# Interfaces in Lithium-ion batteries: Advanced chemical and morphological characterization of the Solid Electrolyte Interphase

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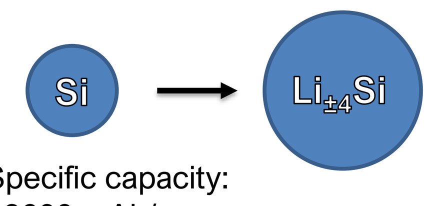
## Introduction:

As the market share of electric vehicles (EVs) and mobility is expected to rise immensely over the next decades, the demand for improved energy storage technologies is currently at an all-time high. Li-ion batteries attract most attention due to their high stability alongside excellent volumetric and gravimetric energy density. One of the most important factors influencing performance and lifetime of a liquid-electrolyte battery is the solid-electrolyte interphase (SEI), formed at the interface between anode and electrolyte. A stable SEI is critical towards the cyclability of the cell. The SEI formation process leads to the (irreversible) trapping of lithium ions inside this layer. This is especially the case for Si-based anodes, as their large volume changes during cycling will damage the integrity of the SEI layer. SEI reformation after each cycle eventually leads to undesired capacity fading. Beyond silicon-based anodes, metallic Li could be considered as the ultimate anode material due to its exceptional theoretical capacity and lowest electrochemical potential. However, many challenges surround its practical application in both liquid electrolyte and all-solid-state batteries. Due to the high reactivity of Li metal, reactions and degradation processes taking place at the interface often have a strongly negative impact on the battery stability and performance. In addition, dendrite formation issues are well known, even for solid-state electrolyte systems. In-depth studies of these interfaces often rely on advanced characterization methods for the (local) investigation of morphology, dynamic thickness, chemical composition and mechanical properties. However, due to the complex nature and reactivity of these interfaces, this is often challenging. Alongside real electrode samples, planar model systems with a well-structured interfacial region could provide supporting information and a better understanding of the processes taking place at the surface. By combining cross-sectional electron microscopy (FIB-SEM) with surface sensitive imaging (AFM), the morphology of the interface region can be investigated in detail. Compositional analysis of the SEI and (buried) electrode surface can be achieved with XPS/HAXPES. By combining multiple X-ray energies, the chemical environment can be probed at various depths, which allows non-destructive profiling. The ultimate goal of this study is to integrate these results, providing a deeper look into the early stages of SEI formation and reduction processes taking place at Si-based materials ($Si/SiO_x$ or Si/C composites) and metallic Li anode interfaces. This knowledge could lead to advancements of current state-of-the-art battery systems and even provide further insights towards new generation Li-ion battery technologies.

## Si anode design




Specific capacity: ~3600 mAh/g

Volumetric capacity: ~2200 mAh/cm³

Alloying type

Very high volume changes (~400%)

**Main challenge**
**for Si-based anodes: Volume changes during cycling**

→ Degradation, fracture, loss of contact
→ Additional SEI formation
→ Capacity fading

