points in time during lithiation. The acceleration of intensity reduction with time already anticipated from the main Figure is more obvious here. As already visible from the main Figure remarkably no shift of the peak position of the Au peak is noticeable during the decrease of intensity. Consequently no formation of an solid solution of Li in Au as it can be expected from the phase diagram of the Li-Au system⁷⁷ can be assumed. The inset in Fig. 6.16 in addition makes clear that during the lithiation no increase of the FWHM is observable. In consequence a loss of structural order inside the crystal structure of Au can be also excluded. However the above mentioned limitation in angular resolution of the detector caused by the pixel size could possibly hinder the detection of an in fact present possibly small increase of peak width with time. Alternatively possibly the Au gets directly transformed into an alloy phase of different atomic structure or into an intermediate amorphous alloy phase.

In contrast Renner¹⁵ et al. and Taillades et al¹⁶ observed a peak evolving at slightly higher diffraction angles than Au assigned to the α -Li-Au solid solution phase showing a composition range from 0-39% Li. Taillades also reported about the reformation of crystalline Au at the end of the lithiation-delithiation cycle. Both studies presented only a limited set of (lower energy) XRD data.



Figure 6.16: Vanishing of the Au peaks during the first lithiation of the Au thin film sample. Fig. 6.16 shows the intensity evolution with time within the designated range of angle. The Au(111) peak at 3.775° decreases in intensity from the beginning of the lithiation experiment until no Au (intensity) remains. The decrease gets steeper from the beginning towards the disappearance. After 2500 s no intensity of Au is left. The inset in Fig. 6.16 shows the Au(111) peak at equidistant points in time. The inset points out the increasing steepness of intensity decay with time clarifies that during the accelerated decrease of intensity no shift of the peak position and no gain in FWHM occurs. Consequently no solid solution of Li in Au is formed and no successive loss of crystalline order can be determined.



Figure 6.17: Fig. 6.17 shows the intensity evolution on time normalized to the maximum intensity at three selected 2ϑ -angles: the angle of the Au(111) peak (3.775°), an angle at which an alloy phase peak arose (3.225°) and an angle where a newly formed phase at the end of the lithiation-delithiation cycle remained (3.895°) together with the galvanostatic potential-time curve during the first lithiation-delithiation cycle. During lithiation in the first cycle the intensity of the Au peak vanishes. Meanwhile the intensity of the alloy phase comes up. Gold is converted into alloy phase. At the end of the delithiation half-cycle no crystalline Au is recovered. Instead a newly formed phase remains showing peaks at different 2ϑ -angles, for example at 3.895° arising at the very end of the cycle. The vertical line at 2790 s marks the end of the lithiation half-cycle.

Concluding the previously presented observations Au seems to transform during the first lithiation of the Au film into an alloy phase without passing the formation of a solid solution of Li in Au expectable from the phase diagram and without a successive loss of order of the Au structure.

Fig. 6.19 (a) shows intensity evolutions with time normalized to the respective maximum intensity.at selected angles. 3.775° is the peak position of the Au(111) peak. At 3.225° a polycrystalline alloy phase (compare Fig. 6.14) features a peak. The intensity evolution at 3.895° will be discussed below. In addition the potential-time curve during galvanostatic lithiation/delithiation of the Au thin film is plotted as a reference.

During lithiation the intensity of the Au(111) peak (at 3.775°) decreases until all the Au is converted into alloy phase and no Au intensity is left. The shape of the decreasing intensity-time curve of Au is worth mentioning. At the beginning of the cycle the decrease occurs at a specific rate. After about 1600 s the rate gets higher. This behavior is not expected during just continuous lithiation of Au. A possible explanation will be discussed in chapter 7. At the same time the intensity of the Li-Au alloy phase (at 3.225°) arises.

When all the Au has vanished after 2400 s the alloy phase shows a maximum. When no pure Au is present anymore there is no starting material for the formation of the Li-Au alloy phase anymore. Consequently subsequently inserted Li is probably used to raise the Li content in already formed Li-Au alloy phase(s) or to form new alloy phase(s). Since the intensity of the initial alloy phase (peak at 3.225°) starts to drop after complete consumption of Au, as can be seen from the drop in intensity, rather the formation of a new alloy phase can be expected here. This alloy phase is observed to arise until the lower potential limit is reached.

Furthermore, from Fig. 6.17 after switching the direction of galvanostatic current (vertical line at 2790 s) to extract the Li from the formed alloy(s) a reformation of the initial alloy phase (at 3.225°) can be ascertained resulting in the observed renewed increase of the corresponding intensity curve. At the same time the assumed higher lithiated second alloy phase is supposed to dissolve. At the end of the lithiation/delithiation cycle interestingly the intensity at the peak position of Au (at 3.775°) does not increase again. There is no crystalline Au recovered at all. Instead at the end of the first cycle at diffraction 2- ϑ -angles different from the Au diffraction angles intensity arises (for example at 3.895°).

The ranges of angle where new peaks come up at the end of the first cycle are marked in Fig. 6.18. Fig. 6.18 shows diffractograms of the starting state (see Figs 6.4), the final delithiated states of the first (see Fig. 6.14) and the second cycle and a state during the delithiation in the third cycle (intermediate state) within a selected range of angle. The diffractogram of the "intermediate state" during the third cycle features some peaks assigned to Li-Au alloy phase(s). In the final delithiated states of the first and the second cycle the peaks of the alloy phase(s) are not present anymore. They dissolve before the potential limit of 1 V is reached. But the diffractograms of the final delithiated states feature peaks not present at the intermediate state during discharging. Five of such peaks can be distinguished (compare magnifications and arrows in Fig. 6.18. They are located at 2.715°, 3.185°, 3.895°, 4.155° and 5.015°. But their peak width is not uniform. While the peak at 2.715° is very broad the peak at 3.185° is remarkable narrow. Usually peaks of the same phase should feature uniform peak widths. One explanation for non-uniform peak widths could be for example anisotropy in structural ordering in the crystal. An other explanation could be two different phases.

Fig. 6.19(a) compares the intensity evolutions with time at 2.715° , 3.185° , 3.895° , 4.155° and 5.015° . Apart from small features the intensity evolutions are very similar (At 5.015° the intensity evolution is superimposed by another phase). In Figure 6.19 (d) the intensity evolution with time for the peak at 3.185 V of this phase is plotted during the first three lithiation/delithiation cycles. The phase appears at the end of each delithiation



Figure 6.18: In Figure 6.18 the set of diffraction peaks arising only at the very end of the delithiation half-cycle can be distinguished. The Figure assembles the diffractograms of the starting state, the states after the first and after the second delithiation and a state during third lithiation. As it becomes clear the diffractograms of the delithiated states features some peaks not present in signicant amout in the starting state and not at all present in the partially lithiated state. Some of them are relatively broad others are relatively narrow. Probably the newly arisen peaks origin from two different phases.



Figure 6.19: In Fig. 6.19 (a) intensity evolutions at the 2 ϑ -angles of the peaks newly arisen at the end of the first lithiation-delithiation cycle are displayed during the third cycle. They show high similarity. The curve at 3.185° differs slightly since it is superimposed by another phase (see also below). In Fig. 6.19 (b) the intensity evolution with time of the newly arisen peak at 3.185° is shown during three lithiation/delithiation cycles at different currents. Although there is a small amount of the corresponding phase already present at the beginning of the first lithiation (due to previously conducted CVs), the phase evolves actually the first time during first delithiation. In the subsequent cycles it is reversibly dissolved and formed again.

process and vanishes during each lithiation process. Although the phase(s) are formed in large amounts only at the end of the first lithiation-delithiation cycle indicated by the pronouncedly arising intensity they are already present in small amounts at the beginning of the first lithiation. The reason for presence of the phase(s) already before the first lithiation is probably the fact that CV measurements were performed before the galvanostatic measurements to test the performance of the cell (see chapter 6.2). As discussed in context with the lab-based CV measurements (see Fig. 5.8 in chapter 5.3) during the CV measurements a thin surface near region of the sample was already lithiated to the highest lithiated state. The formed alloy phases were transformed during subsequent delithiation into the phase(s) under discussion here.

Two of the so far unidentified peaks marked by a star in Fig. 6.4 (b) at 2.715° and 3.185° can be attributed to the phase previously described by showing the typical intensity evolution with time (6.19 (a)). As can be seen from Fig. 6.18 the third peak marked by a star disappears under the broad peak at 2.715°. Since the peak at at 2.925° does not appear again when the peak at 2.715° disappears during charging suggests that the peak at 2.925° also shows a behavior as shown in Fig.6.19 (a). The peak at 2.925° is very narrow as the peak at 3.185°. Hence, taking also into account their similar intensity evolution with time, the two peaks at 2.925° and 3.185° could be provoked by the same phase. Also

the very left peak marked by a star in Fig. 6.4 (b) at 2.455° features quite narrow width. Even though it is not possible to determine the intensity evolution of the peak at 2.445° , since it gets superimposed by a peak of an alloy phase (intermediate state in Fig. 6.18) and can not distinguished any more after delithiation as mentioned above, possibly also the peak at 2.455° is of the same origin as the peaks at 2.925° and 3.185° . The peak at 4.155° is overlapped by some other peaks, but its width seems also to be much smaller than the width of the peaks at 2.715° , 3.895° and 5.015° .

Considering the issues discussed her there may be possibly two phases showing similar intensity evolution with time during the lithiation-delithiation cycles (compare Fig. 6.19 (a)). One phase showing small peak widths at 2.455°, 2.925°, 3.185° and 4.155° and a second phase featuring broad peak width at 2.715°, 3.895° and 5.015°. In Fig. 6.19 (b) the intensity evolution with time both previously distinguished phase have in common is shown over the first three lithiation-delithiation cycles exemplified at the peak at 3.185°. At the beginning of the first cycle the intensity is low due to the previously discussed preliminary CV measurements. At the end of the first cycle the phase(s) are formed for the first time in large amounts. In the following cycles the phases show their characteristic intensity evolution with time already known from Fig. 6.19 (a). The first two cycles in the here described galvanostatic in-situ lithiation-delithiation experiments were measured at 22.7 μ A and the third cycle at 16.6 μ A. With respect to the extraordinary long duration of the first lithiation half-cycle please refer to chapter 6.1. The gap in the intensity-time curve is attributed to translating and turning of the fully lithiated sample at ocp after the first lithiation (see chapter 6.7).

