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Visualization of Early Li Growth Morphology

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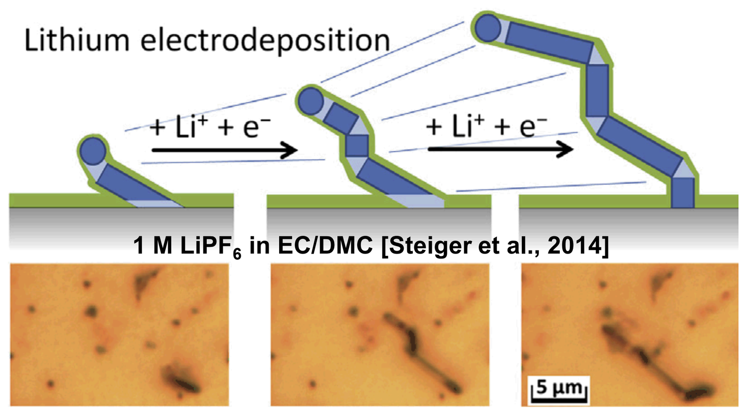
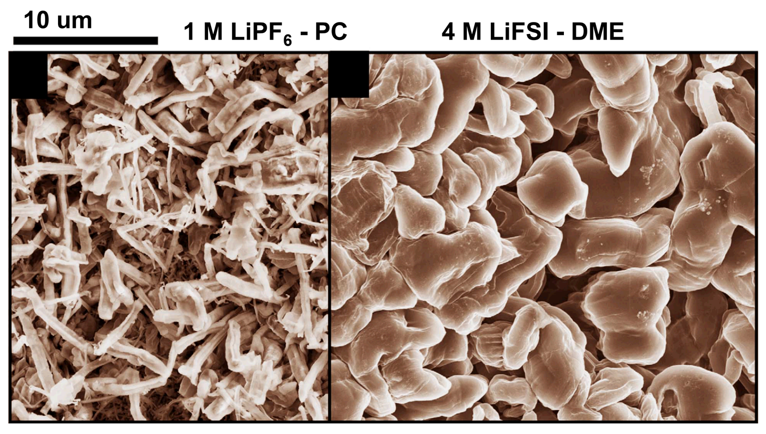
Li Anodes: Understanding Dendrite Growth

In the application of Li-S and Li-O battery systems, Li anodes provide increased energy density, though dendrite formation upon charging prevents their use in commercial systems. 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.



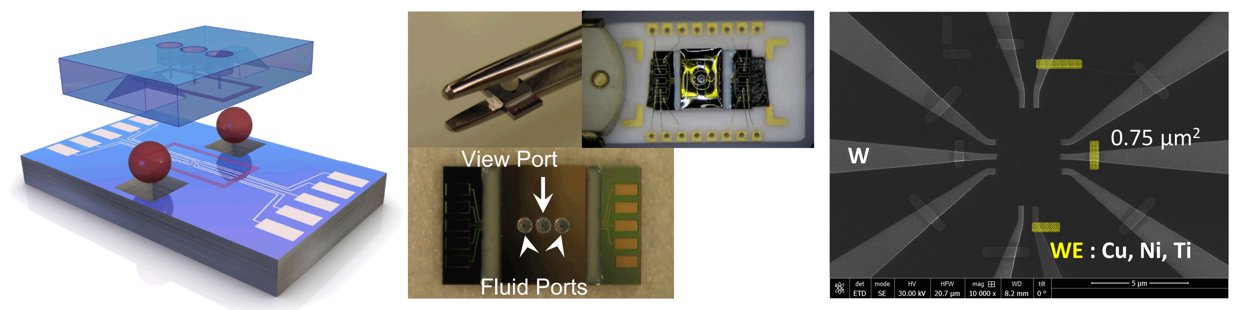


[Qian et al., 2015]
No Li dendrites on right

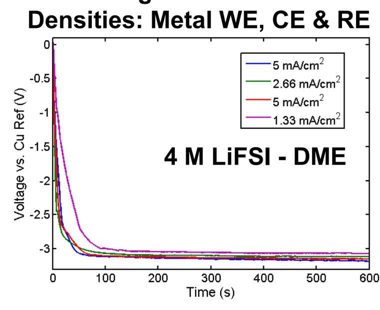
Competing Li Dendrite Growth Models:

- 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]

Electrochemical S/TEM Imaging

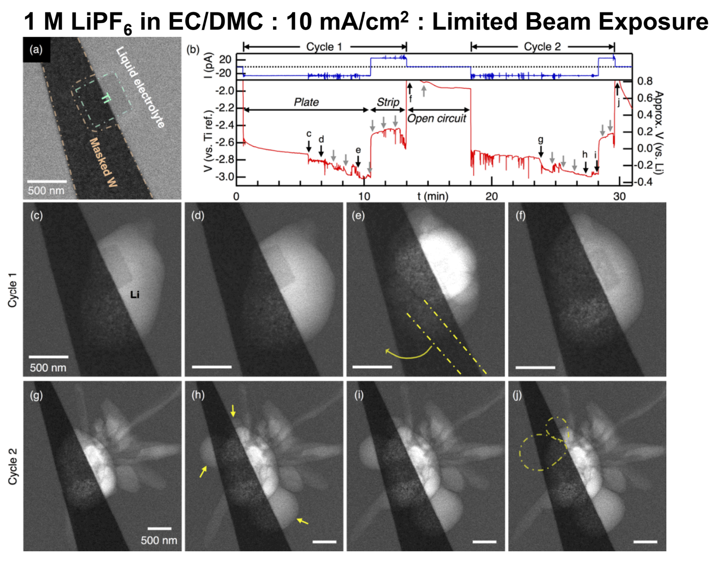


Li Plating at Varied Current Densities: Metal WE, CE & RE

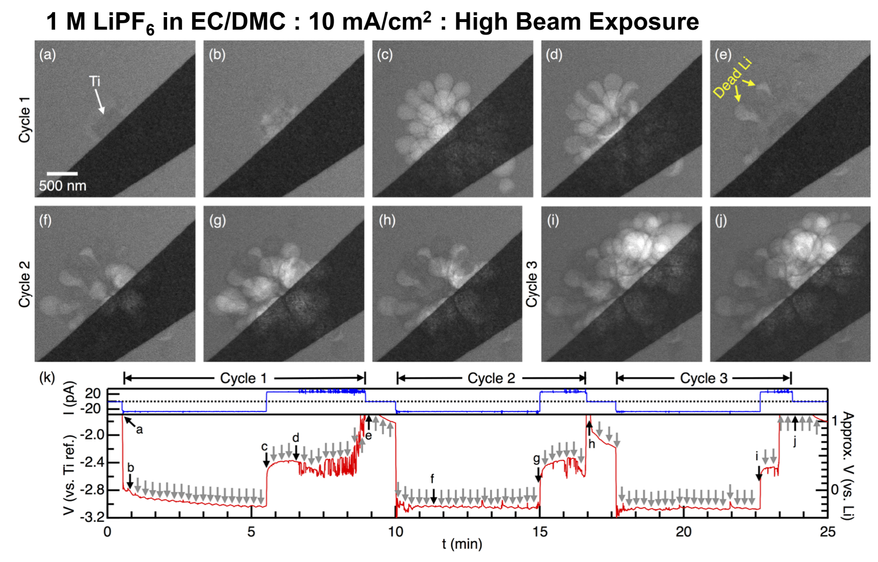


Direct imaging of early stage Li growth can be observed using electron microscopy coupled with an electrochemical platform for enclosure of volatile electrolytes within the high vacuum environment in the TEM. Quantitative cycling of electrodes is demonstrated with picoampere current control of 10 independent ultramicroelectrodes. Controlled even liquid layers of 150 nm have been achieved. Li deposition/dissolution observation to formulate a growth model.