**Basic building blocks**

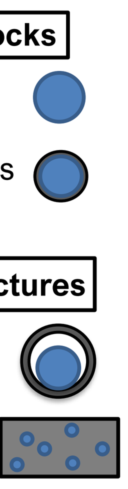
Nanoparticles

Core-shell coatings

**Advanced architectures**

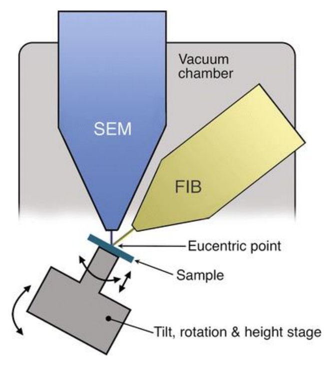
Yolk-shell particles

Composite matrix

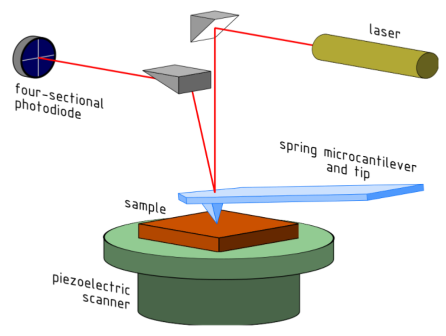


## (Buried) interface characterization

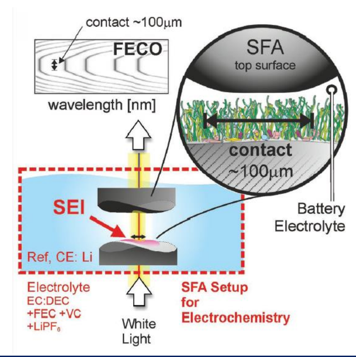
### FIB-SEM



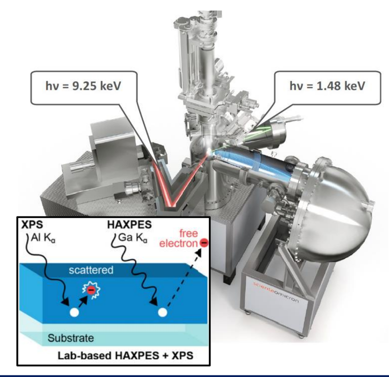

