

Screening of Coatings for an All-Solid-State Battery using *In Situ* Transmission Electron Microscopy

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Abstract

With the ever-increasing use of Li-ion batteries, especially due to their adoption in electric vehicles, their safety is in prime focus. Thus, the all-solid-state batteries (ASSBs) that use solid electrolytes instead of liquid electrolytes, which reduce the risk of flammability, have been the center stage of battery research for the last few years. However, in the ASSB, the ion transportation through the solid-solid electrolyte-electrode interface poses a challenge due to contact and chemical/electrochemical stability issues. Applying a suitable coating around the electrode and/or electrolyte particles offers a convenient solution, leading to better performance. For this, researchers are screening potential electronic/ionic conductive and nonconductive coatings to find the best coatings with suitable thickness for long-term chemical, electrochemical, and mechanical stability. Operando transmission electron microscopy (TEM) couples high spatial resolution with high temporal resolution to allow visualization of dynamic processes, and thus is an ideal tool to evaluate electrode/electrolyte coatings *via* studying (de)lithiation at a single particle level in real-time. However, the accumulated electron dose during a typical high-resolution *in situ* work may affect the electrochemical pathways, evaluation of which can be time-consuming. The current protocol presents an alternative procedure in which the potential coatings are applied on Si nanoparticles and are subjected to (de)lithiation during operando TEM experiments. The high volume changes of Si nanoparticles during (de)lithiation allow monitoring of the coating behavior at a relatively low magnification. Thus, the whole process is very electron-dose efficient and offers quick screening of potential coatings.

Introduction

Today, Li-ion batteries are all around us, from various electronic devices such as smartphones and laptops to electric vehicles, the numbers of which are steeply rising to move away from the fossil fuel-based economy^{1,2}. With this continuously increasing, safety features of Li-ion batteries are a high priority requirement³. The liquid electrolytes that are typically used in traditional Li-ion batteries are flammable, especially at higher operating voltages and temperatures. In contrast, using nonflammable solid electrolytes in all-solid-state batteries (ASSBs) reduces the risk of flammability⁴. This, and potentially high energy density, has brought ASSBs to the research limelight over the last few years. However, the solid-solid electrolyte-electrode interface in ASSBs brings its own challenges that are quite different from the traditional liquid-solid electrode-electrolyte interface⁵. Many of the electrolytes used in ASSBs are not chemically and/or electrochemically stable against lithium and cathodes. Thus, decomposition reactions at electrode-electrolyte interfaces cause the formation of passivating layers, resulting in restricted ionic transport and an increase in internal resistance leading to capacity degradation over battery cycles⁶. One of the most common ways to prevent such a reaction is to apply a coating to the electrodes and/or electrolytes, which ensures there is no direct contact between the electrode-electrolyte and results in a stable interface. For this purpose, different electronic and ionic conductive coatings are currently being investigated^{7,8}.

The main requirements for ideal coating are: it must allow ion conduction; it must not increase the battery's internal resistance; and it must be chemically and mechanically stable throughout many battery cycles. Other questions like coating thickness, single layer or multilayer, and ideal coating process

are of prime interest for the commercialization of ASSBs. Thus, a screening method is needed to find out the best coatings.

A transmission electron microscope (TEM) has been used to investigate the solid-solid interface in ASSBs up to the atomic scale^{9,10}. Furthermore, operando TEM offers the possibility to build a micro battery inside a TEM and study the battery processes during battery cycling. To track Li-ion movements in the battery, imaging at a high resolution is needed¹¹. However, the inherent high electron beam dose of such high-resolution imaging over the entire duration of the experiment may alter the electrochemical pathways. An alternative to that is coatings that are applied on Si nanoparticles (NPs) and subjected to (de)lithiation. During operando TEM experiments, lithiation process though the coating can be monitored at low magnification, thanks to the high volume changes of Si nanoparticles during (de)lithiation^{12,13,14}. Thus, the entire battery cycling process can be monitored at a relatively low electron dose. Further, the stress generated on the coating due to high volume changes of Si will be analogous to the stress generated on the coating over multiple cycles. Thus, long-term mechanical stability of the coatings can also be probed. This article aims to share, with examples of different thicknesses of TiO₂ coating, how such an operando TEM experiment can be conducted for screening the potential ASSB coatings. The protocol will explain loading the coated Si NPs on an *in situ* TEM holder, observing the lithiation of coated Si NPs in a TEM, and analyzing the TEM images.