1 M $LiPF_6$ in EC/DMC : 10 mA/cm² : Limited Beam Exposure



1 M $LiPF_6$ in EC/DMC : 10 mA/cm² : High Beam Exposure

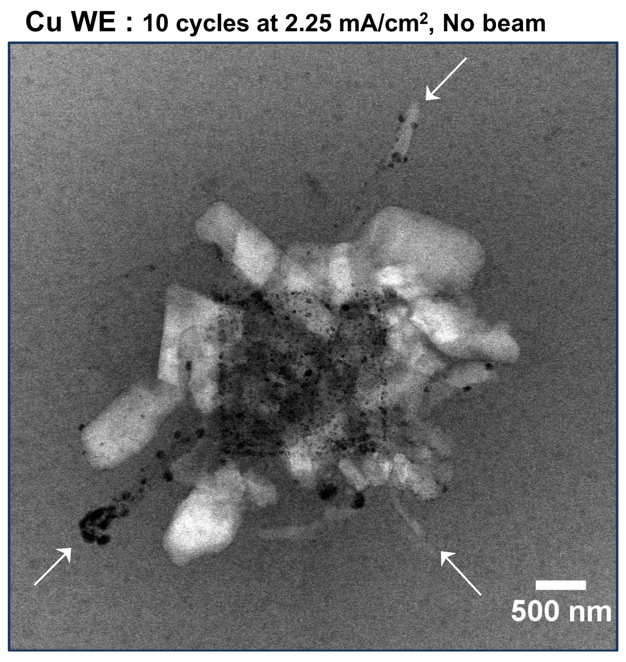


[Leenheer et al., 2015]