### AFM



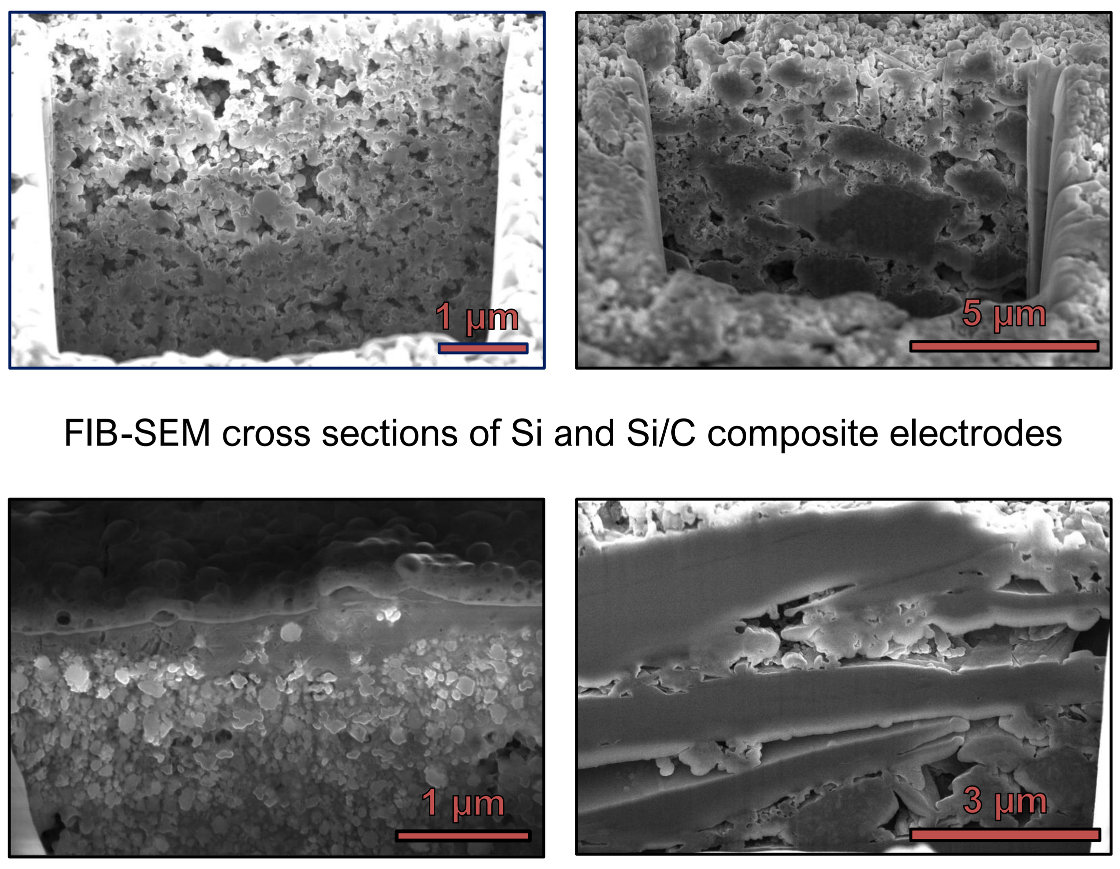

### SFA




### XPS/HAXPES

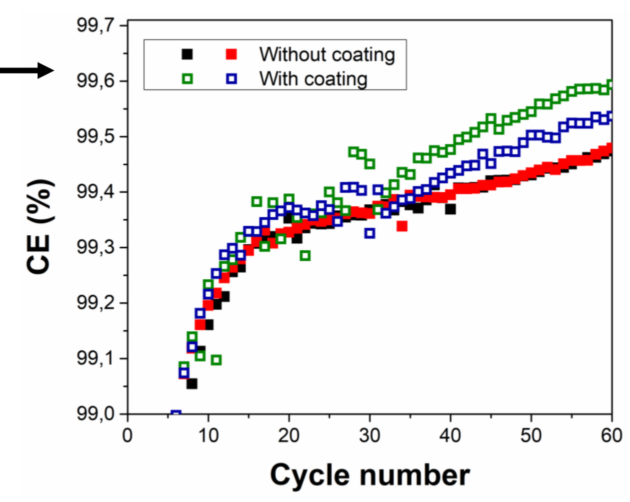



## From Si to Si/C composite anodes

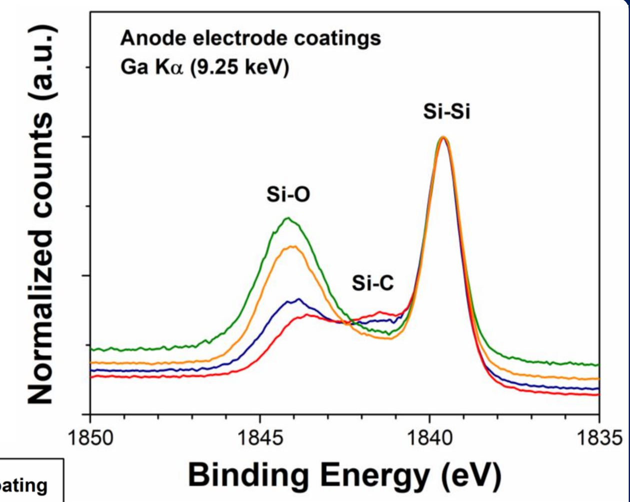


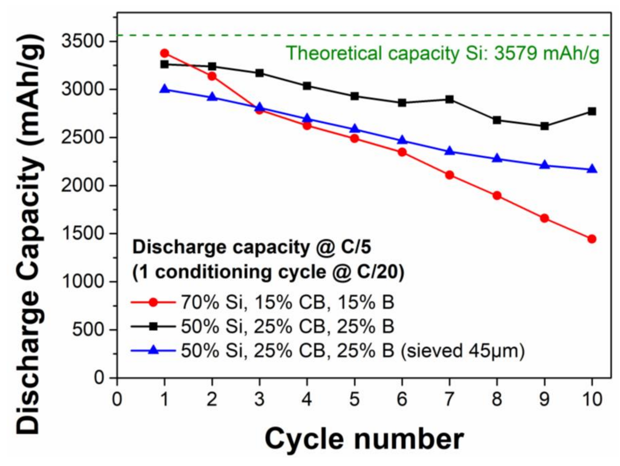

FIB-SEM cross sections of Si and Si/C composite electrodes

CE of Si/C/graphite composite electrodes with and without carbon coating

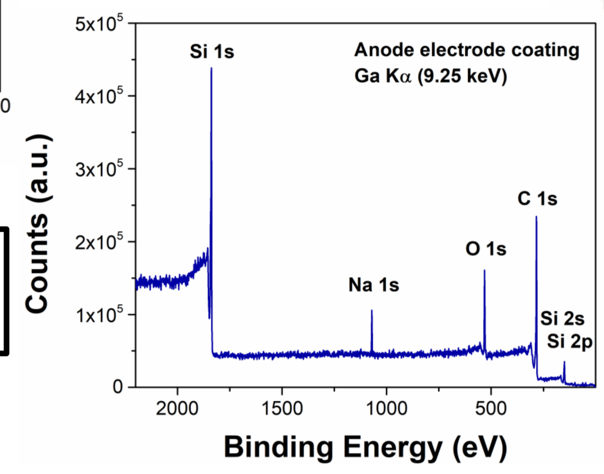