The conclusions of the discussion of Figs. 6.17, 6.18, and 6.19 point to Li-Au alloy formation during the galvanostatic treatment. Accordingly the intensity of the Au peaks vanishes with time. Instead Li-Au alloy phases are formed. During the dealloying process, however the crystalline Au is not recovered. Instead two phases can be assumed to be formed which are probably poor in Li since the corresponding diffracted intensity only arises at the very end of the delithiation half-cycle. One of these phase features peaks at 2.455°, 2.925°, 3.185° and 4.155 showing a characteristic narrow peak width and the other phase features peaks at 2.715°, 3.895° and 5.015° with very broad peak widths. According to the different peak widths the phase showing narrow peak width is probably present in a crystallographically higher crystallographically ordered state and the phase showing broad peak width in a lower ordered state since usually the peak width is the broader the smaller the grains are and the less ordered the phase is. However this classification is not strict. Interestingly both Li-poor phases featuring broad or narrow peak width show the same shape of intensity evolution with time.

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Figure 6.20: Intensity evolution in dependency of diffraction angle (2ϑ) and time. Shown is the evolution of the diffracted X-ray intensity in the range of diffraction angle of interest during the lithiation-delithiation cycle at 16.6 µA. The red line at 2683 s marks the end of the lithiation half-cycle. At different diffraction angles, partly in very close vicinity, during the cycle intensities arise, merge, grow out of each other and disappear. The arising and vanishing intensities are assumed to occur due to Li-Au alloy formation and dissolution. Since the intensities seem to feature different evolutions with time different alloy phases can be assumed to occur.

In the following both phases will be subsumed and referred to as Li-poor phases or also phase 6.

In Fig. 6.20 the evolution of diffraction intensity during the third complete lithiationdelithiation cycle (16.6 μ A) is displayed in dependence of the diffraction angle and time. The lithiation starts a t = 0 s and the delithiation ends at t = 3680 s. The point of switching the current is marked in red. The Figures are obtained by plotting all the 1-D diffractograms yielded from the 2-D diffraction patters by radial integration with respect to intensity in chronicle order along a time axis. Since every 6 s a diffraction pattern was recorded the temporal resolution is 6 s. For the sake of clarity only every tenth diffractogram is plotted resulting in an actual temporal resolution in Figure 6.20 of 60 s. During the electrochemical treatment obviously there are specific changes in the diffractograms. At different angles and at different points in time intensities arise, grow, merge, grow out of each other or vanish. Obviously new phases featuring crystal structures different from the Au starting material occur.

Obviously there is not only one additional phase involved in the lithiation-delithiation process since the temporal behavior of intensity is different for different angles at which new intensities occur. Some intensities arise already near the beginning reaching their maximum before the end of lithiation, others only start raising during delithiation, for example. In consequence temporal evolution of the diffractograms shown in Fig. 6.20 points to the conclusion that several phases are involved during the electrochemical lithiationdelithiation cycles, probably Li-Au alloy phases.

Above we described the vanishing of pure Au during the first lithiation of the sample and the appearance of unknown Li-poor phases at the end of delithiation. Consequently from the second cycle on the Li-poor phases described above are starting material for subsequent lithiations. According to the discussion of Fig. 5.10 in chapter 5.14 the difference in starting material between the first and the subsequent cycles only affects the first lithiation plateau in the galvanostatic measurements. Moreover the above discussed findings point to the conclusion that the difference between the first and all the subsequent cycles observed in the galvanostatic measurements origins from the difference between lithiation of Au and the discussed Li-poor phase(s).

Fig. 6.21 shows some enlarged ranges of angles from Fig. 6.20 displaying the temporal evolution of the diffracted intensity or of the 1-D diffractograms, respectively. In the shown particular ranges of angle the multitude of peaks occurring at different lithiation states overlapping within small ranges of angle is more obvious. Consequently the observations from Figs. 6.20 and 6.21 strongly suggest the (co)existence of several different possible Li-Au alloy phases. Since the peaks are frequently overlapping to a large extend it is not straightforward to separate the peaks and attribute them to the respective underlying phase.

The issue of peak separation and phase identification was addressed by regarding intensity evolutions with time at fixed diffraction angle. These intensity evolutions with time are cross sections through the "intensity landscape" in Figs. 6.20 and 6.21 parallel to the time axis (perpendicular to the angle axes, compare Fig. 6.21 (c) and (d)). Consequently intensity evolutions with time reproduce the evolution of intensity at a fixed diffraction angle with time. Depending on the angle chosen the intensity evolutions with time show peaks at different points in time. At all the angles a respective phase features diffraction peaks in the diffractograms the intensity evolution with time should feature qualitatively the same behavior with time (if it would not be superimposed by another phase). Following this approach the intensity evolutions were compared in small steps of angle (0.01°) with the previous and the subsequent intensity evolutions in search for specific shapes of intensity evolution occurring repeatedly at different diffraction angles.

The result of the procedure described above is reproduced in Fig. 6.22. Including the shape of intensity evolution already introduced in Fig. 6.19 (a) six different characteristic shapes of intensity evolution could be found each repeating at different diffraction angles. In Fig. 6.22 (b) in addition to the characteristic potential evolutions the points in time are marked in the respective colors where the different phases feature their maximum intensity. The six different characteristic intensity evolutions suggest the prevailing of



Figure 6.21: Intensity evolution in dependency of diffraction angle (2ϑ) and time. Shown is the evolution of the diffracted X-ray intensity in the ranges of diffraction angles shown during the lithiation-delithiation cycle at 16.6 µA. The red line at 2683 s marks the end of the lithiation half-cycle. Figs. 6.21 (a-c) represent excerpts from Fig. 6.20. The multitude of peaks in a partly very narrow range of angle prevailing at different points in time corresponding to different states of lithiation comes even more obvious here. Several alloy phases are supposed to occur. But since the peaks are in very close vicinity the problem arises to attribute the individual peaks to the underlying alloy phases. The aim is to separate the different phases, count them and set up a peak-list for the respective phases. This will be approached by means of intensity evolutions with time (see text). Fig. 6.21 (d) shows exemplarily the intensity evolution associated with the cross section plate marked in Fig. 6.20 (c)



Figure 6.22: Typical intensity evolutions assigned to different alloy phases. Comparing evolutions of intensity with time within the whole measured range of angle in small steps of angle six different shapes of intensity evolutions turned out to be typical in terms of occurring and repeating at different diffraction angles (Fig. 6.22 (a). The point of switching from lithiation to delithiation is marked. The intensity evolution termed by "phase 6" was already addressed in Figure 6.19 to represent the phase(s) remaining after the delithiation up to 1.0 V was finished. Consequently these phase(s) are assumed to be very low in Li content (Li-poor). Also the other curves are assumed to represent specific phases. Since they feature their maximum intensity during the lithiation-delithiation process they are considered to be higher in Li content than phase 6. The alloy phase with highest Li content is assumed to be represented by the intensity evolution termed phase 2, since this curve features its maximum intensity at the end of the lithiation half-cycle. In Fig.6.22 in addition the points in time are marked by vertical lines, where phases 1-5 show their respective maximum intensity. Diffraction patterns taken at these points are assembled in Fig. 6.23.

at least six different phases. One of the characteristic intensity evolution was already introduced discussing Figs. 6.17, 6.18, and 6.19 attributable to probably two Li-poor phases. It is called in Fig. 6.22 phase 6. At the beginning of the lithiation-delithiation cycle it shows highest intensity. With time the intensity vanishes signifying a vanishing of the corresponding phase(s). At the end of the lithiation-delithiation cycle, however, the phase(s) get reformed again, the corresponding intensity increases again. So far the Licontent of phase 6 cannot be determined. Also no exact phase determination is possible. The other five phases, however, are assumed to be Li-Au alloy phases with higher Li content. Three of the typical intensity evolutions with time (denoted with "phase 1, phase 2 and phase 3 in Fig. 6.22) increase on insertion of increasing amount of Li while the intensity of phase 6 decreases. Consequently the Li content in the unit cells of the materials causing the peaks associated with the observed intensity evolutions denoted with "phase 1, phase 2 and phase 3 is supposed to be higher than in phase 6. After the intensity of the phase 6 has vanished the intensity evolution called "phase 2" starts raising. Phase 2 proceeds raising until the end of lithiation process marked by the orange line, while phase 1 and phase 3 lose in intensity. Consequently the atomic arrangement represented by "phase 2" is supposed to be the arrangement featuring highest Li content. After switching the current the reverse behavior is expectably observed. Phase 1 and phase 3 regain in intensity and phase 2 decreases. Also it is expected to see the Li poor phase(s) increasing in intensity again after phase 2 has disappeared. Not expectable is however the unsymmetric evolution of intensity with time associated to "phase 4" and "phase 5". They feature very intense peaks between the decrease of "phase 1 and "phase 3" and the increase of phase 6 during the delithiation half-cycle. In contrast in the lithiation half-cycle their evolution of intensity with time is remarkably different.

It remains to remark here that it cannot be excluded that there is more than one phase showing the same intensity evolution. As discussed above the shape of intensity evolution of phase 6 is reproduced by two different phases. The other intensity evolutions observed also may represent different phases.

Fig. 6.23 shows diffraction pattern acquired at the points in time where the different phases feature their maximum intensity. The color code is adopted from Fig. 6.22. In all the diffraction pattern there are diffraction rings visible. In the diffraction pattern of the unlithiated sample (Fig. 6.5 (b) there were only diffraction spots indicating large grains (singlecrystal) or high structural order (texture). In contrast the material causing the diffraction rings in Fig. 6.23 is supposed to be of much smaller grain size and statistical orientation, since the diffraction rings are of uniform intensity. Consequently most of the supposed Li-Au alloy phases are supposed to be of powder-like morphology. The images



Figure 6.23: Diffraction patterns of the assumed Li-Au alloy phases (phase 1 to phase 5). The diffraction patterns shown were taken at the points in time marked in Fig. 6.22 (b). The colors of the frames correspond with the colors of the marks in Figure 6.22 (b). In all the diffraction patterns diffraction rings are visible. Only the pattern at the maximum of phase 2 and in smaller amounts the pattern at the maximum of phase 3 feature distinct diffraction spots (marked by rings in Fig. 6.23 (b). Consequently most of the assumed Li-Au alloy phases are obviously nanocrstalline without preferential orientation. But at least one phase (phase 2) shows considerably larger grains or a preferred orientation. The diffraction patters taken at the point of maximum intensity of phase 1, phase 3 and phase 4 show similar patterns of diffraction rings. Consequently these three phases could feature very similar structure. Phase 5 shows a clearly different diffraction pattern pointing to significant structural difference to phases 1, 3, 4.

acquired at the maximum of the intensity evolution of "phase 1", "phase 4" and "phase 5" only show diffraction rings, only polycrystalline phases are prevailing at these states of lithiation/delithiation. But in the diffraction patterns assigned to "phase 2" and "phase 3" also (not only) distinct diffraction spots are present. These diffraction spots point to the existence of large grains or preferred orientation. Since the occurring reflections are the same in the image of "phase 2" and "phase 3" in both patterns the same crystallographic structure is represented by the reflections. The explanation for seeing the spots in both patterns is that the atom arrangements which give rise to the typical intensity evolutions observed (see Fig. 6.22) do not occur isolated. Rather most of the time phase mixtures are present.

