Development and Use of a Lithium-Metal Reference Electrode in Aging Studies of Lithium-Ion Batteries

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The development and implementation of an in situ lithium-metal reference electrode for use in lithium-ion cells is described. The reference electrode is inserted into cylindrical, commercially available 1.2 Ah lithium-ion cells via perforation of the cell’s outer metallic casing. The reference electrode is used to investigate voltage characteristics of the individual electrodes throughout calendar (i.e., zero duty) aging and duty cycle aging regimes. The response of the electrode voltages (vs. reference) to a given current pulse prior to and during interruptions of the aging regime indicates that the resistance of the positive-electrode is much larger than that of the negative electrode. Prior to aging, the ratio of the positive electrode resistance to that of the negative electrode is approximately two. After aging, the resistance of the positive electrode nearly triples, resulting in a ratio of approximately six, with the resistance of the negative electrode remaining approximately unchanged for both calendar- and cycle-aging regimes. The changes in the cell’s coulombic capacity at various discharge rates are also characterized and indicate the additional contribution of cycle aging over the calendar aging alone to the capacity loss of cells. Furthermore, both “charge depletion” and “charge sustaining” cycle aging were investigated and indicates the added stress of charge depletion operation.

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The service life of rechargeable lithium-ion batteries has certainly improved from the early days1,2 by using more robust materials and better manufacturing methods and has contributed in the wide-spread adoption of these batteries. While many aging parameters can affect life, such as depth-of-discharge, discharge or charge rate, and state-of-charge (SOC), increased temperature has been shown to greatly accelerate the aging processes and is very often used to expediently obtain aging information.3,4 Aging is generally characterized by measurements of coulombic capacity and power (and/or resistance) at specified reference conditions during temporary interruptions of a certain aging regime. Proposed degradation mechanisms by Liu et al. for capacity loss6 focus on buildup of a solid-electrolyte inter-phase (SEI)7 on the negative electrode and for resistance rise focus on decrепitation (micro-cracking, structural disordering, and dissolution) of the active material of the positive electrode.8–10 Although the cell voltage (i.e., positive vs. negative electrode) response is typically measured during aging studies, the employment of a reference electrode allows changes in the cell voltage to be ascribable to contributions from the individual electrodes.11 The use of a reference electrode can therefore add crucial information to the understanding of the degradation mechanisms that lead to cell aging and is the primary focus of this work. The development of an in situ lithium-metal reference electrode is described, whereby the electrode is placed within the cell through a perforation and provides direct contact with the liquid electrolytic solution that saturates the cell’s components.

A reference electrode provides a potential against which the potentials of the indicator electrode can be measured.11,12 The reference electrode also allows the measurement of the potential in the solution. The potential difference between the solution and either electrode can be used to isolate electrode performance. An ideal reference electrode should be reversible (i.e., non-polarizable)12 and the potential should remain constant during the measurement. However, no electrode can absolutely meet these criteria since no reference electrode is completely reversible or stable. In a lithium-ion system, the lithium metal reference electrode must be sufficiently stable in the electrolytic environment by not contributing to the reaction in the system and provide a known and stable thermodynamic potential over the period of use. Lithium metal with an electrolyte that is similar to the electrolyte in the cell is often the reference electrode of choice in these systems. This reference electrode, while not ideal, is sufficiently reversible and easily produced, and thus used for this work.12

Reference electrodes have been used previously in a variety of ways to study lithium-ion cell behavior. Commonly used reference electrodes are inserted into the cell prior to the sealing of the outer casing material;15–18 however, this approach is not amenable to mass production and may alter the performance of the cell relative to one without an inserted reference electrode. Liu et al.12 utilized a reference electrode by removing the end cap of a cylindrical cell and immersing both the cell and reference electrode in an electrolyte-filled vessel, with the reference electrode located outside of the cell.19 These researchers conducted a cycle-aging regime on a cell in this configuration and reported voltage of the negative electrode (vs. Ref.) during several capacity tests as the cell aged. In contrast, in our studies the cells are aged prior to reference electrode insertion in order to minimize the impact of the lithium reference electrode insertion on the chemical processes involved in the cell over the long term. Liu et al. utilized a variety of cell resistance characterization methods (via full cell voltage measurements) to show that the cell resistance did not increase during any of aging regimes imposed on their graphite/iron phosphate cells. Although the cells in our study employ a different positive-electrode material, a significant increase was observed in cell resistance throughout life that is attributable to the positive electrode through our reference electrode measurements. This is contrary to the generally accepted idea that the SEI build up on the negative electrode results in cell failure,15,14 presumably due to resistance rise.