HAXPES study of Si particle surface termination within a composite coating



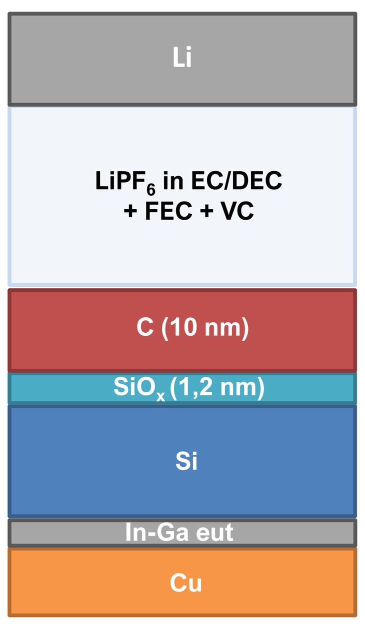



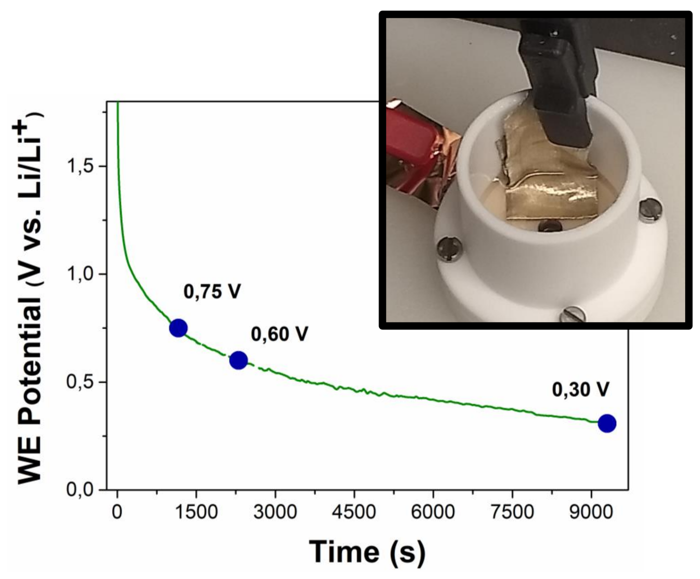

CE of Si electrodes at different Si loadings




HAXPES survey of typical Si/C composite electrode

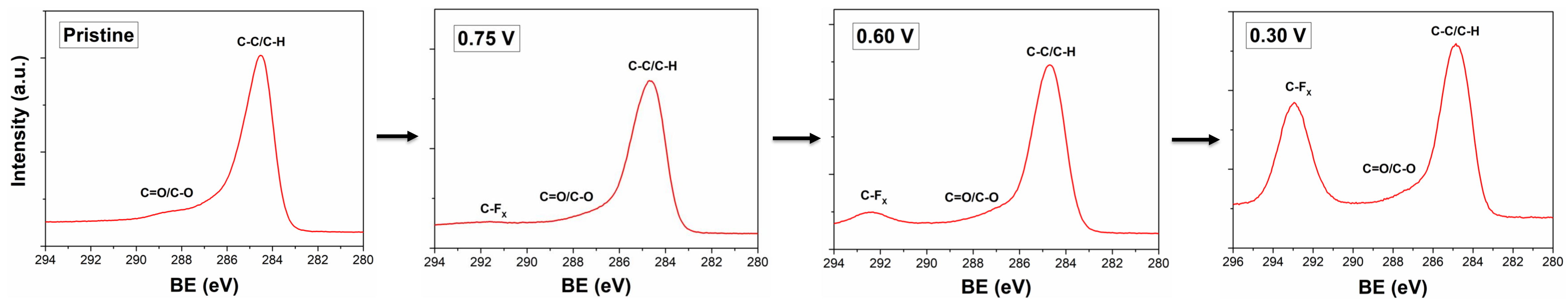
## Si/C planar model system



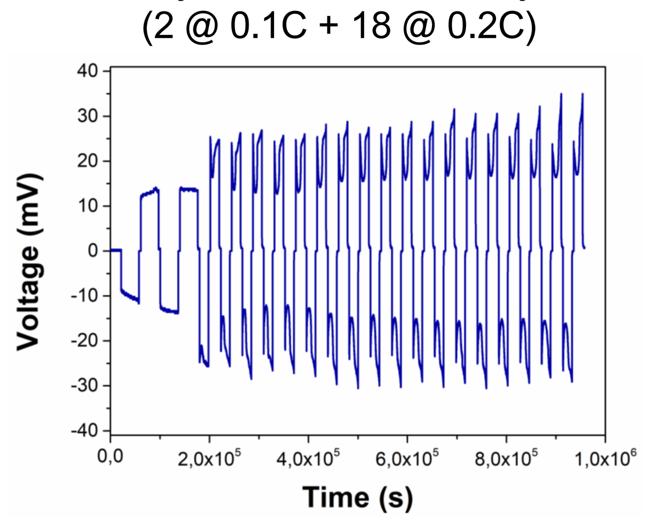

Constant current: -5 µA

