Thin-film lithiation phase progression observed in a TEM liquid cell

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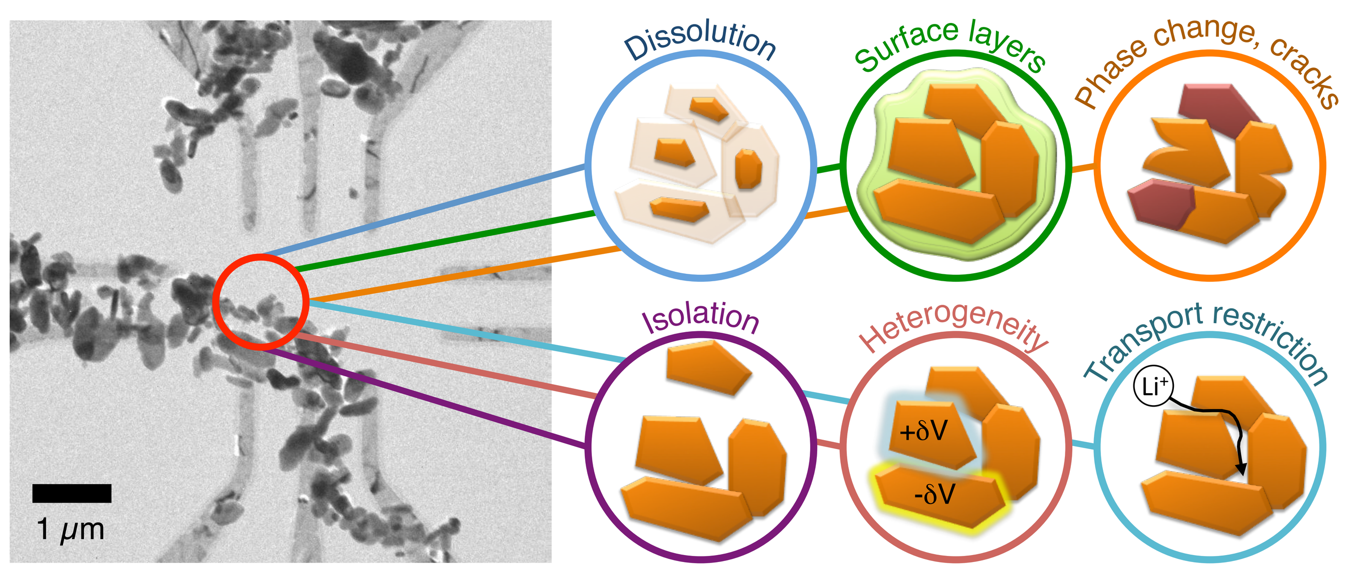
Lithium Battery Degradation

- Lithium ion batteries degradation mechanisms are linked to nanoscale materials changes during cycling:

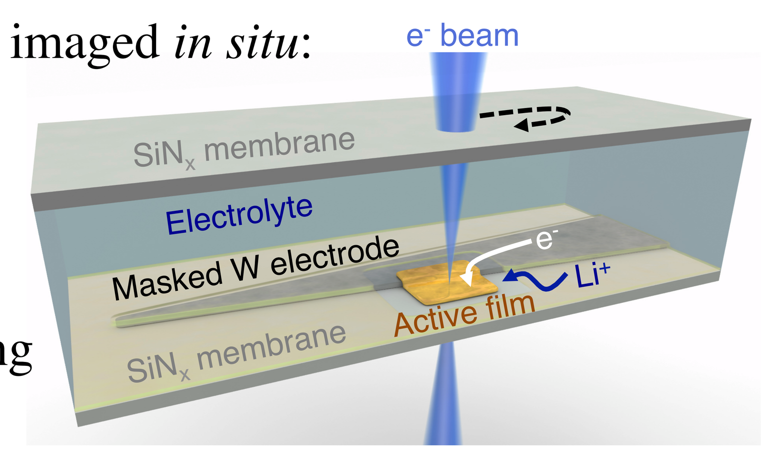


TEM image of $LiFePO_4$ particles on liquid cell electrodes.

Detrimental effects accompany Li movement during electrochemical cycling.

