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Title: Cryogenic Scanning Electron Nanobeam Diffraction Workflows for Structural Characterization of Beam-sensitive Battery Interfaces

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Author Questionnaire

1. Microscopy: Does your protocol require the use of a dissecting or stereomicroscope for performing a complex dissection, microinjection technique, or something similar? **No**

2. Software: Does the part of your protocol being filmed include step-by-step descriptions of software usage? **Yes**

If **Yes**, we will need you to record using screen recording software.

We recommend using the screen capture program [OBS](https://review.jove.com/v/5848/screen-capture-instructions-for-authors?status=a7854k). JoVE's tutorial for using OBS Studio is provided at this link: <https://review.jove.com/v/5848/screen-capture-instructions-for-authors?status=a7854k>

3. Filming location: Will the filming need to take place in multiple locations? **Yes**

If **Yes**, how far apart are the locations?

Filming will be between rooms and 10 - 20 meter distances

4. Testimonials (optional): Would you be open to filming two short testimonial statements **live during your JoVE shoot**? These will **not appear in your JoVE video** but may be used in JoVE's promotional materials. **No**

Current Protocol Length

Number of Steps: 17

Number of Shots: 54

Introduction

Videographer: Obtain headshots for all authors available at the filming location.

INTRODUCTION:

~~REQUIRED: Summarize your research focus and the main questions it aims to answer.~~

- 1.1. **Hyeonjun Koh:** Our research characterizes battery interfaces using diffraction-based studies at low electron beam dose without introducing any water frost formation.
 - 1.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

~~Describe the research gap or limitation in existing methods and how this protocol addresses them.~~

- 1.2. **Eric Stach:** Characterizing nanoscale solid-electrolyte interphases requires electron microscopy, but high-energy electrons cause damage; this protocol uses cryogenic diffraction to preserve structures.
 - 1.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

CONCLUSION:

~~What does this protocol allow researchers to study or measure?~~

- 1.3. **Eric Stach:** This protocol allows researchers to determine the structure and composition of solid-electrolyte interphases at nanoscale, without introducing electron beam artifacts.
 - 1.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

~~Describe the most important consideration or challenge when performing this protocol.~~

- 1.4. **Hyeonjun Koh:** In this protocol, minimizing frost formation during cryo-FIB/SEM to TEM transfer is critical, because solid-electrolyte interphases are extremely beam-sensitive.
 - 1.4.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera.

Videographer: Obtain headshots for all authors available at the filming location.

Protocol

Videographer: Please always record an audio slate while filming each shot mentioned in the shotlist.

2. Transmission Electron Microscopy (TEM) Sample Preparation (On-Grid Method)

Demonstrator: Hyeongjun Koh

- 2.1. To begin, obtain the lithium coin cells after lithium deposition [1]. Use decrimping tools to open the lithium coin cells inside a glovebox [2]. Check for lithium metal deposits on the TEM (T-E-M) grids kept on the copper foil and remove the grids [3].
 - 2.1.1. WIDE: Show the lab set up and then focus on the lithium coated coin cells. NOTE: 2.1.1. and 2.1.2 are filmed in a single shot
 - 2.1.2. Talent using decrimping tools to open lithium coin cells inside a glovebox.
 - 2.1.3. Talent removing TEM grids with visible lithium metal deposits from the copper foil. NOTE: 2.1.3 and 2.2.1 are filmed in a single shot
- 2.2. Remove the separator to take out the TEM grids [1]. To rinse the grid, select the solvent appropriate to the electrolyte used [2]. Drop the solvent onto the TEM grids, then repeatedly wick around the edges with laboratory wipes to remove residual solvent [3]. Dip the grids into a TEM grid box containing the appropriate solvent to remove any salt residues [4]. Place the grids in an argon-filled antechamber and dry them under vacuum for 5 to 15 minutes [5].
 - 2.2.1. Talent removing the separator to access the TEM grids.
 - 2.2.2. Shot of the selected solvent.
 - 2.2.3. Talent applying solvent to the TEM grids and wicking the edge with laboratory wipes.
 - 2.2.4. Talent dipping the TEM grids into a TEM grid box.
 - 2.2.5. Talent placing the TEM grids into an argon-filled antechamber for vacuum drying.
- 2.3. Place the dried grids in cryo-TEM grid boxes [1] and close the grid boxes with pin-type lids [2]. Put the closed grid boxes into a press-to-close bag [3]. Remove the bag through the antechamber and immediately place it into a long-neck liquid nitrogen flask [4]. Then, cut the submerged bag in half to release the grid boxes into the liquid nitrogen [5].
 - 2.3.1. Talent placing dried TEM grids into cryo-TEM grid boxes.
 - 2.3.2. Talent closing the cryo-TEM grid boxes with pin-type lids.
 - 2.3.3. Talent placing the closed grid boxes into a press-to-close bag.

