Video Article

Three-electrode Coin Cell Preparation and Electrodeposition Analytics for Lithium-ion Batteries

Robert D. Minter*[1], Daniel Juarez-Robles*[2], Conner Fear[2], Yevgen Barsukov[3], Partha P. Mukherjee[2]

[1]Department of Mechanical Engineering, Texas A&M University

[2]School of Mechanical Engineering, Purdue University

[3]Battery Management Systems, Texas Instruments Inc.

*These authors contributed equally

Correspondence to: Partha P. Mukherjee at pmukherjee@purdue.edu

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Abstract

As lithium-ion batteries find use in high energy and power applications, such as in electric and hybrid-electric vehicles, monitoring the degradation and subsequent safety issues becomes increasingly important. In a Li-ion cell setup, the voltage measurement across the positive and negative terminals inherently includes the effect of the cathode and anode which are coupled and sum to the total cell performance. Accordingly, the ability to monitor the degradation aspects associated with a specific electrode is extremely difficult because the electrodes are fundamentally coupled. A three-electrode setup can overcome this problem. By introducing a third (reference) electrode, the influence of each electrode can be decoupled, and the electrochemical properties can be measured independently. The reference electrode (RE) must have a stable potential that can then be calibrated against a known reference, for example, lithium metal. The three-electrode cell can be used to run electrochemical tests such as cycling, cyclic voltammetry, and electrochemical impedance spectroscopy (EIS). Three-electrode cell EIS measurements can elucidate the contribution of individual electrode impedance to the full cell. In addition, monitoring the anode potential allows the detection of electrodeposition due to lithium plating, which can cause safety concerns. This is especially important for the fast charging of Li-ion batteries in electric vehicles. In order to monitor and characterize the safety and degradation aspects of an electrochemical cell, a three-electrode setup can prove invaluable. This paper aims to provide a guide to constructing a three-electrode coin cell setup using the 2032-coin cell architecture, which is easy to produce, reliable, and cost-effective.

Video Link

The video component of this article can be found at https://www.jove.com/video/57735/

Introduction

Although the origin of lithium-batteries can be traced arbitrarily far back into the past, the large-scale production and commercialization of many of today's commonly found lithium-ion batteries began in the 1980s. Many of the materials developed during this era, one example being Lithium Cobalt Oxide ($LiCoO_2$), are still commonly found in use today[1]. Many current studies have been focused towards the development of various other metal oxide structures, with some emphasis placed towards reducing or eliminating the use of cobalt in place of other lower cost and more environmentally benign metals, such as manganese or nickel[2]. The continuously changing landscape of materials used in lithium-ion batteries necessitates an effective and accurate method of characterizing both their performance and safety. Because the operation of any battery involves the coupled electrochemical response of both the positive and negative electrodes, typical two electrode batteries fall short of being able to characterize the electrodes independently. Poor characterization and the subsequent lack of understanding may then lead to dangerous situations or poor overall battery performance due to the presence of degradation phenomena. Previous research has been aimed at standardizing the processing techniques for typical two-electrode cells[3]. One method that improves upon the shortcomings of standard cell configurations is the three-electrode cell.

A three-electrode setup is one method to decouple the two electrodes' responses and provide a greater insight into the fundamental physics of the battery operation. In a three-electrode setup, a reference electrode is introduced in addition to the cathode and anode. This reference electrode is then used to measure the potential of the anode and cathode dynamically during operation. No current is passed through the reference electrode and hence, it provides a singular, and ideally stable, voltage. By using a three-electrode setup, the full cell voltage, the cathode potential, and the anode potential can be collected simultaneously during operation. In addition to potential measurements, the impedance contributions of the electrodes can be characterized as a function of the cell state of charge[4].

Three-electrode setups are very useful for studying degradation phenomena in lithium-ion batteries, such as the electrodeposition of lithium metal, also known as lithium plating. Other groups have proposed three-electrode setups[5,6,7,8,9,10,11,12,13] but they often use the inherently

unstable lithium metal as a reference and include custom, difficult to assemble setups leading to reduced reliability. Lithium plating takes place when instead of intercalating into the host electrode structure, lithium is deposited on the surface of the structure. These deposits commonly assume the morphology of either a (relatively) uniform metallic layer (plating) or small dendritic structures. Plating can have effects ranging from causing safety issues to impeding cycling performance. From a phenomenological perspective, lithium plating occurs due to an inability of lithium to intercalate into the host electrode structure effectively. Plating tends to occur at low temperature, high charging rate, high electrode state of charge (SOC), or a combination of these three factors[12]. At low temperature, the solid-state diffusion inside the electrode is reduced, due to the Arrhenius diffusivity dependence on temperature. The lower solid-state diffusion results in a buildup of lithium at the electrode-electrolyte interface and a subsequent deposition of lithium. At a high charging rate, a similar phenomenon occurs. The lithium attempts to intercalate into the electrode structure very quickly but is unable to and thus is plated. At a higher SOC, there is on average less available space for the lithium to intercalate into the structure, and thus it becomes more favorable to deposit on the surface.

Lithium dendrites are of particular importance due to the safety concern they cause. If dendrites form inside a cell, there is a potential for them to grow, pierce the separator, and cause an internal short between the anode and cathode. This internal short can lead to very high-localized temperatures in the flammable electrolyte, often resulting in thermal runaway and even in an explosion of the cell. Another issue related to dendrite formation is the increased surface area of the reactive lithium. The newly deposited lithium will react with the electrolyte and cause increased solid electrolyte interphase (SEI) formation, which will lead to increased capacity loss and poor cycling performance.

