Understanding in-situ structure and chemistry at battery interfaces through time-resolved cryo-EM

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Background

Cryo-EM aids characterization of sensitive battery interfaces

Cryogenic electron microscopy (cryo-EM) is **a valuable tool for characterizing sensitive materials**, as the low temperatures minimize many electron beam-induced artifacts & damage. In lithium-ion battery research, this has enabled transmission & scanning transmission electron microscopy (TEM & STEM) characterization of electrode-electrolyte interphases at high spatial resolution.

Cryo-EM sample prep is a challenge; samples must be:

(1) Frozen quickly to preserve native structures
(2) Thin enough for S/TEM characterization
(3) Protected from air/moisture (for batteries).

Traditional sample prep methods are ex situ and leave significant time between sample cycling & freezing:

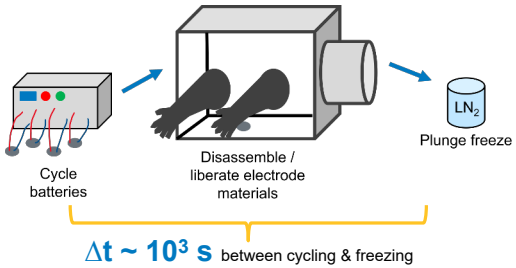

Fig. 1: Typical cryo-EM sample prep workflow for batteries.

This **limits time resolution**, allowing structural relaxation, diffusion, or other processes to occur between cycling & cryo-EM, and **fails to capture interfacial structures in their electrified state**.

»» Goal: Time-resolved method to capture in-situ structures at electrified interfaces.

Methods

In-situ freezing of electrified state

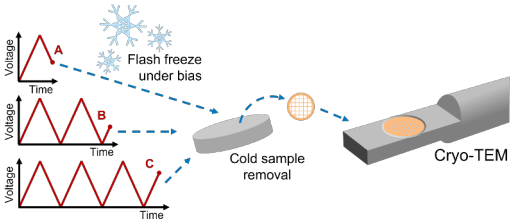

Fig. 2: Freezing samples in-situ under applied bias (or current) allows cryo-EM of structures correlating with times A, B, & C.

1. Integrating plunge freezing with in-situ electrochemical testing

Sample holder developed for Thermo Fisher Vitrobot connects to current/voltage source, allows sample to be plunged into liquid nitrogen (LN_2) at programmed points in electrochemical testing.

Fig. 3: Biasing sample holder in Vitrobot.

$\Delta t_s \approx 1.5$ s, for step-based plunging (e.g. "plunge at 1.5 V")

$\Delta t_t \approx 0.1$ s, for time-based plunging (e.g. "plunge after 10 s")

2. Modified coin cell for cold retrieval of active material

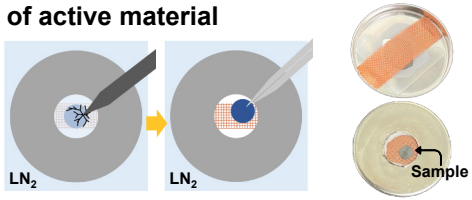

Fig. 4: (a) Retrieving sample, (b) modified cap & cell.

Electrode, on TEM grid, retrieved while continuously submerged in LN_2, for **fast, protected transfer**.

Results

Test case: Silicon nanoparticle half cell with GenF electrolyte

Half cells: Si nanoparticle (NP)-coated TEM grid or Si wafer grid working electrode, Li metal counter electrode, Celgard separator, & GenF electrolyte ([1.2 M $LiPF_6$ in 3:7 w/w EC:EMC] + 3 wt.% FEC).

Control samples show:

(1) Consistent electrochemistry between modified or conventional cells, cycled in in-situ holder or conventional cycler
(2) Suitability for multimodal cryo-EM, with vitrified electrolyte around active materials.

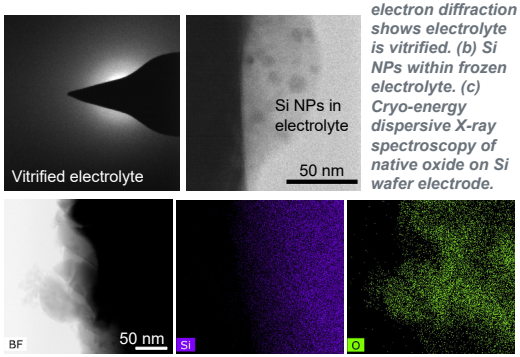

Fig. 5: (a) Cryo-electron diffraction shows electrolyte is vitrified. (b) Si NPs within frozen electrolyte. (c) Cryo-energy dispersive X-ray spectroscopy of native oxide on Si wafer electrode.

Impact: Preservation of electrified state for cryo-EM characterization

By integrating plunge freezing with electrochemical testing of battery materials, we have achieved **3-4 orders of magnitude improvement in time resolution** over conventional cryo-EM sample prep techniques and **preservation of interfaces in their electrified state**.

Future work can **extend this method to other systems** with sensitive materials & dynamic structure under bias, such as perovskite photovoltaics or biohybrid catalysts.

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