In consequence the diffraction patterns in Fig. 6.23 does not only contain diffraction intensities of the phase announced. According to their typical intensity evolution the spots are attributable to phase 2 and the diffraction rings in the pattern of phase 2 origin from phase 1 and phase 3. Accordingly the diffraction patterns cannot be interpreted quantitatively. Qualitatively, however, there seems to be only little difference between the patterns of phase 1, phase 3 and phase 4. Consequently the underlying atomic arrangement seems to be highly similar in "phase 1", "phase 3" and "phase 4". However, the diffraction pattern of "phase 5" can be distinguished clearly on the first view from the others indicating also a considerable structural difference in atom arrangement. Also "phase 2" can be clearly distinguished from the other phases. The reflections do not coincide with the rings of one of the other phases. That is why "phase 2" can be excluded to represent just significantly bigger grains of "phase 1" or "phase 3". The latter also can be seen nicely in Fig. 6.24.

Fig. 6.24 compares the peak positions of phases 1-6 and Au. The peak positions of Au are calculated based on the Au lattice constant of 0.40784 nm.⁷⁷ The peak positions of phase 1 to phase 6 were yielded evaluating the intensity evolutions as described in context of Fig. 6.22. In table 6.5 the peak positions visualized in Fig. 6.24 are compiled. Obviously there is a significant difference between the peak positions of the starting material Au and the Li-poor phase, phase 6, remaining after delithiation pointing to an also structurally considerable difference. However the difference between the peak positions of phase 1, phase 3 and phase 4 is quite small. Consequently also the underlying phases are assumed to be similar in structure. Phase 2, occurring between phases 1, 3 and 4 around the point of switching the direction of galvanostatic current features a unique peak position pattern; sign for an outstanding crystal structure. Having a closer look at Fig. 6.24 similarities of the diffraction pattern of phase 2 to the pattern of Au can be detected. The ratio of the peak positions are similar in case of phase 2 to the ratio of the peak positions observed in the case of Au. However, the absolute values of the peak



Figure 6.24: Overview over the peak positions of Au and the phases correlating with the six typical intensity evolutions shown in Fig. 6.22. A big difference is obvious between the peak positions of the starting material Au and the peak positions of the phase(s) remaining after delithiation (phase 6). The sets of peak positions of phase 1, phase 3 and phase 4 appear quite similar pointing to closely related structures. Phase 5 features a significantly different set of peak positions pointing to also a considerable structural difference. The peak positions of phase 2 also differ strongly from the peak positions of phase 1, 3 and 4. As discussed in chapter 6.7 phase 2" can be identified to be in fact Li-Au alloy phase, namely Li₃Au.

Au	1	2	3	4	5	6 n	6 b
3.772	2.365	2.445	2.395	1.445	1.415	2.455	2.715
4.356	3.235	2.815	3.245	2.405	2.455	2.925	3.895
6.161	4.015	3.985	4.025	3.245	2.835	3.185	5.015
7.226	4.080	4.680	4.105	4.035	3.205	4.155	
7.548	4.135	4.885	4.165	4.135	3.745		
8.717	4.725	5.645	4.790	4.185	4.045		
9.501	5.205	6.145	5.225	4.745	4.245		
9.749	5.725	6.315	5.275	4.815	4.915		
10.6682	6.235	6.90	5.775	5.255	5.105		
11.332	6.335	7.335	6.256.	5.295	5.335		
12.340	6.475	7.975	6.365	5.745	5.855		
12.908	6.895		6.485	5.815	6.030		
	7.030		6.905	6.335	6.170		
	7.095		7.075	6.405	6.475		
	7.675		7.140	6.490	6.505		
	7.805		7.695	6.915	6.865		
	8.025		7.885	7.115	7.250		
			8.055	7.175	7.495		
				7.210	7.695		
				7.695	7.775		
				7.835	8.155		
				7.925			
				8.085			

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Table 6.5: In table 6.5 the peak positions (in degree using a wavelength of 0.0155 nm) of Au and of phases 1-6 are compiled. For phase 6 the positions of the narrow (n) and the broad (b) peaks are listed separately.

positions seem to be shifted to smaller angles in the case of phase 2 in comparison to Au. Accordingly from the observation just stated the Bravais lattice of phase 2 may also be a face centered cubic lattice, as in the case of Au, but the lattice constant of the structure is supposed to be larger than in the case of Au. Also "phase 5" is supposed to be structurally significantly different from "phase 1", "phase 3" and "phase 4". The peak position pattern is significantly different as it is also obvious from Figure 6.23.

In the following the Li-Au alloy phases observed (phase 1 to 5) will be compared to the results of previous investigations on the lithiation behavior of Au model electrodes.

Taillades et al.¹⁶ performed XRD-measurements at Au thin film electrodes at the first and second lithiation plateaus and at the first and third (second according to their nomenclature) delithiation plateau of a galvanostatic lithiation-delithiation cycle. Within their limited range of diffraction angle they observed at the first delithiation plateau two peaks not occurred before in the cycle at q = 1.7 Å⁻¹(Cu K_{α}: 12.1°) and q = 2.3 Å⁻¹(Cu K_{α}:
Au	1	2	3	4	5	6 n	6 b
2.67	1.67	1.73	1.69	1.02	1.00	1.74	1.92
3.08	2.29	1.99	2.30	1.70	1.74	2.07	2.76
4.36	2.84	2.82	2.85	2.30	2.01	2.53	3.55
5.11	2.86	3.31	2.90	2.85	2.27	2.94	
5.34	2.93	3.46	2.95	2.93	2.65		
6.16	3.34	3.99	3.39	2.96	2.86		
6.61	3.68	4.35	3.70	3.36	3.00		
6.89	4.05	4.47	3.73	3.41	3.48		
7.55	4.41	4.88	4.08	3.72	3.61		
8.01	4.48	5.19	4.42	3.75	3.77		
8.71	4.58	5.64	4.50	4.06	4.14		
9.11	4.88		4.59	4.11	4.26		
	4.97		4.88	4.48	4.36		
	5.02		5.00	4.53	4.58		
	5.43		5.05	4.59	4.60		
	5.52		5.44	4.89	4.85		
	5.67		5.57	5.03	5.13		
			5.69	5.07	5.30		
				5.10	5.44		
				5.44	5.50		
				5.54	5.77		
				5.60			
				5.72			

Table 6.6: In table 6.6 the q-values (in Å⁻¹) of Au and of phases 1-6 are compiled. For phase 6 the positions of the narrow (n) and the broad (b) peaks are listed separately.

16.43°). At these q-values also phase 3, which was observed during the first and the second lithiation and delithiation plateaus of lithiation-delithiation cycle experiments presented in this work, features peaks (see table 6.6). Further peaks of phase 3 are outside the range of angle investigated by Taillades. Hence, maybe the peaks at $q = 1.7 \text{ Å}^{-1}(\text{Cu}$ K_{α} : 12.1°) and $q = 2.3 \text{ Å}^{-1}(Cu K_{\alpha}$: 16.43°) indicate the occurrence of phase 3 also in the measurements of Taillades. But it contrast to the here presented measurements Taillades only observed these peaks at the first dissolution plateau. At the lithiation plateaus the intensity may be too weak. But there are also no peaks of phase 1 in the diffractograms of Taillades and also no hints of phase 2, 4, and 5 all featuring peaks in the range of angles of Taillades. The only further peak arising and vanishing during the lithiation-delithiation cycle of Taillades is a peak at $q = 3.1 \text{ Å}^{-1}(\text{Cu K}_{\alpha}: 22.34^{\circ})$. It is present at the first lithiation and delithiation plateau. However, there is no correspondence to this peak in table 6.6. Hence, even though the galvanostatic potential-time curve of Taillades is very similar to the galvanostatic potential-time curves presented in sections 5.4 and 5.5, Figs. 5.10 and 5.12 the observed diffraction patterns show only a few coincidences. Most probably the reason for this is, that Taillades performed only ex-situ XRD measurements. Also ex-situ XRD measurements performed at MPIE (not shown here) resulted in different diffraction patterns than the in-situ measurements. This observation is probably related to limited stability of the alloy phases involved in the lithiation delithiation cycles and underlines the importance and necessity of in-situ experiments.

Hence, the six Li-Au alloy phases observed in the present work turned out to be stable "in-situ" in a relatively wide current range and during galvanostatic lithiation-delithiation cycles (including GITT measurements) as well as during potentiostatic cycles. But after removing the sample from the cell and transferring it to an ex-situ XRD device they degrade. Maybe the peak at q = 3.1 Å⁻¹(Cu K_{α}: 22.34°) observed by Taillades origins from a decomposition product of the original alloy phases.

Renner et al.¹⁵ performed in-situ XRD measurements during their potentiostatic lithiationdelithiation experiments at a Au single-crystal, a Au thin film and Au nanoparticles. In the case of the Au single-crystal they observed the evolution of one set of new peaks after setting the potential to -0.1 V. After subsequent raising of the potential to 0.1 V a different set of peaks is formed. Within this second set of peaks Renner named peaks at q = 1.7 Å⁻¹, q = 2.98 Å⁻¹, q = 3.11 Å⁻¹, q = 3.48 Å⁻¹ and q = 3.64 Å⁻¹explicitly. The lithiation of the thin-film and the nanoparticles gave rise to similar results. Peaks at q = 1.7 Å⁻¹ and q = 3.11 Å⁻¹ were also reported by Taillades (see above). The q-values reported by Renner do not match the peak positions of phase 3. Only the q-value of 1.7 Å⁻¹correlates with phase 3 or maybe phase 1. According to this finding and substantiated by a comparison of the diffraction patterns reported by Renner and the patterns of phases 1 to 5 resulting in no complete matching probably phases 1 to 5 were not present in these experiments. An explanation for this finding could be the harsh potentiostatic conditions of setting the potential directly to -0.1 V.