One issue associated with the design of a three-electrode system is the selection of the appropriate reference electrode. Logistics relating to the location and size of the reference, positive, and negative electrodes can play an important role in acquiring accurate results from the system. One example is that the misalignment of the positive and negative electrodes during the cell construction and the resulting edge effects can introduce error in the reference reading[14,15]. In terms of material selection, the reference electrode should have a stable and reliable voltage and have a high non-polarizability. Lithium metal, which is often used as a reference electrode by many research groups, has a potential that depends on the passive surface film. This can produce issues because cleaned and aged lithium electrodes display different potentials[16]. This becomes a problem when long-term aging effects are studied. Research by Solchenbach *et al.* has attempted to eliminate some of these instability issues by alloying gold with lithium and using it as their reference[11]. Other research has looked at different materials including lithium titanate, which has been studied experimentally and shows a large electrochemical potential plateau range around 1.5 - 1.6 V[17] (~50% SOC). This plateau helps to maintain a stable potential, especially in the event of accidental perturbation to the electrode's state of charge. The potential stability of LTO, including carbon-based conductive additives, is maintained even at different C-rates and temperatures.[18] It is important to emphasize that the selection of the reference electrode is an important step in the three-electrode cell design.

Many research groups have proposed experimental three-electrode cell setup. Dolle *et al.* used thin plastic cells with a lithium titanate copper wire reference electrode to study changes in impedance due to cycling and storage at high temperatures[19]. McTurk *et al.* employed a technique whereby a lithium plated copper wire was inserted into a commercial pouch cell, with the main goal being to demonstrate the importance of noninvasive insertion techniques[9]. Solchenbach *et al.* used a modified Swagelok-type T-cell and a gold micro-reference electrode (mentioned earlier) for impedance and potential measurements.[11] Waldmann *et al.* harvested electrodes from commercial cells and reconstructed their own three-electrode pouch cells for use in studying lithium deposition[12]. Costard *et al.* developed an in-house experimental three-electrode cell housing to test the effectiveness of different reference electrode materials and configurations[13].

Most of these research groups use pure lithium metal as the reference, which can have concerns with stability and SEI growth, especially with long-term use. Other issues involve complicated and time-consuming modifications to existing or commercial setups. In this paper, a reliable and cost-effective technique for constructing three-electrode Li-ion coin cells for electrochemical tests is presented, as shown in **Figure 1**. This three-electrode setup can be constructed using standard coin cell components, copper wire, and lithium titanate-based reference electrode (see **Figure 2**). This method does not require any specialized equipment or elaborate modifications and follows standard laboratory scale electrochemical procedures and materials from commercial vendors.

Protocol

1. Reference Electrode and Separator Preparation

1. **Reference electrode preparation**
    1. **Wire preparation**
        1. Cut one 120-mm length of size 32 AWG (0.202 mm diameter) enameled copper wire.
        NOTE: Each wire will become 1 reference electrode and will be used inside 1 three-electrode cell.
        2. Place one end of the wire in a laboratory press. Gently press approximately 10 mm of wire at one end to a pressure of about 4 MPa. Cut the excess wire off the wire tip so that the flattened section is ~2 mm in length.
        NOTE: The average thickness of the tip is approximately 0.1 mm. Be careful not to bend the flattened tip as it may fatigue and break off.
        3. Place the wire on a polytetrafluoroethylene (PTFE) cutting board. Carefully use a scalpel to remove the outer insulation on the flattened wire tip. Make sure to remove the insulation from both sides; the final product should be a flat, shiny section of exposed copper.
        4. Weigh the wire using a laboratory scale.
        NOTE: This mass will be used after the slurry has been cast to determine the exact amount of active material present in each reference electrode.
        5. Repeat steps 1.1.1.1 - 1.1.1.5 for a typical batch size of 36 wires. Place the wires on a receptacle for storage. A good option is to tape the wires around the edge of a small glass jar.

    2. **Slurry preparation**
        1. Prepare the 10%-wt. polyvinylidene fluoride (PVDF) solution in N-methyl-2-pyrrolidinone (NMP).

1. Using a small rectangular weigh paper, a stainless-steel scoop, and a laboratory scale, measure out the desired mass of the PVDF powder (0.1 g).
2. Transfer the PVDF powder from the weigh paper into a 500-mL plastic bottle. Measure and transfer the appropriate mass of NMP liquid (0.9 g) into the bottle by using a 1-mL-capacity laboratory pipette.
3. Insert a magnetic stirring bar into the solution; place the bottle on a magnetic stirring plate and leave it to mix indefinitely. Allow the solution to mix for at least 24 h prior to the first use. It is recommended to prepare the PVDF solution in bulk to avoid having to make smaller batches for each slurry batch.

2. Before weighing any more powder, clean the stainless-steel scoop, the pestle, and the mortar with isopropyl alcohol to avoid any contamination.
3. Using a weigh paper, the laboratory scale, and the stainless-steel scoop, measure out the appropriate amount (0.8 g) of lithium titanate ($Li_4Ti_5O_{12}$) powder. Carefully transfer the powder to the mortar and pestle. Clean the scoop with isopropyl alcohol after use.
4. Similarly, weigh out the appropriate amount (0.03 g) of KS-6 synthetic graphite and (0.09 g) conductive additive. Carefully transfer the powder to the same mortar and pestle. Clean the scoop with isopropyl alcohol as before.
5. Lightly mix the three powders in the mortar until they become uniformly dispersed. Grind the powder mix using the pestle until the mixture becomes homogenous. Carefully transfer the powder mix to a 20-mL disposable mixing tube.
   NOTE: This will serve as a high-shear mixing vessel to ensure the homogeneous distribution of all the materials inside the slurry.
6. Add the appropriate amount of NMP (2.2 mL) to the mixing tube using a laboratory pipette. Add sixteen 6-mm diameter silicate glass-mixing balls and screw on the cap. Place the mixing tube on the high-shear mixing device, lock the tube into place, and mix the slurry for 15 min on the maximum setting (about 6000 rpm).
7. Add 0.8 g of the PVDF solution (prepared earlier in step 1.1.2.1) to the mixing tube. Continue mixing the slurry for another 5 min to ensure an even distribution of the binder. Immediately cast the slurry on the wires. If the slurry sits for longer than 5 min, mix the slurry for an additional 15 min prior to use, to ensure a homogeneous mixture.

