

Amorphous and perovskite  $\text{Li}_3\text{xLa}_{(2/3)-\text{x}}\text{TiO}_3$  (thin) films via chemical solution deposition: solid electrolytes for all-solid-state Li-ion batteries

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# ***Amorphous and perovskite $\text{Li}_{3x}\text{La}_{(2/3)-x}\text{TiO}_3$ (thin) films via chemical solution deposition: solid electrolytes for all-solid-state Li-ion batteries***

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## ***Abstract***

Thin films of amorphous and crystalline perovskite  $\text{Li}_{3x}\text{La}_{(2/3)-x}\text{TiO}_3$  ( $x=0.117$ ) are prepared by means of aqueous chemical solution deposition onto rutile  $\text{TiO}_2$  thin films as an anode, yielding an electrochemical half-cell. The Li-ion conductivity of the pin-hole free, amorphous LLT thin film (90 nm thick) is  $3.8 \cdot 10^{-8} \text{ S} \cdot \text{cm}^{-1}$  on Pt and  $1.3 \cdot 10^{-8} \text{ S} \cdot \text{cm}^{-1}$  on rutile  $\text{TiO}_2$ , while measuring perpendicular to the thin film direction with impedance spectroscopy. Grazing angle attenuated total reflectance - Fourier transform infrared spectroscopy (GATR-FTIR) shows that all organic precursor molecules have been decomposed at 500°C. In addition, in-situ (heating) X-ray diffraction analysis shows that phase pure crystalline perovskite  $\text{Li}_{3x}\text{La}_{(2/3)-x}\text{TiO}_3$  ( $x=0.117$ ) is formed on top of the rutile  $\text{TiO}_2$  anode at 700°C. Furthermore, thickness control is possible by varying the precursor solution concentration and the number of deposition cycles. The current study presents a promising synthesis route to develop all-solid-state battery devices based on multi-metal oxide materials using aqueous precursor chemistry.

## 1. Introduction

In order to power autonomous electronic devices of tomorrow, such as wireless devices and body implants, efficient energy storage methods are required. Among other options, lithium-ion batteries (LIBs) in particular are interesting because of their high energy and high power density [1, 2]. Although widely applied, contemporary LIBs suffer from safety hazards and capacity fading [3]. Fabrication of all-solid-state batteries, where the liquid electrolyte is replaced with a solid electrolyte, is opted to circumvent these issues [4]. Recently, it was shown that excellent battery lifetimes can be established when a solid electrolyte is used [5]. In addition, solid electrolytes enable operation in a broader temperature range and exhibit a higher structural stability [3, 4]. Despite these advantages, most of solid electrolytes exhibit significantly lower Li-ion conductivity compared to their liquid counterparts. To ensure sufficient power density of the battery, ohmic loss over the electrolyte should be prevented. Since the charge transfer resistance follows the thickness of the electrolyte, thin films of solid electrolyte materials are required [1, 6].

Various solid electrolyte materials are available as bulk powder with a broad Li-ion conductivity range [7]. Based on its high Li-ion conductivity, perovskite  $\text{Li}_{3x}\text{La}_{(2/3)-x}\text{TiO}_3$  (LLT) with  $x=0.117$  is a promising solid electrolyte to be implemented in all-solid-state Li-ion batteries [8, 9]. In addition to the high conductivity of the perovskite phase ( $10^{-3}$  S/cm), the bulk material retains a high conductivity in the amorphous state ( $10^{-5}$  S/cm) [10, 11]. The main disadvantage of this electrolyte is its incompatibility with metallic lithium as an anode due to reduction of titanium (IV) around 1.5 V [9, 12]. However, other anode materials with higher operating voltages are compatible with LLT. More specifically, LLT was synthesized in combination with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as an anode using macro porous morphologies to maximize the electrolyte-anode interface [10].

Several synthesis routes such as solid state synthesis [8] and sol-gel synthesis [13] yielding bulk LLT are known. In addition, several attempts have been made to combine anode or cathode materials with LLT, such as creating LLT coated  $\text{LiCoO}_2$  particles [14] as well as preparing 3D ordered macro porous LLT to create an electrolyte network with high Li-ion conductivity surrounded by a  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  matrix [10]. However, only a limited number of studies focus on thin film synthesis of this material: pulsed laser deposition was applied several times to yield epitaxial LLT layers (approximately 40 nm thick) on  $\text{SrTiO}_3$  and  $\text{NdGaO}_3$  substrates [15],

amorphous LLT films of approximately 500 nm were grown on quartz glass substrates [11] and both amorphous and crystalline LLT were deposited on Pt substrates with 400 nm thickness [16]. In addition, lanthanum deficient amorphous LLT ( $\text{Li}_{0.32}\text{La}_{0.30}\text{TiO}_2$ ) was deposited on Si by atomic layer deposition, but crystallization yielded relatively rough morphologies combined with slow growth rates between 0,30 and 0.50 Å·cycle<sup>-1</sup> [17]. A first attempt at preparing crystalline perovskite LLT films ( $x=0.167$ ) on indium tin oxide using chemical solution deposition was carried out by Kitaoka et al [18]. Using three different organic precursors solutions based on metal alkoxides or acetates dissolved in 2-methoxyethanol, films with thicknesses ranging from 200 nm to 1 µm were obtained by dip coating in combination with a post-deposition anneal of 700 to 1300°C [18].