Protocol

NOTE: For accelerated curing, heat the specimen on a hot plate at around 100 °C for 10 min.

1. Preparation of TiO₂ coated Si nanoparticles (TiO₂@Si NPs) on half-cut TEM grids

1. Prepare a half-cut TEM grid.
 1. Place the 3 mm TEM grids with lacey film (see **Table of Materials**) on a clean glass slide.
 2. Cut the TEM grid into half-cut grids with a razor blade.

2. Drop-cast the TiO₂@Si NPs on the half-cut TEM grid.

NOTE: In this study, 100 nm sized Si NPs coated with 5 nm/10 nm TiO₂ by atomic layer deposition¹⁵ were used. Researchers can prepare coated Si NPs in various ways.

1. Disperse the TiO₂@Si NPs into 10 mL of acetone and dropcast onto one of the half-cut TEM grids with a pipette.

NOTE: Around 10–5 µL drops would result in sufficient TiO₂@Si NPs at the edge of the half-cut TEM grid.

2. Check that the TiO₂@Si NPs are placed at the edge *via* TEM.

NOTE: This is not necessary, but recommended.

3. Attach tungsten (W) wire on a half-cut TEM grid.

1. Cut the W wire using a nipper (see **Table of Materials**) into small pieces, with a length of 0.5–1 cm.
2. Mix two components of conductive glue on the clean slide glass. Glue the W wire on the half-cut grid with conductive glue.
3. Cure the conductive glue by drying it at room temperature in a safe place for 4 h.

2. Preparing the W needle

1. Cut the W wire using a nipper into small pieces, with a length of ~2 cm. Mount the W wire on the electropolishing machine (see **Table of Materials**).
2. Mix 50% of 1.3 mol/L NaOH and 50% of ethanol in a 10 mL beaker. Set the proper moveable range of a counter electrode to carry the electrolyte from the beaker.

NOTE: The electropolishing region can be adjusted by moving the loop up and down iteratively. The polishing region is confined to 2–4 mm by setting the range of the vertical movement of the loop. The number of vertical movements of the loop is set to five times per each trip to dip the loop in the electrolyte beaker.

3. Apply the voltage until the W wire is cut into two pieces—two sharp W needles.

NOTE: The polishing condition used in this study was voltage (4.0 V), and the vertical iterative movement of the loop (2–4 mm) with five iterations per electrolyte.

4. Load the prepared W needle on the probe head.

3. Loading the drop-casted TEM grid and W needle into the *in situ* TEM holder

1. Insert the drop-casted half-cut TEM grid, W needle-loaded probe head, *in situ* TEM holder, and small glove bag (opened) into the air-free glove box (see **Table of Materials**).
2. Scratch the Li metal with the prepared W needle (Li/Li_xO@W needle) probe head.

NOTE: Li is easily oxidized (Li/Li_xO) by a tiny amount of water.

3. Mount the $\text{Li/Li}_x\text{O@W}$ needle probe head to the *in situ* TEM holder. Load the drop-casted half-cut TEM grid to the *in situ* TEM holder (**Figure 1**).

4. Put the assembled *in situ* TEM holder into a small glove bag. Close the small glove bag and take it out of the glove box.

NOTE: Take out the assembled *in situ* TEM holder just before the *in situ* experiment so that the air contact is as low as possible.

4. Inserting the assembled *in situ* holder into the TEM

NOTE: The $\text{Li/Li}_x\text{O@W}$ needle can be oxidized by air or water in the glove bag, so be careful.

1. Seal around the empty TEM goniometer (see **Table of Materials**) with a large glove bag. Put the closed small glove bag containing the assembled *in situ* TEM holder into the large glove bag.

2. Pump and purge the large glove bag with inert gas (Ar or N_2) more than three times.

NOTE: The single pumping and purging process can take around a few minutes.

3. Open the small bag and insert the assembled *in situ* TEM holder. Connect the cables to the *in situ* TEM holder.

NOTE: One cable is for the needle movement from the control equipment, and the other is for applying the voltage or current from the power supply (see **Table of Materials**).

5. Performing the *in situ* biasing experiment in the TEM

1. Align the electron beam.

NOTE: All TEM techniques and principles can be learned from reference¹⁶.