3. **Casting and drying of reference electrode**
   1. Dip by hand the exposed copper, at the tip of each reference electrode, into the mixed slurry. Alternatively, drop-cast the slurry from a pipette onto the wire tip. Be sure to coat only the flattened, exposed section of the copper wire.
   2. Attach the cast RE wires to a base with the cast end suspended for drying. Tape the cast RE to a holder to avoid contact of the wet slurry with any surface (see **Figure 3a**). Dry the electrodes for at least 8 h in a laboratory oven at 70 °C.
   3. Measure the reference electrodes mass after drying and estimate the dried mass of the slurry (0.1 mg average over more than a 100 samples).
   4. Transfer the reference electrodes into the inert argon glovebox for use in the cell manufacturing process.

2. **Cathode and anode electrode preparation**
   1. Select the desired electrode to be studied.
      NOTE: For these tests, prefabricated electrode sheets will be used for demonstration purposes. In-house made electrodes or electrodes harvested from commercial cells can also be used.
   2. Punch out a circular disc of cathode material using a hollow 1.27-cm (1/2-in) punch. The electrode disc shape can be mechanically modified according to the desired test (see **Figure 4**). Weigh the electrodes and calculate the percentage of active material.
   3. Repeat steps 1.2.1-1.2.2 for the anode material, and the additional cells desired. Place each electrode disc into a small glass vial and carefully transfer the vials into the inert argon glovebox where they will be used during the cell construction process.

3. **Separator preparation**
   1. Fold a piece of paper (22.6 cm x 28 cm / 8.5 in x 11 in) in half lengthwise. Cut approximately a piece of 25 cm x 8.5 cm of polypropylene (PP) separator and gently place it inside the folded printer paper.
      NOTE: The paper provides some protection and rigidity when the separator is being punched out by hand.
   2. Place the paper and separator sandwich on top of a self-healing cutting mat. This provides a firm surface and will help avoid dulling of the hollow punch. Using a hollow 1.905-cm (3/4-in) punch, punch out one circular separator disc for each three-electrode cell. Prepare the separators in bulk and store them in a glass vial for later use.
   3. In addition, cut several small squares of separators approximately 5 mm x 8 mm; one of these separators will be used for each cell. Store these in a small glass vial. Transfer the vials of the separators into the inert argon glovebox for use in the cell construction process.

2. Construction of the Preparation Cell

1. Prepare the reference electrode by using a pair of pliers to bend the wire into a spiral shape (see **Figure 3b**). Make sure that the final spiral shape will fit inside the gasket of the coin cell (approximately 1.58 cm diameter). Place each electrode spiral into a small weigh boat and set them aside.
   NOTE: The extra wire spiral provides stability and will also be unfolded and later used in the working cell.
2. Clean both sides of a lithium metal ribbon by using a scalpel or a razor blade. Scrape off any surface oxidation until the shiny lithium shows through. Make sure to clean both sides of the lithium. Take extreme caution when using sharp objects inside the glovebox.
3. Punch out two 1.58-cm (5/8-in) discs for each cell from the cleaned lithium ribbon using the hollow punch.
4. Place one disc of lithium at the center of a 0.5-mm stainless-steel spacer. Press the lithium metal with the spacer firmly together; typically, a thumb press would suffice. Ensure that the lithium disc sticks to the spacer.
5. Place the coin cell case inside a small weigh boat. Fit the second disc of lithium inside the coin cell case. Make sure the lithium is centered and press firmly so that the lithium sticks to the bottom of the case.Place several drops of electrolyte [1.0 M $LiPF_6$ in EC/DEC (1:1 by volume)] on the lithium disc and several drops around the edge of the lithium to fill the outside gap.

NOTE: If insufficient electrolyte is added, there will be bubbles under the separator and inside the cell, which is undesirable.

6. Place one 1.905-cm (3/4-in) PP separator on top of the wetted lithium disc. Make sure that separator is completely wetted and there are no bubbles trapped underneath. Place the gasket in the cell with the gasket lip facing upwards; this lip is where the cap will seat into. Press firmly to fit the gasket into the case.
7. Using a pair of plastic tweezers, gently place the reference electrode spiral into the center of the cell. Add a few drops of electrolyte around the reference electrode. Place a small, rectangle separator on top of where the wire crosses over the gasket and the cell case.
   NOTE: The separator helps prevent shorting between the wire and the metal cell cap.
8. Place one 1.58-cm (5/8-in) separator on top of the reference electrode spiral. Make sure the separator is completely wetted and that there are no bubbles trapped underneath. Place the lithium-spacer disc on top of the reference electrode, with the lithium-coated side facing downwards.
9. Place the wave spring on top of the spacer. Make sure all components are centered inside the cell. Fill the cell to the brim with electrolyte. When the cell is crimped, the extra electrolyte will be squeezed out.
10. Using plastic tweezers, carefully place the cell cap on top of the assembly. Press firmly to seat the cap into the lip of the gasket. Bend the reference electrode wire such that it lays flat over the top of the cap. This is done to make sure the wire is not cut short when crimping the cell (see **Figure 2**).
11. Carefully transfer the cell to the coin-cell-crimping device by using plastic tweezers. When transporting, hold the cell flat to avoid the loss of any additional electrolyte. Crimp the coin cell to approximately 5 MPa (750 psi).
12. Remove the coin cell from the crimper and bend the exposed wire back up away from the top of the cell. This is to avoid any possible shorting between the cap and the reference electrode.
13. Remove the completed coin cell from the Argon glovebox. Using isopropyl alcohol and a lint-free task wiper, carefully clean the cell exterior. Take care to avoid disturbing the wire or the location where the wire exits the cell.
14. **Cell sealing**
    1. Carefully dry the coin cell using a lint-free task wiper. Take extra care to dry the location where the wire exits the coin cell.
    2. Mix equal parts resin and hardener to form a non-conductive epoxy. Using a toothpick or small probing device, carefully apply a small amount of epoxy to the location where the wire exits the coin cell. This is the location where the cell is most likely to leak.
    3. Allow 1 h for the epoxy to dry before connecting the coin cell to any testing equipment. Note that it can take up to 24 h for the epoxy to fully cure and harden.
       NOTE: The purpose of the epoxy is to seal the cell (see **Figure 5**) and not to provide any mechanical strength.