In the current study, amorphous and crystalline perovskite LLT thin films were prepared directly on a rutile  $\text{TiO}_2$  anode film (with Pt underneath) or on a blank Pt current collector by chemical solution deposition using an aqueous precursor solution containing  $\text{Li}^+$ ,  $\text{La}^{3+}$  and  $\text{Ti}^{4+}$ . While the latter stack allows determination of the material's Li-ion conductivity, the former allows studying the interfacial reactions between a suitable anode material (rutile  $\text{TiO}_2$ ) and the electrolyte under study, which is important with respect to the material's final application in a functioning battery device.

## ***2. Experimental***

### ***2.1 Precursor synthesis***

Aqueous precursor solutions were prepared for  $\text{Li}^+$ ,  $\text{La}^{3+}$  and  $\text{Ti}^{4+}$ . Lithium nitrate ( $\text{LiNO}_3$ , Sigma Aldrich, ≥98.5%) and lanthanum nitrate hexahydrate ( $\text{Li}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Sigma Aldrich, ≥99%) were both dissolved in water by stirring at room temperature, yielding concentrations of 1.5 mol·L<sup>-1</sup> and 1.0 mol·L<sup>-1</sup> respectively. Titanium isopropoxide ( $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , Sigma Aldrich, ≥97%) was added to water to form titanium hydroxide, followed by addition of citric acid (CA, Sigma Aldrich, ≥99%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , Acros Organics, 35%) and ammonia ( $\text{NH}_3$ , Merck, 32%) to yield a citrate-peroxo-Ti(IV) solution with a 0.9 mol·L<sup>-1</sup>. A detailed description of the citrate-peroxo-Ti(IV) precursor was reported earlier by Hardy et al. [19].

The concentrations of the mono-ion solutions was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima 3300, PerkinElmer) before mixing them together in stoichiometric amounts at room temperature (Fig. 1). The final multi-metal ion precursor solution was prepared in a high (0.95

M) and low (0.38 M) total metal ion concentration with a  $\text{Li}^+:\text{La}^{3+}:\text{Ti}^{4+}$  molar ratio of 0.35:0.55:1.00 (i.e.  $x=0.117$ ).

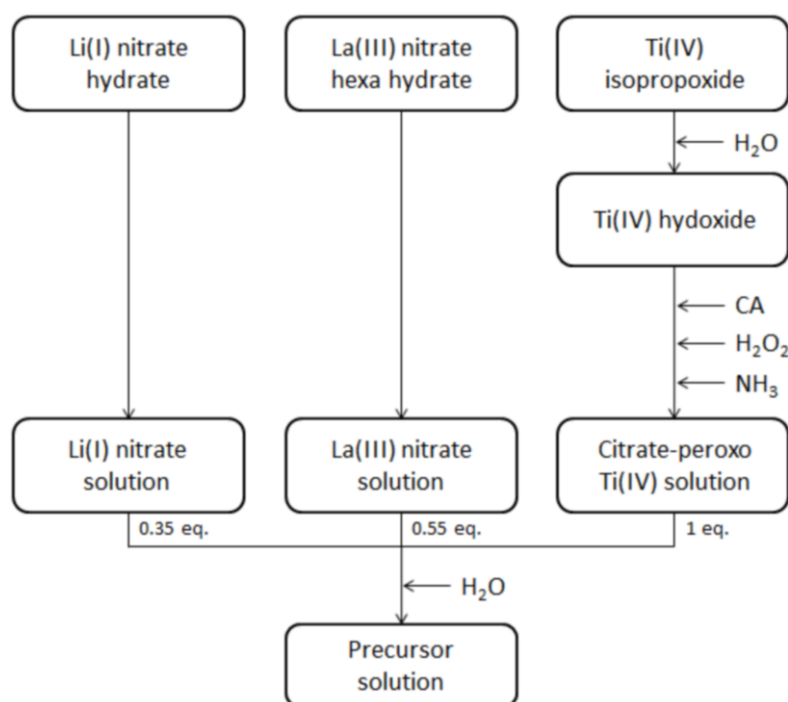


Figure 1: Synthesis scheme of the aqueous precursor solution.

## 2.2 Thin film deposition

The aqueous multi-metal ion precursor solution was spin-coated (3000 rpm, 30 s, 1000 rpm/s) onto small pieces (3 x 3 cm) of different substrates, designated as follows:  $\text{TiO}_2$  (Si); a stack of  $\text{TiO}_2/\text{Si}$  (p-type Si with 90 nm  $\text{TiO}_2$  [20]),  $\text{TiO}_2$  (Pt); a stack of  $\text{TiO}_2/\text{Pt}/\text{TiN}/\text{Si}$  (40 nm TiN coated p-type Si with 70 nm Pt with 90 nm  $\text{TiO}_2$ , deposited as mentioned in [20]) and Pt; a stack of  $\text{Pt}/\text{TiN}/\text{Si}$  (40 nm TiN coated p-type Si with 70 nm Pt).