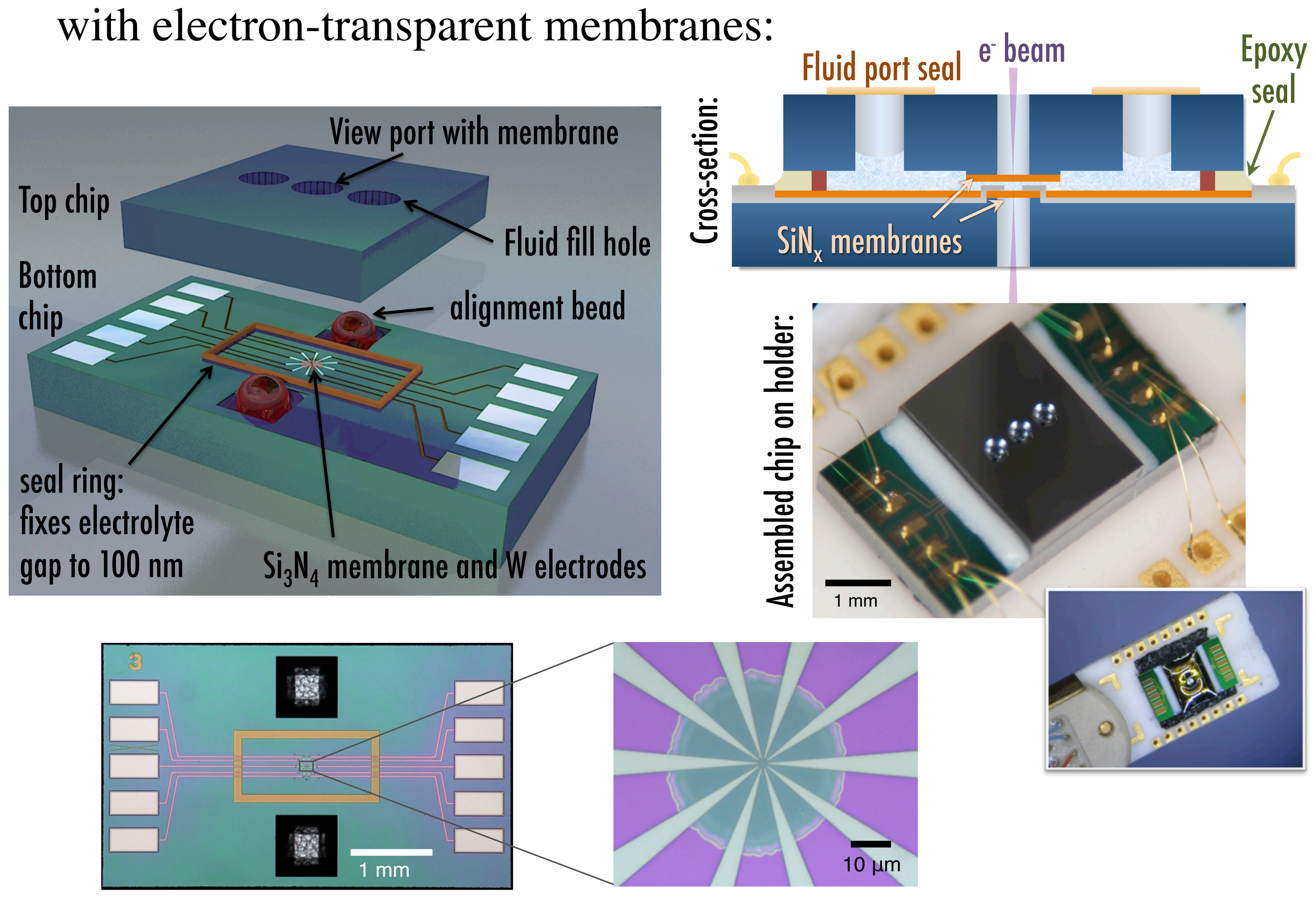
Imaging nanoscale structures during electrochemical cycling in a transmission electron microscope (TEM) shows battery degradation mechanisms and informs mitigation strategies.

- Lithiation of thin film anodes imaged *in situ*:
  (1) Amorphous silicon
  (2) Crystalline Aluminum
  (3) Crystalline Gold
- Understand phase change propagation and corresponding stress localization.



