TITLE:

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

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SUMMARY:

Utilizing the volume change of Si nanoparticles during (de)lithiation, this paper presents a screening method of potential coatings for all-solid-state batteries using in-situ transmission electron microscopy.

ABSTRACT:

With the ever-increasing use of Li-ion batteries especially due to their adoption in the electric vehicles, the safety of same is in prime focus. Thus, the all-solid-state batteries (ASSB) that make use of solid electrolytes instead of liquid electrolytes, which reduce the risk of flammability, have been at the center stage of battery research for the last few years. In the ASSB though, the ion transportation through the solid-solid electrolyte-electrode interface poses a challenge due to contact and chemical/electrochemical stability issues. Application of suitable coating around the electrode and/or electrolyte particles offers a suitable solution, leading to better performance. For this researchers are screening potential electronic/ionic conductive and nonconductive coatings to find out the best coatings with suitable thickness for long-term chemical, electrochemical and mechanical stability.

Operando transmission electron microscopy (TEM) couples high special resolution with a high temporal resolution to allow visualization of dynamic processes and thus is an ideal tool for evaluating the 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. Here we present 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 relatively low magnification. Thus the whole process is much electron dose efficient and offers quick screening of potential coatings.

INTRODUCTION:

Today Li-ion batteries are all around us, starting from the various electronic devices such as smartphones and laptops, to the electric vehicles, numbers of which are in a steeply rising curve in order 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 requirement[3]. The liquid electrolytes that are typically used in traditional Li-ion batteries are flammable, especially at higher operating voltages and temperatures. In contrast, the use of nonflammable solid electrolytes in the all-solid-state batteries (ASSB) reduces the risk of flammability[4]. This and potentially high energy density brought ASSBs to the research limelight over the last few years. The solid-solid electrolyte-electrode interface in ASSBs though brings its own sets of challenges that are quite different from the traditional liquid-solid electrode-electrolyte interface[5]. Many of the electrolytes used in the ASSBs are not chemically and/or electrochemically stable against lithium and cathodes. Thus, decomposition reactions at the 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 cycles[6]. One of the most common ways to prevent such a reaction is to apply a coating to the electrodes and/or electrolytes, which ensures 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 requirement for the ideal coating is it should allow ion conduction, should not increase the internal resistance of the battery and 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, we need a screening method to find out the best coating. Transmission electron microscope (TEM) has been used to investigate the solid-solid interface in ASSB up to 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 the Li-ion movements in the battery through imaging at high resolution is needed[11]. 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 if coatings are applied on Si nanoparticles and are subjected to (de)lithiation during an 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[12–14]. 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 paper aims to share, with examples of different thicknesses of TiO2 coating, how such 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 TEM, and analyzing the TEM images.

PROTOCOL:

1. Making the TiO_2 coated Si nanoparticles (TiO_2@Si NPs) on half-cut TEM grids.
    1.1. Prepare half-cut TEM grid.
        1.1.1. Place the 3 mm TEM grids with lacey film on clean slide glass.
        1.1.2. Cut TEM grid into half-cut grids with razor blade.
        1.1.3. Check the film near the edge.
    1.2. Drop-cast the TiO_2@Si NPs on half-cut TEM grid.
        NOTE: 100 nm sized Si NPs coated with 5nm / 10 nm TiO_2 by atomic layer deposition were used in this paper[15]. Researchers can prepare coated Si NPs in various ways.
        1.2.1. Disperse the TiO_2@Si NPs into 10 ml Acetone.
        1.2.2. Drop the solution on to one of half-cut TEM grid with pipette.
            NOTE: Around 10 drops would be enough.
        1.2.3. Check the TiO_2@Si NPs placed at the edge via TEM.
            NOTE: Not be necessary, but recommends.
    1.3. Attach tungsten (W) wire on half-cut TEM grid.
        1.3.1. Cut pristine W wire by nipper into small pieces with a length of 0.5-1 cm.
        1.3.2. Mix two components of conductive glue on clean slide glass.
        1.3.3. Glue W wire on the half-cut grid with conductive glue.

1.3.4. Cure the conductive glue by drying at room temperature in a safe place for 4 hours.

NOTE: For accelerated cure, heat the specimen on a hot plate around 100 °C for 10 mins.

2. Making the W needle
   - 2.1. Cut pristine W wire by nipper into small pieces with a length of around 2 cm.
   - 2.2. Mount the W wire on the electro-polishing machine.
   - 2.3. Mix 50 % of 1.3 mol/L NaOH and 50 % of Ethanol in 10 ml beaker.
   - 2.4. Set proper moveable range of a counter electrode to carry electrolyte from the beaker.
     NOTE: Electropolishing region would 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 the vertical movement of the loop is set to 5 times per each trip to dip the loop in the electrolyte beaker.
   - 2.5. Apply the voltage until the W wire is cut into two pieces, two sharp W needles.
     NOTE: Polishing condition used in this paper was voltage (4.0 V), the vertical iterative movement of loop (2-4 mm) with 5 iteration per electrolyte.
   - 2.6. Load the prepared W needle on probe head.

3. Loading drop-casted TEM grid and W needle into in-situ TEM holder (**Figure 1**).
   - 3.1. Insert the drop-casted half-cut TEM grid, W needle loaded probe head, in-situ TEM holder and small glove bag (opened) into air-free glove box.
   - 3.2. Scratch the Li metal with prepared W needle (Li/Li_xO@W needle) probe head.
     NOTE: Li is easily oxidized (Li/Li_xO) by tiny amount of water.
   - 3.3. Mount Li/Li_xO@W needle probe head to the in-situ TEM holder.
   - 3.4. Load drop-casted half-cut TEM grid to in-situ TEM holder.
   - 3.5. Put the assembled in-situ TEM holder into small glove bag.
   - 3.6. Close the small glove bag and take it out from glove box.
     NOTE: Take out the assembled in-situ TEM holder just before the in-situ experiment to prevent the air contact as low as possible.