All these substrates were cleaned by an UV/ $\text{O}_3$  treatment at 60 °C (40 min., Novascan PSD Pro Series). Hot plate treatments were carried out in ambient air after spin coating of the aqueous precursor at 250 °C (2 min.), 375 °C (2 min.) and 500 °C (2 min.). The sequence of spin coating and hot plate treatment was repeated multiple times to obtain films with the desired thickness. The final film was annealed by either a heat treatment at 500 °C (1 to 4 hours) in static air on a hot plate or at 700 °C (1 to 4 hours) under a dynamic air flow ( $0.1 \text{ L}\cdot\text{min}^{-1}$ ) in a tube furnace.

## 2.3 Powder characterization

The thermal decomposition profile of the yellow precursor powder, obtained by drying the precursor solution at 60°C, was investigated by thermogravimetric analysis with coupled differential scanning calorimetry (TGA/DSC, TA instruments SDT Q600). 6 mg of the powder was heated ramped at 10°C/min up to 1200°C using dry air (0.1 L·min<sup>-1</sup>) in an alumina crucible. The crystallization process of the aqueous precursor powder was studied by High-Temperature X-Ray Diffraction analysis (HT-XRD, Bruker D8 with an Anton Paar HTK1200 high temperature chamber with a kapton window) from 250 - 900°C (10°C·min<sup>-1</sup>), in steps of 50°C with a counting time of 52.8 s per step. The yellow precursor powder was submitted to a pre-anneal (250°C in a drying oven overnight) to remove most of the organics before starting the HT-XRD experiment.

## ***2.4 Thin film characterization***

As-deposited and sequentially heated (250, 375, 500 and 700°C) layers were characterized by grazing angle attenuated total reflectance - Fourier transform infrared spectroscopy separately (GATR-FTIR, Bruker Vertex 70 combined with Harrick 65° single reflection Ge-ATR) from 4000 to 600 cm<sup>-1</sup> with 32 scans per sample with a torque of 24 kPa. Crystallization of amorphous LLT thin films was studied by in-situ heating XRD (Bruker D8 Discover with experimental heating chamber [21]). A linear detector was used, recording a diffraction pattern with a 2θ range of 30 to 50° every 5 seconds within a temperature range of 25 to 900°C (with a heating rate of 1°C·min<sup>-1</sup>). The morphology of annealed LLT films was investigated by means of scanning electron microscopy (SEM, FEI Quanta 200F). Finally, the Li-ion conductivity of LLT thin films was studied by means of Impedance Spectroscopy. Hereto, Au electrodes (300 nm thick, 6 mm<sup>2</sup> area) were evaporated (Vactec thermal evaporator, 3·10<sup>-7</sup> mbar) on top of post-annealed LLT thin films with Pt or TiO<sub>2</sub> (Pt) as the underlying substrate. The Li-ion conductivity perpendicular to the film direction is of importance for the power density of the final battery, therefore the electric field was applied in this direction. The impedance was measured using an Autolab PGSTAT302N with frequencies ranging from 1MHz – 10 mHz with an alternating voltage of 3 mV. The results were fitted with equivalent circuit models with resistor (R) and capacitor (C) elements using Nova software (Version 1.9.16, Metrohm Autolab B.V.).

## ***3. Results and discussion***

## Powders

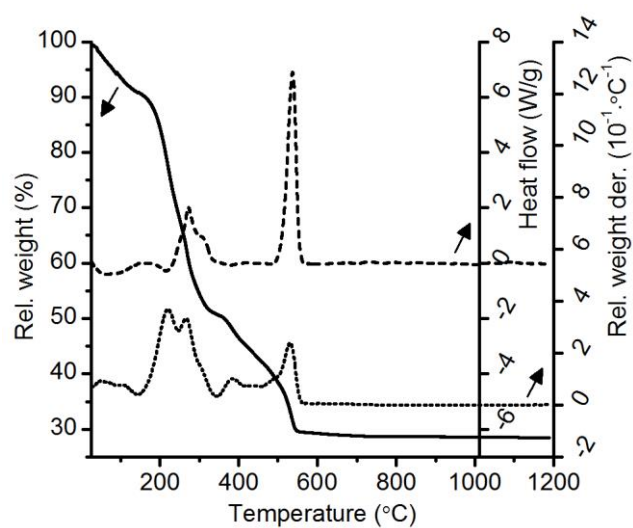
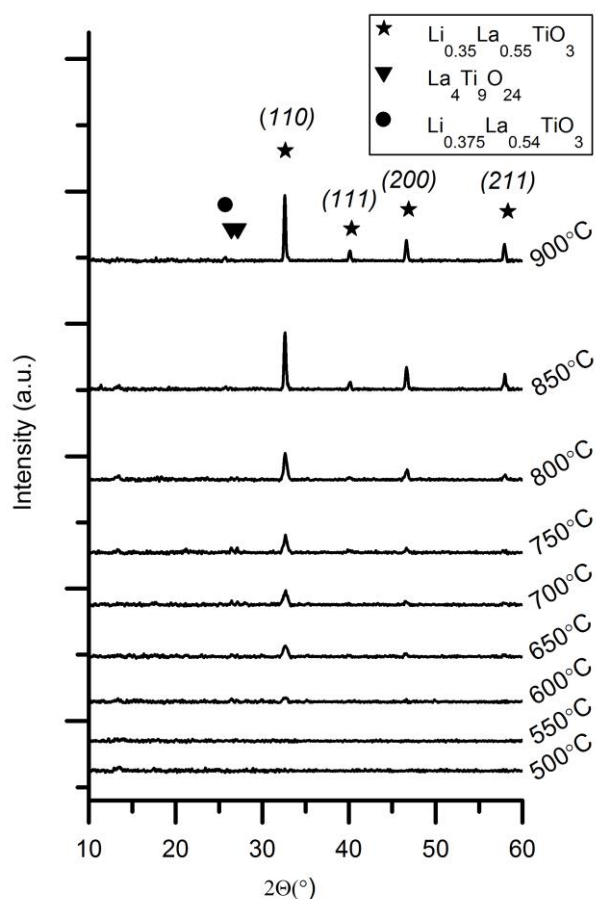