### C 1s XPS series

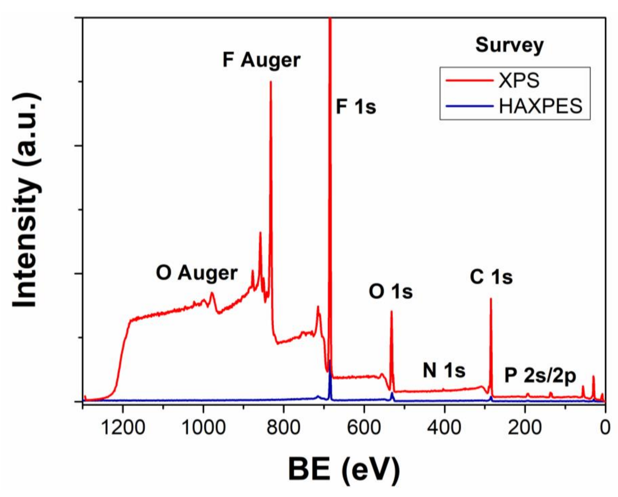


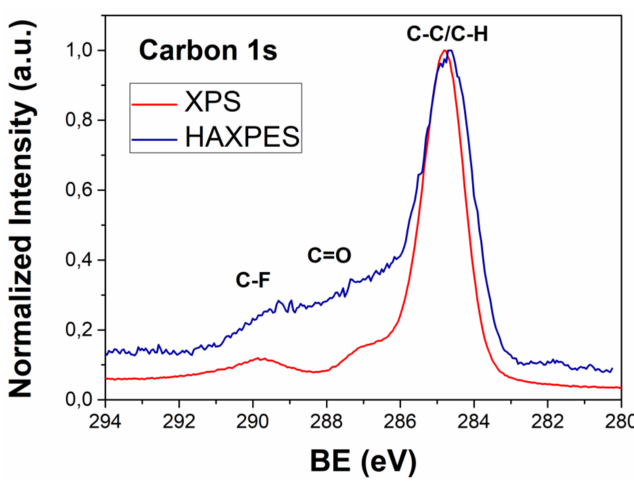

## Li metal anodes

Li-Li symmetrical cell, 20 cycles
(2 @ 0.1C + 18 @ 0.2C)

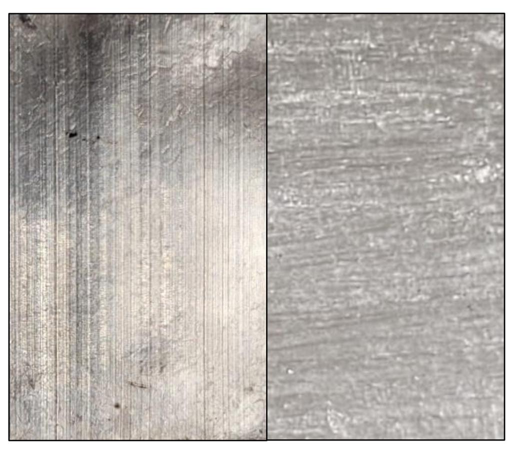



**Main challenge:**
Major issues with lithium plating and dendrite formation
→ Punctures, short-circuits, bad cyclability
**However:** Extremely high capacity (3860 mAh/g) + lowest operational voltage

