



## Comparison of the growth of lithium filaments and dendrites under different conditions



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### ABSTRACT

Although lithium dendrites have important implications on the safety and reliability of lithium-based batteries, an understanding of their growth mechanism is still lacking. Electron microscopy and *in situ* light microscopy were used to investigate the growth of lithium filaments and dendrites. Lithium was deposited by thermal evaporation in vacuum as well as electrochemically using two different electrolytes. Filaments grow in all three cases by an insertion mechanism, suggesting that neither a solid-electrolyte interphase (SEI) nor electrolytes are required to form lithium filaments. The role of the electrolyte becomes apparent in the detailed morphology of the deposits. These findings indicate that instead of ionic transport and electrochemistry, lithium diffusion and crystallization are key processes which need to be modified in order to control the growth of lithium dendrites.

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### 1. Introduction

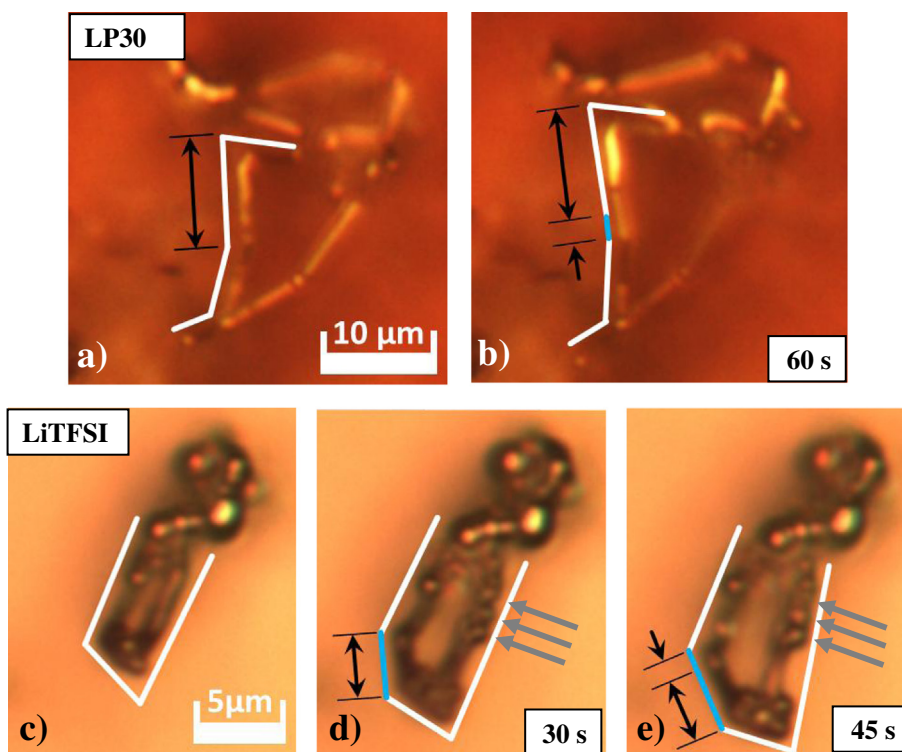
Metallic battery materials have gained considerable attention recently as they enable extreme volumetric and gravimetric energy densities [1]. Especially the lightest metal – lithium – will be the anode of choice for many next generation batteries such as lithium–air and lithium–sulfur if safe and reliable recharging can be achieved [2]. Unfortunately, metals – especially lithium [2] – suffer from the phenomenon of dendritic growth during charging. Dendrites are structures with the shape of needles or bushes that can cause severe problems in batteries such as poor cycling performance and short circuits. Lithium dendrites prevent a widespread commercialization of lithium metal anodes in rechargeable batteries and afflict today's lithium-ion systems under adverse charging conditions [3], i.e. low temperature and/or high charge rates [3,4]. This was shown in the investigations of the Boeing Dreamliner groundings in 2013, where dendrite formation has come under suspicion [5] of having caused short-circuits and ignition of lithium-ion batteries.

Strong efforts have been dedicated to mitigate this issue [2] since its first observation in the 1960s [6]. Attempts that were somewhat successful used mechanical suppression by optimized separators and

solid/gel electrolytes. More fundamental approaches include tuning the solid electrolyte interphase (SEI), stirring the electrolyte or pulsed charging. These countermeasures have beneficial effects on the charging behavior, but so far no attempt has succeeded in tackling both the problem of efficiency and the danger of short circuits. Consequently, it was tried to understand the origins of this phenomenon. However, the varieties of published models are often fundamentally contradicting, e.g. it is still under debate where lithium atoms are incorporated into the structures. Models based on concentration gradients in the electrolyte, electrical field enhancement at protrusions or SEI inhomogeneity predict that lithium atoms aggregate preferably at the tip. In the whisker-based model of Yamaki et al. [7] atoms are added at the base of needle-like structures in the first growth stage, followed by nucleation of spheres at tips and kinks. Some difficulties in understanding lithium dendrite growth are inherent to lithium which shows a very weak interaction with electrons and X-rays. It is challenging to obtain high resolution *in situ* images as the electronically nonconducting electrolyte is opaque for electrons. In our recent *in situ* study by light microscopy we showed that lithium atoms can be added to a dendrite at the base, the tip and into kinks [8,9]. This unexpected behavior was not predicted by previous models of dendritic growth. Hence, we suggested [8,9] that lithium atoms are inserted into the metal lattice of dendrites or filaments at crystalline defects, in particular at interfaces such as high angle grain boundaries (e.g. at kinks, cf. Fig. 1) or the interface at the substrate.