Misra et. al⁴ reported on unexpectedly occurring peaks during their galvanostatic lithiation-delithiation cycles of silicon nanowire anodes possibly correlated to the lithiation of their Au catalyst for Si nanowire growth. To examine this phenomenon in more detail they performed analogous measurements at a 50 nm thin Au film sample and a Au nanoparticle sample (0.5 µm-0.8 µm). In case of the Au nanoparticle sample they again obtained the "unexpected" peaks and could hereby assign them to Li-Au alloy phases. In dependence of the degree of lithiation they found two phases. One phase featuring peaks at q = 1.66 Å⁻¹, q = 1.69 Å⁻¹, q = 2.29 Å⁻¹, q = 2.83 Å⁻¹, and q = 2.95 Å⁻¹and the second phase featuring peaks at q = 1.72 Å⁻¹, q = 2.81 Å⁻¹, and q = 3.29 Å⁻¹. By comparison with the q-values of phase 1 to phase 5 in table 6.6 the second phase of Misra is most probably identical to phase 2. The first phase of Misra seems to be a mixture of phase 1 and phase 3. Also in the measurements presented here phase 1 and phase 3 appeared and vanished always together.

The fact that Misra also detected phase 1, phase 2 and phase 3 substantiates the stability and reproducibility of these phases. Interestingly Misra did not observe these phases while lithiating the 50 nm thin Au film. He assigned the difference in lithiation behavior he found between the Au nanoparticles and the Au film to differences in stress during lithiation of different Au morphologies.

Moreover the intensity evolutions of the two phases observed by Misra is admittedly similar to the intensity evolutions observed for phase 1/3 and phase 2 in this work, but it is not identical. Misra reported his second phase to quasi immediately disappear to the benefit of his first phase after switching the current direction. The described difference in the intensity evolutions can possibly in fact be attributed to differences in stress during lithiation of different Au morphologies.

In addition Misra performed galvanostatic potential relaxation experiments. Potential relaxation after the second phase had appeared led to a disappearance of the second phase and a reappearance of the first phase. In contrast the galvanostatic potential relaxation experiments presented in chapter 5.9 revealed phase 2 (which should be identical to the second phase of Misra according to the comparison of peak positions) to be very stable during potential relaxation. In addition phase 2 identified as Li_3Au in chapter 6.7 is expected to be stable since it appears in the Li-Au phase diagram.

As shown in the present work using a 100 nm Au film not only the two (three) phases

observed by Misra but also some additional phases are involved in galvanostatic and mild potentiostatic lithiation-delithiation cycles.

6.6 Discussion X-ray diffraction: Alloy Phase Formation-Dissolution

In the following discussion the typical intensity evolutions with time observed in the third in-situ galvanostatic lithiation-delithiation cycle (see Fig. 6.22) will be set into relation to the phase transitions occurring during lithiation and delithiation.

Interpreting Fig. 6.22 in terms of Li alloy formation the following procedure is suggested. At the beginning the amount of Li in the sample is only small. The sample contains mainly the Li-poor phase(s), called here phase 6, and leftovers of phase 5 obviously not completely dissolved during the previous cycle. With progressing lithiation the intensities of phase 5 and the Li-poor phase(s) decrease to zero. Instead higher lithiated alloy phases arise, namely phases 1,3 and 4 as denoted here. These three phases start to appear at about the same time (even though they will show different time behaviors along the lithiation cycle). However it cannot be said which of the three phases (1, 3, and 4) increases quicker since the peak intensities are most probably not directly comparable. The increase of the phase 4 (blue) seems from Fig. 6.25 to increase most steeply at the beginning of its appearance. With time the rate of increase reduces. The increase of phase 3 (green) turns out to be rather linear. The increase of phase 1 in contrast seems to be the least pronounced at the beginning. But it get's steeper with time. After about 1400 s phase 4 starts quickly decreasing in intensity as visible in Fig. 6.25. The structure of phase 4 seems to be not stable any more. The intensity of phase 4 reaches zero shortly after also phase 5 and phase 6 have disappeared. Instead at about 1300 s phase 1 and phase 3 start to increase pronouncedly and very uniformly. Their underlying crystal structure seems to be favored now over the crystal structure of phase 4. At about 1500 s the intensity of phase 3 stops increasing abruptly and starts decreasing slowly but more and more pronounced, while the intensity of phase 1 keeps increasing unchanged. The further formation of phase 3 is hindered, but the crystal structure assigned to phase 3 obviously does not become that unpreferable that the phase would be quickly dissolved for example to the benefit of phase 1. After 1700 s also the increase of intensity of phase 1 weakens significantly and the intensity evolution turns to a slow decay, more pronounced in time. Interestingly the shape of the decay of phase 1 is very similar to the one of phase 3. Only the transition between strong increase and slow decrease is less abrupt in case of phase 1. The decrease of intensity of phase 1 and phase 3 continues until the point of inverting the current (end of lithiation). During this decrease, however, intensity of phase 2 arises almost linearly until lithiation is finished. A new Li-Au alloy phase is formed.

After switching the direction of the galvanostatic current after 2750 s phase 2 gets dissolved again. In a very small time window after switching of the direction of galvanostatic current the intensity of phase 1 drops, remarkably, very quickly to about the previous level of phase 3 while he intensity of phase 3 increases very quickly to about the previous level of phase 1. Possibly the energies of phase 1 and phase 3 are very close and already small outer influence effects a conversion between the phases. Or the phenomenon described is only a kinetic effect. Subsequently the intensities of phase 1 and phase 3 increase again, while phase 2 is decreases linearly in intensity. On extracting Li from phase 2 phase 1 and phase 3 seem to be recovered. Their intensity increases until phase 2 has vanished after 3300 s. Already before the intensities of phase 1 and phase 3 reach their second maximum and phase 2 vanishes phase 4 starts arising anew at 3100 s. Phase 4 reaches a very sharp and intense maximum (three times more intense than the first maximum of phase4) during the decay of phases 1 and 3. Phases 1 and 3 seem to be converted into phase 4. Phase 4 seems to feature also a similar structure and energy like phases 1 and 3 as can be anticipated from the quick transformation of phases 1 and 3 into phase 4 and their simultaneous appearance and presence at the beginning of lithiation. When phase 4 is at its second intensity maximum at 3400 s phase 5 starts arising. The steep increase is followed by a sharp maximum at 3600 s and an subsequent decrease less pronounced than the increase. At the end of the lithiation-delithiation cycle, however there is still intensity of phase 5 left as also observed in the previous cycle. At the point of maximum intensity of phase 5 phases 1 and 3 are vanished completely. At the point of maximum intensity of phase 4 phase 6 starts to increase again in intensity. At the end of the cycle the Li-poor phase and phase 5 coexist. The other phases are completely dissolved.

The phase evolutions described above are not compatible with assuming exactly the same mechanism for lithiation and delithiation since the intensity evolutions are not symmetric with respect to the point of switching the current. While the evolutions of phase 1, phase 3 and phase 2 are nearly symmetric with respect to the point of switching the direction of galvanostatic current, the evolutions of phase 4 and phase 5 are highly unsymmetric. Only during delithiation phase 4 and phase 5 show intense and narrow peaks in intensity evolutions. During lithiation they are also present but at much lower intensity and much broader peak width.

Since phase 2, identified to be the Li-Au alloy phase Li_3Au by comparison with database data (see. Fig. 6.26), is the only one increasing towards the point of switching direction of galvanostatic current it can be assumed to be the highest lithiated phase observed in

the presented experiments. Consequently the highest lithiated phase found in the present work is Li_3Au and not $Li_{15}Au_4$. $Li_{15}Au_4$ is the phase with highest Li content in the phase diagram of the binary Au-Li system.

6.7 Gold-Lithium Alloy Phase Characterization

6.7.1 Identification of the Li₃Au alloy phase

Diffractograms of Li-Au alloy phases such as Li_4Au_5 , Li_3Au or $Li_{15}Au_4$ and also Au-Cu alloy phases registered in crystallographic databases were compared to the alloy phases observed (see chapter 6.5). Li-Cu alloy phases are not known in the phase diagram of the Li-Cu-system. Only a solid solution of Li in Cu with low Li content exists.

Comparing the measured peak positions with diffractograms from the ICDD database was successful in the case of phase 2. Fig. 6.26 (a) shows a comparison of the peak positions found for phase 2 in the present work with a diffractogram of the Li₃Au alloy phase from the database (ICDD entry number: 03-065-8632). A match between the peak positions of phase 2 and the Li₃Au alloy phase is obvious. The intensities could not be extracted trustworthily from the measured XRD data due to the overlapping of peaks from different phases. Consequently intensities will be compared here.

 Li_3Au crystallizes in the cubic crystal system with a face-centered Bravais lattice. Au atoms occupy here all the four corners of the unit cell and all the centers of the 6 faces. The Li atoms are located inside all the four octahedral voids and all the eight tetrahedral voids between the Au atoms. Li_3Au crystallizes thus in the BiF₃ or Cu₃Al structure type. Fig. 6.26 (b) displays a sketch of a unit cell of Li_3Au .

According to the previously described identification of phase 2 to be the Li-Au alloy phase Li_3Au the highest lithiated alloy phase observed in the presented lithiationdelithiation cycles is Li_3Au . It has to be pointed out here, that no $Li_{15}Au_4$ alloy phase has been observed which is the Li-Au alloy phase with the highest known Li content and which is widely assumed to be formed using Au anodes and is mostly used as reference for the calculation of the theoretical specific capacity of Au.

6.7.2 Ordering of the Li₃Au alloy phase

As mentioned above, phase 2 is the only phase showing distinct Bragg reflections in the diffraction pattern. The other phases show diffraction rings featuring homogeneous azimuthal intensity distributions. As stated in chapter 2.2 homogeneous diffraction rings in the pattern indicate the presence of a powder-like sample featuring many randomly



Figure 6.25: Typical intensity evolutions observed during the lithiation-delithiation cycles of the Au film model electrode. When comparing cross sections of Figs 6.20 and 6.21, respectively, parallel to the time axis in small steps of angle some particular evolutions of intensity turn out to repeat at different diffraction angles. Together these are the six typical intensity evolutions plotted in Figure 6.25. One of them is was already shown and discussed above with Figure 6.19. In Fig. 6.25 it is plotted in purple and refers to the Li-poor phase (phase 6) remaining after delithiation. The other intensity evolutions can be interpreted to represent different Li-Au alloy phases featuring different Li contents. The orange line marks the end of lithiation. This is the point where phase 2 identified as the Li-Au alloy phase Li₃Au in the following chapter (6.7.1) is found to show maximum intensity. According to Fig. 6.25 Li₃Au is the highest lithiated alloy phase found.



Figure 6.26: Phase identification of phase 2. Fig. 6.26 (a) shows a comparison between the peak positions found for phase 2 in chapter 6.5 (red peaks, please note: a corresponding intensity cannot be given due to experimental issues (see text); in addition the peak width shown here is arbitrarily chosen) and the peak positions and corresponding intensities of a Li₃Au phase from the ICDD database (blue streaks). Based on the correlation found phase 2 could be identified to be the Li-Au alloy phase Li₃Au. In Fig. 6.26 (b) a sketch of a unit cell of Li₃Au crystallizing in the face centered cubic BiF₃ or Cu₃Al structure type is displayed. Au atoms occupy the four corners and the six faces, Li fills all the octahedral and tetrahedral voids within the cubically densest packing of the Au toms.