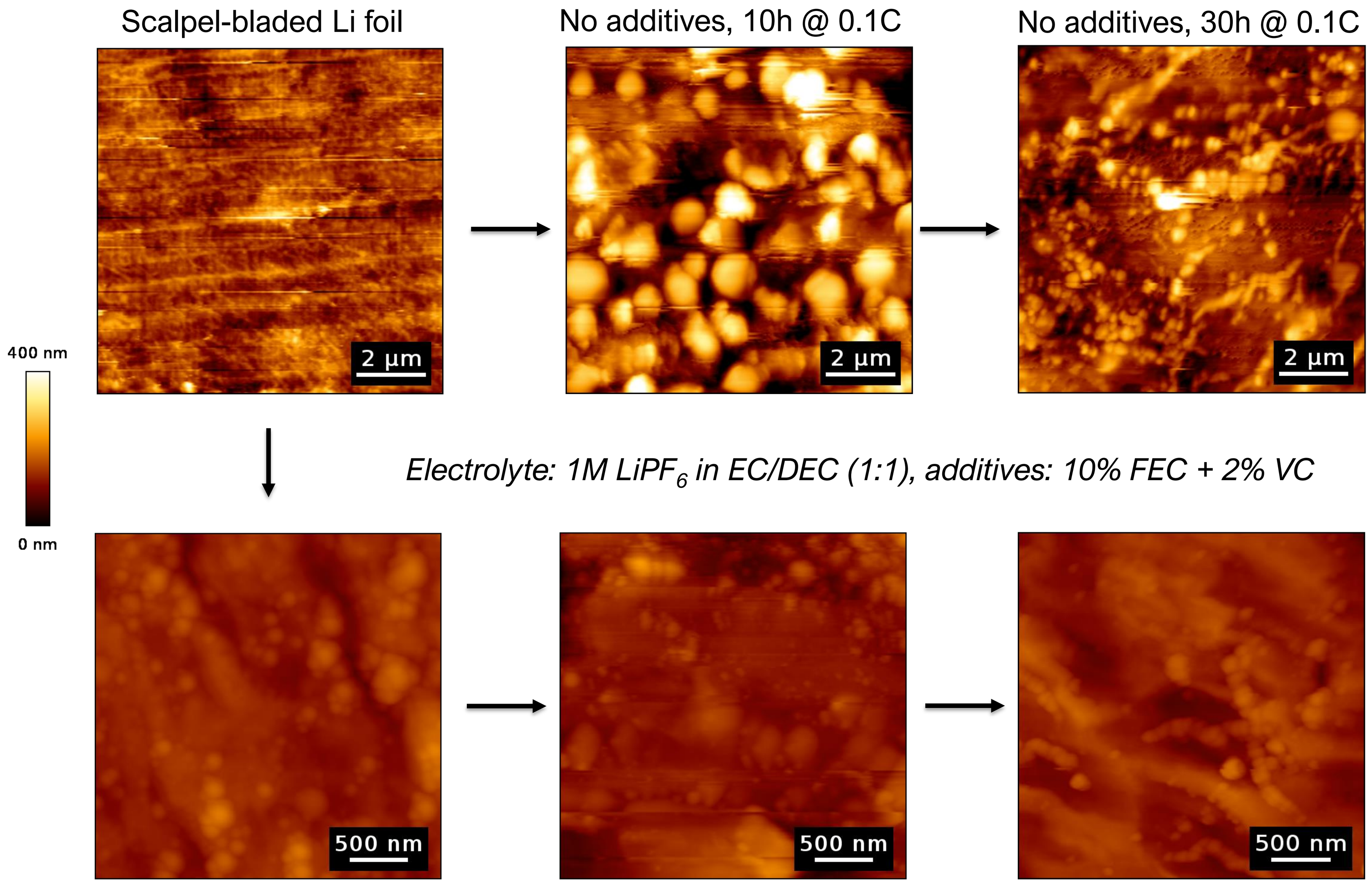



No additives, 10h @ 0.1C



Left: Raw Li foil
Right: Bladed foil




*Electrolyte: 1M $LiPF_6$ in EC/DEC (1:1), additives: 10% FEC + 2% VC*


**References:**
Buried interface characterization – schematic images: *FIB-SEM: Brüggeman et al. (2014) / AFM: Wielgoszewski et al. (2011) / SFA: Moeremans et al., In Situ Mechanical Analysis of the Nanoscopic Solid Electrolyte Interphase on Anodes of Li-Ion Batteries, Adv. Sci. 2019, 6 (16), 5 / HAXPES: scientaomicron.com; Razek et al., 2020 Electron. Struct., 2, 023001*