TEM Liquid Cell Design

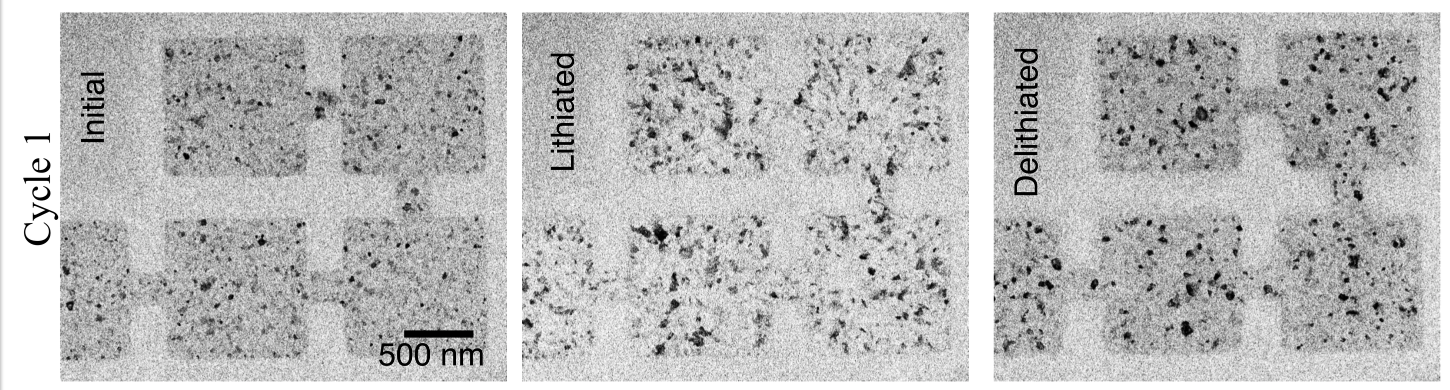
- High-resolution TEM imaging of materials in standard, volatile liquid electrolytes enabled by a microfabricated, sealed liquid cell with electron-transparent membranes:



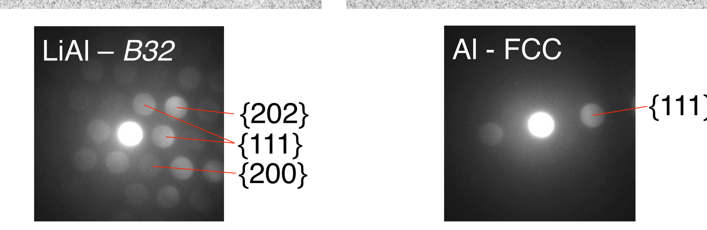
- Quantitative current/voltage control at pA-levels links images to electrochemical signatures.

