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Visualizing Li Deposition in Solvate Electrolytes

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Abstract

Li-S is a promising prototype for transportation batteries for its potential to achieve \$100/kWh and 400 Wh/L. To achieve these metrics, the barriers for the Li anode and electrolyte stability must be overcome. In focusing on the Li anode, protection schemes are being pursued to protect the Li metal interface for reduction of Li dendrite formation and control over the overall Li deposition morphology. Morphology control should provide conditions for reproducible Li deposition and stripping, whereby the energy density is conserved by reducing the amount of dead Li on the anode surface.

Direct imaging of Li nucleation and growth on electrode surfaces in solvate electrolyte systems allows for a greater understanding of the mechanisms that control Li morphology. This nanoscale view of the process is achieved using in-situ electrochemical transmission electron microscopy (TEM) for quantitative relationship between the electrochemical signals and the Li structural evolution on the electrode surface.

Goals

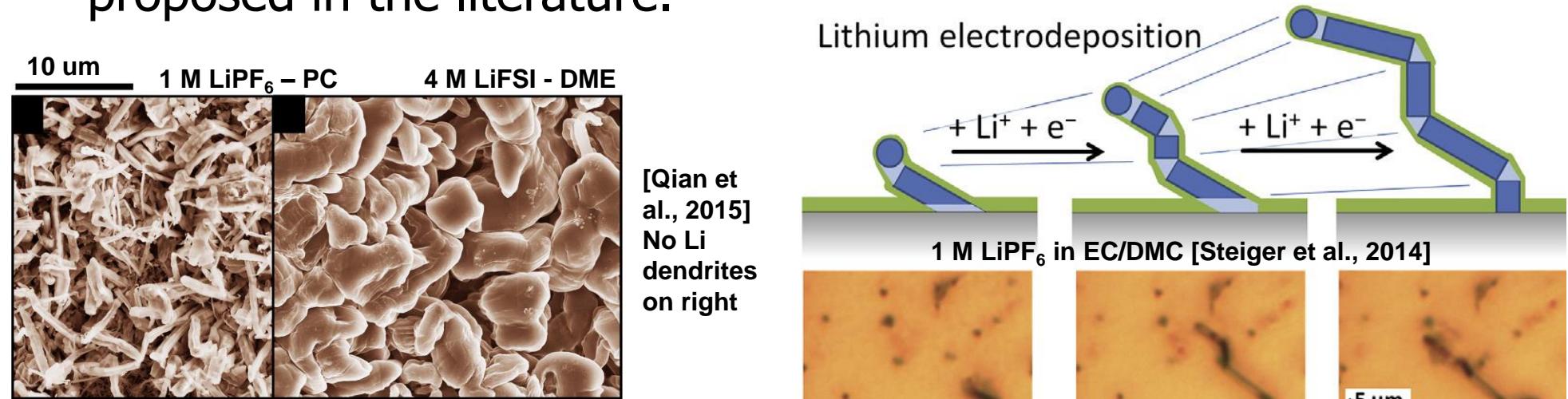
Overall Goal: To determine the controlling factors for initial Li deposition/dissolution in solvate electrolytes that can cause dendrite formation.

Hypothesis: Initial Li nucleation occurs at specific locations on a metal electrode, possibly due to defect electrode surface structure, solid-electrolyte-interface (SEI) structure/composition in that region, or current focusing through surface structures. Li morphology is a result of ion transport to the depositing Li grains in these specific regions.

Project Goal: Implement protection strategies at the Li surface to control Li morphology during cycling and to prevent reduction of active Li in the system.

Background

Visualization of Li morphology using optical microscopy has provided evidence of Li growth on high aspect ratio grains to occur at the base, tip and at kinks. This is in contrast to the multiple Li dendrite growth models that have been previously proposed in the literature.