3. Lithiation Procedure

1. **Connection setup**
    1. Using a handheld lighter, burn off about 2 cm of insulation at the end of the reference electrode wire protruding from the cell; this is where the wire will connect to the testing device. Bend the exposed wire back on itself to improve the connection when connecting the three-electrode cell for testing.
    2. Place a small square of electrical tape (2 cm x 2 cm) across the top of the coin cell case; this should prevent any electrical contact between the top of the coin cell and the coin cell holder. Place the preparation cell in the cell holder.
       NOTE: The top of the cell should be insulated from any connection and the bottom of the cell should be connected to the negative reading on the cell holder.
    3. Using an alligator clip, connect the reference electrode to the top clip on the cell holder (positive connection).
       NOTE: The cell should be set up to test with the reference electrode acting as the positive electrode and the bottom lithium disc (cell case) acting as the negative electrode.

2. **Reference calibration voltage**
    1. Calculate the amount of active material present for the reference electrode.
       NOTE: For a typical electrode mass of 0.1 mg and an 80% active material composition, this comes out to 0.08 mg.
    2. Using the active material mass and the theoretical specific capacity of lithium titanate[20], determine the appropriate current to charge the cell at C/16.
    3. Cycle the reference electrode several times within the appropriate voltage range (1.25 - 2.25 V *vs.* Li/Li^+) at C/16; this range will change depending on the reference electrode in use. Take note of the plateau voltage/reference voltage, which should occur during both the charging and discharging processes.
       NOTE: For a $Li_4Ti_5O_{12}$ electrode this value is typically around 1.56 V *vs.* Li/Li^+.
    4. Record the reference voltage and the corresponding cell with which it is associated. Use this voltage later to calibrate the potential of the electrodes when used in a working cell.
    5. Rest the cell for 24 h and monitor that the reference electrode potential is steady.
    6. Transfer the lithiated cell into the inert argon environment for use in the working cell construction. Avoid any possible contact between the reference electrode and the cap or the cell case; this could short the reference electrode and alter its potential.

4. Construction of Working Cell

1. Place the coin cell case inside a small weigh boat. Place the cathode disk in the center of the cell case. Place several drops of the DEC electrolyte on the cathode and several drops around the edge to fill the outside gap.
2. Place one 1.905-cm (3/4-in) separator on top of the electrode. Make sure the separator is completely wetted and that there are no bubbles trapped underneath. Place the gasket with the small lip for the cell cap facing upwards. Press firmly to properly fit the gasket into the case. Set the coin cell assembly aside and locate the lithiated preparation cell.
3. **Extraction of the lithiated reference electrode**

1. Apply a small square of electrical tape to the top of the lithiated preparation cell. This helps prevent shorting between the case and cap during disassembly.
2. Hold the preparation cell firmly, with the cap side facing up, by using the thin-nosed pliers. Be careful not to short the cell with the metal pliers. Use the end-cutting pliers to carefully, yet firmly, pry open the coin cell along the edge. Take care not to short the top and bottom of the cell with the metal pliers.
3. Once approximately 70% of the cell has been pried open, hold the case with the end-cutting pliers and carefully separate the cell case and cap using the thin-nosed pliers. Carefully extract the lithiated reference electrode. Discard the other cell components.

4. Using a pair of pliers, unbend the spiral-shaped reference electrode wire and straighten. Re-bend the wire such that the tip sits in the center of the electrode and the wire extends over the edge of the cell. Cut off the exposed, uninsulated wire.
5. Add a few drops of electrolyte on and around the reference electrode. Place a small, rectangular separator on top where the wire crosses over the gasket and cell case. This helps prevent shorting between the wire and the metal case and cap.
6. Place one 1.58-cm (5/8-in) separator on top of the reference electrode; this helps to prevent shorting between the reference electrode and the anode. Place the prepared anode disc on top of the reference electrode in the cell. Take care to properly align the shape of the cathode with that of the anode.
   NOTE: The reference electrode tip should be in the center and the wire should exit in the rectangular gap.
7. Carefully place the 1.0-mm stainless-steel spacer on top of the anode. Place the wave spring on top of the spacer. Make sure all the components are centered in the cell. Fill the cell to the brim with electrolyte.
8. Using plastic tweezers, carefully place the cell cap on top of the assembly. Press firmly down to seat the cap into the lip of the gasket. Carefully fold the remaining wire back over the cell cap prior to crimping. This prevents the wire from being cut off during crimping.
9. Carefully transfer the cell to the coin cell crimping device by using a pair of plastic tweezers. When transferring the cell, keep it flat to avoid the loss of additional electrolyte. Crimp the cell to approximately 5 MPa (750 psi).
10. Remove the coin cell from the Argon glovebox. Carefully clean the cell using isopropyl alcohol and a lint-free task wiper.
11. **Cell sealing**
    1. Carefully dry the coin cell using a lint-free task wiper. Take extra care to dry the location where the wire exits the coin cell.
    2. Mix equal parts resin and hardener to form a non-conductive epoxy. Using a toothpick, carefully apply a small amount of epoxy to the location where the wire exits the coin cell. This is the location where the cell is most likely to leak.
    3. Allow 1 h for the epoxy to dry before connecting the coin cell to any testing equipment.
       NOTE: It can take up to 24 h for the epoxy to fully cure and harden. However, the purpose of the epoxy here is to seal the cell and not to provide any mechanical strength.