Other reference electrode designs have focused on the removal of a sample of one of the electrodes, which is introduced into a specially designed cell with a counter electrode and a reference electrode.25,16 These designs are capable of quantifying the capacity of the electrode but are inadequate to determine the original resistance contribution of the individual electrodes in the original configuration. Another disadvantage of these designs is that at a given cell SOC the individual electrode voltages relative to the reference voltage cannot be determined; this information is lost when the cell is disassembled.

The work reported here focuses on several cells selected for reference electrode measurements before and after aging and is a subset of a larger aging study of over 170 cells20,21 conducted at Idaho National Laboratory. In contrast to other studies, the aging regimes in our cell life studies are specifically designed to represent usage in the
environment of a plug-in hybrid (PHEV). Three general types of aging regimes are investigated: (1) calendar (i.e., zero-duty) aging that minimizes the effects of the chemical and mechanical stresses induced by current throughput, (2) charge-sustaining (CS) cycle aging that would include these additional stresses in a limited range of SOC, and (3) charge-depleting (CD) cycle aging which would include further additional stresses due to operation throughout a larger SOC range. Aging data can aid in the development of improved battery control strategies. The ability to evaluate changes in the performance of the individual electrodes during life studies with a reference electrode will be of particular importance to the development of computer battery-aging models; elucidation and validation of proposed aging mechanisms will lead to model improvements.

Experimental

This work focuses on several cells that were aged at 60°C and selected from a larger aging study of 170 cells to undergo performance characterization with in situ reference electrodes. The commercially available 1.2 Ah, 18650-size cylindrical, high-power lithium-ion cells employed a blended positive-electrode active material (i.e., Ni–Mn–Co layered oxide and spinel manganese oxide), dissolved lithium salts in organic solvents, and a carbonaceous negative electrode. First, the reference electrode insertion and construction techniques are described, and then the aging regimes and the reference performance test (RPT) methods that ensued after interruptions of the aging regime are described. The aging regimes and RPTs are based on the United States Department of Energy's PHEV battery test manual for a 10-mile electric-range vehicle and test plan, which includes the appropriate ratings, safety precautions, specific procedures to be performed, and final disposition of the batteries upon completion of the test.

Reference electrode implementation.— Since the intrusion of oxygen and water into a cell would result in severe performance degradation, perforation of the cell was accomplished in the confines of an Argon-filled glove box as well as all testing after the insertion of the reference electrode. A specifically designed apparatus (see Figure 3) was used to cut a plug out of the negative end of the cell for reference electrode insertion after the cell was X-rayed to determine the optimal location of the perforation.

X-Ray imaging.— Figure 1 gives an X-ray image of the cell focused to show the electrode coatings of the winding, which appear as the whiter annulus-shaped region that fills the can. This figure indicates that it is more appropriate to drill into the negative terminal than the positive because there is less material to drill through. The cell’s burst disk resides in the crimped region, which is part of the positive cap shown in the figure.

Figure 2 shows an X-ray of the negative end of the cell focused to show the internal tab and the external nickel foil tab that was welded to the negative terminal to assure a low-ohmic connection. The optimal location for perforation (denoted as an “X” in the figure) was chosen based on avoidance of the internal folded metal tab and the external tab and the opportunity to drill into empty gas space. The figure’s insert gives an expanded view of the negative end of the cell shown in Figure 1, where the feathery, thin gray lines protruding above the winding annulus are the individual sheets of separator between the positive and negative electrode coated foils.

The X-ray in Figure 2 also reveals the exterior of the can and the external tab on the outside of the cell and the internal folded metal tab in the interior of the cell, which runs along the inside face and also along the length of the cell wall. This internal folded metal tab running along the length of the cell is also somewhat visible on the right side of the image in Figure 1. Note that the external tab is not

Figure 1. X-ray of the 18650 cell focused to show the electrode winding that fills the can. The negative end of the cell is at the top of the figure and the positive terminal is at the bottom.

Figure 2. X-ray of the negative end of the 18650 cell focused to show the internal and external welded metal tabs. The “X” marks the optimal location for perforation. Insert: expanded view of the negative end of the cell shown in Figure 1.
visible in the insert because the image was taken before the tabs were welded to the cell.

**Cell perforation.—** Even in an inert atmosphere, perforation of a lithium ion battery can be hazardous because of the risk of shorting. Shorting the electrodes can cause the cell to proceed into a thermal runaway condition that could result in explosion. The use of a traditional drill bit can produce small shavings of metal that can be introduced into the cell during the cutting operation and result in localized shorting. Consequently, cell perforation was performed from the bottom (i.e., with the negative end facing downward) with the customized hole-cutting apparatus shown in Figure 3. The apparatus employed a 13/64 inch Brad point drill bit that had the center hollowed out to transform the bit into a plug cutter. This hollowed-out design greatly reduced the risk of shorting by minimizing the production of metal shavings during the perforation process. The cutting head approached the negative end of the metal can from the bottom, so the metal shavings that were produced did not fall back into the hole. The cutting bit was magnetized to collect both the metal plug and the metal shavings as they fell away from the can. The customized hole-cutting apparatus was designed to allow the alignment of the cutter in the horizontal and vertical direction, by moving the cell in relation to the cutting head, while firmly holding the cell. The cutting process was viewable from the side or above via the proper placement of mirrors. The highly accurate controls allowed movement in the thousands of an inch.