Figure 6.27: Diffraction pattern of the lithiated Au thin film at an arbitrarily chosen angle of rotation around the vertical axes of the sample . In addition to the polycystalline alloy phases represented by the diffraction rings there is also an oriented crystalline alloy phase present which gives rise to distinct diffraction spots. The orientation of the alloy phase giving rise to the occurrence of these spots is clearly defined if all spots can be adequately indexed.

oriented crystallites within the footprint of the beam. In contrast the presence of distinct diffraction spots points to the presence of a rather small amount or even only one rather big crystallites. In addition, the possible presence of a texture has to be considered. Indexing of the diffraction spots will help to get to a more detailed knowledge about the orientation of the phase in relation to the Cu substrate.

It turns out that it is not possible to assign all the diffraction spots visible in the diffraction patterns to a single crystallite. This becomes clear nicely considering Fig. 6.27. Fig. 6.27 shows a diffraction pattern of the model electrode lithiated to 5 mV recorded during the rotation of the sample around its normal ($\Delta \omega = -45^{\circ}$).

The diffraction pattern features a multitude of different spots. If all the spots originate from only one crystallite they will be located on one single mesh spanned by two vectors in reciprocal space (compare section 2.2). But this is obviously not the case. No single mesh featuring a mesh width of minimum the length of the (111) vector is able to cover all the spots visible.

It has to be taken into account that a couple of spots present in the diffraction pattern

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Figure 6.28: (111)x(111) mesh assigned to the Cu single-crystal substrate. All the spots this mesh originate from the Cu singlecrystal substrate. It is apparent that the Cu substrate is indeed an (100) oriented singlecrystal.

do not belong to the alloy phase but stem from the Cu-substrate. These spots however match with a mesh spanned by two Cu(111) vectors including an angle of 70,5°, the angle between two (111)-type planes in a cubic crystal. A mesh like this will be noted in short by the expression (111)x(111) in the following. In table 6.7 the short nomenclature of the meshes discussed in this chapter is correlated with the exact indexing of the vectors spanning the meshes and the angle included by them. Furthermore the angle of rotation around the vertical axis associated with each crystal orientation (mesh) can be read out from the table.

Fig. 6.28 shows the diffraction pattern known from Fig. 6.27 with the Cu(111)x(111) mesh superimposed. All the spots in the diffractogram at 2 ϑ -angles assigned to Cu coincide with this mesh.

Hence, as expected the Cu substrate is a single crystal. Moreover the nominal orientation of the substrate, namely (100) is proven by the fact that the Cu(200) spot is located on the vertical axis of the pattern.

In the case of the Li_3Au phase the situation is more complex. Here a mesh formed by (111) and (220) vectors, where the (220) vector coincides with the vertical axes and the implemented angle is 90°, leads to obvious coincidences. Fig. 6.29 shows the diffraction



Figure 6.29: (111)x(220) mesh assigned to the Li_3Au alloy phase. The corresponding alloy crystal is oriented with a (220) plane parallel to the surface of the Cu(100) substrate. The (111)x(220) grit does not cover all the diffraction spots of the alloy phase and there is no other one that does so. In consequence there is not a single-crystal of Li_3Au present. Instead several crystals are supposed to be present.



Figure 6.30: Addition of an (220)x(220) mesh covers additional diffraction spots. The represented crystallite is as the first crystallite oriented with a (220) plane parallel to the surface of the substrate. However the represented crystallite is rotated with respect to the first crystallite around the vertical axes of the substrate.

pattern together with the (111)x(220) mesh.

The corresponding crystallite is oriented with the (220) plane parallel to the surface of the Cu substrate indicated by the coincidence of the (220) vector with the vertical axis. But not all the diffraction spots of Li₃Au coincide with the (111)x(220) mesh. The spots not covered by the (111)x(220) mesh origin from other crystallite(s) represented by other mesh(es) (other crystal orientations). The next smallest mesh fitting a considerable amount of spots is an (220), (220) mesh with angles of 60° and 120°. It is oriented to result in two grid-lines including the 60° angle tilted by 30° against the horizontal axes each to both sides. In Fig. 6.30 this (220)x(220) mesh is added.

The orientation of the (220)x(220) mesh implies, that this mesh also coincides with the (220)-reflection on the vertical axes. Hence, also the crystallite giving rise to the (220)x(220) mesh is oriented with a (220) plane parallel to the horizontal plane and therefore also to the surface of the Cu(100) substrate as it was also found for the crystallite associated with the (111)x(220) mesh. Hence obviously both crystallites feature an (220)plane parallel to the (100) surface of the Cu substrate. The difference is a rotation around the vertical axis (see table 6.7). The finding that both so far drawn meshes represent a



Figure 6.31: Another mesh assigned to another crystal orientation is the (220)x(331) mesh. Again the orientation parallel to the substrate's surface is (220). The orientation perpendicular to the surface is different from the previous crystallite.

crystal orientation featuring a (220) crystal plane parallel to the surface may already indicate that (220) orientation parallel to the surface is possibly favored by the Li_3Au phase. This hypothesis yields additional orientations drawn here as meshes to explain the remaining reflections so far not covered by the two initial meshes.

The (220)x(311) mesh added in Fig. 6.31 covers further diffraction spots. Also the crystallite corresponding to this mesh is oriented with one (220) plane parallel to the Cu substrate. To cover all the remaining reflections further crystal orientations represented by additional meshes have to be assumed. In fact, all of them include the (220) spot on the vertical axes. They are listed with the associated included and and vertical angles in Table 6.7. In Fig. 6.32 the meshes of the most prominent crystal orientations visible in the diffraction pattern are plotted. Fig. 6.32 nicely shows all the drawn meshes to have the (220) reflection (and (440) reflection) on the vertical axes in common. From the observation that all the crystallites of Li₃Au represented by the different meshes are oriented with the (220) atomic plane parallel to the Cu surface substantiates the above stated hypothesis, that (220) orientation parallel to the surface is favored. Moreover the presence of various different crystal orientations perpendicular to the Cu(100) surface gets apparent. While in the case of Cu only one single lattice can cover all the diffraction spots,

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Figure 6.32: Some more meshes are necessary to cover all the diffraction spots in the diffraction pattern. All these meshes represent crystallites featuring (220) orientation parallel to the Cu substrate. Perpendicular to the substrate all the crystal orientations are rotated by a different angle.

Table 6.7: Possible meshes defined by the two vectors spanning the mesh (hkl) 1 and (hkl) 2 and the angle included in the range of angle measurable in the chosen setup. These meshes correspond to different reciprocal lattice planes. "Angle (vertical)" denotes the angle of rotation of the (220) oriented crystal (and the corresponding reciprocal lattice with respect to the reference orientation shown in Fig. 6.33 to achieve coincidence between the respective reciprocal lattice plane and the Ewald-sphere (paper plane).

	angle (vertical) /°	(hkl) 1	(hkl) 2	angle (included) /°	abbreviation
1	0.0	(200)	(0-20)	90	(200)x(200)
2	8.0	(220)	(5-5-1)	90	(220)x(551)
3	10.1	(5-3-1)	(3-5-1)	27.66	(531)x(531)
4	13.3	(220)	(3-3-1)	90	(220)x(331)
5	15.8	(6-4-2)	(4-6-2)	21.79	(642)x(642)
6	19.5	(3-1-1)	(1-3-1)	50.48	(311)x(311)
7	23.0	(220)	(5-5-3)	90	(220)x(553)
8	25.2	(4-2-2)	(2-4-2)	33.56	(422)x(422)
9	28.0	(5-3-3)	(3-5-3)	24.91	(533)x(533)
10	35.3	(220)	(1-1-1)	90	(220)x(111)
11	41.5	(5-3-5)	(3-5-5)	21.22	(553)x(553)
12	43.3	(4-2-4)	(2-4-4)	27.27	(442)x(442)
13	46.7	(3-1-3)	(1-3-3)	37.86	(331)x(331)
14	49.7	(220)	(3-3-5)	90	(220)x(533)
15	54.7	(20-2)	(0-2-2)	60	(220)x(220)
16	60.6	(3-1-5)	(1-3-5)	27.66	(531)x(531)
17	64.8	(220)	(1-1-3)	90	(220)x(311)
18	68.0	(3-1-7)	(1-3-7)	21.22	(731)x(731)
19	70.5	(20-4)	(0-2-4)	36.87	(420)x(420)
20	74.2	(220)	(1-1-5)	90	(220)x(511)
21	76.7	(20-6)	(0-2-6)	25.84	(620)x(620)
22	78.6	(220)	(1-1-7)	90	(220)x(711)

this is not the case for Li_3Au where 22 are necessary.

The sample, lithiated until the lower potential limit of 5 mV was reached, giving rise to the diffraction patterns under discussion here, was rotated around the vertical axis after switching to ocp to clarify, if within the footprint of the X-ray beam there is only a limited number of relatively large crystals present showing different distinct rotational orientations with respect to the vertical axis or if there are many (smaller) crystallites present showing a (homogeneous) random rotational orientation with respect to the vertical axes (2-D powder).

Already after a small rotation the diffraction pattern changed. At some positions reflections disappeared while at other positions new reflections appeared. This finding is in contrast with the consideration of facing a multitude of relatively small crystallites



Figure 6.33: Reference orientation of the reciprocal lattice of the Li3Au phase showing (220)-orientation parallel to the Cu(100) substrate. Starting from an orientation featuring all faces of the cube perpendicular to the axes the reference orientation is reached by 45° rotation around the x-axis. Referring to this reference orientation in table 6.7the angles (angle (vertical) /°) are listed the specified meshes or reciprocal lattice planes coincide with the (sufficiently large) Ewald sphere approximated by the paper plane if the X-ray beam incides perpendicular to the paper plane.

showing random rotational orientation with respect to the vertical axis (2-D powder) and strengthens the consideration of facing a limited amount of relatively large crystals. In particular they are considerably larger than the crystallites of the other crystalline phases (phase 1,2,4,5), since the latter phases give rise to uniform diffraction rings in the diffraction patterns.

In the idealized case of an infinite radius of the Ewald sphere all the reflections coinciding with a specific mesh (originating from the same plane in reciprocal space), with exceptions of the reflexes on the vertical axis, are expected to appear or disappear during rotation concertedly. However, in the performed measurements during rotation it was often observed that first the reflections belonging to a specific mesh first appeared (dependent on the direction of crystal rotation) only on the left side of the pattern. In the next image also the central spots belonging to this mesh were visible and in the next image the spots at the left side were gone while the central spots of the mesh remained and the spots on the right side of the mesh had appeared. One image later only the spots on the right side remained and in the following image all the spots on the mesh disappeared.

