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Microscopic observations of the formation, growth and shrinkage of lithium moss during electrodeposition and dissolution

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ABSTRACT

Lithium electrodeposition and -dissolution in a commercial battery electrolyte (1 M $LiPF_6$ in EC:DMC) has been studied *in situ* by light microscopy and *ex situ* by scanning electron microscopy (SEM). We describe the transition between lithium filaments, which are most likely whiskers, and lithium moss and report in detail on the growth of mossy lithium structures. In the case of mossy lithium, the deposition can occur at the tips or the base of the growing structure. However, the growth is not limited to these locations, but can also occur by insertion at further growth points distributed inside the mossy Li deposit. We show that two different growth modes have to be distinguished: the unusual non-tip-growth by lithium metal insertion into the metallic moss backbone, and the condition where the deposition at the top of the mossy structure is not possible anymore because it was electrically isolated from the current collector due to a previous lithium dissolution step. After a dissolution period causing insulation of Li ("dead Li"), whole moss remnants can get pushed outside by metal structures growing underneath.

1. Introduction

The use of lithium electrodes for high energy batteries has been suggested decades ago [1], and lithium metal has been used and is still used for primary batteries. For secondary batteries, however, Li metal anodes have been abandoned due to their strong tendency to form rough, dendritic deposits during charging, which use up electrolyte and cause safety problems such as internal shorts. Although tailored electrolytes [2], additives [3,4] and optimized separators [5] mitigate the related problems, their success has been limited [6]. This suggests that to implement safe rechargeable lithium electrodes, the empirical approach of testing should be complemented with experiments aiming at identifying different growth modes and mechanisms [6]. Previous studies of the growth behavior have already elucidated a number of key points: 1. Dendritic electrodeposition can result in the isolation of metallic lithium, which is the so-called dead lithium [7,8]. 2. The solid electrolyte interface (SEI) layer on the lithium, especially its homogeneity, is important [9]. 3. It has been observed that bush-like or mossy lithium does not grow at the outermost tip [10,11]. Instead, the growth occurs in regions closer to the substrate and has been described as growth from the base [10,11]. This surprising result is not expected from the typical growth models of dendritic structures. A previous explanation suggested the growth of whiskers from the base by pressure-induced extrusion [10]. This model has been criticized [12,13], but other previously proposed models did not describe the growth at concealed points. Other models like the one proposed in [12] focus on the growth of single filaments; however, their applicability for the growth of very dense moss might be limited. The present study focuses on the growth mode of mossy lithium; the growth of individual filaments is discussed in a separate publication [13]. Since we observed spatially separated, freestanding lithium deposits rather than a dense moss grown together in a quasi-homogeneous layer, we use the term "lithium bush" instead of the more common "moss". In the present work, *in situ* light microscopy was used to observe the growth to reveal the position of the growth zone and the direction of growth.

2. Experimental

The substrate electrodes were either strips of 10 μm thick battery grade copper foil or created by sputter coating borosilicate glass slides with tungsten and subsequent structuring of the resulting film by a simple lift-off process. The sputtering and transfer was done as described before [13]. The *in situ* microscopy electrochemical cells consist of a polyethylene frame in between borosilicate

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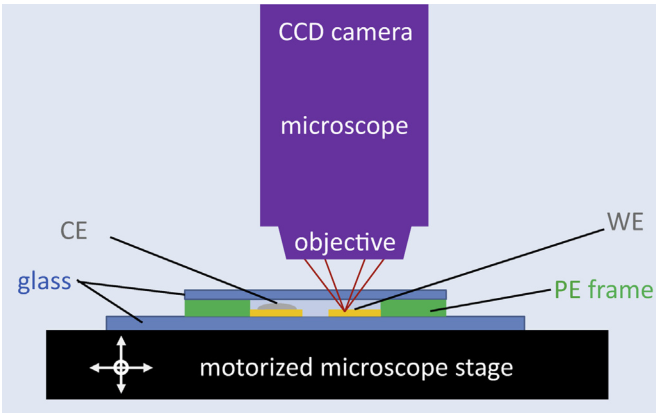

Fig. 1. Schematic of the experimental **setup** for the *in situ* imaging of structural changes during metal deposition and dissolution. A cell consisting of glass and PE was filled with electrolyte and sealed air-tight. A two electrode arrangement was used with metallic current collectors shown in orange. The counter electrode (CE) is a piece of lithium, the working electrode (WE) is the current collector within the focus of the microscope. Images of it are recorded with a CCD camera.

glasses (Fig. 1) and were assembled inside an argon-filled glove box. On one electrode we placed a piece of lithium metal (99.9 % from Alfa Aesar) and the other untreated one was used for deposition. The cells were filled with a commercial LP30 electrolyte (1 M $LiPF_6$ in a 1:1 weight ratio mixture of EC and DMC) and were sealed gas tight. The microscopy was done in air at ambient conditions in bright field, using an Olympus BXFM microscope with a CCD camera (Fig. 1). A Compactstat.e portable potentiostat from Ivium Technologies B.V. was used to galvanostatically cycle our cells at current densities of 2 $\mu A\,cm^{-2}$ for the tungsten electrodes and 10 $\mu A\,cm^{-2}$ for the copper electrodes. To obtain images of cross sections, a dual beam FIB was used (FEI Nova NanoLAB 200).