Figure 2: TGA/DSC graph of dried (60°C overnight) LLT precursor gel, showing the relative weight (solid line), heat flow (dashed line) and relative weight derivative (dotted line) as a function of temperature (10°C·min<sup>-1</sup>, with dry air flow of 0.1 L·min<sup>-1</sup>). The arrows indicate the signal specific Y-axis.



**Figure 3:** HT-XRD patterns of a dried and pre-calcined (250°C) precursor powder measured at several temperatures with a heating rate of 10°C·min<sup>-1</sup> in dry air (0.1 L·min<sup>-1</sup>). Reference patterns of LLT (stars,  $x=0.117$ , JCPDS 46-0465) are shown, along with the most intense peaks of  $\text{La}_4\text{Ti}_9\text{O}_{24}$  (triangles, JCPDS 036-0137) and  $\text{Li}_{0.375}\text{La}_{0.54}\text{TiO}_3$  (circles, JCPDS 47-0668).

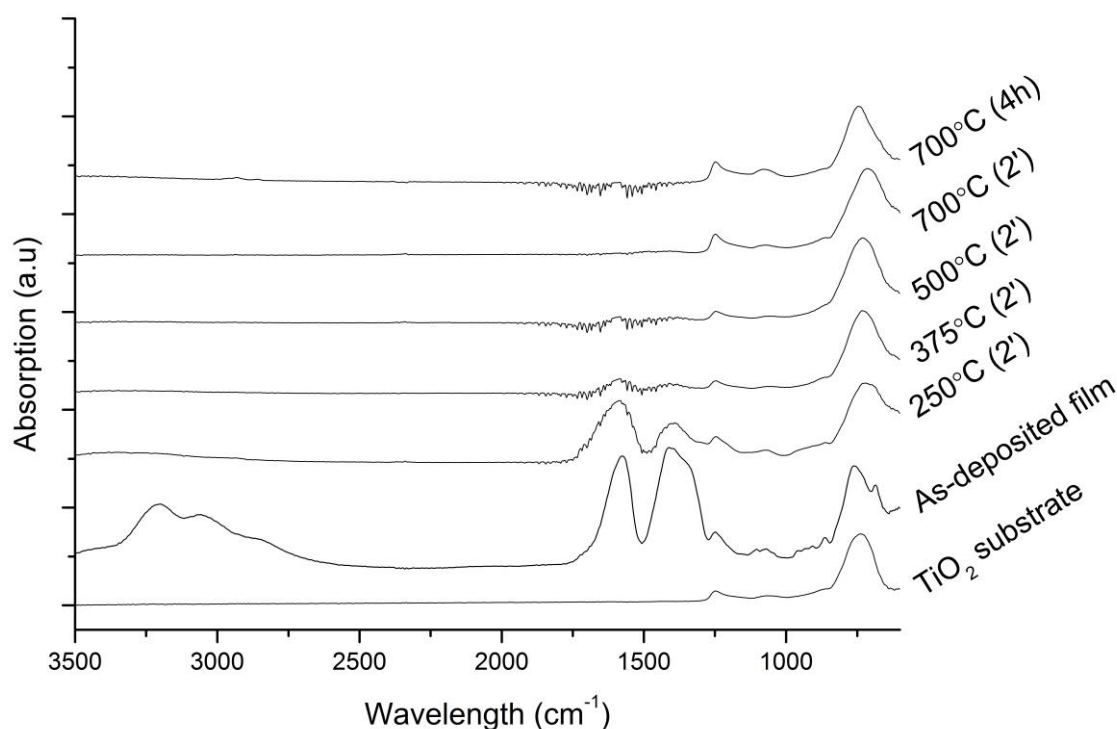
The thermal decomposition pathway of the dried aqueous precursor gel (Fig. 2, solid line) shows a weight loss between room temperature and 150 °C, which is most likely the loss of water. Above 150 °C, a major weight loss is observed while the heat flow (Fig. 2, dashed line) indicates that this is accompanied with small endothermic step at 220°C followed by a sequence of exothermic events at 270 and 535°C, respectively. This sequence is possibly related to the decomposition of organics and nitrates. Above 600 °C, no significant weight loss is observed, indicating that the precursor has completely decomposed, and most probably only oxide phase(s) remain. HT-XRD analysis (Fig. 3) indeed indicates that the onset of perovskite LLT crystallization (JCPDS 46-0465) occurs at 600°C. From 600 to 850 °C small peaks are present around 26,4 and 27,2° 2θ, suggesting the presence of  $\text{La}_4\text{Ti}_9\text{O}_{24}$  (JCPDS 036-0137) as a secondary phase. These small peaks disappear at 900°C, but at this temperature a small single peak at 25,7° 2θ can be observed, suggesting that  $\text{La}_4\text{Ti}_9\text{O}_{24}$  transformed into