**Reference electrode insertion and construction.—** Once the hole in the cell was cut, a small plastic ampoule was placed into the hole (see Figure 4) and filled with electrolyte. The lithium utilized in the reference electrode consisted of a small piece of lithium metal foil (9.5 mm × 25 mm × 1 mm) that was pressed and flattened onto an 80 mm long, 26 gauge nickel wire. The same reference electrode was used for all four cells. The foil was fed through the ampoule and set on top of the separator layers inside the cell, just past the bottom of the ampoule. The electrolyte was made with LithChem lithium hexafluorophosphate (1.2M LiPF$_6$) in a 2:8 volumetric ratio of ethylene carbonate to ethyl methyl carbonate, which was similar to the electrolyte found in the cell. The process of adding the reference electrode to the cell in its original can is novel in that it places the reference electrode as close as possible to the cell in its original container, which allows the cell resistance and capacity to be measured and compared to test results of cells without the reference electrode. Figure 4 shows the specially designed device that firmly holds both the cell and reference electrode during testing. The figure also shows the positive, negative and reference electrode connections to the tester.

Prior to the insertion of a reference electrode, the cells were subjected to a series of capacity and power tests to stabilize performance. Because the aging-study RPTs were all performed at 30°C, these tests were conducted at both 30°C and glove-box temperature (~25°C) to establish a baseline of initial performance. After reference electrode insertion these capacity and power tests were repeated (and in some cases a C/25 discharge was performed) at ~25°C inside the glove box, which included the collection of voltage data relative to the reference electrode. The reference electrode was placed as close as possible to the electrode winding within the cell, such that the ohmic potential drop in the measurement was minimized and a resistance measurement of greater accuracy was obtained.

New, unaged cells were fit with reference electrodes and tested for power and capacity performance to serve as a baseline to measure the performance degradation that occurred after aging; however, cells fitted with reference electrodes were not subjected to the aging regime studies. Reference electrodes were inserted into the cells after aging in order to eliminate the influence of the reference electrode on the aging process and preserve the integrity of the reference electrode itself. This article focuses on reference electrode results of four cells, one not aged and three aged at 60°C, although three other cells were aged at 50°C and tested with reference electrodes as well; the 60°C-aged cells showed the best resolution for performance degradation and are therefore the primary subject of discussion of results.

**Reference performance testing.—** The RPTs were used to track the capacity fade, power fade, and resistance rise every 32 days throughout the aging process. The RPT data of cells that were not instrumented with reference electrodes were presented previously.26 During most of the RPTs, 7.1 W discharge capacity tests (to a 2.7 V cutoff) as well as pulse power tests were performed.22 Selected RPTs included a C/25 discharge (i.e., 50 mA to a 2.7 V cutoff) capacity test, where the C/1 is based on the manufacturer's rated capacity of 1.2 Ah. Charging in all RPTs was performed at the C/1 rate, except for the C/25 capacity tests. In both capacity tests, discharge from a fully-charged state is preceded and followed by a 1 h rest at open circuit and is terminated on the manufacturer's specified cutoff voltage, 2.7 V. The fully charged state is obtained by charging at the C/1 rate to 4.2 V, which is maintained until the current drops below 50 mA (e.g., Figure 9).

The 7.1 W capacity test corresponds to the discharge rate of a single cell in a 1400-cell pack at the 10 kW rate for 10 miles of all-electric range. This rate is not changed as capacity changes during aging from the original 1.2 Ah. This constant-power discharge test is used in place of the more common C/1 constant current discharge test used in HEV testing.31 Depth-of-discharge (DOD) is taken to be the fraction of the rated capacity (i.e., 1.2 Ah) removed from the cell during a discharge, whereas in this work SOC is defined by the open-circuit voltage (as measured at the beginning-of-life [BOL, i.e., RPT 0] in a hybrid pulse power characterization [HPPC] test). This

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**Figure 3.** Custom-built hole-cutting apparatus.

**Figure 4.** Cell in holder with reference electrode, positive, and negative terminals connected to the battery tester.

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1Approximately 10 kW will sustain an average passenger vehicle at typical freeway velocities. The 1400-cell pack meets the power and energy targets for a 10 mile PHEV in accordance with the Battery Test Manual.22
definition of SOC simplifies the programming of the test equipment because the test programs do not have to be changed at each RPT. Therefore, only at BOL is SOC = 1 − DOD. In the majority of published works SOC is based on a C_{1/2} discharge capacity at each RPT to define 100% SOC, and intermediate values are Coulombic fractions thereof.

