Ion-Depleted Microenvironments During Lithium Deposition Revealed by *Operando* Freezing Cryogenic Electron Microscopy

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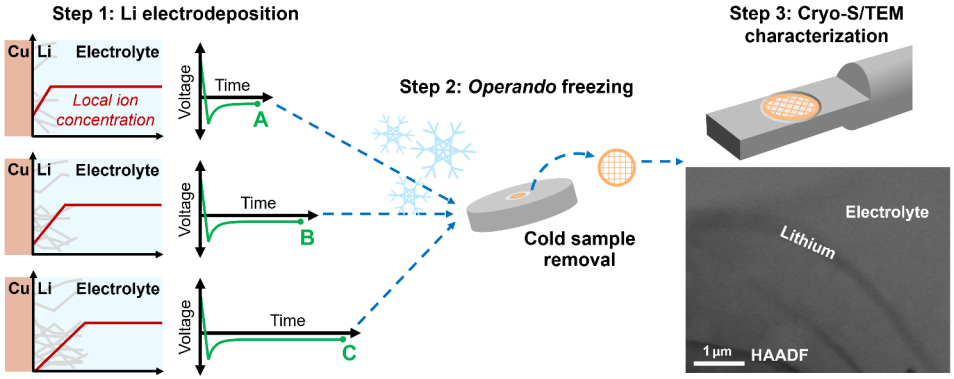
Operando Freezing Cryo-Electron Microscopy

Reveals electrochemically active-state structures & chemistry



Operando freezing cryo-electron microscopy allows electrochemical interfaces to be frozen:

- In active state, e.g., under applied current or bias
- In their native device context (e.g., coin cell)

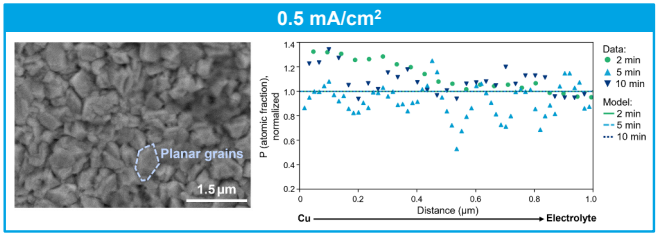
This enables cryo-S/TEM imaging and spectroscopy of site-specific nanostructures & chemical microenvironments that arise during operation.

Fig. 1: Operando freezing cryo-EM workflow involves (1) plunge freezing modified coin cells during an electrochemical process, (2) removing active material via a window in the modified cell, and (3) transferring for cryo-S/TEM characterization.

Ion Depletion Microenvironments During Lithium Deposition

Arise locally and are correlated with heterogeneous growth morphologies

Operando freezing during lithium deposition onto copper in lithium metal batteries reveals local ion depletion in the electrolyte near the active interface at high current densities.



Presence of this depleted region is correlated with heterogeneous lithium morphologies, and its width increases with time.

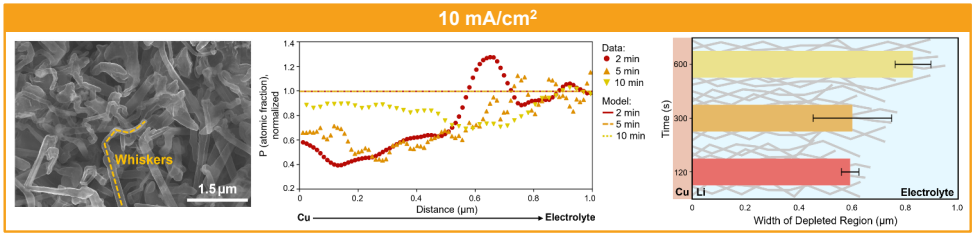
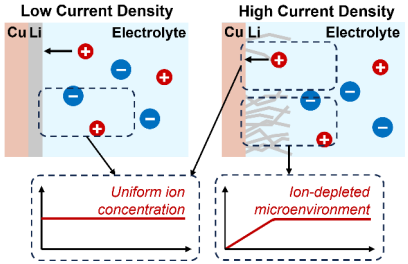


Fig. 2: Left – Scanning electron micrographs of Li deposited onto Cu for 10min shows planar Li growth at the lower current density, versus heterogeneous Li whiskers at the higher current density. Center – Ion depletion is revealed by cryo-energy dispersive X-ray spectroscopy (EDS) line scans showing the phosphorus atomic fraction in the electrolyte adjacent to the Cu (circle & triangle points); here, P acts as a proxy for the PF_6 counterion concentration. The P atomic fraction predicted by a finite-element diffusion model (solid & dashed lines) shows ion depletion is not predicted in either system at steady state; thus, the observed depletion is a local, nonequilibrium microenvironment. Right – The depleted width increases with time.



Local ion depletion provides an explanation for why unstable, often dangerous, lithium morphologies propagate in these systems!

Read the paper:
Dutta et al., 2024,
ACS Energy Letters.

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