Characterizing dynamic structure in battery electrodes by time-resolved cryo-TEM

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Background

Cryo-TEM aids characterization of sensitive battery materials

Cryogenic transmission electron microscopy (cryo-TEM) is **a valuable tool for characterizing sensitive materials**, as the low temperatures minimize many electron beam-induced artifacts & damage. This has opened new doors in structural analyses of battery materials, where electrode structures & interfaces can now be imaged at higher spatial resolutions than previously accessible.

Sample preparation is a key challenge in cryo-TEM, as samples must be:

(1) frozen quickly to preserve native structures,
(2) thin enough for TEM characterization, and
(3) protected from air or moisture, in the case of battery materials.

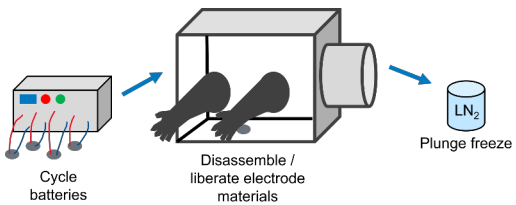

Fig. 1: Schematic of a typical cryo-TEM sample prep workflow. After electrochemical testing, batteries are disassembled in a glovebox, removed, & plunge frozen. Materials of interest can be isolated before freezing or afterwards by cryo-focused ion beam.

Traditional sample prep methods (Fig. 1) leave significant time between electrochemical testing & cryo-TEM characterization. This **limits the time resolution**, allowing for structural relaxation, diffusion, or other dynamic processes & hindering study of transient structures.

$\Delta t \sim 10^3$ **s**, between electrochemical testing and sample freezing

»» Goal: Improve time resolution to study dynamic structures

Methods

In-situ freezing to improve temporal resolution of cryo-TEM

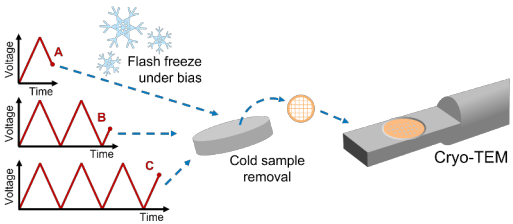

Fig. 2: Flash freezing samples in-situ under applied bias (or current) allows cryo-TEM characterization of transient structures correlating with time points A, B, & C.

1. Integrating plunge freezing with in-situ electrochemical testing

Sample holder developed for Thermo Fisher Vitrobot connects to external potentiostat & allows sample to be plunged into liquid nitrogen (LN_2) at programmed points in electrochemical testing.

$\Delta t_s \approx 1.5$ **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")

Fig. 3: Biasing sample holder in Vitrobot.

2. Modified coin cell to remove sample while cold

Electrode prepared on TEM grid. Investigating window materials to break under LN_2 & remove grid for cryo-TEM.

Fig. 4: Coin cell with sapphire window.

Results

Test case: Silicon nanoparticle half cell with GenF electrolyte

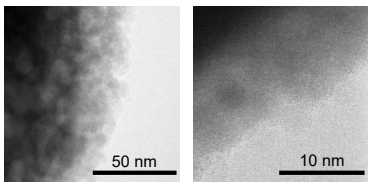

Fig. 5: Silicon nanoparticles deposited onto copper TEM grid.

Modified coin cell with a silicon nanoparticle-coated TEM grid as an anode (Fig. 5), lithium metal counter electrode, Celgard separator, & GenF electrolyte ([1.2 M $LiPF_6$ in 3:7 w/w EC:EMC] + 3 wt.% FEC).

Plunge freezing & removing TEM grid under LN_2 shows:

(1) Electrolyte is vitrified (Fig. 6a)
(2) Nanoparticles visible; electrolyte layer thickness needs to be optimized for high resolution (Fig. 6b)

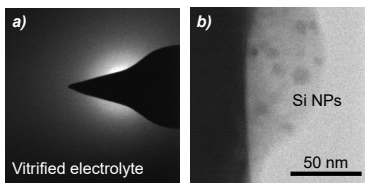

Fig. 6: (a) Cryo-selected area diffraction shows electrolyte is vitrified. (b) Si nanoparticles within the frozen electrolyte layer.

Impacts: Faster time resolution opens doors for future work

We have integrated plunge freezing with electrochemical testing in cryo-TEM sample prep of battery materials, **improving time resolution by 3-4 orders of magnitude**.

In future work:

- Optimize modified coin cell window electrochemically
- Study fast structural & chemical evolution at electrode interfaces
- Extend to other device systems

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