The HPPC test\textsuperscript{23} is a means of assessing power and resistance by using both discharge and charge pulses and establishes an open-circuit voltage (OCV) vs. DOD relationship. This test is performed during initial cell characterization as well as during the interruptions of calendar and cycle aging regimes as part of the RPT. The test as executed in this work provides 10-second (or less) discharge and charge resistances at 10% depth of discharge increments.

The HPPC test is made up of single repetitions at 10% DOD increments of a 5.3 A discharge pulse, 40-second rest, a 4.0 A charge pulse, separated by 2.13 A constant-current discharge segments to the next DOD, and followed by a 1-hour rest to allow the cell to return to an equilibrium state at open circuit. The test is initiated at 0% DOD, or full charge, and ends after completing the final profile at 90% DOD or when the manufacturer’s minimum voltage is reached. Results of voltage and current profiles during the HPPC portion of an RPT (i.e., between 400 and 1000 minutes) are shown in Figure 11a and Figure 11b, respectively. Every cell that was fit with a reference electrode was subjected to five sequential RPTs at 25°C before reference electrode insertion and five after insertion, whereas only a single RPT (at 30°C) was performed during the interruptions of the aging studies.

Cell aging.— A Maccor 4000 programmable tester capable of providing a voltage from 0 to 5 V and current from 0 to 30 A was utilized to generate the cell aging profiles. Temperature and reference electrode measurements were made via connection to the auxiliary voltage inputs. The cells were aged in a temperature-controlled chamber to maintain the desired test temperature and isolate them from the temperature fluctuations of the environment. The test matrix followed in the full aging study is shown below in Table I. Additional details of the full aging study can be found in Refs. 23 and 24. Each of the baseline conditions included 10 cells, with 5 cells being tested at the other conditions to give good statistical replication.

In the full study, the effects of temperature on calendar life, CS cycle life, and CD cycle life\textsuperscript{1} and the effects of SOC on calendar life were investigated. During calendar aging a cell is exercised once daily for 1 hour to generate the cell aging profiles. Temperature and reference electrode insertion and five after insertion, whereas only a single RPT (at 30°C) was performed during the interruptions of the aging studies.

Table I. Abbreviated Testing Matrix.

| Test Number | Cell #’s | Condition          | Temperature (°C) | SOC      | Testing Focus               |
|-------------|---------|--------------------|------------------|----------|----------------------------|
| 1           | 1–10    | CD Cycle Life      | 30               |          | CD Cycle Life Temp.         |
| 2           | 31–35   | ”                   | 40               |          | ”                          |
| 3           | 41–45   | ”                   | 50               |          | ”                          |
| 4           | 51–55   | ”                   | 60               |          | ”                          |
| 5           | 26–30   | Calendar Life      | 30               | 90% SOC  | Calendar Life SOC           |
| 6           | 11–20   | ”                   | 30               | 60% SOC  | ”                          |
| 7           | 21–25   | ”                   | 30               | 30% SOC  | ”                          |
| 8           | 11–20   | ”                   | 30               | 60% SOC  | Calendar Life Temp.         |
| 9           | 36–40   | ”                   | 40               | 60% SOC  | ”                          |
| 10          | 46–50   | ”                   | 50               | 60% SOC  | ”                          |
| 11          | 56–60   | ”                   | 60               | 60% SOC  | ”                          |
| 12          | 61–70   | CS Cycle Life      | 30               |          | CS Cycle Life Temp.         |
| 13          | 71–75   | ”                   | 40               |          | ”                          |
| 14          | 76–80   | ”                   | 50               |          | ”                          |
| 15          | 81–85   | ”                   | 60               |          | ”                          |

\textsuperscript{1}Note that this corresponds to 80% of the 3.4 kWh for the 1400-cell pack.

Results and Discussion

Cell capacity from reference performance testing.— The curves in Figure 7 indicate capacity loss throughout calendar aging as measured by 7.1 W (dashed) and C_{1/25} (solid) discharge capacity tests (Cell 60) prior to reference electrode insertion. Figure 8 gives the 7.1 W and C_{1/25} data for CD-aging (Cell 53) prior to insertion. Both cells encountered six RPTs and were therefore aged for the same time period (~6 months). The green diamonds in Figure 7 give the OCVs obtained from the BOL HPPC test. The C_{1/25} maximum capacity is reflective of the theoretical maximum capacity of Cell 60 because the BOL C_{1/25} voltages are in good agreement with these OCV values. Calendar aging resulted in the cell retaining only 53% of the BOL capacity, as measured by the C_{1/25} test. The capacity retention after CD aging of 42% indicates the additional reduction in the theoretical maximum capacity due to cycling. Comparison of the dashed curves (~2-hour discharge) voltages to those of the solid curves (~25-hour

\textsuperscript{2}A modified dynamic stress test or “DST.”
Figure 5. Daily pulse current profile (and example voltage profile) used to reset the cell OCV during the calendar aging regime. (Note: in all figures discharge current is shown as positive in sign and charge current is shown as negative in sign).