Crystalline material lithiation: Aluminum and Gold films

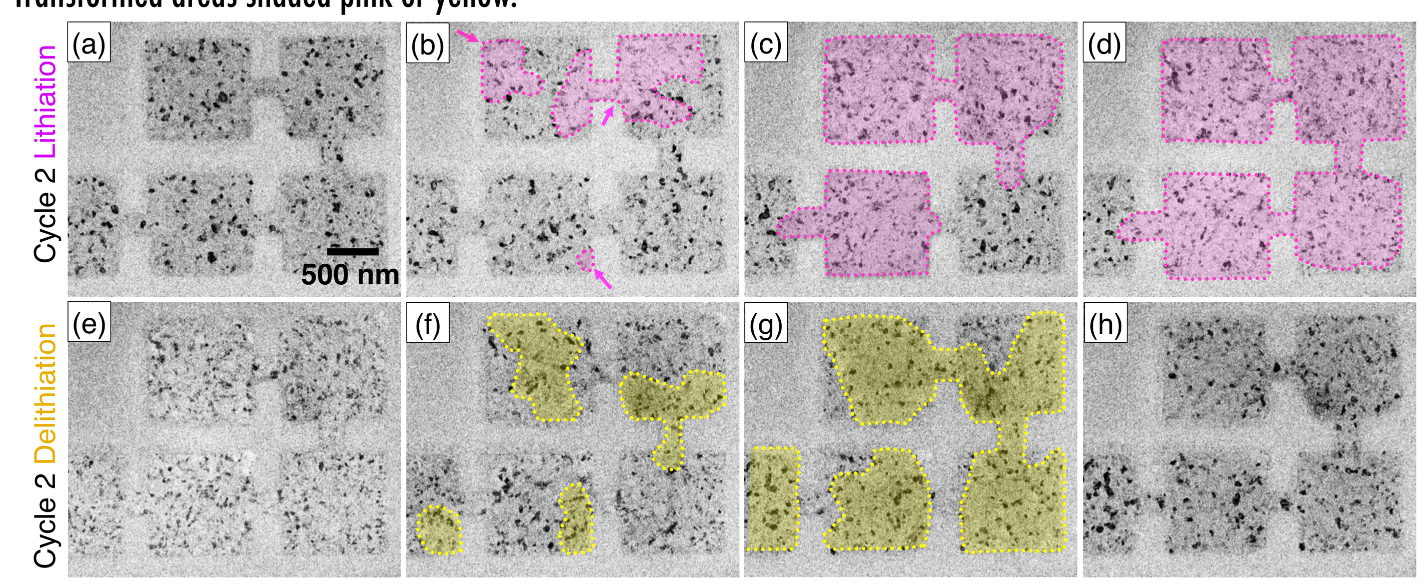
- **Al** electrodes show rapid capacity fade: is material unstable?
- Cycle thin film in liquid electrolyte (1:1 EC:DMC/1 M $LiPF_6$)

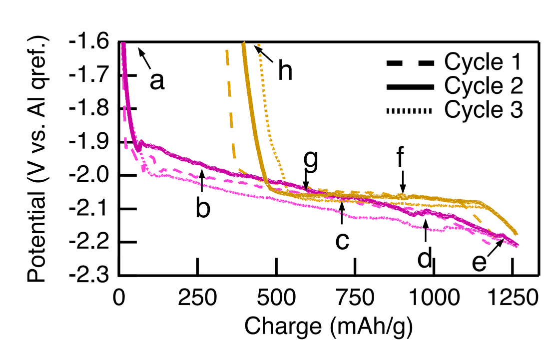


Experiment:
- Apply galvanostatic current to "chain" geometry of 50-nm-thick Al to cycle at 4C rate
- Counter / reference electrodes are 750-μm² Al