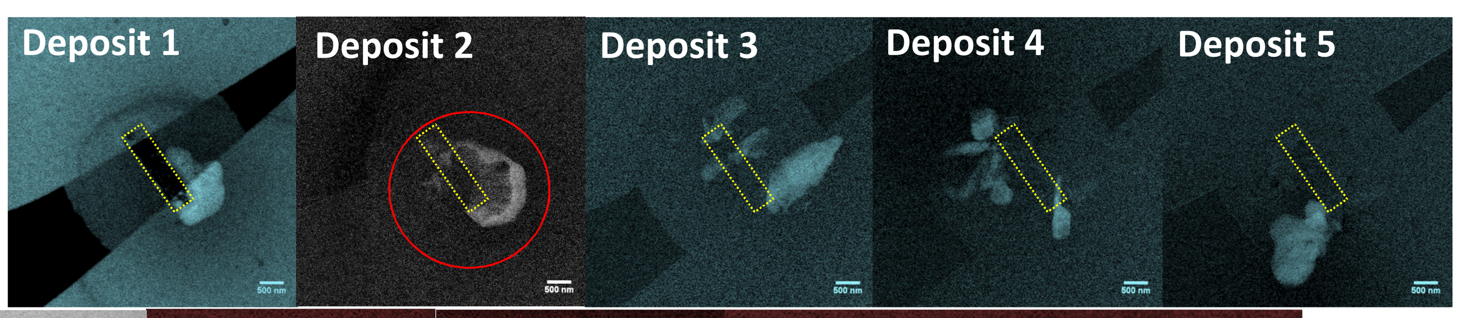
Cycling Li in 4 M LiFSI in DME

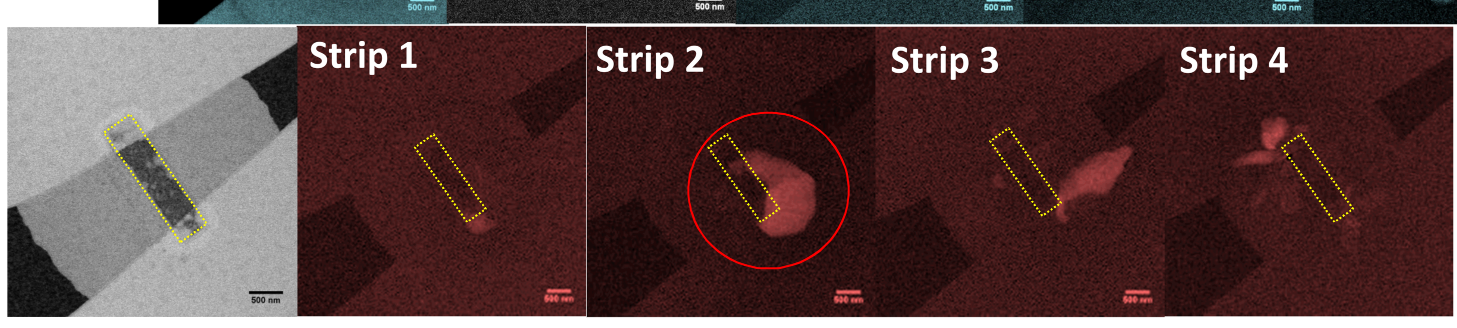
In the development of Li anodes for a Li-S transportation battery, development of electrolytes and surface coatings are being pursued to prevent Li dendrite growth. Zhang's group at PNNL has demonstrated reduced Li whisker formation upon deposition in 4 M LiFSI in DME electrolyte. We began testing this electrolyte in comparison to previous results with 1 M $LiPF_6$ in EC/DMC to determine differences in the Li growth model between the electrolytes to explain this observation. In the absence of a separator, we still observe high aspect ratio grains forming.

Cu WE : 10 cycles at 2.25 mA/cm², No beam

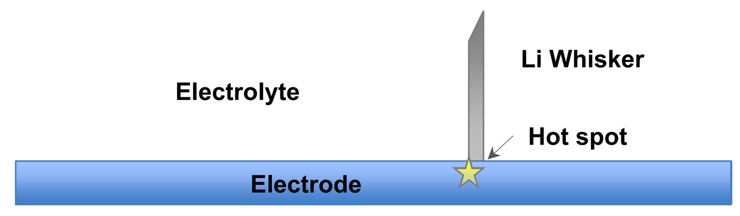


Ni WE & CE : 10 cycles at 10 mA/cm² (50 pA), beam current: 0.12 nA





Li Whisker Growth at Base



The hot spot usually allows for multiple grains to nucleate from the same point, generally multiple grans are observed when a whisker forms. This has led to disconnection of the Li whisker from the electrode if a low-aspect ratio grain forms. SEI is possibly carried away during growth, so SEI remains thin at insertion site [Steiger et al., 2014]. Commonly we observe Li nucleation and growth in the same 'hot spots' even though SEI has build up around the region.

- Incorporation of SEI into Li grains?
- Growth dependent on crystallinity?
- Inactive region at tip of whiskers?
- SEI composition can create local electron transport regions to plate Li on top of Li deposits?
- Local ion concentration? Space Charge?