$\text{Li}_{0.375}\text{La}_{0.54}\text{TiO}_3$  (JCPDS 47-0668) at higher temperatures, possibly by reacting with a lithium containing amorphous phase.

## Thin films

After showing the suitability of the water based precursor system to obtain LLT powders, the behavior of thin films formation was studied. Due to differences in the surface to volume ratio between powders and thin films, leading to different heat transport and gas diffusion phenomena, their decomposition process may differ [22]. Therefore, the decomposition process was indirectly studied on the thin films, by identification of the organic residuals using GATR-FTIR.



**Figure 4:** GATR-FTIR of the blank  $\text{TiO}_2(\text{Si})$  substrate, the as-deposited aqueous precursor and different heat treated LLT layers on  $\text{TiO}_2(\text{Si})$ . The spectra were recorded directly after spin coating (as-deposited) or after consecutive hotplate steps for 2 minutes at 250°C, 250°C+375°C or 250°C+375°C+500°C under static air. Samples annealed at 700°C (for 2 minutes or for 4 hours) were placed in a pre-heated tube furnace in dry air after completing all consecutive hotplate steps.

GATR-FTIR was applied on a single layer deposited onto the TiO<sub>2</sub> (Si) substrate; measured as-deposited and directly after different heat treatments (Fig. 4). The TiO<sub>2</sub> (Si) substrate shows a strong band at 750 cm<sup>-1</sup>, arising from TiO<sub>2</sub> lattice vibrations [23, 24]. Si-O-Si longitudinal and transverse modes are also observed at 1250 and 1050 cm<sup>-1</sup>, respectively [25]. For the as-deposited aqueous precursor several bands could be observed: the (broad) band at 3500 to 2750 cm<sup>-1</sup> is associated with C-H stretching vibrations, O-H stretching vibrations of (unbound) water and NH<sub>4</sub><sup>+</sup> anti-symmetric stretching vibrations broadened by hydrogen bond formation [26, 27]. At 1600 and 1400 cm<sup>-1</sup> strong bands are observed, associated with COO<sup>-</sup> asymmetric and symmetric stretching vibrations of the citrate ligands [27]. In addition, the 1400 cm<sup>-1</sup> band overlaps with the asymmetric stretching vibration of NO<sub>3</sub><sup>-</sup> [28]. The (weak) band at 1250 cm<sup>-1</sup> is assigned to C-OH stretching of a carboxylic acid, related to citric acid [27]. Finally, the (weak) bands at 850 to 800 cm<sup>-1</sup> and 770 to 715 cm<sup>-1</sup> are both related NO<sub>3</sub><sup>-</sup>, respectively out-of-plane and in-plane bending vibrations [26, 28].

At 250°C the broad band from 3500 to 2750 cm<sup>-1</sup> is strongly reduced, associated with the removal of water and NH<sub>4</sub><sup>+</sup>. Furthermore, a large reduction of the 1400 cm<sup>-1</sup> band combined with absence of the weak bands at 850-800 cm<sup>-1</sup> and 770-715 cm<sup>-1</sup> suggest that NO<sub>3</sub><sup>-</sup> has been removed from the sample. At 375°C, the 1600 and 1400 cm<sup>-1</sup> band have strongly been reduced, indicating that most of the organic materials have been decomposed. At 500°C and above only bands related to substrate can clearly be observed. Furthermore, above 375°C no bands are observed between 1550-1300 cm<sup>-1</sup>, indicating that no (oxy)carbonates [23, 26, 29] are formed. In literature no FTIR results could be found regarding (perovskite) LLT. However, bands of closely related titanates are only visible at lower wavenumbers than recorded in this study [26, 30]. In-situ XRD was therefore employed to study the crystallization of the films obtained with little organic residuals prepared at 500°C.