- 2.3.4. Talent placing the press-to-close bag into a long-neck liquid nitrogen flask.
NOTE: 2.3.4 and 2.3.5 are filmed in a single shot
- 2.3.5. Talent cutting the submerged bag in half to release the grid boxes into the liquid nitrogen.

2.4. Next, use long tweezers to place the grid boxes into a 50-milliliter conical tube before cryogenic scanning TEM characterization [1].

- 2.4.1. Talent transferring grid boxes with long tweezers into a 50 mL conical tube.

NOTE: There was some confusion in sections 3.3 and 4.x.x. First the client got confused, then shortly after I got confused, resulting in a few shots being mislabeled. The editor should definitely read over the shot log before assessing the footage; hopefully I captured everything you need to know there. All shots should be accounted for. I shot 3 or 4 extra shots. I usually slated them as ".X", although one I didn't slate at all -- I was just alone in a room with an electron microscope and couldn't help myself. :) Shot log is attached here, and included with the footage upload

3. TEM Sample Preparation (Cryo-FIB/SEM Method)

- 3.1. Collect the lithium coin cells after lithium deposition [1]. Use decrimping tools to open the lithium coin cells inside a glovebox [2]. After removing the lithium-deposited copper foil from the coin cells, place it onto a focused ion beam and scanning electron microscopy or SEM (*S-E-M*) stub [3]. Put the stub into a press-to-close bag [4] and remove the argon-filled bag through the glovebox antechamber [5].
 - 3.1.1. Talent keeping the lithium coin cells ready after lithium deposition.
 - 3.1.2. Talent using decrimping tools to open lithium coin cells inside a glovebox.
 - 3.1.3. Talent placing the lithium-deposited copper foil onto a focused ion beam and SEM stub.
 - 3.1.4. Talent placing the focused ion beam and SEM stub into a press-to-close bag.
 - 3.1.5. Talent removing the argon-filled bag through the glovebox antechamber.
- 3.2. Quench the argon-filled bag in liquid nitrogen [1] and cut it in half to release the sample [2]. Carefully place the SEM stub in a 50-milliliter conical tube before the focused ion beam and SEM session [3].
 - 3.2.1. Talent quenching the argon-filled bag in liquid nitrogen. **NOTE: 3.2.1 and 3.2.2 are filmed in a single shot**
 - 3.2.2. Talent cutting the bag in half to release the sample.
 - 3.2.3. Talent placing the SEM stub into a 50 mL conical tube.
- 3.3. Move the cold samples through a vacuum transfer system to the cryogenic focused ion beam and SEM stage [1]. Use a lidded cryogenic focused-ion-beam and SEM shuttle to

minimize ice deposition [2]. Load the vacuum transfer system to the cryogenic focused ion beam and SEM [3].