5. Electrochemical Tests

1. **Performance and cycling**
    1. Calculate the theoretical capacity for both the cathode and anode electrodes.
        1. Using the total dry weight of the electrode disc, the mass of the aluminum/copper substrate, and the weight percentage of the active material, determine the mass of the active material present for each electrode.
        2. Determine the capacity of each electrode by multiplying the mass of the active material by its respective theoretical capacity. Using the most limiting electrode capacity (typically the cathode), determine the overall cell capacity.

    2. Connect the cell to the electrochemical measuring device, taking care with connecting the positive power and positive sensor to the cathode and the negative power and sensor to the anode. Connect the reference to the reference electrode via the copper wire (see **Figure 6b**).
    3. Double-check that the cell is connected and working properly by checking the open circuit voltage and potentials. Use the reference voltage recorded during the lithiation procedure to calibrate the cathode and anode potential readings.
    4. Cycle the full cell at the desired C-rate, for example C/10, and measure the full cell, cathode, and anode potentials simultaneously. Repeat steps 5.1.1 - 5.1.4 for other cells and C-rates as desired, depending on the specifications and requirements for each cell.

2. **Electrochemical impedance spectroscopy**
    1. **Full cell impedance**
        1. Connect the cell to the EIS measurement device. Use the following configuration: the positive power and positive sensor to the cathode, the negative power and negative sensor to the anode.
           NOTE: The reference sensor should be connected to the anode. The reference electrode should remain disconnected.
        2. Select the potentiostatic control for the EIS with an amplitude of 10 mV. Select a frequency range of 1 MHz to 1 mHz. Collect the impedance of the full cell. Plot a Nyquist plot and Bode plot to analyze the response of the cell.
           NOTE: The frequency range may not always be required and can be modified after collecting the preliminary results.

    2. **Cathode impedance**
        1. Connect the cell to the EIS measurement device with the following: the positive power and positive sensor to the cathode, the negative power and negative sensor to the anode, and the reference sensor to the reference electrode via the copper wire.
        2. Repeat the same steps as for the full cell impedance (steps 5.2.1.2 - 5.2.1.3).

    3. **Anode impedance**
        1. Connect the cell to the EIS measurement device with the following: the positive power and positive sensor to the anode, the negative power and negative sensor to the cathode, and the reference sensor to the reference electrode via the copper wire.
        2. Repeat the same steps as for the full cell impedance (steps 5.2.1.2 - 5.2.1.3).

    4. **Impedance as a function of state of charge**

1. Connect the cell to the EIS measurement device according to the desired impedance measurement: either full cell, cathode, or anode. Use steps 5.2.1.1, 5.2.2.1, or 5.2.3.1, respectively, for the appropriate connection.
2. Charge the cell using a constant current at C/2 until the cell reaches the upper voltage limit. Hold the voltage at the upper limit using a constant voltage control method until the applied current drops below C/100. The cell should now be fully charged.
3. Discharge the cell at C/2 for 3 min; the cell should now be at 90% SOC. Allow the cell to rest for 1 h to reach thermal and electrochemical equilibrium conditions.
4. Collect the impedance using the same procedure presented in steps 5.2.1.2 - 5.2.1.3. Repeat steps 5.2.4.3 and 5.2.4.4 to collect the impedance as a function of the SOC.

Representative Results

Typical results for the voltage and potential profiles for the three-electrode cell can be seen in **Figure 7**. In an ideal setup, the full cell voltage should be identical to that produced from a two-electrode cell using the same electrode couple. This is one method to determine whether the insertion of the reference electrode modifies the performance of the cell. If there is a significant difference between the two- and three-electrode full cell performance (for identical working and counter electrodes), then it can be assumed that the insertion of the reference electrode modifies the behavior of the cell and the results are no longer meaningful.

During the charging process, lithium moves from the cathode to the anode electrode. As lithium is being removed from the cathode microstructure, its potential with respect to Li/Li^+ increases. The opposite occurs with the anode, as the structure is continually filled with lithium. During discharge, the reverse situation occurs. These changes in potential are reflected in the three-electrode potential profiles, which can be seen in **Figure 7**.

A powerful outcome of the three-electrode cell setup is the detection of the onset of lithium plating. **Figure 8** shows an example of an anode potential profile during the fast charging of a coin cell. From the zoomed-in portion of the plot, it can be seen that the anode potential reaches negative values towards the end of the CC charging process. This is indicative of the presence of lithium plating in the cell. This measurement is not possible when using a standard two-electrode setup.

The impedance results for the three-electrode setup are shown in **Figure 9**. A typical impedance response consists of three characteristic regions: a high-frequency semicircle, a medium-frequency semicircle, and a low-frequency diffusion tail. The Re(Z) intercept of the plot, the radii of the semicircles, and the slope of the diffusion tail can be used to characterize important electrochemical phenomena occurring within the cell.

