

***In situ* Electrochemical TEM for Quantitative Nanoscale Imaging Dynamics of Solid Electrolyte Interphase and Lithium Electrodeposition**

Robert L. Sacci¹, Jennifer M. Black², Nina Balke², Nancy J. Dudney¹, Karren L. More², and Raymond R. Unocic²

¹ Materials Science Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

² Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Recently, *in situ* electrochemical scanning transmission electron microscopy (ec-STEM) has enabled the direct visualization of lithium battery chemistry [1–4]. In this study, we seek to understand the Li electrodeposition process, dendrite formation, and solid electrolyte interphase (SEI) growth mechanisms *via* ec-STEM. Annular dark field (ADF) STEM imaging is used to extract quantitative information on the density of the SEI and Li nano-electrodeposits.

A limiting factor in the performance of many portable electrical devices is the need for higher power energy storage devices, such as Li-metal batteries. Li-metal batteries are prone to short-circuiting when dendrites form during Li-electrodeposition (battery charging), which leads to spontaneous discharge and thermal runaway, making them unsafe for general use [5]. It is speculated that dendrite growth can be mitigated by controlling or quickly repairing the SEI that develops at the electrode/electrolyte interface [5]. The formation of the SEI and Li-electrodeposition are studied using an ec-STEM sample holder (Protochips Poseidon™) that allows for electrochemical experiments and simultaneous STEM imaging within a volatile liquid electrolyte environment. The electrochemical microchip, shown in **Figure 1a–b**, consists of a microfabricated glassy carbon (GC) working electrode with Pt pseudo-reference and counter electrodes.

Negative potential sweeps show cathodic currents that stimulated SEI formation and the nucleation and growth of Li electrodeposits on the GC electrode in 1.2 M LiPF₆ in EC:DMC (**Figure 1c**). Simultaneous quantitative ADF STEM imaging tracks the dynamic nature of SEI formation, which appears as a bright thin layer at the GC edge (**Figure 1d**) and shows that the thickness and brightness of the SEI increases (**Figure 1e**), which correlates with the SEI exhibiting a maximum density near the electrode surface of 2.3 g cm⁻³. This value is similar to Li-salts (e.g., LiF density is 2.6 g cm⁻³) and agrees with the present model of the SEI: a dense inorganic inner layer and porous organic outer layer [6]. At more negative potentials, dark contrast, irregularly shaped nano-deposits form at the GC/SEI interface (**Figure 1f**). These dark electrodeposits are determined to be Li metal from quantitative ADF STEM image contrast analysis and confirmed by electron energy loss spectroscopy (EELS). The image analysis and electrochemical measurements are complementary techniques and are used to estimate the thickness of the electrodeposited thin film.

The direct observation of SEI formation and Li electrodeposition dynamics on GC electrodes show the utility of *in operando* TEM investigations. Moreover, quantitative ADF STEM imaging provides detailed chemical information that offers further insight into the design of safer and longer lasting batteries [7].

References:

- [1] Z Zeng et al. *Nano Letters* 14 (2014) p. 1745-1750.
 [2] RL Sacci, et al. *Chemical Communications* 50 (2014) p. 2104-2107.
 [3] ME Holtz et al. *Nano Letters* 14 (2014) p. 1453-1459.
 [4] RR Unocic et al. *Microscopy and Microanalysis* 20 (2014) p. 1029–1037.
 [5] W Xu et al. *Energy and Environmental Science* 7 (2014) p. 513-537.
 [6] PB Balbuena and Y Wang, eds. *Lithium-Ion Batteries: Solid-Electrolyte Interphase*. Imperial College Press, London, (2004).
 [7] This work was supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. Electron microscopy conducted as part of a user proposal at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), a U.S. DOE Office of Science User Facility.

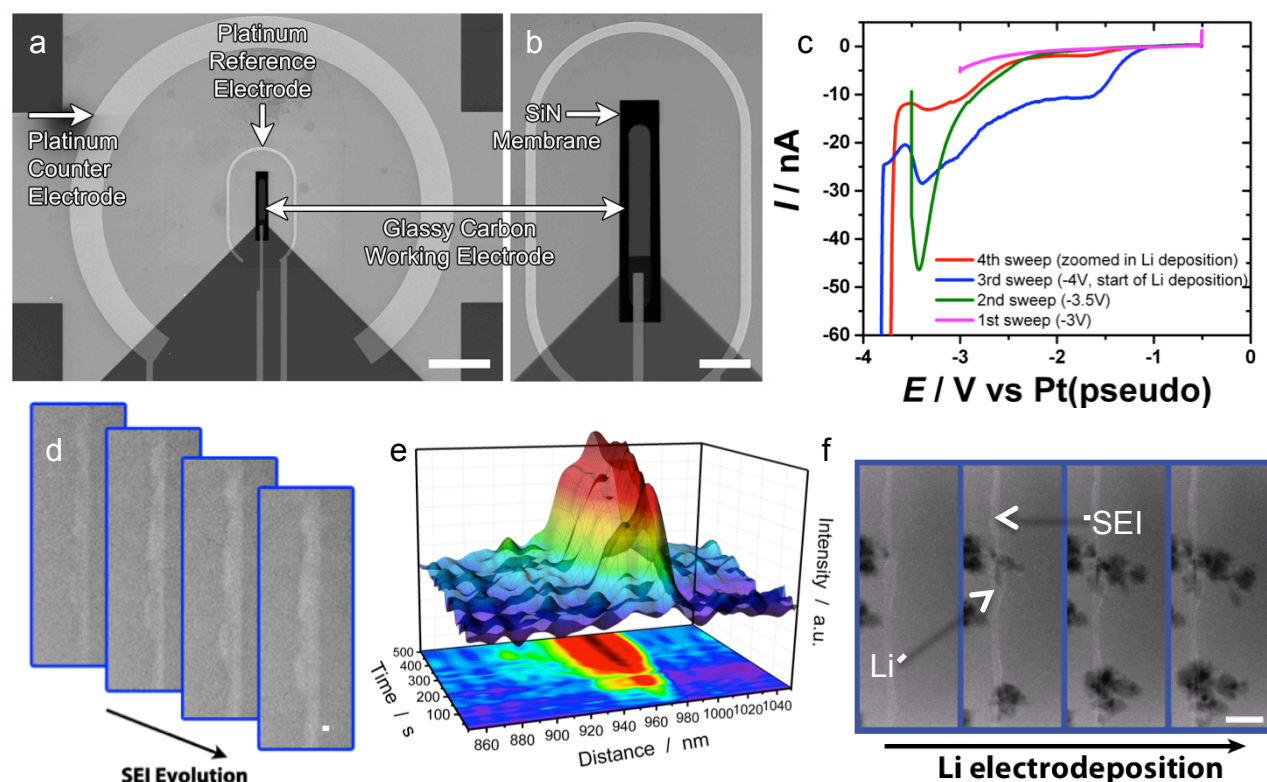


Figure 1. (a, b) SEM images of three-electrode electrochemical microchip. Scale bars are 200 and 50 μm , respectively; (c) Cyclic voltammogram (CV) of glassy carbon in 1.2 M LiPF_6 in EC:DMC showing Li electrodeposition; (d) *operando* ADF STEM images showing progressive SEI formation during negative potential sweep; (e) transient cross-section of *operando* ADF-S/TEM image intensities from SEI growth region. Scale bar is 0.5 μm ; (f) *operando* ADF STEM image showing SEI (bright edge) and Li electrodeposits (dark particles). Scale bar is 2 μm .