In situ light microscopy on lithium plating and dendrite growth: New insights into an old problem

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Lithium-ion secondary batteries are the state of the art technology for portable electric energy storage. They have taken a leading role in the power supply of mobile electronics and are about to supersede lead acid batteries in electric cars. This is due to their superior energy density while exhibiting a high power density. Lithium-ion batteries usually use graphite anodes and intercalation materials as cathodes [1].

The use of pure lithium metal instead of graphite strongly improves the volumetric energy density of cells [1]. Lithium metal electrodes are further required for possible future technologies such as Li-S or Li-O_2 cells. This is due to the superior capacity and low electrochemical potential of lithium metal. While pure lithium metal anodes are common in primary batteries, lithium dendrite growth during charge is the main inhibitor of the usage of those anodes in secondary batteries. Even though state of the art lithium-ion batteries do not contain metallic lithium, they can still suffer from dendrite growth for high rates of charge especially at low operating temperatures.

The phenomenon of dendritic growth of lithium is well known since the 1960’s but so far only limited understanding of this process exists.

Several explanations have been proposed:

- The concentration of the electric field at protrusions is expected to attract the lithium cations in the electrolyte. This causes the localization of growth, further enhancing the electric field [2].
- A Gradient in the ionic concentration that forms in the electrolyte during cycling may be another reason. Supposedly it can either cause protrusions to grow faster than flat areas as they reach further into the electrolyte where the concentration is still higher [3] or due to an excess amount of cations at the negative electrode which causes a high local space charge [4].
- A spherical diffusion flux model was proposed to explain the preferred plating at protrusions, as protrusions benefit from an enhanced three-dimensional flux, while a flat surface will be dominated by a two-dimensional flux [5].
- Inhomogeneities in the SEI are suspected to cause localization of plating through the SEI at areas with higher ionic permeability. This causes stress in the SEI and eventually the cracking of the same. This reveals an area with no SEI which further localizes the plating [6].
- A lithium extrusion model predicts that the stress that forms between the lithium and the SEI is released by crack formation and the extrusion of the lithium through the crack, causing a whisker-like growth [7].

As of now, there is no general agreement on the basic growth mechanisms. While the first four models predict that dendritic growth happens by plating of atoms onto the tip of a dendrite, there is also experimental proof for the addition of the atoms at the base of a dendrite [7, 8].

In order to develop a better picture of the lithium plating process, we have conducted in situ light microscopy of lithium plating on metallic foils and on smooth sputtered films. Additional detailed ex situ observations were performed by SEM.

For this purpose we designed thin cells made from borosilicate glass where large sections of the electrode can be monitored through a thin layer of electrolyte. With this design we were able to record movies with unprecedented resolution (Fig. 1). In the dendrite growth regime, we studied growth modes as well as growth velocities and directions. The nucleation stage of lithium plating was investigated on various substrates to gain insight into the process of lithium plating and its transition to dendrite growth.

In this presentation we report on the details of the lithium plating and stripping processes and show observations of dendrite nucleation and growth. Our observations do not clearly confirm one of the existing growth models and suggest that interfacial SEI effects can strongly affect nucleation and growth of lithium dendrites during plating.

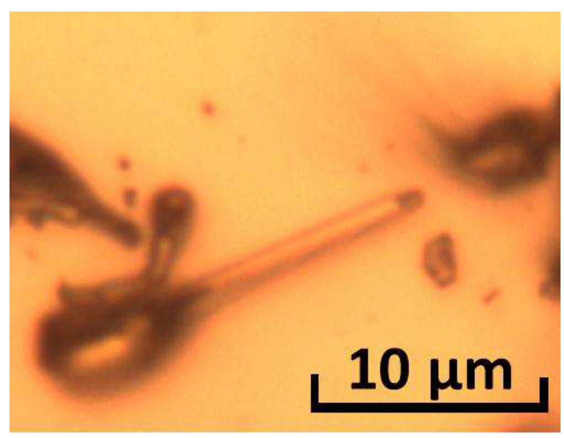

Fig. 1: Image taken from an in situ movie that shows growth and shrinkage of whisker-like plated lithium.

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