- 3.3.1. Talent transferring the cold samples through a vacuum transfer system.
- 3.3.2. Talent loading the samples in a lidded cryogenic focused ion beam and SEM shuttle. NOTE: Use 2nd take at the end of the clip
- 3.3.3. Talent loading the vacuum transfer system to cryogenic focused ion beam and SEM. NOTE: We took a video with the videographer additionally on the day. If you cannot find the clip just ignore this change

3.3.X: Wide shot of vacuum transfer. 4.1.1.X is part of 3.3.

4. Characterization of Battery Interphases/Interfaces Through Cryo-SEND

NOTE: The shots labelled as SCREEN are filmed by the videographer

- 4.1. Remove the cryogenic box containing the previously prepared cryo-scanning TEM samples [1]. Transfer it into a liquid nitrogen flask, following standard experimental procedures [2].
 - 4.1.1. Shot of talent removing the cryogenic box containing the previously prepared samples.
 - 4.1.2. Talent pouring the cryogenic box content into the nitrogen flask.
- 4.2. After ensuring that the cryogenic TEM working station is filled with liquid nitrogen, immerse the grid box [1]. Open the pin-type lid and take out a TEM grid [2]. Gently place it into the tip of the cryogenic TEM holder maintained at minus 160 degrees Celsius [3]. Close the shutter [4], then immediately insert the holder into a TEM goniometer, following the manufacturer's instructions [5].
 - 4.2.1. Talent placing the grid box into liquid nitrogen in the cryogenic TEM working station.
 - 4.2.2. Talent opening the pin-type lid and taking out a TEM grid.
 - 4.2.3. Talent loading the TEM grid into the tip of the cryogenic TEM holder maintained at -160 °C.
 - 4.2.4. Talent closing the shutter on the cryogenic TEM holder.
 - 4.2.5. Talent inserting the holder into the transmission electron microscope goniometer.
- 4.3. Locate the sample at low magnification [1]. Select a region of interest such as a solid electrolyte interphase or SEI (S-E-I) layer [2]. Draw a region of interest and collect the nanobeam diffraction [3]. Adjust the pixel time and step size to limit the total accumulated dose [4].
 - 4.3.1. Talent locating the sample at low magnification on the transmission electron microscope.

- 4.3.2. SCREEN: Show selection of a region of interest containing the SEI layer.
- 4.3.3. SCREEN: Show the region of interest being drawn and nanobeam diffraction being collected.
- 4.3.4. SCREEN: Show adjustment of the pixel time and step size in the transmission electron microscope software.
- 4.4. To ensure a successful point, check whether the lamella is sufficiently thin and all components are distinctly visible [1]. Check if lithium appears very dark in dark-field scanning TEM mode while the SEI shows the brightest contrast [2]. Verify that the SEI surrounds the lithium metal plating and is sandwiched by vitrified electrolyte and lithium metal [3]. Confirm that the vitrified electrolyte is continuous and free of substantial pores [4].
 - 4.4.1. SCREEN: Show a sufficiently thin lamella with clearly distinguishable components.
 - 4.4.2. SCREEN: Show lithium appearing very dark and the solid electrolyte interphase appearing brightest in dark-field scanning TEM mode.
 - 4.4.3. SCREEN: Show the SEI surrounding lithium metal plating and lying between vitrified electrolyte and lithium metal.
 - 4.4.4. SCREEN: Show continuous vitrified electrolyte without substantial pores.
- 4.5. Then, adjust the center beam position without parking the beam on the region of interest [1]. Use a vacuum area to align the transmitted beam at the center [2] and remove the high-angle annular dark-field detector to acquire diffraction patterns at high angles [3].
 - 4.5.1. SCREEN: Show adjustment of the center beam position away from the region of interest.
 - 4.5.2. SCREEN: Show the transmitted beam being aligned in a vacuum area.
 - 4.5.3. SCREEN: Show the removal of high-angle annular dark-field detector.
- 4.6. Next, optimize the camera resolution, data storage and transfer, and total acquisition time based on the experimental needs [1]. Perform software or hardware binning in the TEM software [2].
 - 4.6.1. SCREEN: Show optimization of camera resolution, data storage or transfer, and acquisition time settings.
 - 4.6.2. SCREEN: Show data binning in the TEM software.
- 4.7. Set the acquisition parameters as presented to collect the data [1]. Once data is collected, use a shutter or blank the beam to avoid beam damage during repeated rastering over the region [2]. After the 4-dimensional scanning TEM acquisition, acquire a scanning TEM image to observe any noticeable change relative to the image before the measurement [3].