Another powerful use of the three-electrode tool is impedance characterization as a function of the state of charge. This impedance can be correlated to various degradation phenomena, including the electrodeposition of lithium. **Figure 10** shows an example of impedance spectra collected for the full cell, cathode, and anode for a single coin cell. The changing impedance can be used to characterize the individual contributions of electrode impedance as the cell SOC is changing. For the anode, the impedance can be correlated to the various degradation phenomena, including the growth of the SEI layer and lithium plating and dendrite formation. Distorted impedance measurements including inductive loops (see **Figure 11**) can be correlated to two different factors. A bad sealing of the cell along with electrolyte leaking (see **Figure 5**) can induce an inductive impedance response. The electrode shape and the position of the reference electrode tip (see **Figure 4**) can also induce inductive loops on the impedance response[21].

The behavior of the individual electrode potentials can be used to provide analysis, which is not available in traditional two-electrode setups. For example, plateau regions in the potential profile can represent phase changes in the electrode structure. These phase changes can be corroborated with additional electrochemical testing, such as cyclic voltammetry. Also, the value of the anode potential can be used in conjunction with other methods to determine lithium plating, which occurs once the anode potential has reached a value below 0.0 V *vs.* Li/Li^+.

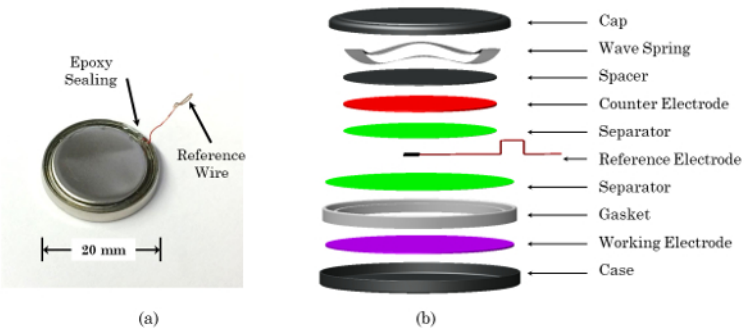

Figure 1. In-house three-electrode cell setup. (**a**) This panel shows a photograph of a completed three-electrode coin cell. (**b**) This panel shows an exploded view of the internal cell components. Please click here to view a larger version of this figure.

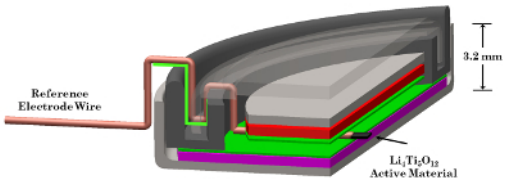

Figure 2. Three-electrode coin cell showing the entry point of the reference electrode as well as the internal layout. Note that in this figure, the cap is transparent and the wave spring (not shown) is located just above the top spacer. Please click here to view a larger version of this figure.

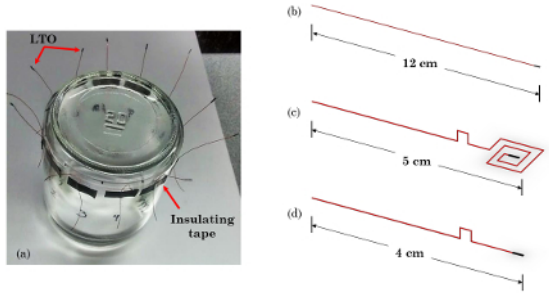

Figure 3. Reference electrode configurations. (**a**) This panel shows a reference electrode batch taped to a holder element (*e.g.*, clean glass container) with the coated ends suspended for drying. The following panels show reference electrode configurations corresponding to (**b**) the situation immediately after the electrode casting onto a wire, (**c**) the use in a preparation cell, and (**d**) the use in a working cell. The panels are not drawn to scale. Please click here to view a larger version of this figure.

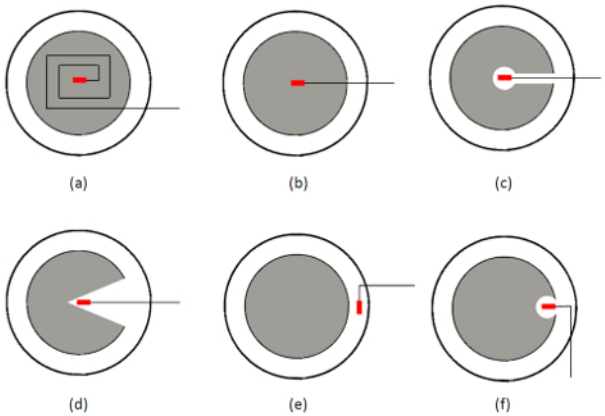

Figure 4. Various electrodes that are possible to use in the construction of three-electrode coin cells. These panels show (**a**) a spiral shape, (**b**) a central reference, (**c**) a keyhole shape, (**d**) a pizza-slice shape, (**e**) on the side, and (**f**) on the side with a small circular cutout. Please click here to view a larger version of this figure.

Figure 5. Improperly sealed three-electrode coin cells, demonstrating leaking and the resultant reaction of electrolyte with environment. Under this condition, it is recommended to remove the cell from the holder, since electrolyte can rust the electrical terminals. Please click here to view a larger version of this figure.