Figure 6. The power vs. time profiles used to cycle-age the cells, where the arrows denote the BOL maximum currents attained during the profile. The 90-second CS-aging and 360-second CD-aging profiles, respectively, are shown in red and navy.

discharge) indicates the voltage losses that are typically associated with the transport and kinetic irreversibilities\(^1\) that are absent in the nearly equilibrated C/25 discharge.

Figure 9 shows the voltage vs. time data during the full 7.1 W capacity test at EOL\(^+\) for the CD-aged cell (Cell 53) after reference electrode insertion. These data indicate that the cell voltage excursions throughout the test (i.e., over 1.5 V) can be attributed to the positive rather than the negative electrode. An expanded ordinate for the negative vs. Ref. is shown to highlight the voltage response of the negative electrode, which varies less than 100 mV throughout the test. The discharge capacity was measured to be 0.54 Ah, which indicates that the cell further lost 7% of its capacity during cold storage (i.e., compared to 0.58 Ah in Figure 8). The variations (±5 mV) in electrode voltages vs. Ref. during the 1 hour rest periods before discharge and after charge demonstrate satisfactory stability of the reference electrode. The precipitous drop in the positive voltage vs. Ref. during the discharge at 76 minutes and the lack of response in the negative voltage vs. Ref. indicates that the positive electrode limits the available capacity of the cell in this test. The lower electronic conductivity of the positive electrode active material relative to that of the negative\(^2\) is the likely explanation for the apparent higher resistance of the positive electrode than that of the negative and will be discussed further in the next section. The electrode voltages vs. Ref. during the rest period between discharge and charge show that the cell voltage relaxation behavior after interruption of discharge also is dominated by the positive electrode. The cell voltage after interruption is within 20 mV of the 1-hour cell OCV after 30 minutes. The rise of the negative

\(^1\)Overvoltage has been associated with ohmic and mass transport in the solid and liquid phases as well as charge transfer, for example.\(^2\)
Figure 7. Capacity test data before and after calendar-aging (60°C, 60% SOC): 7.1 W test (dashed) and Cᵢ/25 (solid) test for Cell 60 prior to reference electrode insertion. The green diamonds are OCVs from the BOL HPPC test.

Figure 8. Capacity test data before and after CD-aging (60°C): 7.1 W test (dashed) and Cᵢ/25 test (solid) for Cell 53 prior to reference electrode insertion. The dots denote 10% DOD.

Figure 9. Voltage vs. time data during the full 7.1 W capacity test at EOL⁺ for Cell 53 (i.e., CD-aged at 60°C) after reference electrode insertion. (CC = constant current, CV = constant voltage).
voltage vs. Ref. of $\sim 55 \text{ mV}$ during this rest period is discussed further (see section entitled “Behavior of the Negative Electrode Voltage vs. Ref. After Discharge Interrupt at High DOD”). The positive electrode is also responsible for the rise in cell voltage during charge to the 4.2 V lid.

Another potential advantage of these types of reference electrode measurements is the ability to map the degree of lithiation of the individual electrodes to cell SOC if the electrode OCV vs. degree of lithiation relationships are known a priori. For example, if the negative electrode active material were graphite, then a stable OCV vs. Ref. of 0.22 and the positive-electrode fractional lithiation could be likewise determined at this certain cell SOC.

Figure 10 shows the 7.1 W capacity results for representative cells subjected to the three aging regimes. Relative to cycle aging, we would expect a lesser degree of capacity decay via calendar aging because the minimized flow of current would greatly limit the effects of parasitic chemical processes and mechanical stresses induced by current throughput. The lithium insertion and extraction that accompanies current flow is associated with particle swelling and shrinking, cracking, and perhaps loss of electrical connectivity or increased area (or polarization) to drive parasitic electrochemical reactions. Thus, relative to CD aging, the CS-aging regime would result in a lesser degree of capacity decay because of the lower average current (see Figure 6) and the smaller average changes in the electrode degrees of lithiation associated with the cell not being swept through the full range of available capacity.