- 4.7.1. TEST ON A PLAIN BACKGROUND:
 - Probing-forming aperture: 10 μm
 - Probe size: 7
 - Camera length: 250 mm
 - Pixel time: 13 ms
 - Step size: 4 nm
 - Camera resolution: 512 pixels
- 4.7.2. SCREEN: Show the beam being shuttered or blanked after data collection.
- 4.7.3. SCREEN: Show acquisition of a post-measurement scanning TEM image.

5. Correction and Analysis of 4-Dimensional Scanning TEM Data

- 5.1. Using PyXEM in a Hyperspy-based python environment, correct the descans and objective stigmation [1]. Correct the center beam positions in each real space coordinate and the ellipticity in reciprocal space [2].
 - 5.1.1. SCREEN: Show descans and objective stigmation correction in the software.
 - 5.1.2. SCREEN: Show corrected center beam positions in real space and corrected ellipticity in reciprocal space.
- 5.2. Acquire diffraction patterns from regions of interest and transform the 2-dimensional data into 1-dimensional data [1]. After obtaining the diffraction intensity signal in scattering-vector space, apply background subtraction to enhance the signal [2]. Multiply the intensity by the scattering vector or by the scattering vector square when required to increase the signal-to-noise ratio [3].
 - 5.2.1. SCREEN: Show diffraction patterns being extracted from regions of interest and transformed from 2D data to 1D data.
 - 5.2.2. SCREEN: Show diffraction intensity in scattering vector space and apply background subtraction.
 - 5.2.3. SCREEN: Show intensity multiplied by the scattering vector or by the scattering vector squared.
- 5.3. Bin the real space data to enhance the diffraction signal [1]. Then, bin the detector pixels to reduce the data processing time according to the workstation computing capability [2].
 - 5.3.1. SCREEN: Show real space data binning to enhance the diffraction signal.
 - 5.3.2. SCREEN: Show detector pixel binning to reduce the data processing time.

Results

6. Results

6.1. The solid - electrolyte interphases formed in both the electrolytes used [1] appeared amorphous under cryogenic scanning electron nanodiffraction at a controlled electron dose [2].

6.1.1. LAB MEDIA: Figure 3A. *Video editor: Highlight the left panel.*

6.1.2. LAB MEDIA: Figure 3A. *Video editor: Highlight the right panel.*

6.2. The solid-electrolyte interphase from the 1 molar lithium bis(fluorosulfonyl)imide in dimethoxyethane electrolyte did not show a detectable structural correlation [1], whereas the solid-electrolyte interphase from the high-concentration electrolyte exhibited short-range order [2].

6.2.1. LAB MEDIA: Figure 3B. *Video editor: Highlight the blue curve.*

6.2.2. LAB MEDIA: Figure 3B. *Video editor: Highlight the red curve.*

6.3. The short-range order in the solid-electrolyte interphase from the high-concentration electrolyte showed maxima at approximately 0.3 inverse angstrom [1] and 0.65 inverse angstrom [2].