4. Inserting the assembled in-situ TEM holder in TEM.
   NOTE: Li/Li_xO@W needle would be getting oxidized by air or water in glove bag, so be careful.
   - 4.1. Seal around the empty TEM goniometer with large glove bag.
   - 4.2. Put closed small glove bag containing assembled in-situ TEM holder into large glove bag.
   - 4.3. Pump and purge the large glove bag with inert gas (Ar) for more than 3 times

NOTE: Single pumping and purging process would take around few mins.

4.4. Open the small bag and insert assembled in-situ TEM holder.

4.5. Connect the cables to in-situ TEM holder.

NOTE: one cable for movement of needle from control equipment, and the other cable for applying the voltage or current from power supply.

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

5.1. Align the electron beam.

NOTE: All TEM techniques and principle can be learned from textbook[16].

5.2. Approach the $Li/Li_xO@W$ needle to $TiO_2@Si$ NPs (**Figure 2**).

5.2.1. Set the lowest magnification.

5.2.2. Find the half-cut TEM grid.

5.2.3. Locate the grid to eucentric height by TEM goniometer.

5.2.4. Find the $Li/Li_xO@W$ needle.

5.2.5. Run TEM stage wobbling.

5.2.6. Locate the needle to eucentric height by coarse movement (inertial sliding with the repeated pulse).

NOTE: Minimization of needle movement indicates the eucentric height.

5.2.7. Move the needle close to the grid by coarse movement.

5.2.8. Increase the magnification.

5.2.9. Move the needle forward to the grid to make a physical contact between needle and $TiO_2@Si$ NPs by Fine Movement (piezoelectric tube).

NOTE: Contrast change of $TiO_2@Si$ NPs indicates the physical contact.

5.3. Set proper magnification and beam intensity.

NOTE: Electron dose rate used in this paper was 10 $e^-/Å^2/s$ comparable condition for biological sample.

5.4. Apply voltage and capture the image or video.

NOTE: Voltage used in this paper was 2 V.

6. Analyzing the TEM images by image processing program.

6.1. Load TEM image.

6.2. Draw polygon to target particle.

6.3. Measure the area of drawn polygon

6.4. 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.

REPRESENTATIVE RESULTS:

Series of TEM images of lithiation on 5 nm and 10 nm TiO_2 coated Si/SiO_2 particles are shown in **Figure 3**. In case of 5 nm coating, significant expansion was occurred at whole area and coating was not broken during huge expansion. In case of 10 nm coating, relatively small expansion was occurred even for longer lithiation time and 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**. 5 nm coating case showed around 2 times areal expansion while 10 nm coating case showed only 1.2 times areal expansion. The expansion rate of 5 nm coating case is 6 times faster than that of 10 nm coating case.

FIGURE AND TABLE LEGENDS:

Figure 1. In-situ TEM Holder assembly (a) Empty In-situ TEM biasing holder, (b) assembling the drop-casted half-cut TEM grid with tungsten rod to right side of holder, (c) assembling the probe head with tungsten needle to left side of holder.

Figure 2. Approaching tungsten needle toward TiO_2 coated Si nanoparticles in TEM (a) Locating the tungsten needle to the eucentric height and moving the needle close to TEM grid, (b) physical contact between the needle and nanoparticles indicated by contrast change.

Figure 3. TEM image series about lithiation (a) 5 nm TiO_2 coated Si nanoparticles, (b) 10 nm TiO_2 coated Si nanoparticles.

Figure 4. Tracking the expansion of nanoparticles during lithiation (a) Measuring the area of nanoparticles (by drawn polygon) from TEM image, (b) graph of area increase vs time[15].

DISCUSSION:

The lithiation of coated Si NPs via in-situ TEM enables simply examining potential coatings for ASSB. One of the important steps which determine 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 the ion conduction. On the other hand, any non-oxidized area of lithium may act as an optional means of battery short circuit. This can be achieved by careful transportation of the assembled holder from the glovebox to the TEM with the use of the so-called glove bag as described in protocols 3 and 4.

The behavior of coating during the lithiation can be investigated more deeply even at this observation at low magnification if the data of coating (signal) is extracted separately from TEM images without the data of Si-core (noise). Before the lithiation, coating and Si nanoparticles are easily distinguished by the contrast. However, during the lithiation, the contrast difference was decreased, so it is hard to investigate the phenomena of coating independently. STEM imaging can enhance the contrast and the intensity of STEM image can be used for volume measurement. Furthermore, machine learning or deep learning technology can enhance feature recognition and finally extract more information to understand the mechanisms that occurred during the in-situ experiments[17].

Since the lithiation of coated Si NPs via in-situ TEM is focused on observing the volumetric expansion at low magnification for low electron dose rate, this method is limited on quick screening to find the potential coating materials and conditions for ASSB. After screening the coating candidates with this method, the candidates should be tested with a real ASSB system. For studying the real system, micro battery prepared by focused-ion-beam on microelectromechanical system (MEMS) chip-based in-situ biasing experiment can provide more detailed information such as interfacial ionic transport mechanism[6, 11].

In principle, volume expansion via in-situ TEM experiment is used as a simple visual sensor not only to determine the phenomena but also to test long-term structural stability. Based on this principle, this method can be adapted near to sodium ion ASSB.

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DISCLOSURES:

We have nothing to disclose.

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