Stability of the reference electrode.— As mentioned earlier, five consecutive RPTs were performed before and after reference electrode insertion in order confirm that the cell voltage behavior was not influenced by the presence of the reference electrode. Although the cell voltages at all respective times during the five RPTs after insertion were within measurement error, the negative (and positive) electrode voltages vs. Ref. exhibited some drift in the first two RPTs. The consistency of the cell voltages points to the stability of the reference electrode, rather than system instability. Within the first two RPTs the drift was typically between 30 and 40 mV, whereas voltages during the $3^{\text{rd}}$, $4^{\text{th}}$, and $5^{\text{th}}$ RPT were within 5 mV. The drift may be related to equilibration of the solution in the ampoule with the cell solution, being that they are not likely to be identical.

We also observed that the reference electrode would develop a surface layer which would dull the original shiny lithium surface after a period of use. In order to prevent excessive buildup of oxidation on the surface of the reference electrode, which could possibly begin to affect the measurements, the surface layer was scraped off approximately half-way through the reference electrode studies. It was confirmed that this scraping caused no difference in the results before and after the scraping process.

Resistances from reference performance testing.— Calculations of cell and electrode resistances (designated as $R_{\text{disPos}}$ or $R_{\text{disNeg}}$) can be made from the HPPC results. Figure 11a shows the overall cell voltage, the positive electrode vs. Ref. (shown in red) and the negative electrode vs. Ref. (shown in blue) that were used for the calculations. The resistance is calculated to be the difference between the 1-hour OCV and the 10-second voltage divided by the HPPC pulse current. For example, the discharge resistance at 40% DOD for Cell 111 is calculated from the following values: $(3.887 \text{ V} - 3.608 \text{ V})/5.0 \text{ A} = 0.0558 \Omega$. However, instead of using the voltage between the positive and the reference electrode, or between the negative and the reference electrode, is used. Table II gives resistances from the first of the five RPTs with the CD-aged cell before and after reference electrode insertion. The resistance (3rd column) from the HPPC that was performed before reference electrode insertion was $\sim 6\%$ larger than the HPPC test (5th column) after the insertion. These values, observed to be close to the measured cell resistance, which is separately measured between the positive terminal and the negative terminal, were as expected. The OCV values in Column 2 and Column 4, between the two tests match, indicating that in terms of OCV, the pulses were performed at the same SOC. For all DODs tested, $R_{\text{disNeg}}$ is $\sim 5$ times smaller than $R_{\text{disPos}}$. Consequently, the information in Table II shows that inserting the reference electrode in the cell decreases the measured resistance approximately 5–6% after the insertion, presumably due to the increased electrolyte added to the system. These results provide confidence for a comparison between the reference electrode results of other cells.

Figure 12 shows the voltage during the 7.1 W capacity test and subsequent four HPPC discharge and charge pulses with a reference electrode for Cell 53 at EOL. (Calculated resistances associated with
the results in these three figures are shown in Figure 14.) Note that the discharge and charge portions up through 250 minutes in Figure 12 were shown previously in Figure 9. A new cell with no capacity loss (e.g., Figure 11) would have 9 pulses, while an aged cell would have fewer pulses, such as the four pulses shown in Figure 12.

Figure 13 gives the HPPC discharge resistances for the full cell, positive electrode, and negative electrode as a function of DOD before and after calendar aging (60 °C, 60% SOC, Cell 60) and Figure 14 shows these resistances before and after CD-aging (60 °C, Cell 53). These figures show increased full cell resistance from BOL to EOL + for both calendar and CD aging. The data in Figure 14 show that the resistance of the negative electrode rises ∼5% and the resistance of the positive electrode rises ∼150% after CD aging. Figure 13 shows that through calendar aging the resistance of the negative electrode rises 20% and that of the positive electrode rises ∼170%. Both figures show little change in the resistance of the negative electrode from

| DOD | OCV (V) | Cell Resistance (Ω) | OCV (V) | Cell Resistance (Ω) | RdisPos + RdisNeg (Ω) | RdisPos (Ω) | RdisNeg (Ω) |
|-----|---------|----------------------|---------|----------------------|-----------------------|-------------|-------------|
| 0   | 4.175   | 0.1067               | 4.178   |                      |                       |             |             |
| 10  | 4.044   | 0.1082               | 4.045   | 0.1006               | 0.1006                | 0.0840      | 0.0166      |
| 20  | 3.943   | 0.1082               | 3.944   | 0.1018               | 0.1022                | 0.0854      | 0.0168      |
| 30  | 3.809   | 0.1185               | 3.810   | 0.1018               | 0.1022                | 0.0856      | 0.0166      |
| 40  | 3.717   | 0.1146               | 3.716   | 0.1093               | 0.1098                | 0.0930      | 0.0168      |
Figure 12. Voltage profiles of Cell 53 during RPT 6 after CD aging (60°C).

Figure 13. HPPC discharge resistances (10-s) for the full cell (black), positive electrode (red), and negative (blue) electrode before and after calendar aging (60°C, 60% SOC) for Cell 60.

The BOL to EOL+ in comparison to the positive electrode. The large change in cell resistance from BOL to EOL+ is the direct result of the large change in the positive electrode resistance.

