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Quantitative Electrochemistry during In Situ S/TEM Imaging for Energy Storage

Katherine L. Jungjohann[1*], Andrew J. Leenheer[1], Katharine Harrison[2], Nathan T. Hahn[2], C. Tom Harris[1], John P. Sullivan[3], and Kevin R. Zavadil[2]

[1.] Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, New Mexico 87185

[2.] Sandia National Laboratories, Albuquerque, New Mexico 87185

[3.] Sandia National Laboratories, Livermore, California 94551

*kljungj@sandia.gov

U.S. DEPARTMENT OF ENERGY

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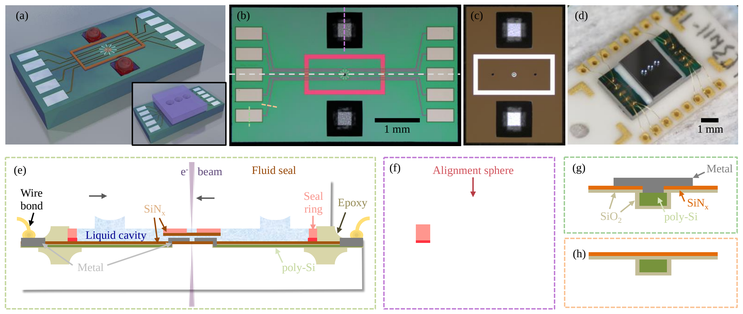
cint.lanl.gov

Electrochemical TEM Platform

The Center for Integrated Nanotechnologies (CINT) has successfully designed a microfabricated liquid cell [1] that can operate with quantitative femtoampere-level current control over 10 ultramicroelectrodes while imaging within a TEM [2]. The electrodes are patterned onto a 50 nm SiN_x membrane window, with a constant fluid gap around 150 nm. Microsphere lenses are used to align the individual top and base of the platform to overlap the 30 μm diameter membrane windows. Liquid is loaded post assembly of the two platform parts by pumping solution into a fluid fill port and allowing capillary forces to fill the cell, then the openings are capped and epoxy sealed. Battery materials are well suited for investigations in this platform for structural changes at electrode surfaces, deposition/stripping, intercalation mechanisms, and solid-electrolyte interphase (SEI) formation. The nanoscale features of these energy materials are clearly visible within the liquid platform with a demonstrated 1 nm spatial resolution [3].

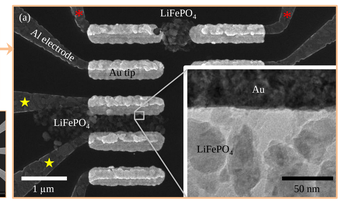


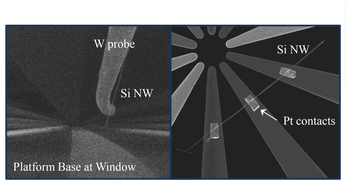
Electrochemical TEM Liquid Platform [2]. (a) Representative schematic of the platform base, inset is the platform top set on the base. (b) Real image of the platform base design, the pink rectangle represents the seal ring, scale bar at 1 mm. (c) Platform top lid from the underneath to show the mating surface to the base, with the SiN membrane in the center with fluid fill ports on either side. (d) Image of the sealed platform wire bonded to a chip carrier that connects to a 16 lead electrical feed through TEM holder. Cross-sectional schematic of the (e) platform operating within the TEM, (f) alignment sphere between the top and base units next to the seal ring, (g) metal electrodes exposed on the base unit, and (h) buried poly-Si traces on the base unit.

Customization and Nanomaterial Integration

Energy storage investigations on nanoscale materials may be conducted by integrating nanoparticles, nanowires, or thin films onto the platform base, then subsequently loading an electrolyte and sealing the cell in an inert atmosphere prior to analysis in the TEM.

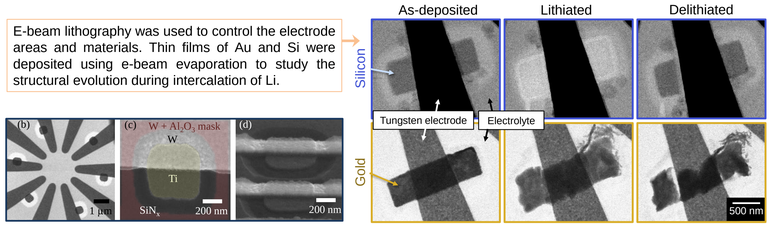
Dielectrophoretic assembly of energy relevant nanomaterials has been demonstrated using patterned Au electrodes with $LiFePO_4$ nanoparticles on the platform base prior to enclosure and liquid loading.

