Use of Asymmetric Average Charge- and Average Discharge-Voltages as an Indicator of the Onset of Unwanted Lithium Deposition in Lithium-Ion Cells

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Unwanted lithium-metal deposition on the negative electrode of a lithium-ion cell causes capacity loss due to poor lithium deposition and stripping efficiency and the possibility for internal short circuits. Internal short circuits may cause thermal runaway, which is especially dangerous in applications requiring many individual cells. This article proposes a method capable of identifying the onset of unwanted lithium deposition in situ using cycles to full depth of discharge in a cell of any form-factor. The two most important factors affecting the average voltage of a Li-ion cell under load are the internal resistance increase and loss of lithium inventory. Increasing internal resistance increases average charge voltage and decreases average discharge voltage. Loss of lithium inventory, which occurs rapidly during unwanted lithium deposition and stripping, increases both average charge and average discharge voltage. Increasing internal resistance and loss of lithium inventory have a linearly additive effect on average voltage; therefore, tracking the average of average charge- and average discharge-voltages versus cycle count allows one to determine where rapid changes to lithium inventory onset, indicative of the onset of unwanted lithium deposition.

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The work in this article proposes a simple method using inexpensive equipment under standard test conditions to detect onset of unwanted lithium deposition. It uses inspection of average charge and discharge voltages for the in-situ identification of the onset of lithium deposition compatible with commercial form-factor cells.

Experimental

Cell build.—Size 402035 machine-made wound pouch cells were obtained heat sealed and without electrolyte from LiF Technologies (Zhuzhou City, China). Cells had a single crystal LiNi0.5Mn0.3Co0.2O2 (NMC532) positive electrode material that was well characterized by Li et al. 14 The positive electrode was made up of active material: conducting carbon: polyvinylidene fluoride (PVDF) binder in a 94:4.2 weight ratio. Positive electrodes had a loading of 21.1 mg/cm² and a density of 3.5 g/cm³. Negative electrodes used artificial graphite with 13.6 mg/cm² loading and 1.55 g/cm³ density. The negative electrodes used active material: conductive carbon black (CB); carboxymethyl cellulose (CMC) and styrene butadiene (SBR) binders in a 95.4:1.3:1.1:1.2 weight ratio. Full cells were balanced for 4.5 V maximum operation with a nominal capacity of 240 mAh.

Electrolyte.—Salt and solvent systems were obtained from BASF. All electrolytes contained 1.2 M lithium hexafluorophosphate (LiPF₆, 99.94% purity, 14 ppm water content.). Solvent was a combination of ethylene carbonate: ethyl methyl carbonate 3:7 w:w (EC:EMC, 99.99% purity, < 20 ppm water content) with and without methyl acetate (MA, 99.99% purity). Fluoroethylene carbonate (FEC, BASF, 99.94% purity) was added to all cells at two weight percent. Ethylene sulfate (DTD, 1,3,2-Dioxathiolane 2,2-dioxide, Sigma Aldrich, 98% purity) was added to half of prepared cells at one weight percent. FEC and DTD are henceforth referred to as additives. All electrolytes were prepared in an argon-filled glove box.

Cell filling.—Cells were cut open along the top edge of the pouch and heated to 100°C in an antechamber under vacuum for approximately 14 hours to remove trace water, then transferred directly into an argon-filled glove box to be filled with electrolyte. All cells contained 1.2 M LiPF₆ salt. Cells were filled with a base electrolyte of EC:EMC 30:70, EC:EMC:MA 24:56:20, or EC:EMC:MA 18:42:40, all weight percent. Cells then had either 2% FEC or 2% FEC + 1% DTD added. Hereafter, cells will be referred to by their additive and MA content. Cells were filled with 1.0 g of electrolyte. Once filled,
they were sealed using a compact vacuum sealer (MSK-115A, MTI Corp.) at -95kPa gauge pressure, 165°C for 4 seconds.

**Cell formation.**—Filled cells were clamped between two rubber blocks to force any gas evolved out of the electrode stack and into the pouch bag. Cells were held at 1.5 V for 24 h at room temperature for proper wetting. They were then moved to a temperature controlled box at 40°C connected to a Maccor 4000 series cycler (Maccor Inc.). Cells were charged at C/20 (11 or 12 mA) to 4.2 or 4.3 V respectively and held at top of charge for one hour. Cells were discharged to 3.8 V and held for 2.5 h. Cells were returned to the argon-filled glove box where they were cut open to release gas evolved during formation and resealed using the same conditions as described previously. Cells were removed from the glove box and re-clamped between rubber blocks.

**Long term cycling**—Cells were cycled using a Neware BTS3000 series charger (100 mA/5V, Shenzhen, China) at room temperature (approx. 23°C). Cells were cycled at C/3 (66.6 mA (4.2 V upper cutoff)) or 70.0 mA (4.3 V upper cutoff)) in constant current-constant voltage (CCCV) mode. Cells were held at top of charge until the current reached C/20. After every 50 cycles, a constant current (CC) cycle at C/20 (10.0 or 10.5 mA) was performed to monitor low rate performance. Cells were removed from test near 80% original C/3 capacity or as necessary for destructive experiments.

