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Cryogenic Electron Microscopy for Understanding Energy Storage

Katherine L. Jungjohann,[1] Katharine L. Harrison,[1] Robert Fischer,[2] John Watt,[3] and Subrahmanyam Goriparti [1]

[1] Sandia National Laboratories, Albuquerque, NM 87185; [2] University of Oregon, Eugene, OR 97405, [3] Los Alamos National Laboratory, Los Alamos, NM 87544

U.S. DEPARTMENT OF ENERGY
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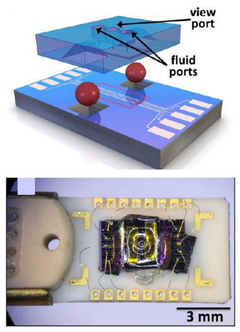
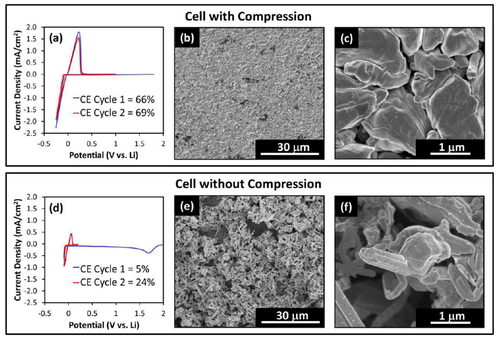
Need for Liquid-Solid Interfacial Characterization for Li-Ion Batteries

Lithium metal electrodes present a 10x increase in energy storage capacity, if the lithium metal can be electrodeposited and removed without the formation of filament structures which cause internal shorts. Many variables impact the electrodeposited Li metal morphology, including temperature, environment, pressure, current density, initial surface roughness, electrolyte, and electrolyte additives.[1] In this work, we have found that contact pressure on the electrodes greatly changes the Li metal morphology. Cryogenic scanning electron microscopy (cryo-SEM) and focused ion beam (cryo-FIB) are necessary to preserve the electron beam sensitive structures. Future implementation of cryo lift-outs for transmission electron microscopy (TEM) and chemical analysis is planned for mapping solid-liquid interfaces.



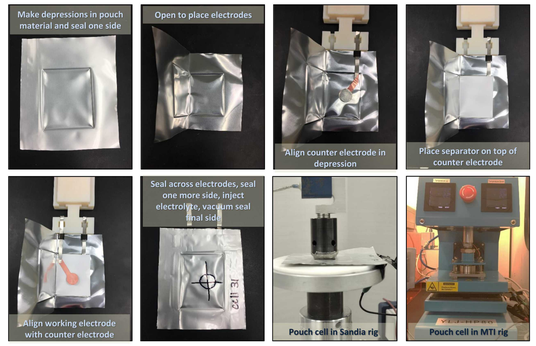


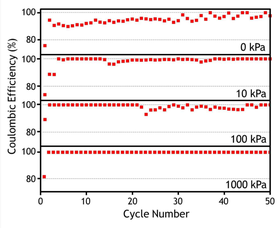
In-situ electrochemical STEM observed Li grain morphology that was uncharacteristic from what was observed in bulk geometries in identical electrolytes with the same current collector material.[2,3] It was determined that the lack of surface compression during the in-situ STEM results was the critical factor for the changes in Li cycling performance and Li morphology, which was proven in bulk electrodes with and without surface compression. Coulombic efficiency greatly improved with compression and a dense filament-free Li layer was observed.[3]

Compression Impact on Li Morphology

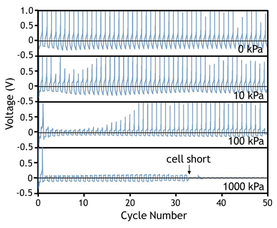
Contact pressure on the surface of the Li electrode will impact the cycling performance and the electrodeposited Li morphology.[4] Constant pressure was applied using load frames on pouch cells.

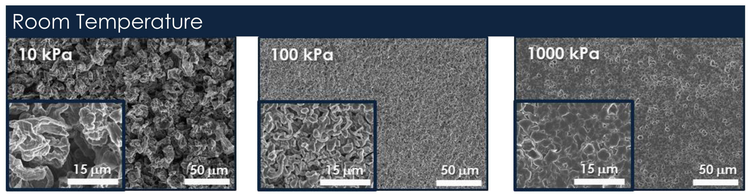
Copper foils were loaded vs. 50 µm Li metal on copper with Celguard separators in between. Extra space in the pouch allowed excess electrolyte to move under compression.