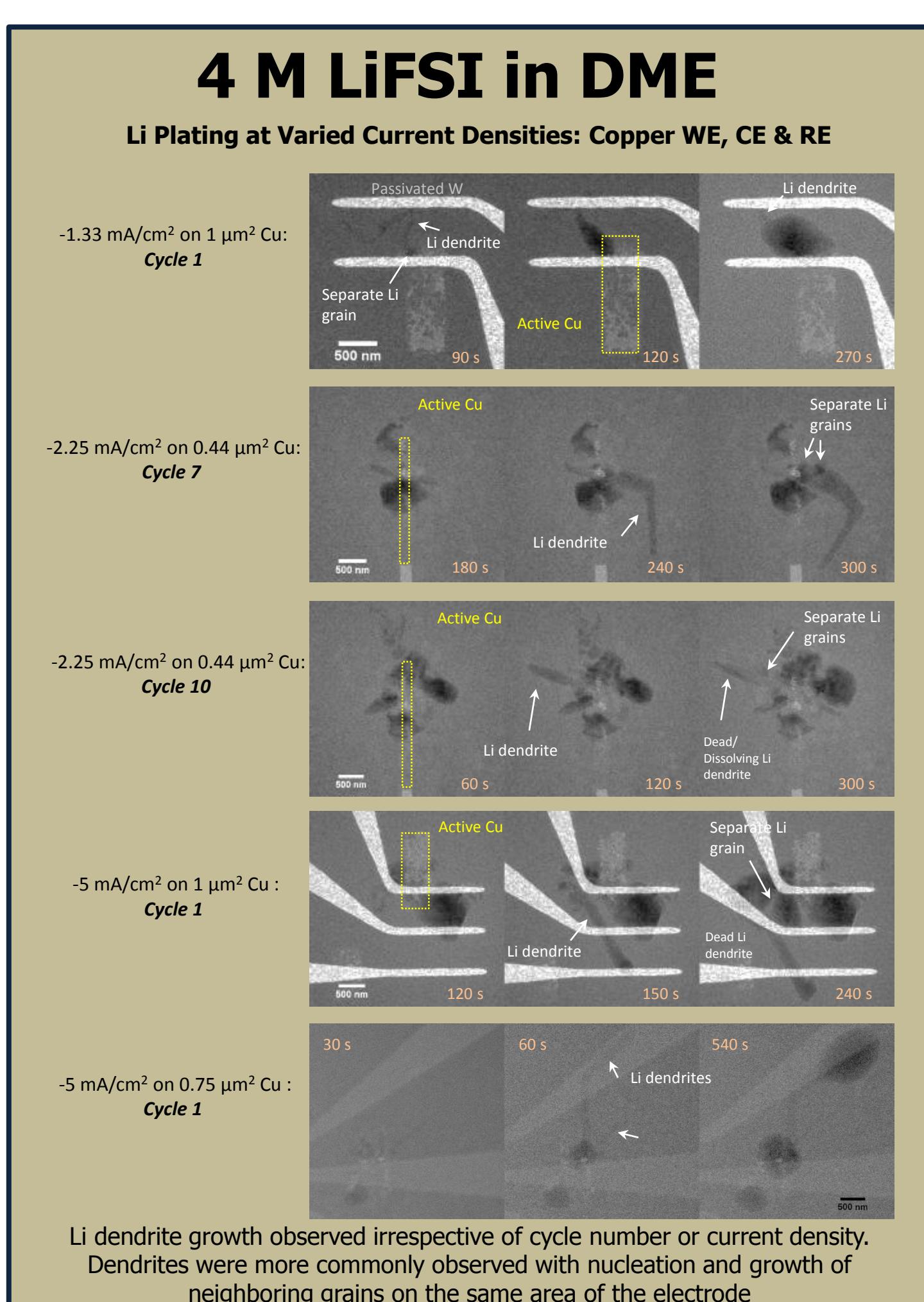