Figure 15 shows the positive and negative electrode voltages vs. reference electrode during the 10% DOD (i.e., 0.12 Ah removed) HPPC discharge pulse at BOL and after CD aging (EOL+), from which the first set of resistances in Figure 14 were obtained. At the onset of current flow, for the negative electrode data (bottom) in Figure 15 both before and after CD aging, a value of initial polarization is exhibited and maintained throughout the 10-second pulse; after current interrupt the voltage rapidly returns to the open-circuit condition (i.e., within 1 second). The increase in the BOL negative OCV vs. Ref. of ~25 mV with aging (from 130 to 155 mV vs. Ref.) may represent reference-electrode drift, but is more likely due to the carbonaceous negative residing in a lower state of lithiation. That the negative electrode polarization remains constant during the pulse after the initial polarization may indicate that the electrode material resides in a two-phase region throughout the pulse. The negative-electrode BOL polarization (above open circuit) is ~90 mV and increases slightly (to ~100 mV) after CD aging, perhaps due to decreased electronic conductivity resulting from particle fracture.

In contrast, the positive electrode (top portion of Figure 15) exhibits a certain value of initial polarization, and polarization increases throughout the pulse, but the voltage vs. Ref. slowly returns to the open-circuit condition (taking several minutes) after the current interrupt. The initial polarization of the positive electrode is ~35% greater than that of the negative prior to aging and is nearly triple that of the

We define “initial” electrode polarization as the magnitude of the difference between the OCV vs. Ref. and the electrode voltage (vs. Ref.) measured at 50 ms (i.e., the first data point after current onset) and likewise for “initial” cell polarization.
negative after aging. Since the initial polarization in these types of cells has been associated primarily with the electronic conductivity of the solid active material, we surmise that the increase with aging may be due to the loss of electrical connectivity resulting from particle fracture. The buildup of positive-electrode polarization after the presentation of the initial value and relaxation after current interrupt has been attributed to the generation and dissipation, respectively, of solid-state lithium concentration variations throughout the positive electrode particles. This buildup of polarization after aging, nearly triple that of the BOL values, may indicate lowered ease of solid-state lithium transport through the degraded active material. The decrease in the BOL positive OCV vs. Ref. of ~10 mV after aging may result from the preferential degradation of the high-voltage component of the blended material or the positive active material residing in a higher state of lithiation. As expected, the full cell OCV (by difference in figure) prior to the onset of current flow is lower after CD aging than at BOL. These BOL and EOL+ OCVs are more clearly denoted by the navy and red dots, respectively, in Figure 8, which show ~30 mV decrease with CD aging.

Table III shows a summary of the reference electrode tests resistance results for representative cells subjected to the three different aging regimes. The BOL capacity results in Table III show a significant difference between the 7.1 W capacity and C/25 capacity, as expected. The EOL+ 7.1 W and C/25 test results do not show the same significant difference that was seen in the beginning of life results. These results indicate that the loss of either available lithium for intercalation within the specified voltage limits or the loss of intercalation sites is more significant than the effects of diffusion at the beginning of life. Additionally, the capacity loss from the charge depleting cycle life test is 18% larger than from the average calendar and charge sustaining cycle life tests in the 7.1-W capacity tests, and 22% larger for the C/25 measurements. These results show that the CD cycle life regime results in slightly greater capacity degradation than in the calendar life and CS cycle life testing (see Figure 7 and Figure 8).

Table III also demonstrates the rise in resistance for the positive electrode. Comparison of the HPPC resistance at 40% DOD shows the same consistency as Table II before and after the insertion of the reference electrode. The rise of resistance in all cases from the BOL to the EOL+ is expected. However, the bulk of the rise in resistance is concentrated at the positive electrode. While there is some difference in the negative electrode resistance, it tends to be much smaller, (6% to 25%), than the difference in the positive electrode resistance (148% to 165%). The rise in negative electrode resistance is either the effect of measurement error or the solid-electrolyte interphase, a nanometer scale buildup of solvent reaction products on the negative electrode. However, the significant rise in resistance of the positive electrode can be attributed to a similar buildup of solid-electrolyte interphase and/or a decrepitation (micro-cracking and structural disordering) of the positive electrode. The decrepitation mechanism accounts for the rise in resistance and loss of capacity through the loss of lithium/lithium intercalation sites. As the structure changes, portions of the electrode will become electronically disconnected, creating an increasingly tortuous path of electron conduction and trapping lithium ions within the structure at the same time. This same phenomenon could also be affecting the negative electrode in a less pronounced way.

