FIRST Center Research Perspective:

In Situ Electrochemical Scanning Transmission Electron Microscopy: Revealing the Dynamics of Localized Electrochemical Processes at Electrode/Electrolyte Interfaces

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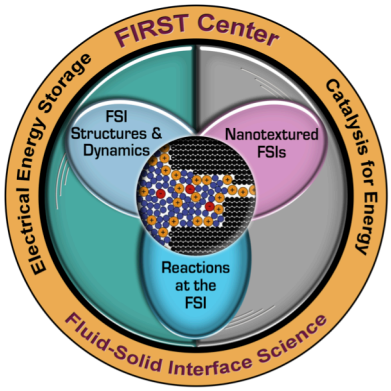

Research Summary: In this research effort we have developed a novel *in situ/operando* characterization platform that has the unique ability to probe localized electrochemical processes at high spatial and temporal resolution. Using the scanning transmission electron microscope (S/TEM) and electrochemical liquid cells as the experimental platform, we have the ability to conduct quantitative electrochemical measurements while simultaneously characterizing localized chemical and electrochemical processes with S/TEM imaging, diffraction, and spectroscopy. We use this method to study fundamental issues related to energy storage and conversion systems such as batteries, fuel cells, and supercapacitors. The system is essentially a microfluidic electrochemical cell (ec) that is sealed within the tip of a vacuum-tight TEM holder. The holder has an integrated microfluidic delivery system and electrical contacts, as shown in the assembly view in **Figure 1A**. The microfluidic flow cell feature of the system enables the controlled delivery of liquid with the aide of a syringe pump and tubing. A flexible circuit with electrical contacts is embedded within the tip of the holder and allows for the electrochemical cell to be interfaced with a potentiostat that resides outside of the S/TEM for electrochemical measurements. The removable microchips (**Figure 1B-C**) also contain integrated features that have been directly microfabricated onto each device, such as a spacer layer and electrical contacts. A close-up view of the microfabricated three-electrode electrochemical microchip is shown in **Figure 1D,** which has a Pt counter/reference electrode and a glassy carbon working electrode. The microchips also contain a central electron transparent Si_3N_4 membranes which are used to directly image and analyze the dynamics of electrochemical processes. With this system, we have shown that it is possible to perform controlled and quantitative electrochemical measurements [1].

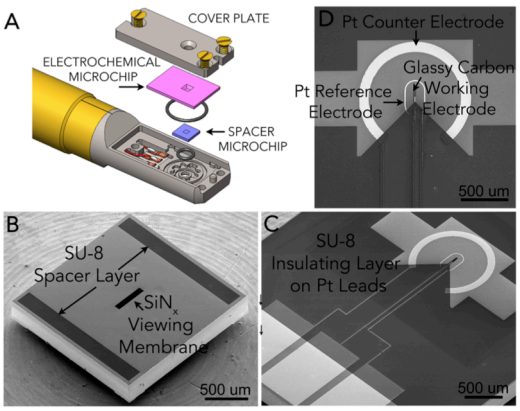

Figure 1. The *in situ* ec-S/TEM system: (A) Assembly view of the in situ TEM holder. (B) spacer microchip with 50x400 um viewing window and SU-8 spacer layer deposited on Si_3N_4 membrane, used to define the microfluidic pathway. (C-D) Electrochemical microchips with micro-fabricated Pt counter and reference electrodes and glassy carbon working electrode [1].

Technical Details: In electrical energy storage systems, interfaces play an active role in controlling the electrochemical energy conversion process. Of crucial importance to the performance and life-cycle of lithium ion batteries is the formation of the solid electrolyte interphase (SEI), which is a passive interfacial, nm-scale film that forms along the electrode/electrolyte (solid/liquid) interface as a result of electrolyte decomposition reactions during electrochemical cycling. Due to the dynamically evolving nature of the SEI, it has proven difficult to design experiments that will reveal details regarding SEI formation mechanisms as well as how its structure and chemistry evolve during electrochemical cycling. The *in situ* ec-S/TEM approach has been used to understand the mechanisms of solid electrolyte interphase formation in lithium ion batteries [2-3]. Within a 1.2M $LiPF_6$ EC:DMC electrolyte, cyclic voltammetry was used to monitor electrolyte reduction while directly imaging SEI nucleation and growth dynamics. **Figure 2** shows the mechanisms of how an electrolyte is reduced from a Au working electrode under electrodeposition conditions. We have also investigated the dynamics of Li intercalation in Si nanowire electrodes [4] and SEI formation on graphite anodes [5-6]. Moreover, this method is currently being used to directly image ion transport at electrochemical interfaces, which is related to electron, charge, and mass transport mechanisms and kinetics.