6.3.1. LAB MEDIA: Figure 3B. *Video editor: Highlight the first raised feature on the red curve near 0.3 inverse angstrom*

6.3.2. LAB MEDIA: Figure 3B. *Video editor: Highlight the second (slightly) raised feature on the red curve near 0.65 inverse angstrom*

1. Decrimping

Pronunciation link: <https://www.howtopronounce.com/decrimping>

IPA: /di:'krɪm.pɪŋ/

Phonetic Spelling: dee·krim·ping

2. Glovebox

Pronunciation link: <https://www.merriam-webster.com/dictionary/glovebox>

IPA: /'glʌv.bɑːks/

Phonetic Spelling: gluv·boks

3. Electrolyte

Pronunciation link: <https://www.merriam-webster.com/dictionary/electrolyte>

IPA: /ɪ'lek.trəˌlaɪt/

Phonetic Spelling: ih·lek·truh·lyte

4. Argon
Pronunciation link: <https://www.merriam-webster.com/dictionary/argon>
IPA: /'ɑːr.gɑːn/
Phonetic Spelling: ar·gon
5. Antechamber
Pronunciation link: <https://www.merriam-webster.com/dictionary/antechamber>
IPA: /'æn.ti.tʃeɪm.bər/
Phonetic Spelling: an·tee·chaym·ber
6. Cryogenic
Pronunciation link: <https://www.merriam-webster.com/dictionary/cryogenic>
IPA: /'kraɪ.oo'dʒen.ɪk/
Phonetic Spelling: kry·oh·jen·ik
7. Cryo-TEM
Pronunciation link: No confirmed link found
IPA: No verified IPA available
Phonetic Spelling: kry·oh tee·ee·em
8. Focused ion beam
Pronunciation link: <https://www.merriam-webster.com/dictionary/ion>
IPA: /'foʊ.kəst 'aɪ.ɑːn biːm/
Phonetic Spelling: foh·kuhst eye·on beam
9. Nanobeam diffraction
Pronunciation link: <https://www.howtopronounce.com/nanobeam>
IPA: /'næn.oo.biːm dɪ'fræk.ʃən/
Phonetic Spelling: nan·oh·beam dih·frak·shuhn
10. Goniometer
Pronunciation link: <https://www.merriam-webster.com/dictionary/goniometer>
IPA: /'ɡoʊ.ni'ɑː.mə.tər/
Phonetic Spelling: goh·nee·om·uh·ter
11. Lamella
Pronunciation link: <https://www.merriam-webster.com/dictionary/lamella>
IPA: /lə'mel.ə/
Phonetic Spelling: luh·mel·uh
12. Vitrified
Pronunciation link: <https://www.merriam-webster.com/dictionary/vitrify>
IPA: /'vɪ.trə'faɪd/
Phonetic Spelling: vih·truh·fyd
13. High-angle annular dark-field
Pronunciation link: No confirmed link found
IPA: No verified IPA available
Phonetic Spelling: hy·ang·guhl an·yuh·ler dark·field
14. Rastering
Pronunciation link: <https://www.howtopronounce.com/rastering>
IPA: /'ræs.tər.ɪŋ/
Phonetic Spelling: ras·ter·ing

15. PyXEM
Pronunciation link: No confirmed link found
IPA: No verified IPA available
Phonetic Spelling: pie·zem
16. HyperSpy
Pronunciation link: No confirmed link found
IPA: No verified IPA available
Phonetic Spelling: hy·per·spy
17. Stigmation
Pronunciation link: <https://www.howtopronounce.com/stigmation>
IPA: /stɪɡ'meɪ.ʃən/
Phonetic Spelling: stig·may·shuhn
18. Ellipticity
Pronunciation link: <https://www.merriam-webster.com/dictionary/ellipticity>
IPA: /ɪˌlɪp'tɪs.ə.ti/
Phonetic Spelling: ih·lip·tis·uh·tee
19. Reciprocal
Pronunciation link: <https://www.merriam-webster.com/dictionary/reciprocal>
IPA: /rɪ'sɪp.rə.kəl/
Phonetic Spelling: ree·sip·ruh·kuhl
20. Amorphous
Pronunciation link: <https://www.merriam-webster.com/dictionary/amorphous>
IPA: /ə'mɔːr.fəs/
Phonetic Spelling: uh·mor·fuhs