4 M LiFSI in DME

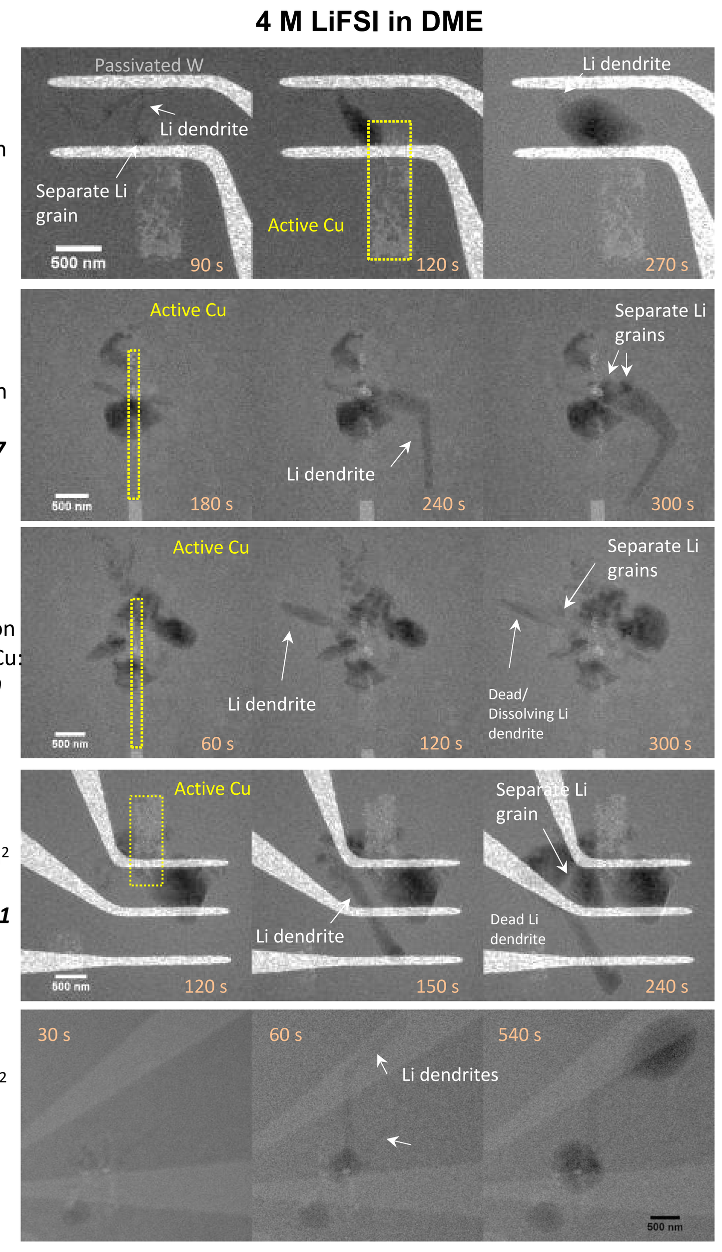
-1.33 mA/cm² on 1 µm² Cu: *Cycle 1*

-2.25 mA/cm² on 0.44 µm² Cu: *Cycle 7*

-2.25 mA/cm² on 0.44 µm² Cu: *Cycle 10*

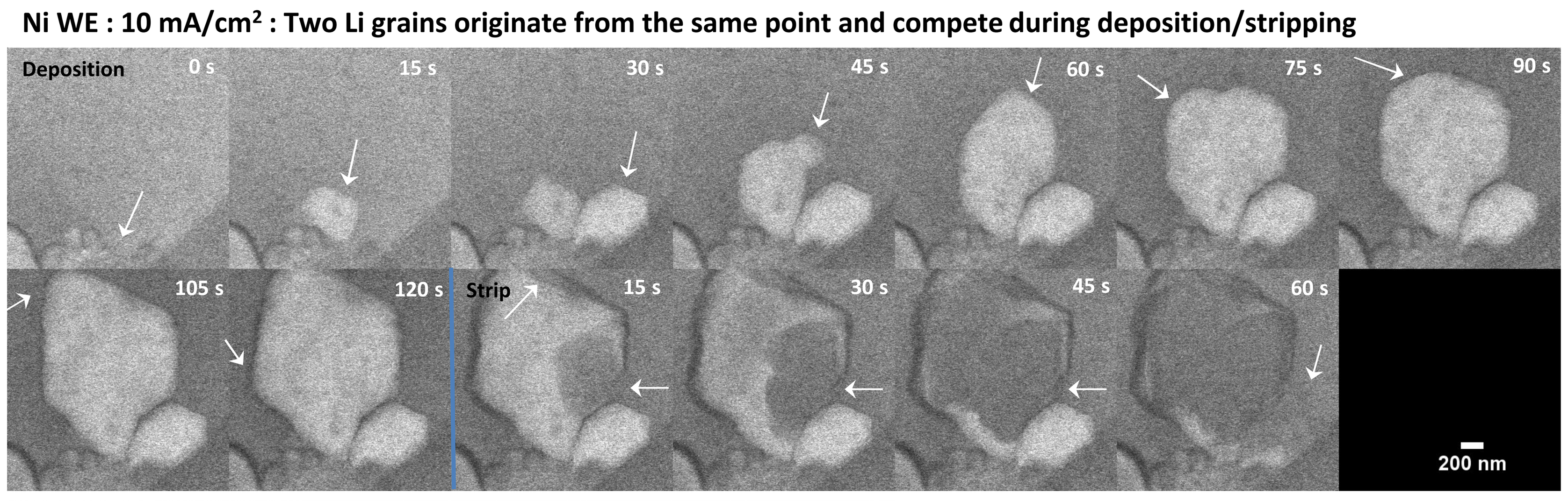
-5 mA/cm² on 1 µm² Cu : *Cycle 1*

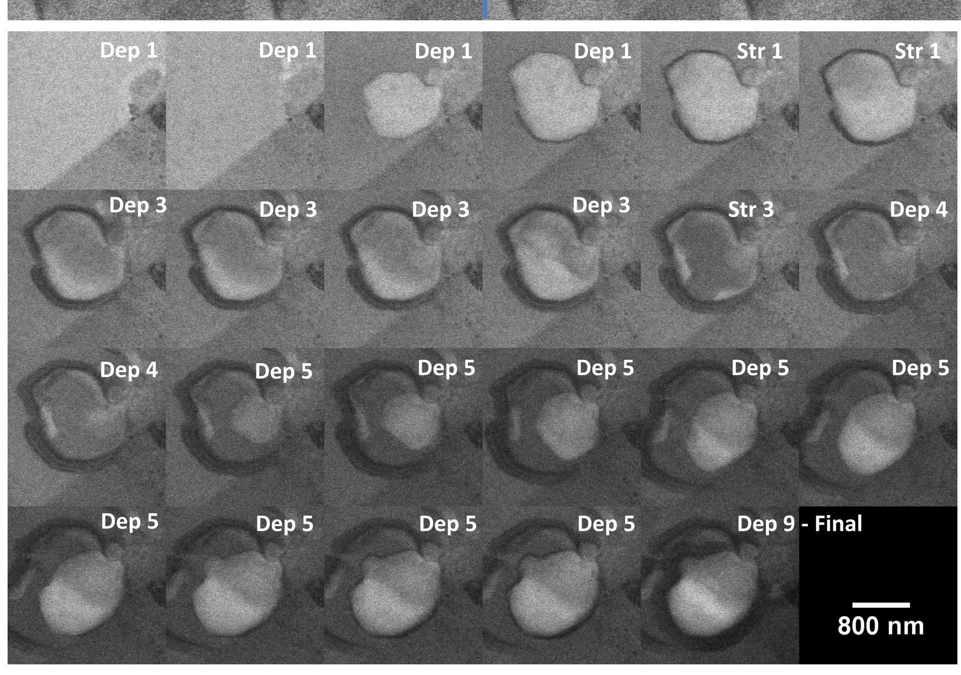
-5 mA/cm² on 0.75 µm² Cu : *Cycle 1*



Li Ion Transport in 4 M LiFSI in DME

Ni WE : 10 mA/cm² : Two Li grains originate from the same point and compete during deposition/stripping



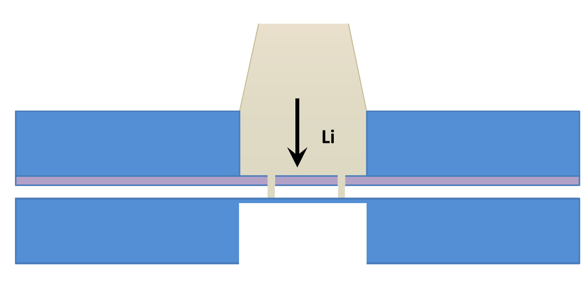


Ni WE : 10 mA/cm² : Grain Regrowth and SEI Crack Formation

Observations:

- Li grain nucleation occurred at high electron conduction regions of the electrode surface
- Ion transport influences 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