2. Move the $\text{Li/Li}_x\text{O@W}$ needle toward the $\text{TiO}_2\text{@Si}$ NPs (**Figure 2**). Set the lowest magnification.

1. Find the half-cut TEM grid. Locate the grid to eucentric height by the TEM goniometer. Find the $\text{Li/Li}_x\text{O@W}$ needle.

2. Run TEM stage wobbling. Locate the needle to eucentric height by coarse movement (inertial sliding with the repeated pulse).

NOTE: Minimization of needle movement indicates the eucentric height.

3. Move the needle close to the grid by coarse movement. Increase the magnification.

4. Move the needle forward to the grid to make physical contact between the needle and the $\text{TiO}_2\text{@Si}$ NPs by fine movement (piezoelectric tube).

NOTE: Contrast change of the $\text{TiO}_2\text{@Si}$ NPs indicates physical contact.

3. Set proper magnification and beam intensity.

NOTE: The electron dose rate used in this study was $10 \text{ e}^-/\text{\AA}^2/\text{s}$, a comparable condition for a biological sample.

4. Apply voltage and capture the image or video.

NOTE: The voltage used in this study was 2 V.

6. Analyzing the TEM images

1. Load the TEM image. Draw a polygon to target particle.
2. Measure the area of the drawn polygon. Compare the measured area among various TEM images.

NOTE: For the quantification purpose, setting the scale (unit: pixel per length) is required before the

measurement. ImageJ (see **Table of Materials**) was used for processing the images in the present study.

Representative Results

A series of TEM images of lithiation on 5 nm and 10 nm TiO_2 coated Si/SiO₂ particles are shown in **Figure 3**. In the case of 5 nm coating, significant expansion occurred in the whole area, and the coating was not broken during huge expansion. In the case of 10 nm coating, relatively small expansion occurred even for a longer lithiation time, and

the coating was broken after 2 min. From the amount of expansion and coating breakage, 5 nm coating is promised to show better capacity and durability than 10 nm coating.

The amount of particle expansion can be obtained by image processing as shown in **Figure 4**. The 5 nm coating case showed around 2x areal expansion, while the 10 nm coating case showed only 1.2x areal expansion. The expansion rate of the 5 nm coating case is six times faster than that of the 10 nm coating case.

(A) Piezo based TEM biasing holder (B) Half-cut TEM grid with Si particles (c) Scratched lithium on W needle

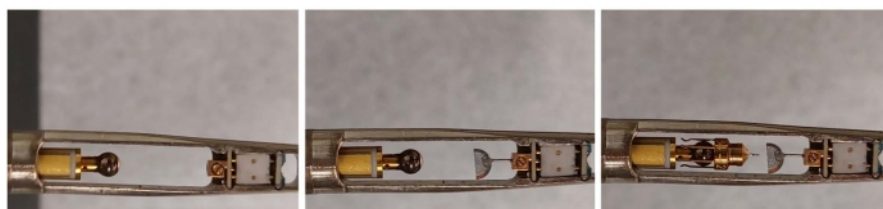
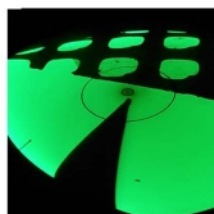
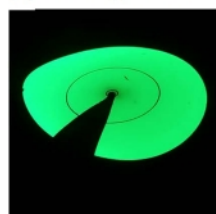


Figure 1: *In situ* TEM holder assembly. (A) An empty *in situ* TEM biasing holder. (B) Assembling the drop-casted half-cut TEM grid with a tungsten rod to the right side of the holder. (C) Assembling the probe head with a tungsten needle to the left side of the holder. [Please click here to view a larger version of this figure.](#)

(A) Coarse approach



(B) Fine approach

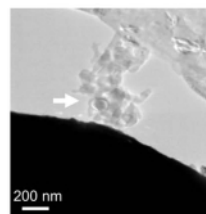
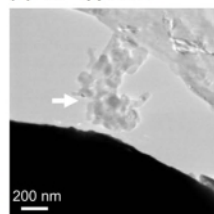
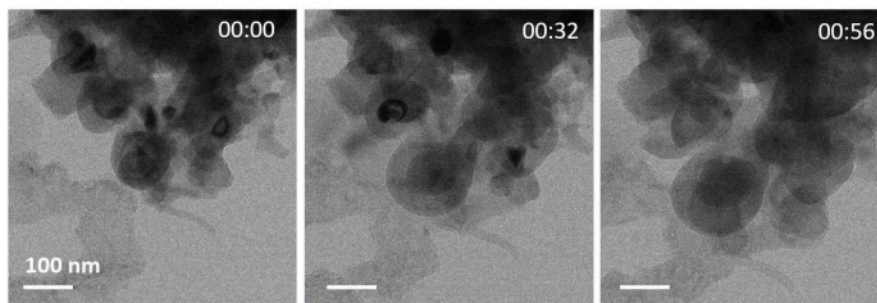