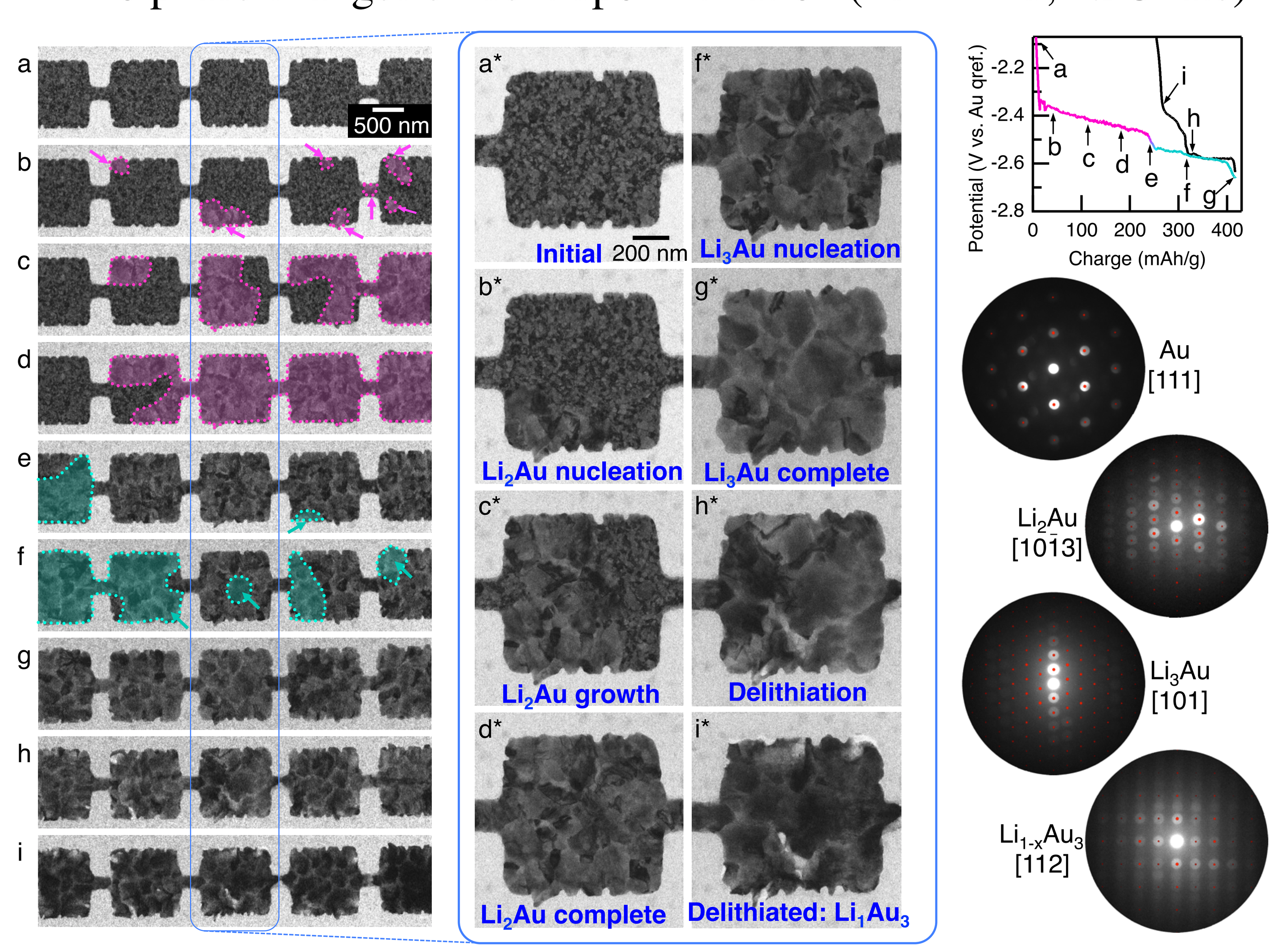
Transformed areas shaded pink or yellow.





- Only 3 initial LiAl nucleation events
- Growth of new grains impeded by defects, but nucleation of new grains facile at phase boundary: **Polycrystalline film results even with few nucleation points.**

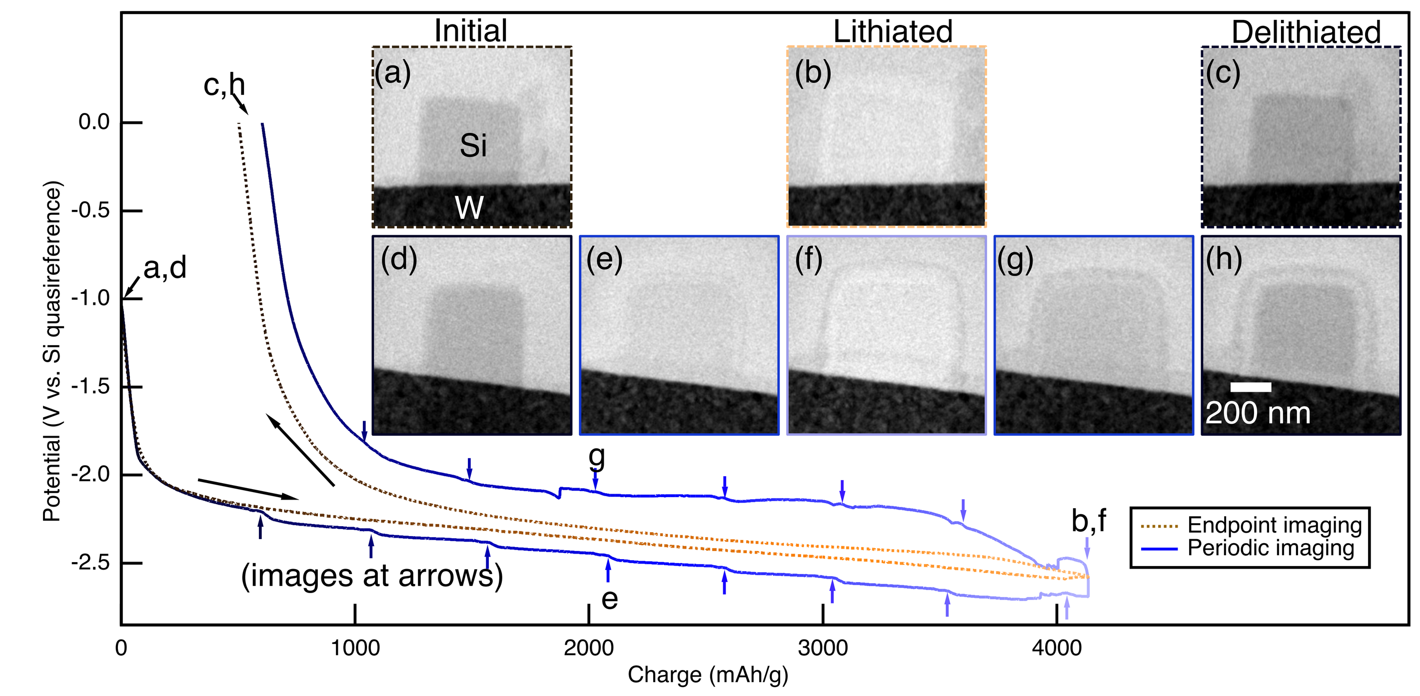
- **Au** electrodes similar but more visible in liquid environment
- Two phase changes evident upon lithiation (40 nm Au, 1.3C rate)