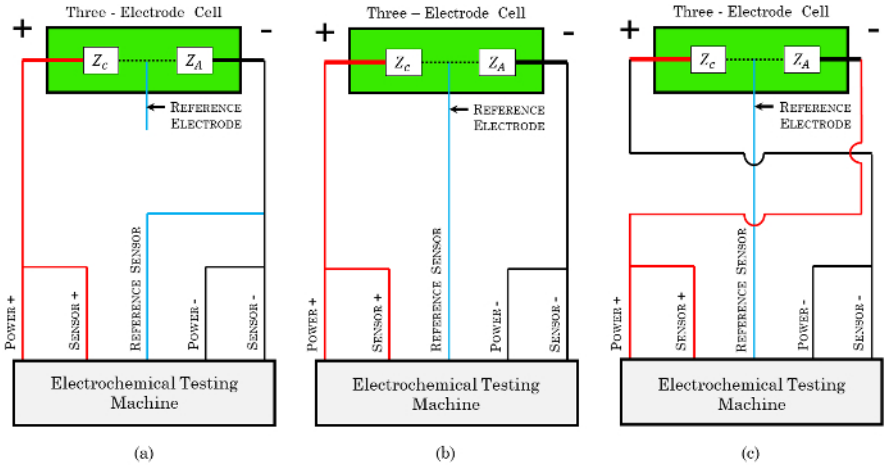

Figure 6. **Connection to the electrochemical testing machine to measure impedance**. Connection configurations are shown for (**a**) a full cell (Z_F), (**b**) a cathode (Z_C), and (**c**) an anode (Z_A). A performance and cycling of the three-electrode cell can be done using the cathode connection shown in panel (**b**). Please click here to view a larger version of this figure.

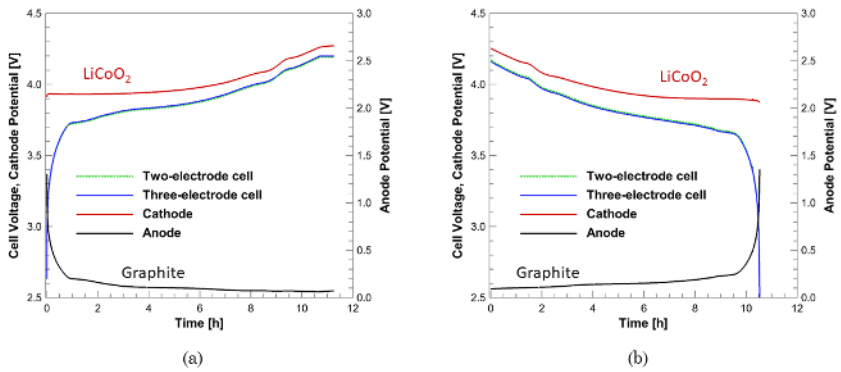

Figure 7. Voltage measurements. These panels show the voltage measurements for an anode, a cathode, and a full cell (two- and three-electrode cell) during (**a**) constant current, constant voltage (CCCV) charging at C/10 and (**b**) constant current (CC) discharging at C/10. Please click here to view a larger version of this figure.

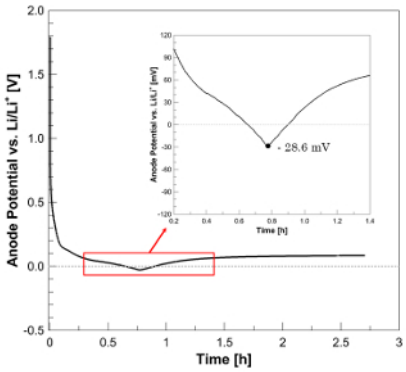

Figure 8. Negative anode potential during fast charging. This panel shows a negative anode potential occurring during the fast charging (1C-rate) of a three-electrode coin cell, indicating the possible presence of lithium plating. Please click here to view a larger version of this figure.

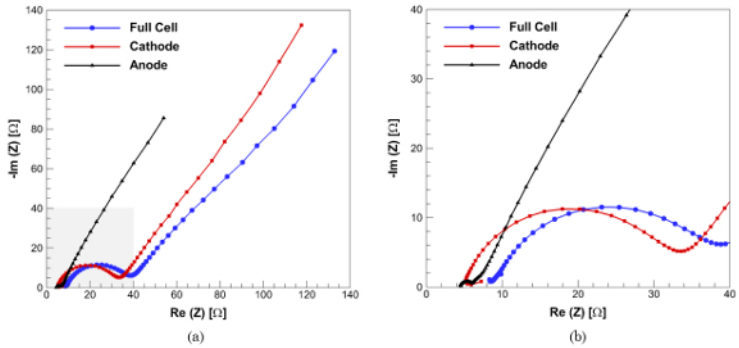

Figure 9. Impedance response. These panels show the impedance response from using a frequency response analyzer for a full cell, a cathode, and an anode showing (**a**) a complete frequency range and (**b**) a low-frequency range. Please click here to view a larger version of this figure.

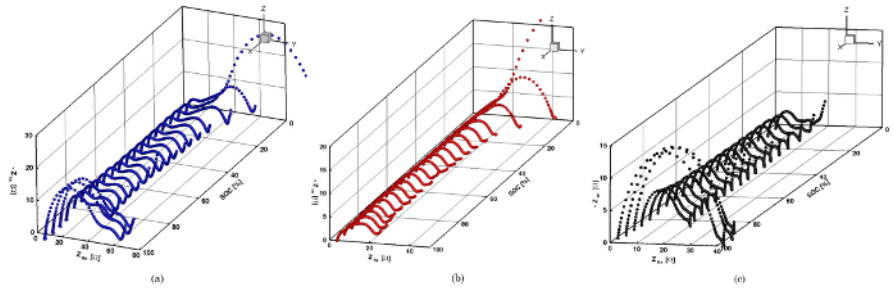

Figure 10. EIS. These panels show the electrochemical impedance spectroscopy corresponding to (**a**) the full cell, (**b**) cathode, and (**c**) anode measurement for a three-electrode coin cell as a function of the SOC. Please click here to view a larger version of this figure.