3. Results

Lithium was deposited and dissolved under galvanostatic conditions. The electrode and the lithium structures were observed *in situ* by light microscopy. Fig. 2 and the corresponding video S 1 shows the growth of a needle-like structure that is surrounded by a bush. Between images a) and c) this structure grew in a straight line and gained in length. Minor variations in the apparent diameter in the video images occur if the filament runs out of focus, but since a decrease of the diameter during electrodeposition is hardly possible, it is reasonable to assume that the diameter did not change at all. The tip seems unchanged during growth; therefore, growth at the tip is unlikely for this structure. The view on the exact growth zone however, is blocked by the surrounding bush. Starting from picture d), the structure started to grow in width at the tip where significant roughness is visible. From there on the straight needle part did not grow extensively anymore and instead the tip widened showing even more structure and curling indicative of, e.g., branching.

Fig. 3 and video S 2 show bush-like growth recorded by laser scanning microscopy; the structure is shown in side view, i.e. perpendicular to the line connecting working and counter electrode. The circles mark arbitrary, but easily traceable structures of the bush. The arrows in image b) mark their shift in position from their original position (image a)). These structures lack a preferred growth direction and they also increase the distance between each other.

To inspect bush structures, we used a micromanipulator (Kleindiek Nanotechnik) inside an SEM to remove the upper parts of a lithium bush, where we found needles underneath (see area marked in red in Fig. S 3). Furthermore, we used the FIB to image cross sections of Li bushes. An example is shown in Fig. 4. It can be seen that large parts of the structure are not directly connected to the substrate.

The dissolution of the bush-like structure depicted in Fig. 2 is shown in Fig. S 4. The process started at the tip and was accompanied by the motion of the whole structure. The images suggest that the lithium of the broadened filament could be dissolved and only a thin shell of the structure remained. In contrast to this case where a large fraction of the metal could be redissolved, the case of an incomplete dissolution is shown Fig. 5 (cf. the video S 5): in image a), a bush structure is shown that was electrodeposited on copper, and image b) shows what remained of the structure after its dissolution up to 3 V vs. Li. The arrows mark a structure at the tip of the bush that did not change its shape while the bush was shrinking. The two following images show a subsequent plating step. No new bushes have been observed; instead the electrodeposition took place at the location of the remaining bush. While the tip structure of the bush remained unchanged both during dissolution and deposition, the bush changed its size and seemed to grow towards the sides and around the inactive tip structure. Again, no obvious general growth direction was observed during electrodeposition. The fact that a large part of the structure of Fig. 5 could not be dissolved is also reflected in the galvanostatic data (see [13] for a representative graph) where it was apparent that the amount of charge transferred during stripping is significantly smaller than the amount of charge transferred during electrodeposition.

Fig. S 6 shows an overview of a tungsten surface during growth showing lithium needles and particles. All structures on the substrate have nucleated at roughly the same time. The arrows mark lithium structures that formed and ceased to grow, while other structures continued to grow. Although Fig. S 6 only shows this effect for bush-like growth, we also observed this effect in needle-like growth. These active structures also remained active after interrupting deposition for one hour for several times.

4. Discussion

4.1. Growth of Li bushes

The observations as exemplified by Fig. 2 clearly demonstrate that growth can happen both at the tip and at lower parts simultaneously. The tip broadening (Fig. 2 d)) proves accretion at the tip; at the same time, the features of the filament tilt and move outwards showing that the base is flexible and still growing. Based on our observations of single Li needles [13] we suggest that lithium is inserted either at the tip, the base or at kinks of whisker-like structures, and we conclude that defects are necessary to allow lithium atom insertion into a filament [13]. In particular, insertion into intact crystal structures is unlikely; therefore, we believe that defects for example such as grain boundaries are required to allow Li atom insertion in the otherwise perfect crystals. Kinks in filaments with straight segments were observed frequently in our microscopic images. They are an experimental indication of high angle grain boundaries which are regions of high defect density containing dislocations and/or vacancies. The tilting movements indicate that these grain boundaries do not have fixed angles, which suggests that their structure is either continuously changing by further Li addition or that it might have a liquid-like flexibility.

During lithium deposition, needle-like growth in length was observed frequently [13], which occurs–within the accuracy of light microscopy–without an increase in thickness [13]. It has been described by the mechanism of insertion at kinks or other defects [13]. Video S 1 and Fig. 2 show that there is a transition between such needle-like growth, which is a quasi one-dimensional, linear elongation, and bush-like growth, which is three-dimensional and