- Material does not fully delithiate: final phase is not Au
- Phases identified *in situ* via convergent-beam electron diffraction

Amorphous material lithiation: Silicon films

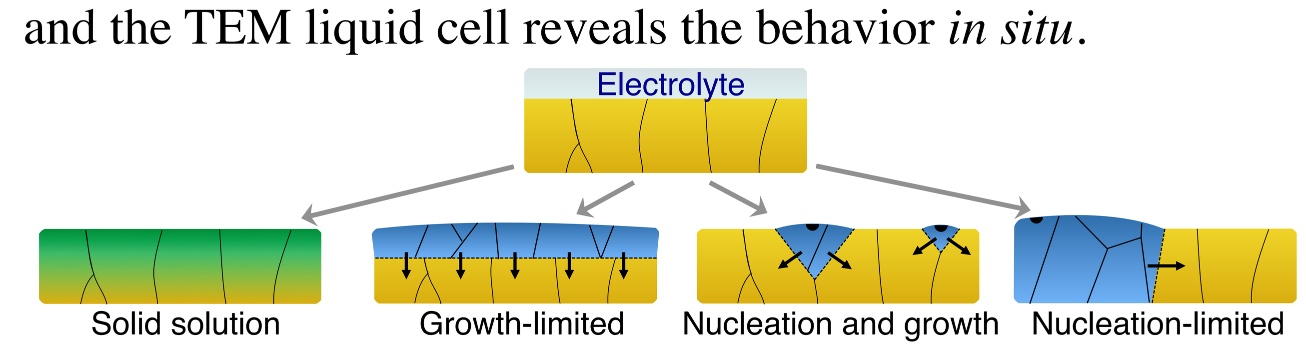
- **a-Si** is fairly stable in thin-film form; how does it differ from Al?
- 90-nm thick film cycled at 6.3C rate, immersed in electrolyte.



- Uniform lateral contrast change: no isolated nucleation events
- Film "disappears" due to lowered density while immersed
- Electron-beam current too high: dark halo around film and altered potential indicates beam-induced chemistry occuring

Analysis and Conclusions

- Lithiation spatially varies during cycle depending on mechanism, and the TEM liquid cell reveals the behavior *in situ*.



- Stress highly localized if a sharp lithiation front exists.
- Al and Au showed clear nucleation-limited behavior, while a-Si showed solid solution behavior.
- Surprising nucleation/growth dynamics: new grains of lithiated phase preferentially nucleated along phase front, not within the host material.
- Thin-film Al lithiation very reversible over a few cycles: no inherent damage seen in thin film material. In contrast, Au fragmented.
- Controlled-rate lithiation of thin films shows unique behavior for each material tested. Other nanomaterials (wires, particles) should obey similar mechanistic principles.

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