Behavior of the negative electrode voltage vs. Ref. after discharge interrupt at high DOD. — As the 7.1-W discharge shown in Figure 9 is interrupted, the typical initial depolarization (~50 mV) due to dissipation of ohmic and charge-transfer processes is exhibited; however, a curious steady increase in negative-electrode voltage (vs. Ref.) of ~55 mV occurs during the hour rest that follows (78 min to 135 min). The relaxation voltage of the positive electrode during the rest appears normal. However, this curious negative electrode behavior is also observed in Figure 11a after the 2.13-A discharges at 20%, 10%, and 0% DOD and after the final 5.3-A discharge to the lower voltage limit (at ~1000 minutes) that leaves the cell at below zero DOD. Normal negative-electrode depolarization is seen after the other higher DOD discharges (i.e., 30% to 90). We note that the behavior is magnified at relatively low negative electrode degrees of lithiation. Additionally, similar curious behavior is exhibited in Figure 12 after each the final four 2.13-A discharges, but not in the first HPPC discharge. The phenomenon is magnified at lower rates of discharge, perhaps because the negative electrode is driven to lower degrees of lithiation. For example, in the 1-hour rest after the C/25 discharge of a CD-aged cell (Cell 53) the negative electrode voltage vs. Ref. increased ~300 mV, while the positive electrode exhibited normal relaxation of ~700 mV. If the behavior were associated with liquid- or solid-phase diffusion processes, we would expect to see magnification at higher rates of discharge rather than lower. Although we would expect magnification at high cell SOC if the behavior were a result of the onset of degradative processes, it is possible that oxidative decomposition is provoked at high values of the negative electrode voltage vs. Li/Li+. If this were the case, then continued delithiation of the negative electrode (reduction) could occur at open circuit concurrent with solvent oxidation. Another explanation that would be consistent with the observations lends to structural reorganization – it is possible that non-equilibrated highly staged phases (i.e., low degrees of lithiation) are formed in which the intercalated lithium distributes itself to more thermodynamically favorable entropic states. We do not believe that the behavior is consistent with instability of the reference electrode which was observed in the first two of the five RPTs after insertion (see section entitled “Stability of the Reference Electrode”).

Conclusions

This work has shown that inserting a reference electrode into the original cell container is achievable and does not disturb the cell’s voltage and current characteristics. Cell perforation inside a glove box, under the guidance of X-ray which allows the placement of a reference electrode that is in electrolytic contact with the cell, is also feasible. This novel approach demonstrates the methodology and
apparatuses necessary to minimize the risk of shorting and disruption of cell performance. While only metal can cells were used in this study, the same process could be implemented with pouch cells with some modifications. Not only can the electrode performance be isolated, but the degree of lithiation of the individual electrodes can be mapped to cell state of charge; this mapping cannot be done once the cell is disassembled.

There are some drawbacks to the proposed methodology. We don’t recommend the cells be aged with an inserted reference electrode because of the evaporation of the solvent through the perforation in the glove box environment. Also the buildup that was observed on the reference electrode foil will likely be exacerbated. However, with some additional effort, after insertion, the plug could be re-welded and/or sealed for additional testing.

While some of the capacity loss from BOL to EOL as measured by the 7.1 W capacity test can be attributed to the rise in resistance, virtually none of the corresponding capacity loss as measured by the C1/25 discharge can be attributed to the rise in resistance. These results imply that usage in a plug-in hybrid will be more challenging than standard hybrid operation versus a vehicle that is purchased and stored in a garage. The rise in positive electrode resistance may be the result of micro-cracking and structural disordering, which could cause a loss of available sites for lithium intercalation.8–10

The work done with reference electrodes shows the degradation of the positive electrode is responsible for the performance degradation of the cell. Even with a large capacity loss, consistent with a thick, non-electronically conducting SEI layer, only a small resistance was rise observed for the negative electrode.11,12 It is commonly suggested that the SEI buildup on the negative electrode is responsible for the increase in resistance and decline in cell performance. However, others have suggested that the SEI, being on the order of nanometers thick, is too thin to cause an appreciable increase in resistance, which is supported by our results. Consequently, in order to further improve lithium ion technology, reference electrodes coupled with long-term testing must be used to identify which electrodes limit overall cell capacity and resistance performance. Capacity fade and resistance rise based on full cell results are common for these types of tests, especially at elevated temperatures. However, this work clearly points to the positive electrode as the cause of the resistance rise.

Utilizing the in situ reference electrode methodology, battery manufacturers can devise new strategies or materials based on which electrode is limiting cell performance to increase life, improve performance, or reduce cost. Additionally, performance testing with a reference electrode identifies which electrode limits performance during aging.

Due to the long term nature of life testing, it is important to identify which electrodes are limiting performance under various life conditions, rather than haphazardly modifying one or both electrodes to improve life. The in situ reference electrode can be used to quantify the electrode capacity, consistent with past work, but its use can also be expanded to evaluate the resistance contributions from each electrode.

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