Figure 2: Moving the tungsten needle toward the TiO_2 coated Si nanoparticles in TEM. (A) Locating the tungsten needle to the eucentric height and moving the needle close to the TEM grid. (B) Physical contact between the needle and nanoparticles is indicated by contrast change. [Please click here to view a larger version of this figure.](#)

(A) Lithiation of 5 nm TiO_2 coated Si nanoparticles



(B) Lithiation of 10 nm TiO_2 coated Si nanoparticles

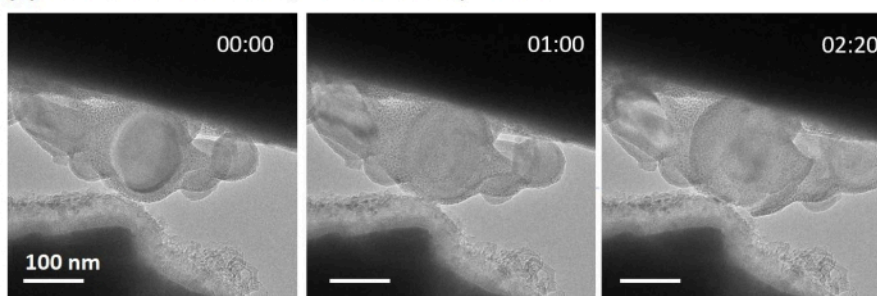


Figure 3: TEM image series about lithiation. (A) 5 nm TiO_2 coated Si nanoparticles. (B) 10 nm TiO_2 coated Si nanoparticles. The figure is adapted from Basak et al.¹⁵. [Please click here to view a larger version of this figure.](#)

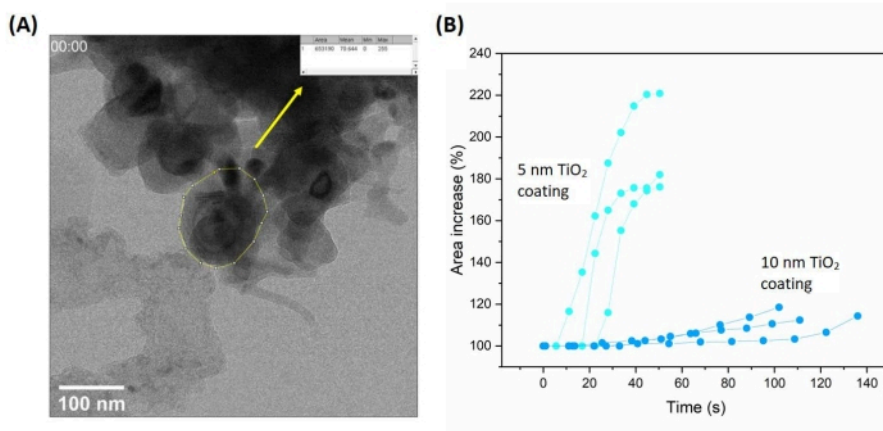


Figure 4: Tracking the expansion of nanoparticles during lithiation. (A) Measuring the area of the nanoparticles (by a drawn polygon) from the TEM image. (B) The graph of area increase vs. time. The figure is adapted from Basak et al.¹⁵. [Please click here to view a larger version of this figure.](#)

Discussion

The lithiation of coated Si NPs *via in situ* TEM enables simple examination of the potential coatings for ASSBs. One of the important steps in determining the success of these experiments is the appropriate thickness of LiO_x , which acts as a solid electrolyte in these experiments. As the ionic conductivity of LiO_x is significantly lower than that of the typical solid electrolyte used in ASSBs, a thicker LiO_x layer would increase internal resistance and hamper ion conduction. On the other hand, any non-oxidized area of lithium may act as an optional means of battery short circuit. The appropriate thickness of LiO_x can be ensured by carefully transporting the assembled holder from the glovebox to the TEM using the so-called glove bag (described in steps 3 and 4).