The reason for this is the mismatch between the planar atomic lattice planes and the bended Ewald-sphere. In result the high indexed lattice points belonging to a plane in reciprocal space penetrate the Ewald-sphere earlier or later than the lattice points closer to the origin of the reciprocal space.

The meshes occurring in Figure 6.32 all are assigned to different crystallites. These crystallites all have a (220)-orientation with respect to the surface of the substrate in common. For face-centered-cubic (fcc) crystals rotating around an axes perpendicular to one of their $\{220\}$ planes the number reciprocal lattice planes (represented by the meshes) that can cross the (large enough) Ewald sphere is limited considering only the part of the reciprocal space imageable by the detector in the here chosen arrangement (see chapter 4.3). By modeling of the the resulting diffraction pattern during rotation of a Li₃Au crystallite round the plane normal of its (220) plane (compare Fig. 6.33) it becomes obvious that considering all the reflections up to (711) only 22 meshes can occur (only 22 reciprocal lattice planes can coincide with the Ewald sphere). Fig. 6.27 contains in fact 22 of them. But in the some of other diffraction patterns acquired during rotation one, two, three four or even five of these crystal orientations (meshes) were not present. An estimation based on statistical evaluation of the number of crystal orientations observed in all the diffraction patterns acquired during rotation suggests 50-150 crystals to be present.

Concluding, the structural investigation of the Li_3Au phase (phase 2) presented in this chapter revealed that the ordering of the Li_3Au phase within the sample is characterized by the presence of only a limited number of relatively large crystallites. These crystallites have a (220)-orientation parallel to the surface of the Cu substrate in common. With respect to the vertical axis they show random orientation, but since their number is limited the resulting arrangement cannot be called a 2-D powder.

The presence of Li₃Au crystallites showing uniform (220) orientation parallel to the Cu surface suggests the crystals to form starting at the interface between electrode material and Cu substrate, since the surface of the Cu(100) substrate provides a highly oriented template the newly formed alloy phase can orient at. The high number of different rotational orientations with respect to the vertical axis on the Cu surface points to the fact, that for the formation of Li₃Au(220) planes parallel to the Cu(100) surface not the interactions between the Cu substrate and the alloy phase are decisive. Obviously the formation of Li₃Au(220) surfaces is attributed to the reduction of the interface energy of the alloy phase.

6.8 Summary of the results of the XRD-measurements

In the following the results of the in-situ XRD experiments presented and discussed in chapters 6.3 to 6.6 will be summed up.

Au Film on Cu Substrate

First the pristine Au film on the Cu substrate before the start of the electrochemical treatment was investigated.

In chapter 6.3 the Cu substrate was proven to be indeed a Cu(100) single-crystal by evaluating the diffraction pattern of the starting state (Figs. 6.4 and 6.6). The diffraction pattern showed distinct reflections which can be explained by a single mesh representing a single crystal orientation. The (100)-orientation of the Cu single-crystal parallel to the surface could be proven, since the Cu(200)-reflection was found to coincide with the vertical axis.

Furthermore in chapter 6.3 the Au thin film was shown to represent two different crystal orientations transferable into each other be rotation by 180° around the vertical axis and assignable to the two possible stacking orders in the cubic densest packing of atoms ABC and ACB. Both crystal orientations featured the (111) lattice plane parallel to the surface of the Cu(100) single-crystal (Figs. 6.4 and 6.6). The diffraction pattern showed distinct reflections explainable by two mirror symmetrical meshes representing two mirror symmetrical crystal orientations. Since for both meshes the Au(111)-reflection was found to coincide with the vertical axis (111)-orientation of the Au thin film parallel to the surface could be proven.

In chapter 6.4 the orientation of the Au crystallites observed in the diffraction pattern with respect to the Cu substrate was determined to differentiate in the case of the Au thin film between a random rotational orientation of the crystallites with respect to the vertical axis and preferred orientation with respect to this axis . Discussing Figs. 6.9, 6.10, 6.12, and 6.13 coincidence of the atomic lattices of Au and Cu along one specific direction was found in this specific orientation. From this finding a preferred orientation of Au on Cu can be assumed leaving the possibilities of either dealing with a bi-crystal featuring all crystallites showing ABC stacking order adjacent and also all all crystallites showing ABC stacking order adjacent or facing a highly textured Au film with crystallites of both stacking orders randomly distributed, but all uniformly oriented.

Lithiation-Delithiation Cycling of the Au film on the Cu substrate

Then the electrochemical treatment (galvanostatic lithiation-delithiation cycles) was started and the associated structural changes of the electrode material were followed.

In chapter 6.5 during the first lithiation of the sample the intensity of the reflections of the Au film were found to vanish without detectable widening of the Au structure or successive loss in crystalline order. Fig. 6.16 shows the Au(111) peak to decrease in intensity without shifting of the peak position or increasing of the FWHM.

After subsequent delithiation no crystalline Au was recovered any more. According to Figs. 6.17 and 6.18 at the end of the delithiation half-cycle no intensity at the peak positions of Au raised. Instead short before the end of the delithiation cycle at different diffraction angles intensity arises. Two different phases, one phase featuring rather sharp peaks indicating high crystalline order and another phase featuring rather broad peaks feature very similar intensity evolution with time arising for the first time at the end of the first cycle and in the following cycles vanishing at the beginning of lithiation and recovering at the end of delithiation (Fig. 6.19). Crystalline Au is never recovered again after the first lithiation half-cycle. The two new phases were pooled due to their analogue intensity evolution with time and termed phase 6. The phases are Li-poor and maybe they contain still a considerable amount of Li to be responsible for the observation discussed in chapter 5.15 that only 2.5 equivalents of Li can be reversibly inserted and extracted.

By means of intensity evolution with time (see discussion of Figs. 6.21 and 6.22) it was possible to distinguish five additional Li-Au alloy phases occurring during the lithiation-delithiation cycles termed phase 1 to phase 5. The nomenclature refers to the point in time the phases show their maximum intensity in the first lithiation-delithiation cycle. Remarkably not all the distinguished phases show phase evolution symmetrical with respect to the point of complete lithiation implicating different reaction paths of

lithiation and delithiation. Regarding their very similar associated diffraction patterns (Fig. 6.23) phases 1, 3, and 4 are structurally very similar. Phase 5 differs structurally significantly expressed by the different diffraction pattern. All the so far mentioned phases (1,3,4,5,6) are poly-crystalline. In the diffraction patterns they only show diffraction rings. Only phase 2 shows distinct spots. By comparison with structure data from the ICDD database phase 2 was identified to be the Li-Au alloy phase Li_3Au (Fig. 6.26). The evaluation of the crystalline order of phase 2 showed that the crystallites of phase 2 are considerably larger than the crystallites of the other (nanocrystalline) phases. An estimation based on statistical evaluation of the number of crystal orientations observed in all the diffraction patterns acquired during rotation suggests 50-150 crystals to be present. All the crystallites are oriented with (220)-lattice planes parallel to the Cu(100)surface but rotational disorder with respect to the vertical axis prevails. Due to the uniform orientation of phase parallel to the Cu(100) surface phase 2 can be expected to be formed starting from the Cu(100) surface and not from the electrode's surface. In addition the presence of an additional amorphous phase during the series of structural changes in the electrode material during the lithiation-delithiation cycles was considered.

Concluding the discussion of structural changes during the first lithiation half-cycle the preferred orientation of the Au film on the Cu substrate disappears first completely while only polycrystalline alloy-phases are formed before again preferred orientation of the Li₃Au phase on the Cu crystal but only parallel to the surface. In contrast to the arrangement of the Au(111) film on the Cu(100) surface which is clearly determined by interactions between substrate and film the tendency of the Li₃Au crystallites to form (220) surfaces on top of the Cu(100) substrate is assigned to a reduction of the surface energy of the Li₃Au crystallites. Obviously Li₃Au(220) interfaces are energetically favored.

7 Correlation between electrochemical treatment and alloy phase formation

7.1 Structural changes during galvanostatic lithiation/delithiation of the Au thin film model anode

To correlate the applied electrochemical treatment with the observed phase transformations the characteristic evolutions of diffracted intensity with time associated with the alloy phases found are compared to the simultaneously recorded current-time curves.

Fig. 7.1 (a) shows representing the third lithiation-delithiation cycle of the galvanostatic in-situ measurements the intensity evolutions with time typical for phase 1 to phase 6 observed by XRD during galvanostatic lithiation-delithiation cycles performed in the in-situ electrochemical cell together with the corresponding galvanostatic potential-time curve. In Fig. 7.1 (b) similar data are given for the first galvanostatic cycle, where pristine Au is still present as the starting material of the cycle. In addition to the galvanostatic potential-time curves acquired during the respective in-situ measurement the potentialtime curves of the third cycle (Fig. 7.1 (a)) and the first cycle (Fig.7.1 (b)) of the lab-based galvanostatic measurements at 1.7 C (16.6 μ A, see Fig.5.10) are shown for comparison. For the lab-based measurements the duration of the lithiation and delithiation half-cycles are adapted to the duration of the lithiation and delithiation half cycles obtained from the synchrotron-based in-situ measurements.

In the in-situ galvanostatic potential-time curves of the first and the third cycle of both, in-situ and lab-based measurements, two potential plateaus in the lithiation halfcycle and three potential plateaus in the delithiation half-cycle can be distinguished, respectively (compare Fig. 5.10). However, in the in-situ measurements they are not as well pronounced as in the lab-based measurements. In the in-situ curves the potential



Figure 7.1: To correlate the results of the lab-based galvanostatic lithiation-delithiation cycle experiments with the results of the in-situ measurements the intensity evolutions with time for the six phases found from the in-situ XRD measurements (compare Fig. 6.22) in the first (Fig. 7.1 (b)) and the third cycle (Fig. 7.1 (a)) are compiled together with the potential-time curves during the first (Fig. 7.1 (b)) and the third cycle (Fig. 7.1 (a)) galvanostatic in-situ (IS) and lab-based (LB) measurements. The duration of the lithiation and delithiation half-cycles from the lab-based measurements were adapted to the duration of the respective half-cycles of the in-situ measurements. The numbers 1 to 6 denote the alloy-phases 1 to 6 introduced in Fig. 6.22. The galvanostatic potential-time curves are labeled (IS) and (LB). The vertical lines mark the point in time where the respective phases show their maximum intensity.

is not as stable over a long time period as it was observed to be the case in the labbased measurements resulting in clearly sloped plateaus. But in the case of the third cycle (Fig. 7.1 (a)) the plateau values observed in the potential-time curves of the in-situ measurements nicely coincide with the plateau values obtained in the lab experiment both measured at a current of 16.6 μ A. The coincidence of the plateau potentials between in-situ and lab-based measurements is better in the third cycle than in the first cycle. Reason for this could be the higher current in the first cycle of the in-situ measurements (22.7 μ A) than in the first cycle of the lab-based measurements (16.6 μ A) and the leak currents assumed to be present in the in-situ measurements. However, the difference between the first cycle (lithiation of Au) and the third cycle (lithiation of phase 6) (compare chapter 6.5, Fig. 6.17) reported in chapter 5.4 can nicely be reproduced and recognized in the in-situ measurements.