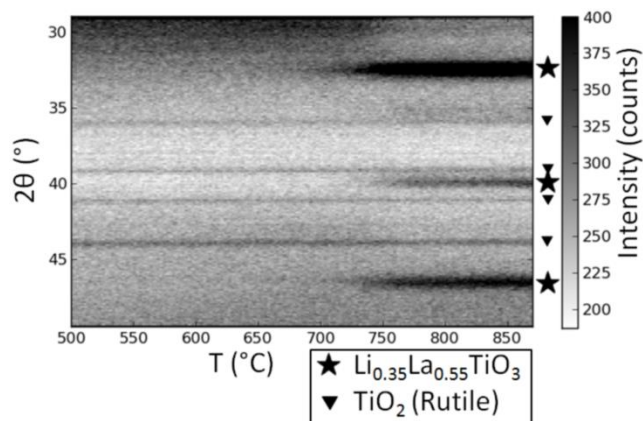


Figure 5: XRD intensity of a 240 nm thick LLT film on  $\text{TiO}_2$  (Si), pre-annealed at  $500^\circ$  for 1 hour in static air, as a function of temperature during non-isothermal heating with a heating rate of  $6^\circ\text{C}\cdot\text{min}^{-1}$  in static air. Reference peak positions of perovskite LLT (stars,  $x=0.117$ , JCPDS 046-0465) and rutile  $\text{TiO}_2$  (triangles, JCPDS 021-1276)

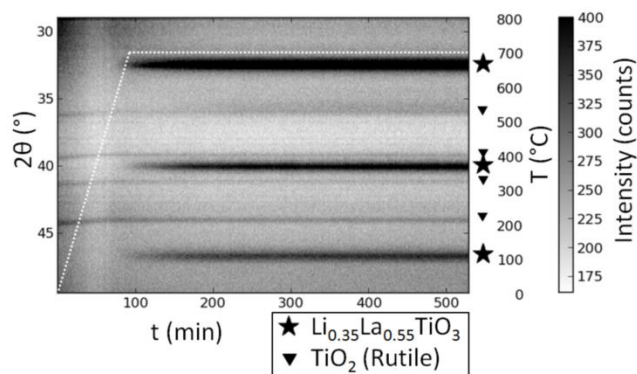
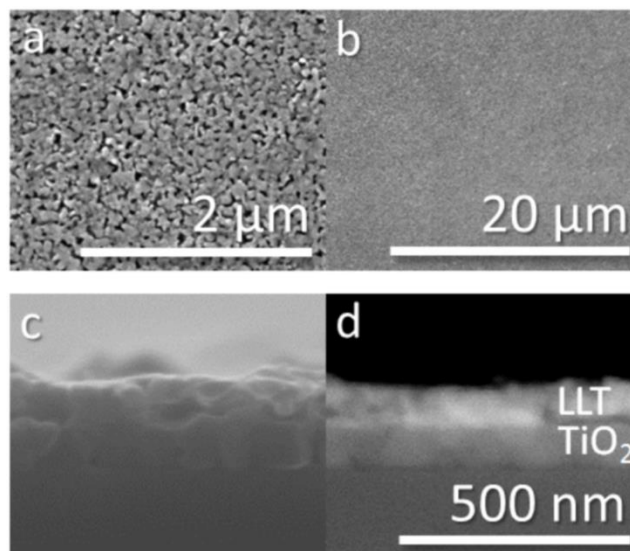


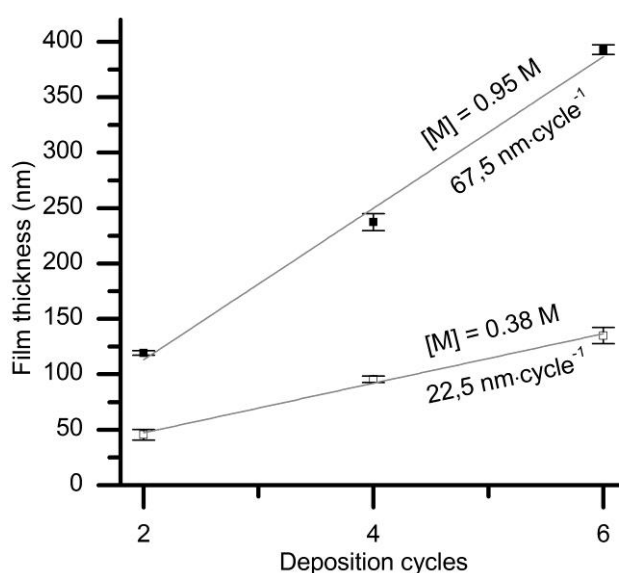
Figure 6: XRD intensity of a 240 nm thick LLT film on  $\text{TiO}_2$  (Si), pre-annealed at  $500^\circ$  for 1 hour in static air, heated isothermally at  $700^\circ\text{C}$  with in static air (after a short period of non-isothermal heating to reach  $700^\circ\text{C}$  with  $10^\circ\text{C}\cdot\text{min}^{-1}$ ). The temperature profile is plotted (dashed line) as a function of time. Reference peak positions of perovskite LLT (stars,  $x=0.117$ , JCPDS 046-0465) and rutile  $\text{TiO}_2$  (triangles, JCPDS 021-1276)