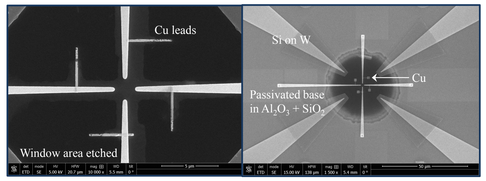




Individual nanowires have been placed on the platform base using a micromanipulator in an SEM with e-beam deposited Pt contacts to the electrodes

E-beam lithography was used to control the electrode areas and materials. Thin films of Au and Si were deposited using e-beam evaporation to study the structural evolution during intercalation of Li.





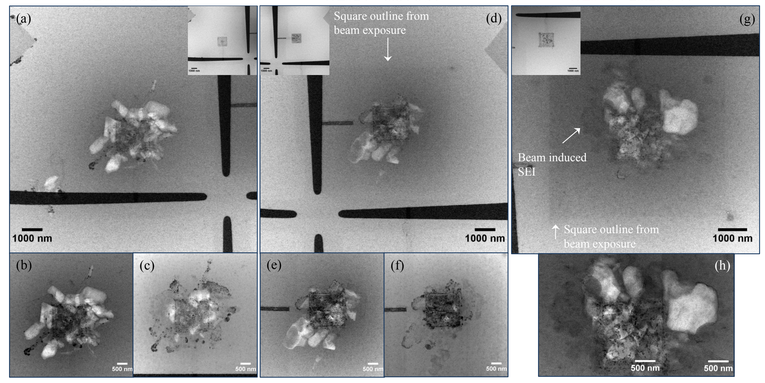
Li deposition/stripping studies in 4 M LiFSI in DME used a custom patterned platform with deposited thin Cu leads coated with a passivation layer of Al_2O_3 and SiO_2. The window regions around the electrodes were etched to minimize increased background scattering during TEM imaging. Cu electrodes of ~1 μm^2 and large >100 μm^2 Si electrodes were exposed to electrolyte.

Electron Beam Artifacts

Electron beam artifacts on liquids confined within a thin gap for investigations on processes and materials in the TEM can be substantial. The electron beam transmits through the sample, resulting in scattering which produces the contrast in the bright-field scanning TEM (STEM) images, shown here. Inelastic scattering of the incident electrons with elements in the liquid transfers energy resulting in breaking bonds and excited states. During electrochemical cycling of energy storage materials in organic solvents this may result in unintended features observed resulting from the electron beam an not from the process under investigation.

4 M LiFSI in DME on Cu: Galvanostatic Control of +/- 10 pA for 2 min of 10 cycles

WE#3 : No Beam WE#1 : < 3.84 e⁻/Å² WE#4 : < 20.16 e⁻/Å²

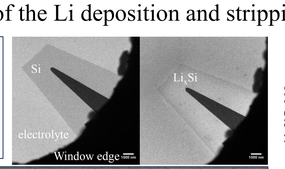


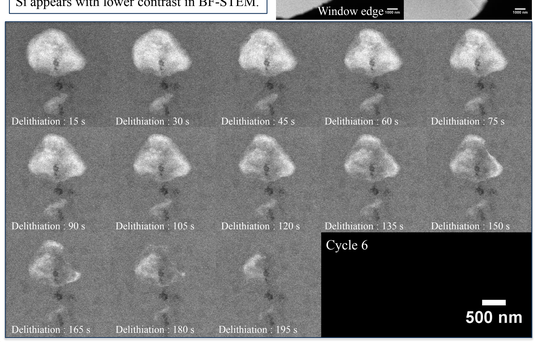
Comparison of electron beam artifacts on cycling of Li deposition and stripping on Cu electrodes. (a-c) No exposure to electron beam during Li cycling. (d-f) Total electron dose of < 3.84 e⁻/Å² with imaging at the end of each cycle step. (g-f) Total electron dose of < 20.16 e⁻/Å² with image acquired every 15 s throughout cycling. Inset images display the electrodes prior to cycling. Images (b),(e), and (h) were taken at the end of cycling the electrode. Images (c) and (f) were acquired at the end of the experiment, where self discharge significantly reduced the volume of residual Li on the electrode surface. A darkened square can be observed about the beam exposed electrodes caused by damage to the electrolyte in the form of polymerized carbon chains. Beam induced SEI was also observed at the highest beam dose.

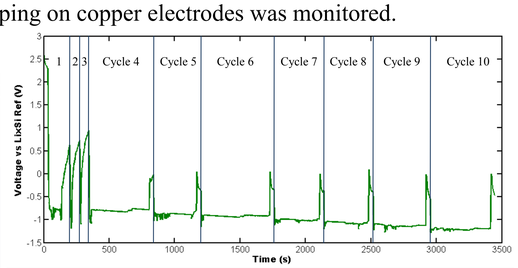
Morphological and Electrochemical pairing of Li Deposition and Stripping on Cu Electrodes

To meet the increased demand for high power energy storage for grid and transportation applications, a stable highly efficient Li metal battery electrode is being investigated. The system is dependent on the formation of a solid electrolyte interphase that is capable of suppressing Li dendrite formation, which is the limiting characteristic that prevents application of high capacity Li metal anodes in current lithium ion batteries (LIBs). The SEI layer that is formed between the electrolyte and the Li metal electrode is dependent on the breakdown of the Li containing electrolyte. We investigated lithium bis(fluorosulfonyl)imide (LiFSI) in dimethoxyethane (DME) for suppressed Li dendrite formation. The morphological evolution of the Li deposition and stripping on copper electrodes was monitored.