Third Lithiation Half-Cycle

Fig. 7.1 (a) shows the intensity evolutions with time typical for phase 1 to phase 6 during the third lithiation-delithiation cycle already shown in Fig. 6.22 together with the corresponding potential-time curve and the potential-time curve obtained in the third cycle of the lab-based galvanostatic measurements.

At the beginning of the cycle, phase 5 and phase 6 are present. The ratio cannot be inferred directly from the curves since the individual peaks may feature different form factors. However an estimation can be made assuming the complete electrode consists of phase 5 at the maximum of phase 5. At the beginning of the cycle the intensity of phase 5 is at half of the value at the maximum of phase 5 (vertical line in Fig. 7.1 (a)). Accordingly, phase 5 and phase 6 are assumed to be present at the beginning of the third cycle in equal amounts. From the beginning of the lithiation half-cycle the intensity of phase 5 keeps constant for about 700 s. Afterwards it starts decreasing and has vanished after 1600 s. The intensity of phase 6 decreases after an initial small increase continuously and has also vanished after 1600 s. At about 250 s phases 1, 3 and 4 start increasing and continue increasing in the following 750 s linearly.

At 250 s in the potential-time curve, after the initial dip (* in Fig. 7.1 (a)), an maximum of intensity (# in Fig. 7.1 (a)) occurs representing the beginning of the first lithiation plateau. Considering the previous observations obviously during the first lithiation plateau phases 1, 3 and 4 are formed first exclusively from phase 6 and later also from phase 5. The fact that phases 1, 3 and 4 are formed at the same time resulting in the formation of only one single plateau strengthens the assumption that the three phase are energetically (due to similar formation potential) and structurally (due to similar diffraction pattern)

very similar. Phase 4 is obviously the most preferred phase at the beginning of the alloy formation, since its increase in intensity is the steepest. At about 1100 s phase 1 and phase 3 turn to increase more pronouncedly than phase 4 while the increasing-rate of the intensity of phase 4 keeps almost constant. At 1300 s the intensity of phase 4 stops increasing and stays constant for a while. At the same time the intensities of phase 1 and phase 3 increase strongly. At 1450 s the intensity of phase 4 starts decreasing very pronouncedly obviously to the benefit of phases 1 and 3. This observation could explain the occurrence of the first intermediate lithiation plateau ($^{\circ}$ in Fig. 7.1 (a)) in the potential-time curve from the lab-based measurements. But the in-situ potential time curve does not show this intermediate plateau as pronounced as the lab-based experiments and seems to have reached the second pronounced potential plateau already at 1400 s. The position of the intermediate plateau in the potential time curve from the lab measurements is an estimation because of the above mentioned adjustment of the time scale in case of the lab-based measurement to match the time-scale of the in-situ measurement. When the intensity of phase 4 has vanished at 1600 s also phase 5 and phase 6 do not show intensity any more (see above). At 1750 s intensity of phase 2 arises and increases linearly during the second pronounced plateau while the intensities of phase 1 and 3 decrease also linearly until the lower potential limit (5 mV) is reached giving rise to the second lithiation potential plateau which is better developed than the first lithiation plateau in the in-situ measurements as well as the lab-based measurements. In both measurements (in-situ and lab-based) the plateau potential was found to be more stable during the second lithiation plateau than during the first lithiation plateau. The galvanostatic measurements with intermediate relaxation periods (GITT, see chapter 5.10) suggested in addition the second lithiation plateau to represent a phase transformation closer to equilibrium potential. During this second lithiation plateau obviously the highest lithiated phase in the in-situ as well as in the lab-based measurements was formed. This phase was identified to be Li_3Au in chapter 6.7. It has to be pointed out here, that no $Li_{15}Au_4$ alloy phase has been observed. $Li_{15}Au_4$ is the Li-Au alloy phase with the highest known Li content and is widely assumed to be formed using Au anodes and is mostly used as reference for the calculation of the theoretical specific capacity of Au. This observation is similar to the case of silicon, where $Li_{15}Si_4$ instead of $Li_{22}Si_5$ was found to be the highest lithiated phase occurring during lithiation-delithiation cycles of lithium-ion battery anodes,

Taking all the evidence collected so far together, the second lithiation plateau represents in comparison to the first lithiation plateau a very clearly defined phase transformation between phases 1 and 3 (already pointed out to be very similar, but nevertheless clearly different) and phase 2. The fact that phases 1, 3, and 4 start to form only after 250 s when the maximum in potential-time curve initiating the first lithiation potential plateau is reached points to SEI-film formation to be the dominating electrochemical process at the beginning of the lithiation half-cycle.

Third Delithiation Half-Cycle

After reversing the direction of galvanostatic current the intensities of phase 1 and phase 3 invert very rapidly. A further hint to the enegetical and structural similarity of these two phases. Phase 2 gains significantly in intensity for a short time after switching the direction of galvanostatic current. Probably after switching the direction of galvanostatic current there prevail for a short period conditions apart from equilibrium. Thereafter, how(Fig. 7.3 (b))ever the intensity of phase 2 decreases linearly as it arose and phase 1 and 3 gain again in intensity during the potential forms the first dissolution plateau. With this the first dissolution plateau can be considered to occur due to the reverse phase transformation from phase 2 to phase 1 and 3. At 3300 s phase 2 has vanished and phases 1 and 3 are at their maximum intensity and start to convert to phase 4 in the next 100 s. Again the conversion of phases 1 and 3 into phase 4 is very fast strengthening the assumption of high similarity in energy and structure of these phases already stated from the phases' behavior in the lithiation half-cycle. The phase transformation from phases 1 and 3 to phase 4 is obviously the reason for the second pronounced (but short) delithiation plateau to occur since it is located between the appearance of the maxima of intensity of phases 1 and 3 and the maximum of phase 4. Between 2400 s and 2600 s phase 4 is converted into phase 5 corresponding with the third pronounced dissolution plateau. During the third dissolution plateau the intensity of phase 5 increases pronouncedly while the intensity of phase 4 decreases. During the subsequent final steep potential increase towards the upper potential limit the intensity of phase 6 finally increases very pronouncedly while the intensity of phase 5 decreases again. Consequently it is possible that the intermediate plateau during the final potential increase after the third delithiation plateau observed in the galvanostatic measurements at 0.17 C (1.66 μ A) (see chapter 5.4) represents the phase transformation from phase 5 to phase 6.

After reaching a potential of 1 V and switching off the electrochemical cell contact (ocp) the increase of the phase 6 and the decrease of phase 5 continues but the respective rate slows down. The further transformation of phase 5 into phase 6 is therefore either enabled by the leak current mentioned above or signifies, together with the observation to see the transformation to occur during steep potential increase, that the transformation of phase 5 into the Li-poor phase(s) is current free.

First Lithiation-Delithiation Cycle

Fig. 7.1 (b) shows the intensity evolutions with time typical for Au and phase 1 to phase 6 during the first lithiation-delithiation cycle (the intensity evolutions with time of Au, phase 1/3 and the Li-poor phase(s), phase 6, were already shown in Fig. 6.19) together with the galvanostatic potential-time curves of the first cycle from the in-situ and lab-based measurements .

During the delithiation half-cycle the processes of phase formation expressed by the shape of the potential time curves are very similar in the first cycle and the third cycle (see above).

But in the lithiation half-cycle some differences are evident. First of all in the first cycle there is neither phase 5 nor phase 6 present at the beginning of the cycle. Instead in the first cycle the starting material for lithiation is pristine Au. The intensity of the Au peaks subsequently decreases with time. Although the current is higher in the first cycle (22.7 μ A) than in the third cycle (16.6 μ A) the intensity of phases 1 and 3 start arising considerably later in the first than in the first cycle. The charge flown before phases 1, and 3 arise is consequently taken by another process.

The explanation considered for this phenomenon is the formation of an amorphous alloy phase. As concluded from the lab-based galvanostatic measurements and also likely regarding the third cycle of the in-situ measurements discussed above, the SEI formation is supposed to be completed also in the case of the first in-situ cycle when the maximum in the potential-time curve after the initial dip is reached (* and # in Fig. 7.1 (b)). Subsequently to this maximum in the in-situ potential-time curve of the first cycle there is a gradual decrease of potential apparent, instead of an actual plateau as observed in the lab-based curves. The reason could be the initial formation of an amorphous phase instead of a crystalline phase.

Also Renner et al. reported on the occurrence of an amorphous alloy phase previous to a retarded arising of a crystalline alloy phase during their potentiostatic lithiationdelithiation experiments at Au nanoparticles on a HOPG substrate.

A crystalline phase was expected to form during the first lithiation plateau in the case of the lab-based experiments in the first and the third cycle and also in the third insitu cycle giving rise to the pronounced first lithiation potential plateau formation of crystalline alloy phases (phase 1, 3, and 4) was observed. However, in the first cycle only after 800 s intensity of phases 1, 3, and 4 came up, probably formed from the remaining crystalline Au and the probable amorphous phase which is responsible for the decrease of the Au intensity before the crystalline phases start be be formed.

A formation of a solid solution of Li in Au at the beginning of the lithiation half-

cycle can be excluded because the accompanying shrinkage of the lattice constant (from 0.40784 nm for pure Au to of the 0.3973 at 33.8 atomic percent of Li) would lead to a shift in peak position from 3.775° to $3.875^{\circ77}$ which is not observed in the XRD-measurements (see Fig. 6.16 in chapter 6.5).

During the first lithiation half-cycle a significant difference between the in-situ measurements just described and discussed, and the lab-based measurements is assumed regarding the difference in shape of the potential-time curves. As just mentioned, in the in-situ potential-time curve of the first cycle there is no actual first lithiation potential plateau observed. Rather a gradual potential decrease is found. From this observation and the observed retarded formation of crystalline alloy phases indicated by the intensity evolutions the formation of an amorphous phase is assumed. In the lab-based measurements the clearly more pronounced plateau suggest the formation of crystalline phases already at earlier stages maybe completely without an appearance of an amorphous phase.