Li Evaporated Electrodes – Test Protection

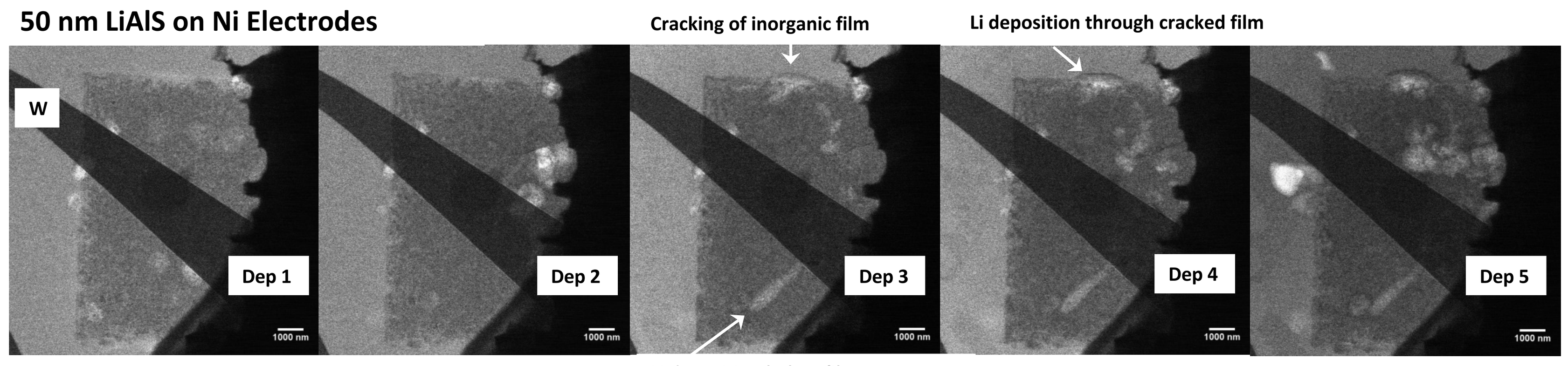


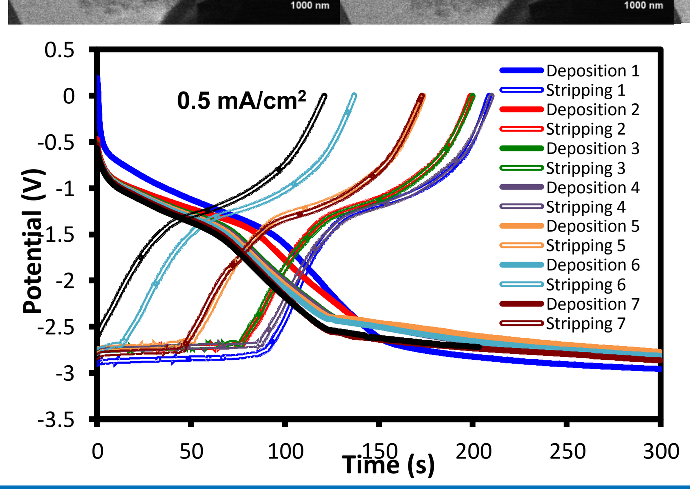
Evaporation of Li using a lid as a shadow mask, with regions cut out for electrode areas using a focused ion beam. Sealing of the pristine Li surface within the closed cell has been a difficulty due to epoxy poisoning of the Li surface during curing. Li electrodes will be coated with ALD protective films, LiAlS and LiPON, to test Li morphology.

50 nm LiAlS on Ni Electrodes

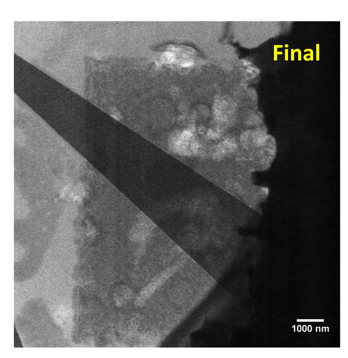
Cracking of inorganic film

Li deposition through cracked film





Li deposition below film



- **Stripping more consistent with ALD film**
- **Li depositing below ALD film**
- **Li nucleation still abundant at specific locations**
- **Li stable in cell, no self discharge observed**
- **Failure of CE at cycle 8**

Future Experiments:

- Li deposition on Li in 4 M LiFSI in DME
- 1 M LiTFSI in DOL/DME with and without 0.2 M $LiNO_3$
- Identify processes of Li metal accommodation at the protective film/electrode interface

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