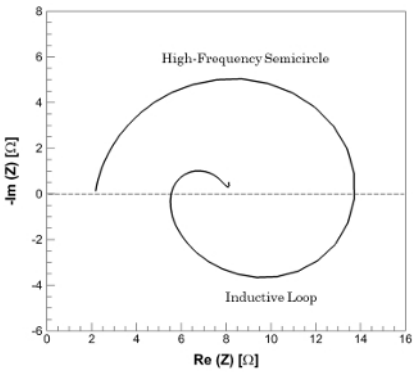

Figure 11. Anode impedance distortion. This figure shows anode impedance distortion measured for a three-electrode coin cell, likely caused by either a misalignment of the reference electrode inside the cell or an improper sealing of the coin cell near the exit location of the wire. Please click here to view a larger version of this figure.

Discussion

Cell crimping pressure plays an important part in the success rate of both the preparation and working cells. If the cell is crimped at too high a pressure (>800 psi), the reference electrode can become shorted with the cell cap due to the reference wire position in-between the cap and the gasket. Note that the wire crossing this interface is a requirement in order to connect the reference electrode reading to an external measurement device. If the cell pressure is too low (<700 psi), the cell can have issues with incomplete crimping which may cause electrolyte leakage and air penetration after the cell is removed from the inert argon environment. It was found that around 750 psi is the optimal pressure for crimping the cell to avoid leaking or shorting issues. In order to provide additional means to prevent these issues with shorting of the reference wire, a vital step in the construction process is the additional square separator that is placed along the gasket where the wire crosses the cell boundary. This separator provides an additional insulating layer that helps prevent internal shorting. In addition, slightly different crimping pressures may be required for the preparation and working cell. The preparation cell uses two lithium discs that are significantly thicker than an electrode cast on a metal foil-which are used in the working cell.

After the lithiation of the reference electrode in the preparation cell, the reference electrode must be extracted and reused in the working cell. During this process, extreme care must be taken. In general, if the reference electrode was prepared properly, there should not be any issue associated with the adhesion of the material to the flattened section of the wire. In any case, the amount of time between when the reference electrode is removed from the preparation cell and used in the working cell should be minimized. The reference electrode should not be placed on any surface or allowed to rest outside for a significant amount of time. Minimizing manipulation of the wire is ideal because it avoids possible fatiguing and breaking of the wire.

Another important consideration when constructing the three-electrode coin cell is sealing the cell properly. Because the wire is sandwiched between the cap and the gasket, there is potential for a small breach in the cell that may allow for electrolyte leakage or air penetration in the cell. If this is not rectified, distortion may be seen in the impedance measurements and the entire cell may fail due to reactions with the environment, especially after an extended period outside of the inert glovebox in which it is fabricated. In the cell construction procedure, the use of the non-conductive epoxy is vital because it completely seals the cell from the outside environment. One interesting observation is that if the cell is not crimped to a high enough pressure, the epoxy will not harden properly and will sometimes bubble up. This may be caused by the electrolyte being wicked up and mixed with the epoxy, or the higher internal pressure of the cell slowly leaking out and causing bubbles to form. Note that the epoxy, both during and after hardening, was soaked in the electrolyte and no obvious sign of any reaction was observed. If used properly, the epoxy-sealed cell should be allowed to dry for a minimum of 1 h inside the glovebox before removal. Afterward, the epoxy can harden in an atmospheric environment. Depending on the epoxy used, it may take 24 h or more for the epoxy to fully cure, and during this process, the cell should be allowed to rest. In the event that the cell is not sealed, or the sealing procedure is not sufficient, the cell will leak into the environment. After a while, the cell may begin to change colors. Some examples of poorly sealed cells can be seen in **Figure 5**.

When constructing the three-electrode coin cells, the shape of the host electrodes can have an influence on the performance of the cell. Various possible shapes can be seen in **Figure 4**. In an ideal case, the reference electrode would be placed at the center of the electrodes. Some problems that can occur involve an uneven pressure distribution within the cell due to the location of the reference electrode. Another issue is that the existence of the reference electrode between the host electrodes creates an artificial increase in the cell impedance, due to the fact that the reference is blocking a portion of the electrode area. Some configurations (**Figure 4C - 4F**) attempt to reduce this issue by carving out a small area in which the reference can sit. The problem is that this reduces the cell capacity as well as introduces complexity in the manufacturing process.

When connecting the three-electrode cell to the electrochemical testing measurement, the connection to the reference electrode can be very sensitive due to the small diameter of the copper wire used. Note that the wire diameter must be small in order to reduce any effects on the cell performance, one of which could be a blockage of the area between the two planar electrode disks. Because of this connection sensitivity, it is advantageous to bend the exposed end of the copper wire back on itself multiple times to increase the surface area for connection. If this is not done, the reference electrode may appear to be shorted or have failed, when in fact the cell is working as expected.

One limitation of using a three-electrode coin cell is that the entire process is done by hand. A certain amount of practice is required when constructing coin cells in order to produce consistent and reliable results. In the case of accidental shifting of the position of the reference electrode, working electrode, and/or counter electrode inside the cell, impedance and potential readings may become distorted or inaccurate.

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This is not as important for the preparation cell because the objective of this cell is simply to prepare the reference by partial lithiation and to determine the value of the plateau voltage (typically ~1.565 V for the lithium titanate electrodes used in this procedure).

One good method for determining the success of the cell is through the observation of impedance distortion for the anode. In the case of an improperly sealed cell, or a poor electrode alignment, inductive impedance loops are often seen when taking the anode impedance. These loops are more easily noticed when the cell is fully discharged (*i.e.*, when the cell is first constructed), so they can be tested for prior to any cycling of the cell. An example of anode impedance spectra with the distortion present is shown in **Figure 9**.

Disclosures

The authors have nothing to disclose.

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