**Results and Discussion**

Figure 1 illustrates the origins of the potential – capacity curve of a full cell. The full cell potential is the difference between the potential of the positive electrode and the negative electrode. The experiments in this article specify that the full cell potential shall not exceed an upper cutoff potential (UCV) of 4.2 or 4.3 V, or fall below a lower cutoff potential (LCV) of 3.0 V. To maintain constant cutoff potential, the locations of the UCV and LCV may move relative to the capacity axis depending on impedance growth, loss of lithium inventory, and loss of active material.

Figure 2 uses illustrative curves in arbitrary units of graph-paper squares to convince the reader that impedance growth and loss of lithium inventory are the processes capable of most change in average voltage. Change in average voltage that is attributable to impedance growth will hereafter be referred to as resistance voltage, or RV. Change attributable to loss of lithium inventory will be referred to as shift voltage, or SV because loss of lithium inventory causes the positive and negative electrode V-Q curves to shift their relative alignment. Figure 2, panels D-G show the negative electrode shift by 0, 1, 2, and 4 capacity units respectively. Graphite stages have been heavily exaggerated relative to positive electrode slope for clarity.

Recall that average voltage is capacity-weighted and can be calculated by,

\[
V_{av} = \frac{1}{Q_T} \int_{0}^{Q_T} V dq
\]

where \(V_{av}\) is the average voltage, \(Q_T\) is the total cycle capacity, and the integral is the area under the V-Q curve of the full Li-ion cell. The V-Q curve of the full Li-ion cell is calculated as the difference between the positive electrode curves and the negative electrode curves in each of the panels of Figure 2. The area between the positive and negative electrode curves has been shaded on the figure so the readers may count the squares to convince themselves that the stated areas are correct.

A perfect lithium-ion cell should have a constant average charge voltage (\(V_{av,c}\)) and a constant average discharge voltage (\(V_{av,d}\)) during its lifetime. However, normally over long times, \(V_{av,c}\) increases and \(V_{av,d}\) decreases. Average charge- and discharge-voltages are nearly mirror images of each other when plotted versus cycle number.

Mirrored \(V_{av,c}\) and \(V_{av,d}\) versus cycle number suggest that impedance growth is the most significant parameter in average voltage change. This is reflected by the common use of the parameter \(\Delta V\), the difference between average charge- and average discharge-voltages. It is expected that cell impedance will increase during life, as SEI layers thicken, parasitic reaction products deposit on one or both electrodes, electrolyte is consumed, or salt is depleted. The left column of Figure 2 (panels A, B, C) shows an illustrative data set that has been manipulated with an ohmic impedance term,

\[
\eta = IR
\]

where \(\eta\) is overvoltage due to the applied current, I is applied current, and R is internal resistance. Magnitudes of the IR terms increase red < blue < green.

It is assumed that impedance does not change depending on the direction of charge movement. Charge and discharge currents of equal magnitude introduce a mirrored offset in the voltage-capacity plot. When voltage limits are fixed (3 and 8 a.u.), impedance growth limits the available capacity near the beginning and end of charge as shown in panel C. Capacity decreases from 9.9, to 9.2, to 8.0 as impedance growth causes endpoints to be reached sooner.

Figure 2 shows that any individual cycle has nearly identical charge capacity (panel A) and discharge capacity (panel B) but significantly different areas under the V-Q curve, which results in charge always having larger average voltage than discharge. Increasing the IR term increases average charge voltage, decreases average discharge voltage, and decreases total capacity.

Figure 2, panels D-G, shows the impact of imperfect alignment between positive (blue) and negative (red) electrode capacities. As cyclable lithium is consumed from a cell’s inventory, the electrode capacities ‘shift’ relative to each other which changes the overlapping areas. Shift voltage (SV), unlike resistance voltage, is unaffected by charging direction.

Figure 2 shows that if a Li-ion cell begins its life in a positive electrode-limited alignment (panel D), average voltage (area between positive and negative curves normalized by total capacity) will decrease until electrodes are in perfect alignment (panel E) while capacity remains the same. This means average voltage will decrease. As the negative electrode slips past the positive due to lithium inventory loss (panels F, G), the area between the curves decreases more slowly than the loss of capacity. This results in an increasing average voltage. Figure 2, panel G shows how previously unused positive electrode capacity may be accessed to achieve the required UCV.