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**Fig. 1.** Image sequences of the growth of lithium filaments in the shape of a loop (marked with parallel white lines) in LP30 (above) and LiTFSI (below). Both filaments elongate by addition of new segments (marked in blue) without elongation of the surrounding segments (white). Hence, the segments must grow by atom insertion into the lattice of the filament, probably at kinks. The arrows mark spheres that were plated at the side of a filament in LiTFSI. Image b) was taken 60 s after a). Image d) was taken 30 s and e) 45 s after c). Similar observations were made on filaments. Changes in segment length can be detected more easily on loops. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 2. Experimental information

We used an *in situ* optical cell based on a polymer frame that connects two glass plates to allow for the observations. The details of the setup can be found in [8]. LP30 (1 M lithium hexafluorophosphate  $\text{LiPF}_6$  in EC/DMC 1:1) and 1 M LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) in DOL/DME (1,3-dioxolane/1,2-dimethoxyethane) were used as electrolytes. PVD (physical vapor deposition) was performed by thermal evaporation of lithium from a tungsten boat inside a commercial thin film deposition system (NANO 36, Kurt J. Lesker). Different commercial foil substrates (battery grade copper, tungsten and tantalum) were used as-received. Polycrystalline copper substrates (Alfa Aesar Puratronic 99,999%) were prepared by several polishing steps and subsequent vibratory polishing to achieve smooth surfaces. Traces of oxides were removed by a heat treatment in a vacuum at small partial pressures of forming gas (5%  $\text{H}_2$  und 95% Ar) at 250 °C for 15 min. The nominal thickness of the lithium and the deposition rate were monitored by a quartz crystal microbalance. Deposition was performed at room temperature; the nominal deposition rate was kept around  $1 \text{ nm s}^{-1}$  (which is equivalent to a current density of  $0.74 \text{ mA cm}^{-2}$ ) for 200 s. The samples were tilted to 0°, 45° and 65°. Needles were found on all substrates with a tendency of increasing density with increasing tilt angle. The residual gas pressure before deposition was  $3.3 \cdot 10^{-6}$  mbar.

## 3. Results and discussion

To investigate the mechanisms of filament growth and to what extent they are affected by the chemical composition of the electrolyte, we compared dendrite formation in two chemically very different electrolytes, the widespread LP30 (1 M  $\text{LiPF}_6$  in EC/DMC) and a 1 M LiTFSI solution in DOL/DME using the electrochemical cell described in [8]. In both electrolytes lithium exhibits the tendency to grow needles and

dendrites. As observed before [8,9], lithium filament growth can occur by insertion at kinks (shown in Fig. 1), at the substrate interface and by growth at the tip. The electrolytes have comparable ionic conductivities ( $11 \text{ mS cm}^{-1}$  for LP30 [10] and  $15 \text{ mS cm}^{-1}$  for LiTFSI [11]), which implies that morphological differences are related to the different SEI compositions (containing e.g.  $\text{Li}_x\text{PF}_y$  in LP30 [12] and  $\text{Li}_2\text{SO}_3$  and  $\text{Li}_2\text{S}$  in LiTFSI [13]). Characteristic differences in the growth morphology were identified: In contrast to LP30, spheres (marked by arrows in Fig. 1) are distributed along the filaments in LiTFSI. In LP30, needles can be elongated by insertion at the tip whereas in LiTFSI, the only growth observed at the tip was the deposition of lithium spheres in the tip area. Besides filament growth, also bushes or mossy lithium can form (Fig. 2). Here, strong differences were found: While LP30 shows strongly branched bushes where the branches resemble the filaments [9], electrodeposition in the LiTFSI exclusively leads to more compact agglomerates containing spheres. Fig. 2 B is an extreme example of such a structure not showing any elongated segments (as the ones in the lower part of Fig. 1).

These differences indicate that the SEI has a strong influence on the growth morphology as reported before [14,15], but filamentary growth was found for both electrolytes which raises the question whether it depends on the composition of the SEI. To fully exclude electrochemical effects, namely electric fields, concentration gradients and the SEI, deposition was additionally performed by thermal evaporation (PVD). Fig. 3 shows SEM images of lithium needles on Cu grown by PVD in comparison with those obtained by electrodeposition. The deposits look very similar: Both contain lithium needles with a length in the micrometer range and a diameter of ca.  $0.1\text{--}0.2 \mu\text{m}$ . PVD filaments – which we observed in all PVD runs on different substrates – can have kinks as the electrodeposited ones.

The strong resemblance of PVD and electrodeposited filaments as exemplified in Fig. 3 indicates that the underlying mechanism could be controlled by the same insertion mechanism. As a consequence,

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