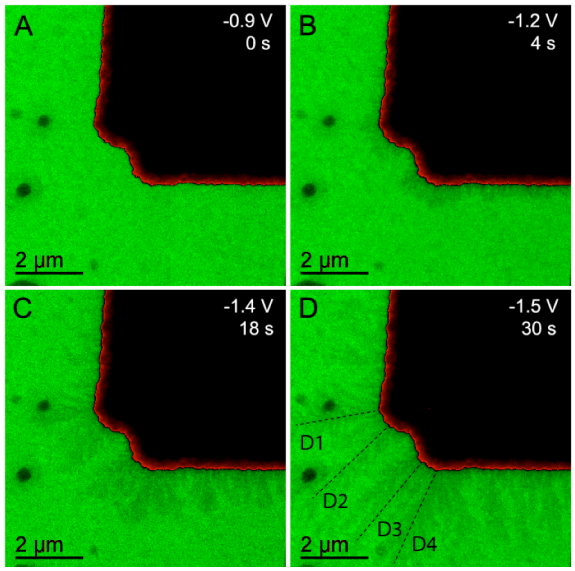

Figure 2. Time-lapsed BF-TEM images (A-D) showing dendritic SEI nucleation and growth from a Au working electrode during electrodeposition.

Significant Impacts on Science and Technology:

The ability to probe electrochemical processes at high spatial and temporal resolution will have a profound impact on how we are able to decipher the fundamental mechanisms of transport phenomena that are related to electrical energy storage and conversion device functionality. The unique suite of advanced *in situ* TEM-based characterization platforms described in this summary will directly benefit a broad scientific user community, where access to unique instrumentation and scientific staff expertise is available for collaborative use through the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory. This is a valuable resource supported by the Department of Energy that can enable innovations that will help solve future challenges in energy-related materials technology.

Publications and Manuscripts:

1. Unocic RR, Sacci RL, Brown GM, Veith GM, Dudney, More KL, Walden FS, Gardiner DS, Damiano D, Nackashi DP, "Quantitative Electrochemical Measurements using *In Situ* ec-S/TEM Devices," Microscopy and Microanalysis, (2013). Accepted.

2. Unocic RR, Sun XG, Adamczyk LA, Alsem DH, Salmon NJ, Dai S, Dudney NJ, More KL, "Visualizing SEI Formation in Li-ion Batteries with *In Situ* ec-TEM," Microscopy and Microanalysis, (2013). Under Review.

3. Sacci RL, Dudney NJ, More KL, Parent LR, Arslan I, Browning ND, Unocic RR, "Direct Visualization of Dendrite Nucleation and Growth Kinetics during Lithium Deposition with *in situ* Electrochemical Transmission Electron Microscopy," Chemical Communications, Accepted and In Press, (2014). [10.1039/C3CC49029G].

4. Gu M, Parent LR, Mehdi L, Unocic RR, McDowell MT, Sacci RL, Xu W, Connel JG, Xu P, Abellan P, Chen X, Zhang Y, Perea DE, Lauhon LJ, Arslan I, Zhang JG, Liu J, Cui Y, Browning ND, Wang CM, "Demonstration of an Electrochemical Liquid Cell for Operando Transmission Electron Microscopy Observation of the Lithiation/Delithiation Behavior of Si Nanowire Battery Anodes," Nano Letters, *13* (12), 6106–6112, (2013). [10.1021/nl403402q]

5. Unocic RR, Sun XG, Alsem DH, Salmon NJ, Dai S, Dudney NJ, More KL, "Application of *In Situ* Electrochemical Liquid Cells for Electrical Energy Storage Research," *Advances in Imaging and Electron Physics,* Proceedings of the Conference on In-Situ and Correlative Electron Microscopy (CISCEM), November 6–7, 2012, Saarbrucken, Germany, 176-177, (2013).

6. Sacci RL, Dudney NJ, More KL, Unocic RR, "Quantitative *In Situ* Electrochemical Liquid Cell Characterization of SEI Formation in Lithium Ion Batteries," Microscopy and Microanalysis, 19, Suppl 2, 418-419, (2013). [10.1017/S143192761300408X]

7. Unocic RR, Baggetto L, Unocic KA, Veith GM, Dudney NJ, More KL, "Coupling EELS/EFTEM Imaging with Environmental Fluid Cell Microscopy," Microscopy and Microanalysis, 18, Suppl 2, 1104-1105, (2012). [10.1017/81431927612007374].

8. Unocic, R. R.; Adamczyk, L.; Dudney, N. J.; Alsem, D. H.; Salmon, N. J.; More, K. In-Situ TEM Characterization of Electrochemical Processes in Energy Storage, Microscopy and Microanalysis 2011, 17, 1564-1565, [10.1017/81431927611008695].