- Coulombic efficiency ↑ with pressure ↑
- Overpotential ↓ with pressure ↑
- Denser, smaller features with pressure ↑
- Cells short at very high pressure→ indicates there is an optimal pressure

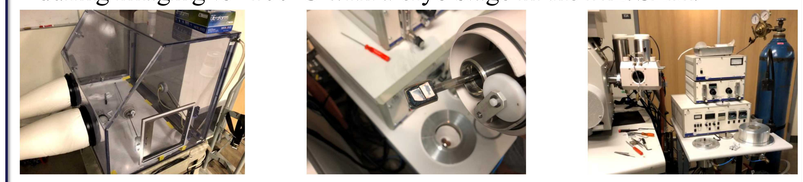




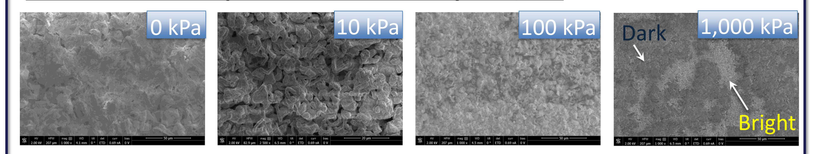
Scanning electron micrographs of the electrodeposited Li metal working electrode surface after removal from a pressure controlled pouch cell at: 10, 100, and 1,000 kPa after 50 deposition/stripping cycles vs. Li metal.

Cryogenic SEM of Li Morphology

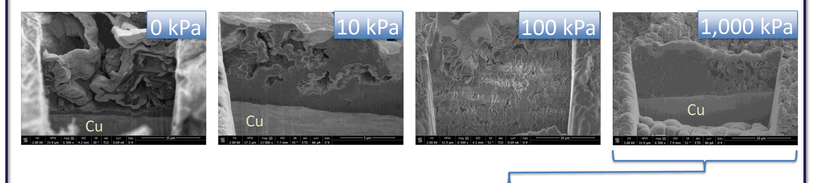
Inert (air-free) transfer of Li working electrodes from the glovebox to the SEM cryo-transfer arm, where Li samples were plunge frozen into a liquid nitrogen slush under vacuum, then cooled during imaging to -100°C with a cryo stage in the FIB/SEM.



Surface of Electrodeposited Li Metal with Cryo-FIB/SEM

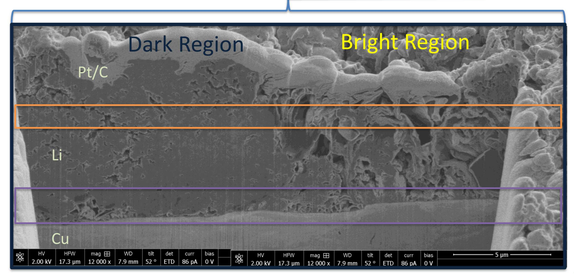


Cross-sections of Electrodeposited Li Metal on Cu with Cryo-FIB/SEM



1,000 kPa
Li porosity changes
- dark (low) vs. bright (high) region

Li nucleation on Cu
- Many deposits initiated in bright region, fewer in dark region



CINT's Cryo-EM Suite

The Center for Integrated Nanotechnologies (CINT) is a DOE-Basic Energy Sciences national user facility to provide expertise and instrumentation free of charge to support accepted peer-reviewed nanoscience research. Access to instrumentation is provided upon acceptance of a 2-page proposal. September 30th, 2019 is the deadline for user proposal submissions for 18-month projects on our website: cint.lanl.gov.

Vitrobot
Captures native, solvated state

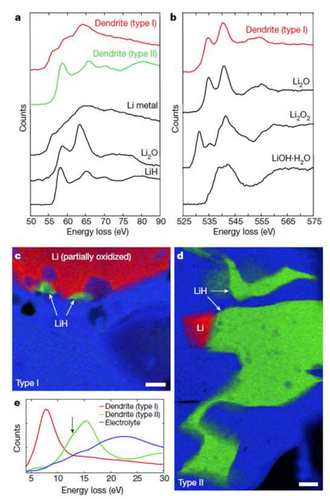
Scios FIB/SEM
Analysis of surfaces & buried interfaces; 3D tomography

Leica Cryo SEM Stage
Includes cryo-FIB milling, lift out, and transfer to the TEM

Talos L120C CryoTEM
Dedicated low dose, low keV TEM for imaging of beam sensitive materials

Future Directions of Using Cryo-EM for Liquid-Solid Interfacial Characterization

Cryo-FIB has allowed for unperturbed imaging of the Li morphology, deposited under varied contact pressures, in order to define limitations in cell performance and causes of failure. The next steps will be the preparation of FIB lift-out TEM samples for atomic-scale imaging and elemental analysis of the solid-liquid interfaces. Understanding of the electrode as a whole is necessary for defining which regimes to investigate within the TEM and how statistically relevant those features are to the morphologically heterogeneous material. Future studies will also use grain mapping with electron backscattered diffraction and energy dispersive x-ray spectroscopy to identify the grain structure of these metal electrodes and the reactions with the electrolyte.



Zachman et al. *Nature* **560**, 345 (2018)

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2. Leenheer et al. *ACS Nano* **9**, 4379 (2015)
3. Harrison et al. *ACS Nano* **11**, 11194 (2017)
4. Jungjohann et al. *Microsc. Microanal.* **25**(S2), 2040 (2019)
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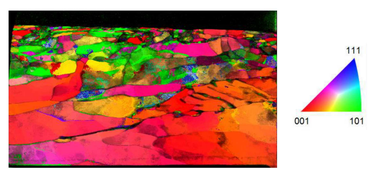

Acknowledgement

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