The crystallization process of LLT thin films, deposited on  $\text{TiO}_2$  (Si) and pre-annealed at  $500^\circ\text{C}$ , was examined by in situ X-ray diffractometry as a function of temperature during its non-isothermal heating with constant heating rate (Fig. 5) and as function of time during isothermal heating at  $700^\circ\text{C}$  (Fig. 6). Before the heating starts, diffractions are only visible at  $2\theta = 36, 39, 41$  and  $44^\circ$ ; all these correspond to the rutile phase (JCPDS 021-1276) of the  $\text{TiO}_2$  anode underneath the amorphous LLT film. While heating the amorphous LLT films, the onset of perovskite LLT ( $x=0.117$ , JCPDS 046-0465) crystallization can be observed at  $725^\circ\text{C}$ , identified

by the 33, 40 and 47° 2 $\theta$  angle diffractions. Isothermal heating at a slightly lower temperature of 700°C leads to perovskite LLT phase formation as well (Fig. 6), but prolonged heating at this temperature is required to fully crystallize the film.

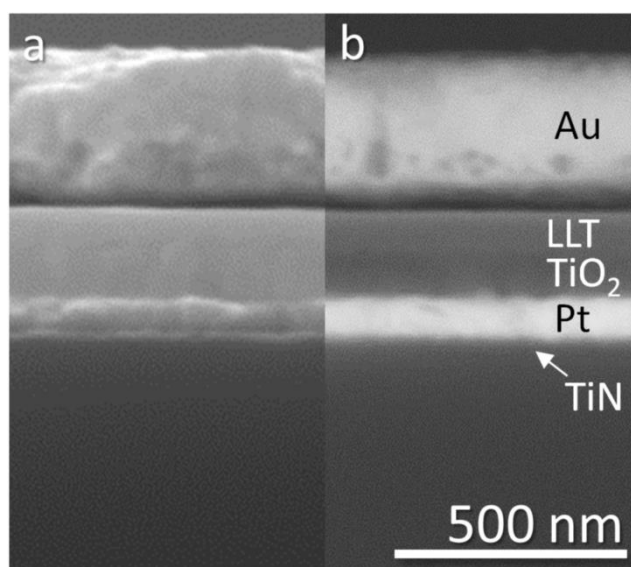


**Figure 7:** Top view SE images at different magnifications (a & b) and cross sections SE image (c) and BSE image (d) and of 4 layers (0.38 M) of LLT deposited on TiO<sub>2</sub> (Si) annealed at 700°C for 1 hour in dry air.

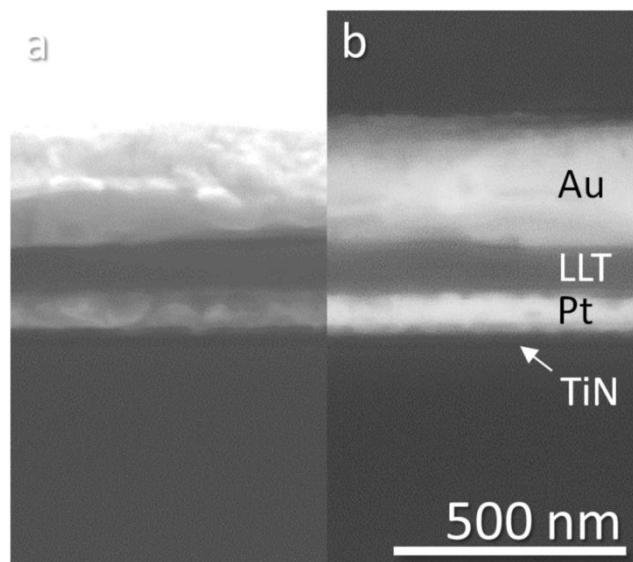


**Figure 8:** LLT film thickness as function of deposition cycles and precursor concentration deposited on TiO<sub>2</sub> (Si), determined by SEM cross sections. After deposition the LLT films were annealed for 1 hour at 700°C in dry air. High (0.95M; black squares) and low concentrations (0.38 M; white squares) were measured with the standard deviation shown for each sample.

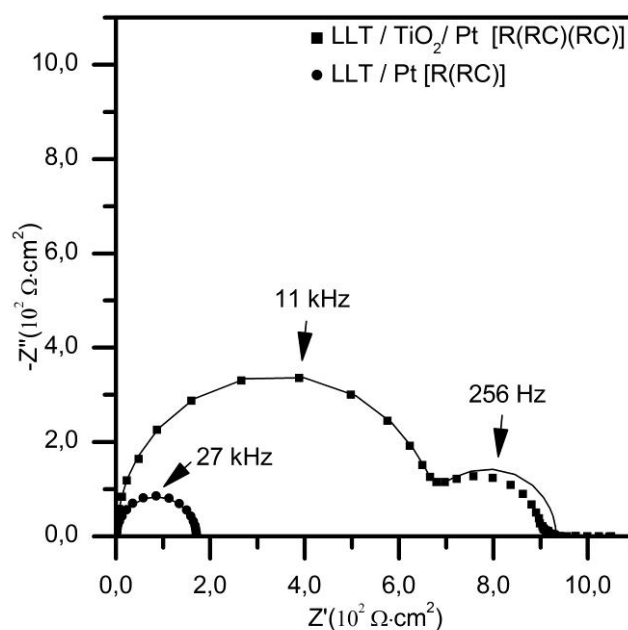
The top view SEM micrographs show crystalline perovskite LLT films on  $\text{TiO}_2$  (Si) (Fig. 7a and 7b), which received an anneal comparable to the isothermal heating during the in-situ XRD study (Fig. 6). The films exhibit a homogeneous morphology with macro porosity. It is speculated (based on properties of the amorphous layers, see further in Fig. 9) that this is introduced during the crystallization of the films. Using the Z contrast in the BSE cross section image (Fig. 7d) the LLT layer (brighter, 90 nm thick) can clearly be distinguished from the rutile  $\text{TiO}_2$  anode layer (darker, 90 nm thick) underneath. The thickness of the LLT layer on  $\text{TiO}_2$  increases linearly with the number of deposition cycles for high and low precursor solution concentrations (Fig. 8).