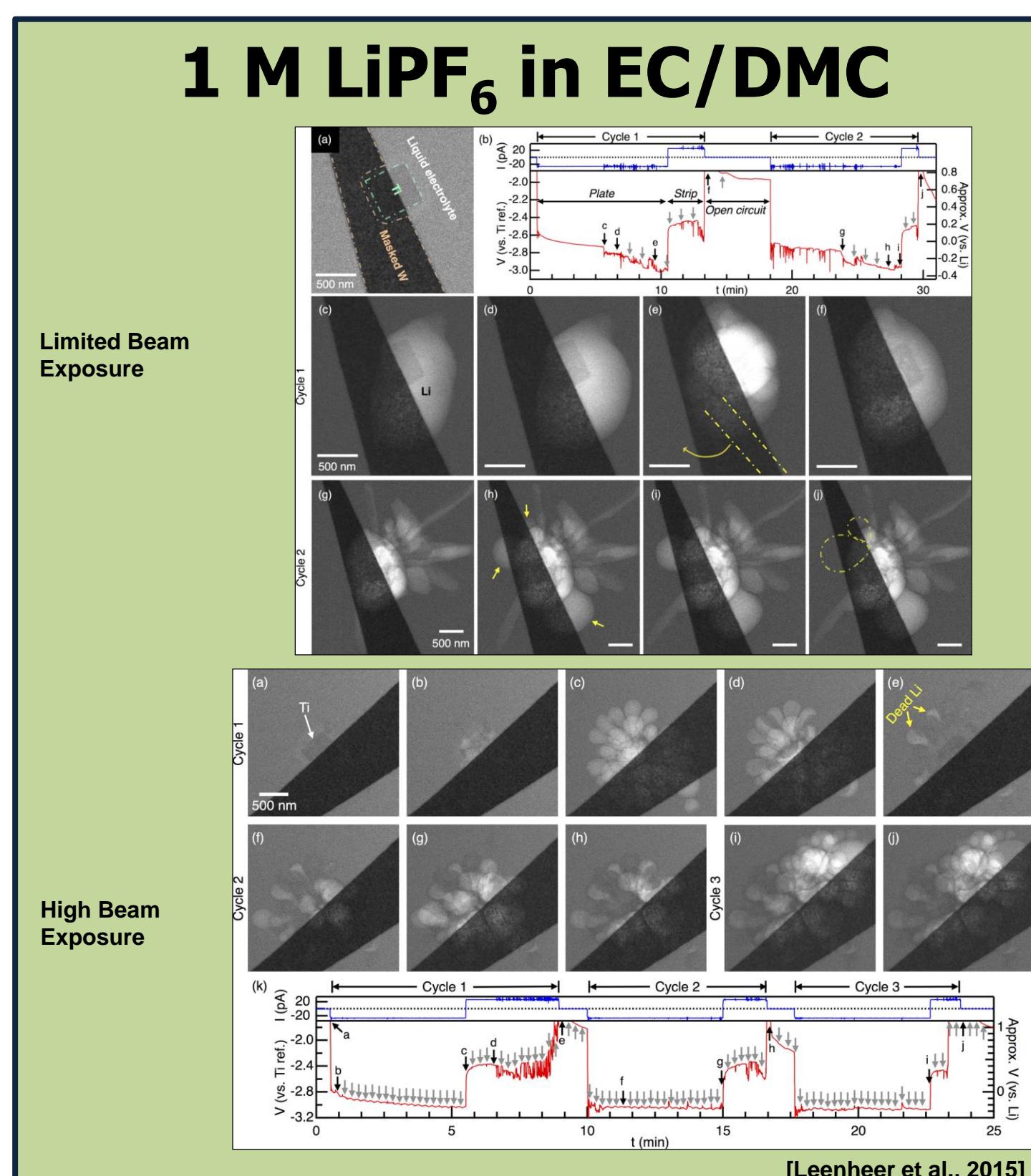
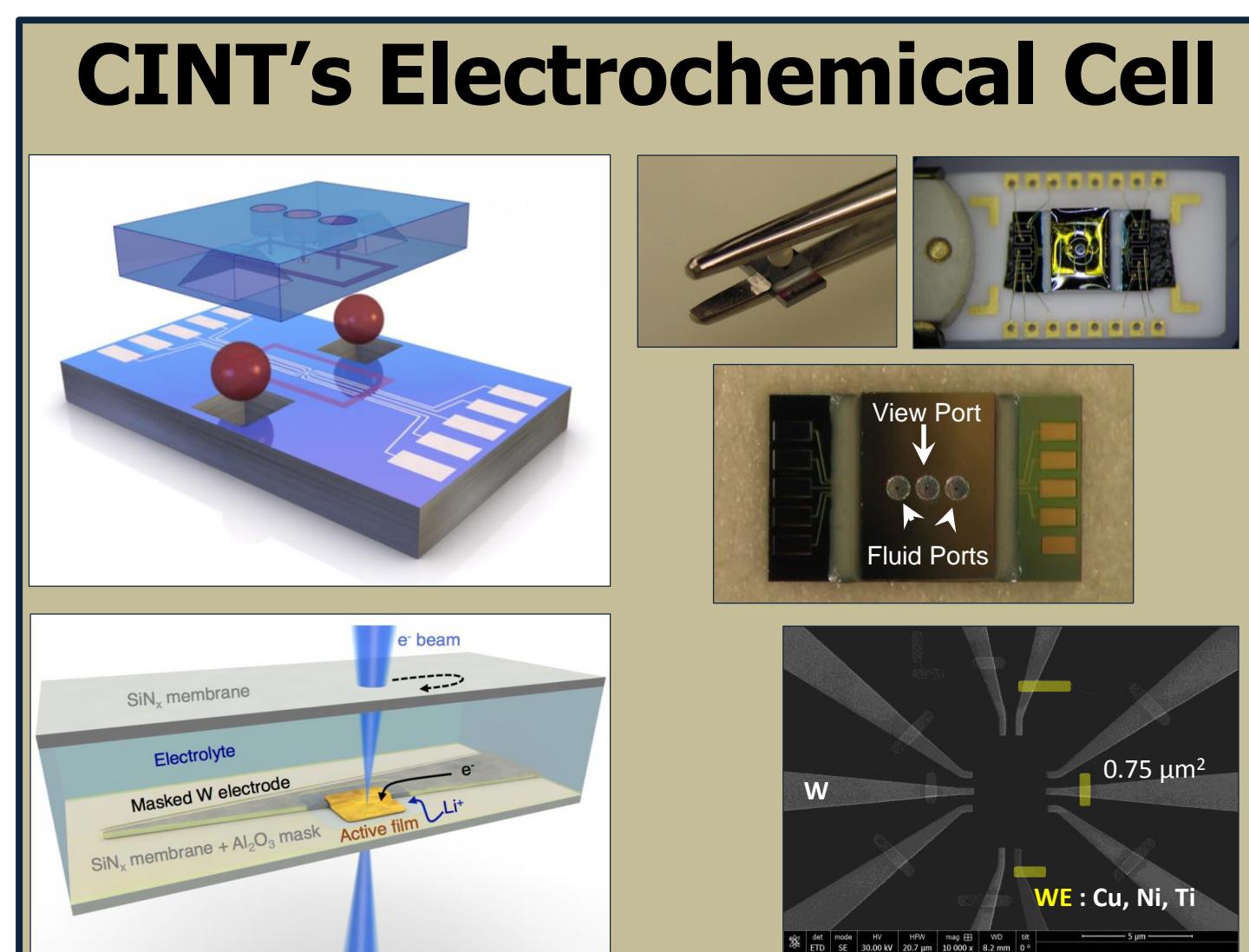
Competing Li Dendrite Growth Models:

- Uneven SEI layers on electrode form cracks [Cohen et al., 2000]
- SEI cracks, dendrite growth from the base [Yamaki et al., 1998]
- Electric field enhancement at the tip or protrusions [Ding et al, 2013]
- 3D ion diffusion dominant at protrusions [Monroe and Newman, 2003]
- Ion concentration polarization causing space charge [Chazalviel, 1990]

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Supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science. Experiments were performed and technology was developed at the Center for Integrated Nanotechnologies, a DOE-BES supported national user facility. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND No. 2011-XXXXP



In-Situ Electrochemical TEM

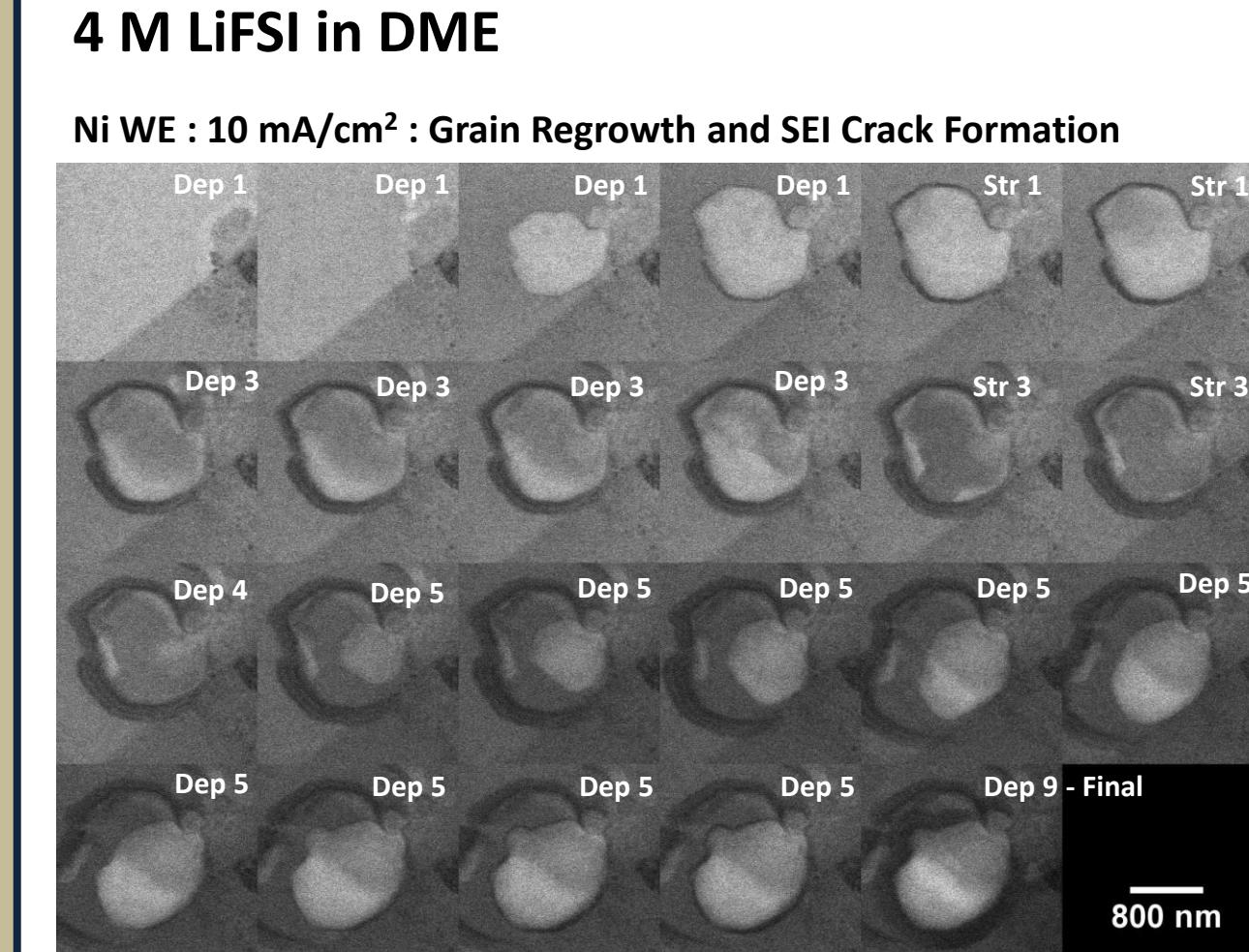
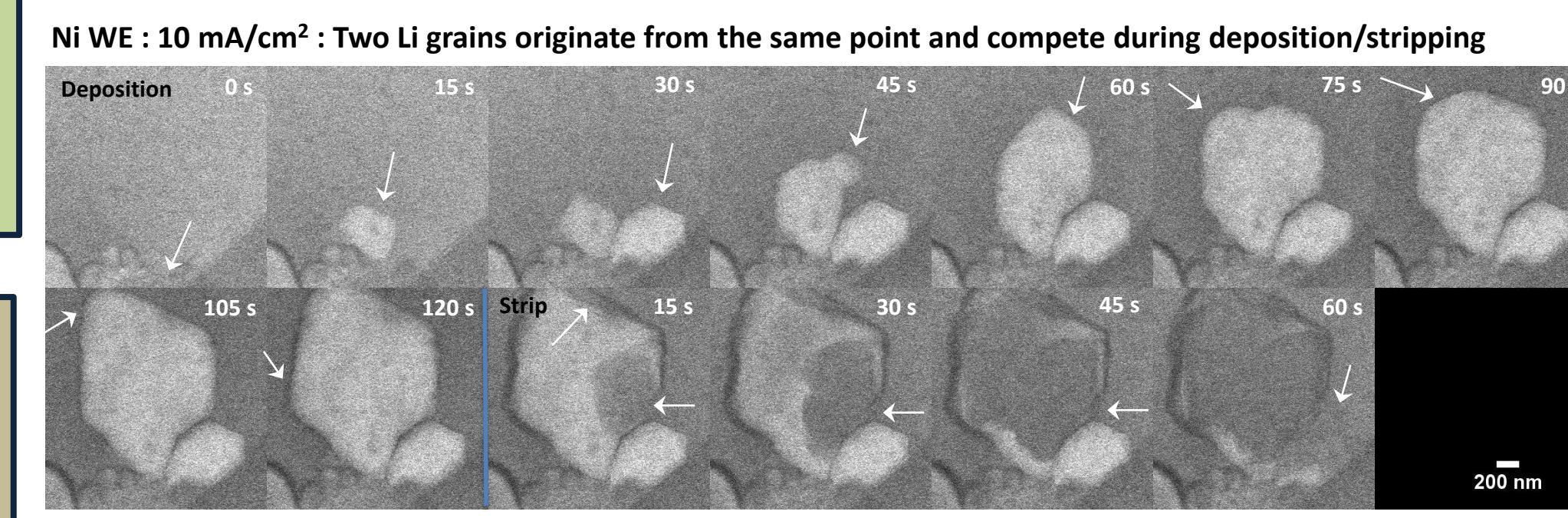
Direct imaging of early stage Li growth can be observed using electron microscopy coupled with an electrochemical platform for enclosure of volatile electrolytes within the high vacuum environment of the TEM. Galvanostatic cycling of ultramicroelectrodes allows for direct correlation between the electrochemical behavior and structural evolution at the electrode. Li deposition/dissolution observation was conducted to formulate a growth model.

