

***In operando* Transmission Electron Microscopy Imaging of SEI Formation and Structure in Li-Ion and Li-Metal Batteries**

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Lithium ion and Li-metal batteries are being used to meet the increased demand for electrical energy storage in electrical vehicle, grid storage, and portable electronic device applications. While Li batteries utilizing Li metal as the anode have one of the highest specific capacities (3840 mAh/g), their use is discouraged given its tendency to form dendrites during charging, which can short the battery. Li dendrite formation mechanisms are not well understood, although it is known that a solid-electrolyte interphase (SEI) spontaneously forms at the Li-metal/electrolyte interface during charge discharge cycling. To obtain a fundamental understanding of the Li electrodeposition/dendrite formation and SEI growth, *in situ* electrochemical TEM (ec-TEM) studies have been conducted.

The SEI is a nm-scaled passivating layer that forms locally at the anode/electrolyte interface as a result of electrolyte decomposition during the initial charging cycle. The ongoing formation of radicals (due to the highly negative reduction potential of Li, -3 V) can lead to the formation of a disordered SEI. Controlling the SEI's structure and chemistry are essential to the development of longer lasting and safer Li-ion and Li-metal batteries; however, SEI formation mechanisms and structural growth and evolution have remained elusive due to the lack of *in situ* high spatial resolution imaging coupled with electrochemical characterization [1-2]. The SEI layer's physiochemical properties and performance depend on several factors including the anion, electrolyte, solvent, electrode material, and electrochemical conditioning.

In operando visualization of electrochemical processes occurring within commercial Li-ion batteries requires the use of a closed cell as a result of the volatile nature of the liquid electrolytes typically used. Electron transparent SiN viewing membranes seal the volatile liquid electrolyte within the high vacuum of the TEM column. With recent advances in vacuum-tight liquid cell TEM holders [REF], it is now possible to directly image the dynamically evolving nature of electrochemical reactions while simultaneously performing quantitative electrochemical measurements [3-6]. In the present study, we use an *in situ* liquid biasing flow-cell holder system within a S/TEM operated at 300 kV. The microchips incorporate Au electrodes patterned on the surface of the SiN membrane. A potentiostat (Gamry Ref 600) is interfaced with the *in situ* TEM holder for electrochemical measurements. Quantitative electrochemical measurements are performed in a two- and three-electrode cell configuration while imaging *in operando*. Liquid electrolyte is delivered to the cell using a microfluidic syringe pump and tubing. During the experiments, electrolyte is continuously flowed to prevent dewetting of the microchip and to flush out any products from the counter electrode.

To conduct the quantitative electrochemical studies, current or charge must be measured at a particular referenced potential. We discuss the *in situ* formation of a reference electrode (RE) for use in studying Li-ion battery electrolytes. The RE was found to maintain potential and was used to record reproducible voltammograms and show that the potential can be controlled and monitored on both the working and counter electrodes. The current profile shows little noise $\sim \pm 0.1$ % with proper instrument grounding.

SEI formation and growth kinetics were studied on Au and glassy carbon electrodes from a commercial organic battery electrolyte - LiPF₆ in ethylene carbonate:dimethyl carbonate. Reduction products from

the electrolyte form porous dendrites on the surface of the electrode *prior* to Li deposition (Fig. 1). The polymeric dendrite growth correlates with the applied potential and charge transfer rates and nanoparticles form within dense polymeric regions due to increased Li insertion occurring at high overpotentials. The direct observation of SEI formation and Li deposition on Au and glassy carbon electrodes serve as proof-of-concept for the utility of *in operando* TEM investigations of electrode/electrolyte interfaces during electrochemistry. In particular, this study provides insight regarding the design of safer and longer lasting batteries [7].

References:

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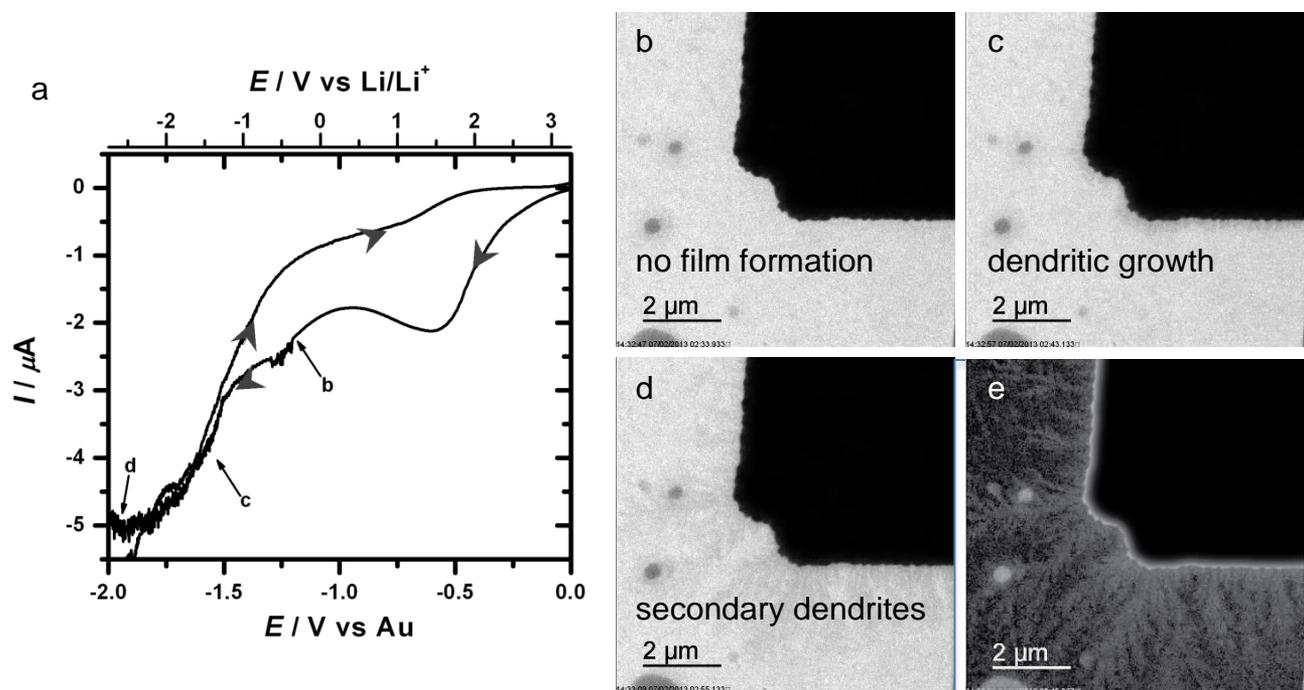


Figure 1. (a) Cyclic voltammogram of Au in 1 M LiPF₆ in EC:DMC. (b-d) *in operando* TEM images acquired during potential cycling showing polymeric dendrite formation (sweep rate: 5 mV s⁻¹). For clarity, the dendrites in (d) are enhanced in (e).