Conclusion

The observed difference between the lab-based and the in-situ measurements for the first galvanostatic lithiation-delithiation cycle could be attributed to higher current (16.6 μ A compared to 22.7 μ A) associated with a different reaction path for alloy phase formation. However the lab-based measurements suggests the phases involved in the lithiation-delithiation process to be stable even at currents above 16.6 μ A (see chapter 5.16). A reason for a possible difference in reaction path between in-situ and lab-based measurements suggested by the first lithiation half-cycle from the in-situ measurements could be the leak currents occurring in case of the in-situ cell (compare chapter 6.1).

In the third cycle during lithiation the in-situ potential time curve is more similar to the corresponding lab-based curve. Consequently the phase evolutions observed during the third in-situ lithiation is assumed to better match the phase evolution during the lab-measurements. In fact in case of the third cycle the phase evolution during both measurements can be imagined to be very similar.

During delithiation in both cycles the typical shape of potential-time curves observed in the lab-based measurements is reproduced in the in-situ measurements. The three plateaus are clearly discernible but less pronounced. Again in the third cycle the correlation is obviously better. In consequence the phase evolution observed in the in-situ measurements during delithiation can be assumed to occur analogously during the labbased measurements.

Concluding the present chapter the crystalline alloy phases involved in lithiation-delithiation cycles of a Au thin film are assumed to be identical during in the lab-based experiments

and the in-situ measurements. Consequently they are not only stable under the more defined conditions in the ex-situ electrochemical cell used for the lab-based measurements in a considerable current range but also under the less defined conditions in the in-situ cell during the in-situ measurements where leak currents are presumably involved.

7.2 Phase evolution diagram

To conclude the previous chapter in Fig. 7.2 the phase diagram for the electrochemical lithiation/delithiation of a Au thin film electrode already shown in chapter 5.7 excluding the first lithiation half-cycle is recalled (compare Fig. 5.28). The involved Li-Au alloy phases together with their Li content calculated based on two different scenarios described in more detail in the context of fig. 5.28 are compiled in table 7.1. In the first scenario the fact that only 2.5 equivalents of Li are extracted in the lithiation-delithiation cycles is attributed to some Li remaining in the sample after the first delithiation cycle (column "remaining Li" in table 7.1). In the second scenario the described phenomenon is assigned to contact loss of parts of the sample already in the first cycle (compare 5.7).

At the beginning of the first lithiation in idealized case (phase 5 has transformed completely into phase 6) only one starting material (starting phase) is present. Phase 6 transform during the first lithiation plateau into a mixture of phases 1, 3 and 4, which are assumed to be energetically and structurally very similar. The intermediate plateau between the first and the second lithiation plateau may occur due to the very quick transformation of phase 4 formed so far into phases 1 or 3 (or both). At the beginning of the second pronounced lithiation plateau accordingly only phases 1 and 3 are present. They fully transform into phase 2 during the second pronounced lithiation plateau. Phase 2 prevails around the point of switching the direction of galvanostatic current. It gets transformed back into phases 1 and 3 during the first delithiation plateau. The narrow second delithiation plateau occurs due to the transformation of phases 1 and 3 into the energetically and structurally closely related phase 4. The transformation of phases 1 and 3 into phase 4 takes only very little time implicating only little necessary charge exchange (due to similar Li content of the structures in structurally similar hosting structure). During the last pronounced delithiation plateau phase 4 gets transformed into phase 5 from which at the very end of the delithiation half-cycle phase 6 is recovered. In the next cycle the different steps of lithiation and delithiation are passed through again.

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	Li content X in Li_xAu	Li content X in Li_xAu			
	remaining Li	contact loss			
phase $1/3$	1.49-1.65	1.15 - 1.32			
phase 2	3.00	3.00			
phase 4	1.49	1.15			
phase 5	0.71	0.22			
phase 6 0.58		0.075			

Table 7.1: Li-Au alloy phases 1-6



Figure 7.2: Phase evolution diagram of the electrochemical lithiation/delithiation of Au. Concluding the previous section a phase diagram for the electrochemical lithiation/delithiation of the Au thin film electrode from the second cycle on can be set up. During the first lithiation plateau the Li-poor phase(s) (phase 5, phase 6 and maybe an additional amorphous phase) transform into phases 1, 3 and 4 which feature most probably similar energy and structure. The intermediate plateau between the first and second lithiation plateau may be attributed to the transformation of phase four formed so far into phases 1 and 3. During the second lithiation plateau the "two phase region" between phases 1 and 3 and phase 2 is established. Phase 2 is formed out of phase 1 and 3. During the first dissolution plateau phase 2 transforms back to phases 1 and 3. The subsequent narrow delithiation plateau is assigned to the transformation of phases 4 which transform into phase 5 during the third delithiation plateau. At the very end of the lithiation-delithiation cycle phase 6 recovered from phase 5.





Figure 7.3: Combining all the results obtained from the lab-based and in-situ electrochemical measurements and from the in-situ X-ray diffraction measurements a model for the processes of phase evolution during electrochemical lithiationdelithiation cycles involving crystalline Au as starting material of the first lithiation-delithiation cycle and phases 1 to 6 described in chapter 6.5 is proposed.

7.3 Phase Evolution Model

Combining all the results obtained from the lab-based and in-situ electrochemical measurements and from the in-situ X-ray diffraction measurements a model for the processes of phase evolution during electrochemical lithiation-delithiation cycles is proposed.

Fig. 7.3 shows a sketch of the phase evolution during electrochemical lithiation-delithiation cycles. At the beginning of the first cycle (Fig. 7.3 (a)) the pristine Au-film is present. After starting the lithiation half-cycle first an SEI-film is formed on top of the Au-film indicated by a dip in the potential time curve. Subsequently during the first lithiation potential plateau the powder-like phases 1 and 3 form starting from pure Au consuming the entire Au material. In result at the end of the first lithiation plateau only phase 1 and

3 are present in the sample (Fig. 7.3 (b)). Two third of the electrode consists of phase 1 and one third of phase 3. The fact that SEI-film formation and alloy-phase formation occur (mainly) in sequence and the fact that the potential rises after SEI-film formation is complete, points to a enhancing effect of the SEI on the Li-insertion by lowering the potential necessary to effect Li-insertion (compare sections 5.3 and 5.7). During the second lithiation plateau phases 1 and 3 are transformed into phase 2 until the entire electrode consists of phase 2 (Li₃Au) (Fig. 7.3 (d)). The process of formation of phase 2 starts at the interface between the Cu(110) substrate and the electrode material to give rise to uniform (220)-orientation of the rather large crystallites of phase 2 parallel to the Cu substrate

At the beginning of the delithiation half-cycle the equilibrium between phase 1 and phase 3 shifts to the benefit of phase 3. In result the sample consists now to one third of phase 1 and two third of phase 3 (Fig. 7.3 (e)). During the first delithiation potential plateau phase 2 dissolves while phase 1 and phase 3 are reformed in a 1:2 ratio (Fig. 7.3 (f)). After the (220)-oriented phase 2 has disappeared the powder-like phases 1 and 3 start to transform in rather short time into the also powder-like phase 4 (Fig. 7.3 (g)) giving rise to the narrow second delithiation potential plateau. During the subsequent broader third delithiation plateau phase 4 is converted into phase 5 (Fig. 7.3 (h)) which is another powder-like phase. When the conversion is completed the potential increases strongly towards the upper potential limit. During this increase of potential phase 5 transforms quickly into phase 6 which probably represents two different phases showing identical evolutions of intensity with time. At the end of the lithiation-delithiation cycle mainly phase 6 is present in the electrode but probably also still phase 5 (Fig. 7.3 (i)).

In the next lithiation half-cycle first the SEI-film partially degraded during the delithiation process is maintained (Fig. 7.3 (j)) announced by a smaller dip in the potential time curve as in the first lithiation half-cycle. Subsequently phases 1, 3 and 4 appear again in approximately equal amounts during the first lithiation potential plateau (Fig. 7.3 (k)). Between the first and the second lithiation plateau phase 4 vanishes to the benefit of phase 1 and 3 possibly correlated to the appearance of the first intermediate plateau in the galvanostatic potential time-curve (compare Figs. 5.10 and 5.12). Afterwards again the electrode consists of two third of phase 1 and one third of phase 3 like after the first lithiation plateau in the first cycle. From this state on the described processes of phase evolution repeat cyclically.

8 General Conclusion

In the present work in-situ investigation of the structural changes associated with alloy phase formation/dissolution in Au thin film model electrodes during electrochemical lithiation-delithiation cycles by means of High-Energy XRD (HEXRD) are presented in order to gain a more profound understanding of the lithiation/delithiation mechanisms.

In-situ HEXRD measurements were conducted during galvanostatic lithiation-delithiation cycles in an especially designed electrochemical cell (in-situ cell) at the synchrotron radiation facility Petra III at DESY (Hamburg).

In addition lab-based electrochemical characterization was performed to compare the results obtained in the in-situ cell with the electrochemical behavior in an dedicated cell for electrochemistry.

By following this approach it was possible to correlate the electrochemical treatment of the Au thin film electrode with the respective structural changes in the electrode material during the electrochemical processes.

The lab-based electrochemical measurements pointed to identical involved mechanisms during galvanostatic and potentiostatic lithiation-delithiation cycles within an associated current range of one order of magnitude of power pointing to a considerable stability of the involved phase transformations and alloy phases. Two potential plateaus during lithiation and three plateaus during delithiation indicating two two-phase regions during lithiation and three two phase regions during delithiation were observed in all the different electrochemical lithiation-delithiation cycles. Accordingly, different reaction paths are obvious for alloying and dealloying. The first galvanostatic cycle differed significantly from the subsequent cycles.

By means of in-situ XRD this difference could be clearly attributed to a change in the electrode material during the first cycle. While at the beginning of the experiment a highly ordered crystalline Au film is present after the first cycle a powder-like Lipoor phase remains, which is the starting material for subsequent cycles. During the lithiation-delithiation cycles six different (alloy) phases are involved. Except from the highest lithiated phase showing strong preferential orientation with respect to the Cu(100) substrate associated with relatively large grains these alloy phases are of powder-like

8 General Conclusion

morphology. Three of the powder-like phases are most probably very similar in Li content, atomic structure and energy. The highest lithiated phase found by XRD showing strong preferential orientation could be identified to represent the Au-Li alloy phase Li_3Au known from the phase diagram of the Li-Au-system.

In combination of purely electrochemical and in-situ XRD measurements it was possible to correlate the observed alloy phases with the electrochemical potential-time curves. Based on the lab-based electrochemical measurements and the in-situ XRD experiments an alloy phase evolution diagram of the Au-Li system was proposed as well as a model of the phase transformations occurring in the Au film model electrode.

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