The coating behavior during the lithiation can be investigated in a more in depth manner, even at this low magnification if the coating data (signal) is extracted separately from TEM images without the data of Si-core (noise). Before the lithiation, coating and Si NPs are easily distinguished by the contrast. However, during the lithiation, the contrast difference was decreased, so it was hard to investigate the phenomena of coating independently. STEM imaging can enhance the contrast, and the intensity of STEM images can be used for volume measurement. Furthermore, machine learning or deep learning technology can enhance feature recognition and extract more information to understand the mechanisms during the *in situ* experiments¹⁷.

The current procedure of (de)lithiation of coated Si NPs *via in situ* TEM is limited to quick screening to find the potential coating materials. The shortlisted coating candidates must be tested in the actual ASSBs. *In situ* biasing studies of the micro batteries, prepared by focused-ion-beam on a

microelectromechanical system (MEMS), can provide further information on the interfacial ionic transport mechanism^{6,11}.

This coating screening technique can be adapted to Na-ion based ASSBs by replacing the lithium with sodium.

Disclosures

The authors have nothing to disclose.

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References

1. Armand, M., Tarascon, J.-M. Building better batteries. *Nature*. **451** (7179), 652-657 (2008).
2. Goodenough, J. B., Park, K.-S. The Li-ion rechargeable battery: a perspective. *Journal of the American Chemical Society*. **135** (4), 1167-1176 (2013).
3. Liu, K., Liu, Y., Lin, D., Pei, A., Cui, Y. Materials for lithium-ion battery safety. *Science Advances*. **4** (6), eaas9820 (2018).
4. Grey, C. P., Hall, D. S. Prospects for lithium-ion batteries and beyond-a 2030 vision. *Nature Communications*. **11** (1), 6279 (2020).
5. Basak, S. et al. Operando transmission electron microscopy study of all-solid-state battery interface: redistribution of lithium among interconnected particles. *ACS Applied Energy Materials*. **3**(6), 5101-5106 (2020).

6. Wang, L. et al. In-situ visualization of the space-charge-layer effect on interfacial lithium-ion transport in all-solid-state batteries. *Nature Communications*. **11** (1), 5889 (2020).
7. Lee, D. J. et al. Nitrogen-doped carbon coating for a high-performance SiO anode in lithium-ion batteries. *Electrochemistry Communications*. **34**, 98-101 (2013).
8. Wu, E. A. et al. A facile, dry-processed lithium borate-based cathode coating for improved all-solid-state battery performance. *Journal of The Electrochemical Society*. **167** (13), 130516 (2020).
9. Liu, Y. et al. Visualizing the sensitive lithium with atomic precision: cryogenic electron microscopy for batteries. *Accounts of Chemical Research*. **54** (9), 2088-2099 (2021).
10. Sheng, O. et al. Interfacial and ionic modulation of poly (ethylene oxide) electrolyte via localized iodization to enable dendrite-free lithium metal batteries. *Advanced Functional Materials*. **32** (14), 2111026 (2022).
11. Gong, Y. et al. In situ atomic-scale observation of electrochemical delithiation induced structure evolution of LiCoO₂ cathode in a working all-solid-state battery. *Journal of the American Chemical Society*. **139** (12), 4274-4277 (2017).
12. Huang, J. Y. et al. In situ observation of the electrochemical lithiation of a single SnO₂ nanowire electrode. *Science*. **330** (6010), 1515-1520 (2010).
13. Liu, X. H. et al. Anisotropic swelling and fracture of silicon nanowires during lithiation. *Nano Letters*. **11** (8), 3312-3318 (2011).
14. Liu, X. H., et al. Size-dependent fracture of silicon nanoparticles during lithiation. *ACS Nano*. **6** (2), 1522-1531 (2012).
15. Basak, S. et al. Operando transmission electron microscopy of battery cycling: thickness dependent breaking of TiO₂ coating on Si/SiO₂ nanoparticles. *Chemical Communications*. **58** (19), 3130-3133 (2022).
16. Williams, D. B., Carter, C. B. *Transmission Electron Microscopy*. Springer US. Boston, MA. (2009).
17. Horwath, J. P., Zakharov, D. N., Mégret, R., Stach, E. A. Understanding important features of deep learning models for segmentation of high-resolution transmission electron microscopy images. *npj Computational Materials*. **6** (1), 108 (2020).