**Figure 9:** Cross section SEM SE (a) and BSE (b) images of 4 layers (0.38 M) of amorphous LLT deposited on  $\text{TiO}_2$  (Pt) annealed at 500°C for 4 hours in static air. Afterwards, the Au electrode was evaporated on top.



**Figure 10:** Cross section SEM SE (a) and BSE (b) images of 4 layers (0.38 M) of amorphous LLT deposited on Pt, annealed at 500°C for 4 hours in static air. Afterwards, the Au electrode was evaporated on top.



**Figure 11:** Nyquist plot of 90 nm thick LLT films annealed for 4 hours at 500°C, with 300 nm Au electrodes evaporated on top. Two semi-circles are observed for LLT on TiO<sub>2</sub> (Pt) (squares) as shown in Fig. 9, whereas one semi-circle was observed for LLT on Pt (circles) as shown in Fig. 10. Results of the fitted equivalent circuit models are also shown (grey lines) with resistor (R) and capacitor (C) elements.

Thus far, XRD and GATR-FTIR results have, respectively, confirmed the formation of perovskite phase LLT on TiO<sub>2</sub> (Si) and the presence of negligible organic contents in the films. To study functional properties of these

films with impedance spectroscopy, an electronically conductive substrate is required; for this study Pt coated substrates are used. To ensure stability of the current collector and limit the macro porosity of the films, the maximum annealing temperature was set at 500°C, yielding smooth amorphous LLT thin films (Fig. 9 and 10). The impedance results (Fig. 11) show one semicircle for LLT on Pt, and two semicircles in case of the half-cell configuration (LLT on TiO<sub>2</sub>(Pt)). Based on this comparison, it is assumed that the high frequency range semicircle is related to the amorphous LLT layer, whereas the small low-frequency range semicircle is related to TiO<sub>2</sub> layer. The latter can either arise from Li<sup>+</sup> ions that have diffused from the LLT layer into TiO<sub>2</sub> during annealing (4 hours at 500°C), or it can be related to the charge transfer resistance at the LLT-TiO<sub>2</sub> interface. Based on fitting with an equivalent circuit, the Li-ion conductivities of amorphous LLT thin films, with thicknesses under 100 nm, on Pt and TiO<sub>2</sub> (Pt) were found to be  $3,8 \cdot 10^{-8} \text{ S} \cdot \text{cm}^{-1}$  and  $1,3 \cdot 10^{-8} \text{ S} \cdot \text{cm}^{-1}$ , respectively. Since the conductivity of amorphous LLT films drops when the lithium contents is reduced [11], the lower conductivity of the LLT thin film on TiO<sub>2</sub> (Si) might arise from a lithium deficiency. The conductivities obtained with the current approach are considerably lower compared to the conductivity of bulk amorphous LLT prepared at 600°C ( $10^{-5} \text{ S/cm}$ , measured at room temperature) [10]. Although a previous study on LLT thin films (with a thickness under 100 nm) prepared at higher temperatures nearly accomplished this value, the reported Li-ion conductivity was measured in lateral direction [15], whereas the current study regards the perpendicular Li-ion conductivity of the thin film, which is of higher relevance for the final battery.

## Conclusion

The results of the current study have shown that amorphous and crystalline perovskite LLT (thin) films could be established using an aqueous precursor system, at respectively 500 and 700°C. The thickness of the films can easily be tuned by varying the number of deposition cycles and the concentration of the aqueous precursor, which is of importance to tailor the ideal electrolyte thickness in a battery device. In addition, the uniform depositions on the rutile TiO<sub>2</sub> anode and Pt current collector indicate that the current approach has potential to be applied to other anode and cathode materials as well. The impedance results of the amorphous LLT thin films showed that an electronic short circuit could be prevented across the films, indicating that no pin holes are present and that the amount of residual organics is sufficiently low at 500°C. The final value obtained for the Li-ion conductivity of the amorphous thin films ( $10^{-8} \text{ S} \cdot \text{cm}^{-1}$ ) still has to be improved in view the

application of LLT as a solid electrolyte. Nevertheless, it is a promising result compared to other studies on LLT thin films.

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