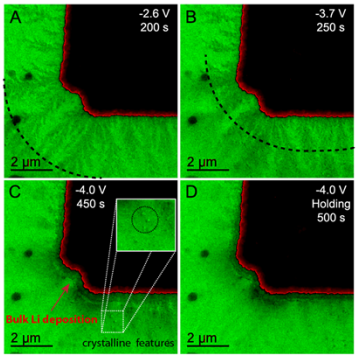
Direct Imaging of Solid Electrolyte Interphase Growth with *In Situ* Electrochemical TEM



Operando characterization using the *in situ* ec-TEM approach allows for direct imaging of the initial stages of SEI growth from the corner of a gold working electrode in a 1.2M $LiPF_6$ EC:DMC electrolyte.

Work was performed as User Project at the Center for Nanophase Materials Sciences and Pacific Northwest National Laboratory

Scientific Achievement

A new *in situ* TEM based characterization method is used to study Solid Electrolyte Interphase (SEI) formation using microfabricated electrochemical cells for transmission electron microscopy.

Significance and Impact

Real time imaging of electrochemical reactions aids in elucidating the fundamental mechanisms of SEI formation in lithium ion batteries. With this method we are able to directly image site-specific reactions occurring along electrode/electrolyte interfaces within organic battery electrolytes at high spatial resolution.

Research Details

- SEI formation and growth was studied using in situ ec-TEM, wherein 1.2M $LiPF_6$ EC:DMC electrolyte was placed within a microfabricated electrochemical cell with electron transparent SiN viewing membranes.
- Imaging is directly correlated with quantitative electrochemical measurements (cyclic voltammetry).

R.L. Sacci, N.J. Dudney, K.L. More, L.R. Parent, I. Arslan, N.D. Browning, R.R. Unocic, *Chemical Communications*, **50** 2104-2107 (2014).

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"Investigating Solid Electrolyte Formation and Growth at the Nano-scale"

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 disordered SEIs. Controlling the SEI's properties essential to the development longer lasting and safer Li-ion batteries; however, its formation mechanism and structural characterization has remained elusive due to the present lack of high spatial resolution imaging coupled electrochemical characterization and its ongoing evolution during electrochemical cycling. Its physiochemical properties and performance are dependent upon a number of factors such as: anion, solvent, electrode material, and electrochemical conditioning. *Operando* visualization of processes occurring within commercial Li-ion batteries requires the use of a closed cell. Electron transparent SiN viewing membranes seal the volatile liquid electrolyte from the microscopy vacuum column. With recent advances in liquid cell TEM holders, it is now possible to image dynamically evolving electrochemical reactions while simultaneously performing quantitative electrochemical measurements. Here we use an *in situ* liquid biasing flow-cell to directly image the early stages of SEI growth.

Figure: The sequence of images are bright-field TEM images of SEI growth, imaged through the SiN viewing window portion of the electrochemical cell. The corner of a gold working electrode (black-upper right) is imaged during the negative sweep of a cyclic voltammogram. Here is is observed the a polymeric-SEI nucleates and grows from the electrode/electrolyte interface in a dendritic morphology.

Reference: R.L. Sacci, N.J. Dudney, K.L. More, L.R. Parent, I Arslan, N.D. Browning, R.R. Unocic, Chemical Communications, **2014**, 50, 2104-2107. **DOI:** 10.1039/C3CC49029G

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