CINT's Electrochemical TEM Platform Attributes:

- 10 Custom Designed Electrodes
- Multiple Experiments on Same Platform
- Beads Simplify Window Alignment
- Liquid Thickness > 120 nm
- Passivated Leads to Localize Electrochemistry
- Picoampere Current Control
- Chemical Compatibility with Cell
- Conduct in-situ & ex-situ testing

Li Deposition/Dissolution

Li deposition morphology on ultramicroelectrodes for the solvate electrolyte (4 M LiFSI in DME) was compared to the standard electrolyte used in Li-ion batteries (1 M LiPF₆ in EC/DMC). Dendrite growth was observed in both electrolytes regardless of cycle number or current density. The electron beam was shown to control the Li morphology under high beam dose conditions.



Observations:

- Li grain nucleation occurred at high electron conduction regions of the electrode surface
- Ion transport influences the preference of neighboring growing Li grains
- SEI continues to deposit on Li grains during deposition steps
- Incomplete stripping of Li observed at SEI interfaces, unless the grain disconnects at base
- SEI crack during Li grain regrowth did not nucleate a dendrite, though a nodule formed
- Growth at the electrode/electrolyte/Li grain interfaces was most commonly observed, second being cap formation on top of a Li grain

Future Work

- Li deposition/dissolution from evaporated Li metal electrodes
- Implement protection layers on Li electrodes to study changes in Li morphology during deposition/dissolution
- Identify processes of Li metal accommodation at the protective film/electrode interface
- Enhanced imaging will be obtained using direct electron detection camera to increase frame rates during imaging while retaining low-dose electron beam conditions