Si electrodes were lithiated from the 4 M LiFSI in DME electrolyte to be used as a quasireference electrodes during Li deposition and stripping on Cu electrodes. Lithiation of the 500 μm^2 Si electrode was conducted for 18 min at -100 pA. Lithiated Si appears with lower contrast in BF-STEM.

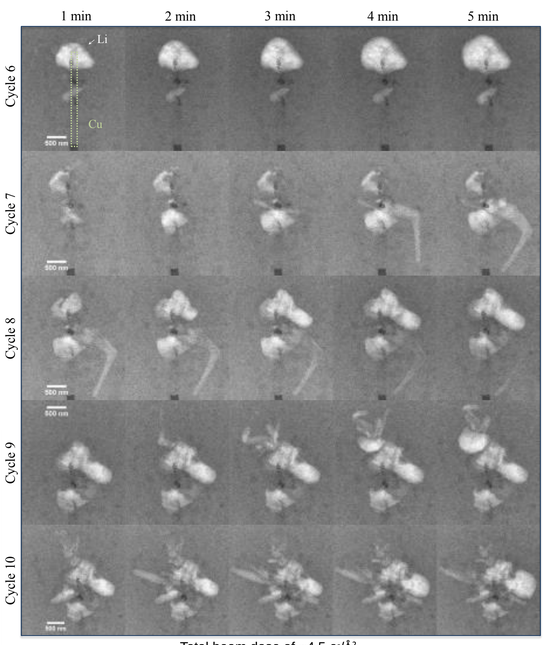






Small patterned Cu electrodes enabled imaging of Li deposition and stripping at a current density of 2.25 mA/cm². The initial three cycles did not deposit Li on the electrode, likely due to a weak passivation barrier on the surface. Cycles 4 and 5 majorly deposited Li on an exposed region of the W electrode, micrometers from the Cu lead. In Cycles 6 – 10, the Li deposition demonstrated increase number of nucleation sites for Li deposits as previous grains become disconnected from the electrode. The initial deposit formed a porous structure, whereas the later cycles grew compact single grains and dendrites. Coulombic efficiency during these cycles was low, ranging from 5 – 58%. Dissolution of Li grain on Cycle 6 shows collapsing of the structure with preferential regions. Li dissolution of disconnected deposits was observed during subsequent Li deposition cycles, cycles 7 - 8. This characteristic may be responsible for the formation of LiF in the SEI, contributing to a stable interphase layer. These results demonstrate the variance of evaluating electrode morphology on the micro to nanoscale compared to bulk properties.

4 M LiFSI in DME on Cu: Galvanostatic Control of - 10 pA



Total beam dose of ~4.5 e⁻/Å²

CINT User Proposals to Access the Platform

CINT is a Department of Energy/Office of Science Nanoscale Science Research Center (NSRC) operating as a national user facility devoted to establishing the scientific principles that govern the design, performance, and integration of nanoscale materials. Through its Core Facility in Albuquerque and Gateway to Los Alamos Facility, CINT provides open access to tools and expertise needed to explore the continuum from scientific discovery to the integration of nanostructures into the micro- and macro world. User proposals are accepted in the months of March and September, active user proposals last a duration of 18 months. Proposals entail a 2 page description of the proposed research project, impact of the research, experimental outline, details on user's contribution, and details on CINT's contribution. The user proposals are evaluated by a team of external reviewers on the merit of the proposal in relation to nanoscience and potential impact on the community.

References:

[1] M. J. Williamson *et al*, Nat. Mater. **2** (2003), p. 532.

[2] A. J. Leenheer *et al*, J. Microelectromech. S. **99** (2015), 10.1109/JMEMS.2014.2380771.

[3] This work was performed at the Center for Integrated Nanotechnologies (CINT), a U.S. DOE Office of Basic Energy Sciences (BES) user facility. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly-owned subsidiary of Lockheed Martin Corporation, for the U.S. DOE's National Nuclear Security Administration under contract DE-AC0494AL85000. Portions of this work were supported as a part of the Nanostructures for Electrical Energy Storage (NEES), an Energy Frontier Research Center funded by the U.S. DOE, Office of Science. Other portions were supported by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. DOE, Office of Science.

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