As has been described, average charge voltage is increased by the cumulative effects of SV and RV. Average discharge voltage is increased by SV but decreased by RV. Therefore,

\[
V_{w,c} = SV + RV
\]

\[
V_{w,d} = SV - RV
\]
Figure 2. The impact of increasing internal resistance (RV) and losing lithium inventory (SV) on average voltage are shown using illustrative curves. Average voltage is the area under the full cell curve, or the area between the positive and negative electrode curves, normalized by the total capacity. Shaded boxes may be counted to confirm values for area. As shown by the left panels, increased internal resistance will increase average charge voltage and decrease average discharge voltage. Three values of R are shown with R_{red} < R_{blue} < R_{green}. The black dashed curve shows a cell with no internal resistance. As shown by the right panels, loss of lithium inventory will increase both average charge and discharge voltage. A curve representing the positive electrode is given in blue, and the negative electrode is in red. If a cell begins its life positive-limited, it is possible for average voltage to decrease as shown. Capacity remains unchanged until the anode capacity is to the right of the cathode, but area between the curves decreases.

It is a trivial rearrangement of Equations 3 and 4 to show,

\[ SV = \frac{1}{2} \left( V_{av,c} + V_{av,d} \right) \]  
\[ RV = \frac{1}{2} \left( V_{av,c} - V_{av,d} \right) \]  

Figure 3 shows the SV:RV analysis technique applied to a real data set. Panel A shows average voltages indicated with solid black lines. Average charge voltage begins near 3.81 V and average discharge voltage begins near 3.71 V. The dashed lines indicate a perfect cell with unchanged average voltage. This guide to the eye promotes the observation that V_{av,c} is increasing faster than V_{av,d} is decreasing. Equations 5 and 6 were used to calculate the values of SV (blue) and RV (red). As expected, SV (panel A) and RV (panel B) increase with cycle count. The right panels show common performance metrics: discharge capacity (panel C) and \Delta V (panel D). It is observed that SV begins to increase faster as discharge capacity begins faster decrease.

Throughout the work that follows below, RV and SV have been zeroed to cycle 20. Values that have been zeroed will be called shift voltage change, SVC, and resistance voltage change, RVC. The initial value of RVC (before zeroing) is captured by \Delta V. The initial value of SVC is less informative than clearly seeing the relative rankings from a matrix of cells.

Shift voltage change is shown to be useful in analysis of cells showing rollover failure. As discussed by Burns et al., rollover is characterized by high capacity retention for many cycles and then
Figure 3. Shift voltage and resistance voltage are shown with standard lifetime parameters discharge capacity and ΔV for a representative cell. Shift voltage is the average of average charge- and discharge-voltages. Resistance voltage is half of the difference between average charge- and discharge voltages. Dashed lines indicate constant average voltage, and highlight asymmetry between charge and discharge. It is obvious that ΔV is twice the resistance voltage, RV. The upward turn in SV occurs near the same cycle count that capacity loss begins to accelerate.

abrupt, rapid capacity loss over few cycles. Figure 4 highlights the strength in the SVC:RVC method for accurately determining the onset of unwanted lithium-metal deposition as a cause of rollover failure. The left graphs show absolute capacity loss, SVC, and RVC for four cells at 1200 cycles. Each of the cells had an initial capacity near 220 mAh. The cell in green triangles, FEC-DTD_40MA, is considered “far from rollover”. It has lost less than 5 mAh capacity (2.4%), and shows minimal change in impedance. The cell in black crosses, FEC, is “not at rollover”. It shows 20 mV of impedance growth, but is similar to FEC-DTD_40MA in capacity retention. The cell in

Figure 4. Destructive experiments on four cell chemistries to confirm the presence of metallic lithium. Capacity retention is very good for FEC (high RVC) and FEC-DTD_40MA (low RVC). The negative electrodes of both cells look pristine. Resistance voltage change is identical for FEC_20MA and FEC_40MA, but FEC_40MA has lost much more capacity. Shift voltage change shows a sharp increase in FEC_40MA that correlates well with rollover (dashed line). Only FEC_40MA shows sharply increasing SVC, and only FEC_40MA shows metallic lithium deposition.
Figure 5. Capacity loss, SVC, and RVC for the full FEC-DTD-MA matrix. Every chemistry shows sharply increasing SVC correlates well with rollover. High RVC does not necessarily indicate a predisposition for shorter cycle life due to rollover failure.

As discussed in Figure 2, loss of cyclable lithium leads to increasing SVC. Lithium deposition rapidly removes lithium from the inventory, which rapidly increases SVC. It was decided that these four cells should be terminated to verify the presence of metallic lithium on the surface of the negative electrode. The right side of Figure 4 shows photographs of the negative electrodes inside an argon-filled glove box. The photographs are labelled and colored to match the graph legend. The electrodes of FEC-DTD-40MA (far from rollover) and FEC (not at rollover) are uniformly red, indicating stage 2 lithiation throughout. The electrodes of FEC_20MA (brink of rollover) and FEC_40MA (at rollover) are red near the edges of the electrode with patchy blue regions (dilute stage 2) down the center of the electrode. Poor lithiation occurs at the center of the jelly roll, far from the electrolyte reservoir at the edges of the jelly roll. As predicted by the non-destructive in-situ SVC analysis technique, only FEC_40MA shows the presence of metallic lithium. Patchy metallic lithium is located at the center of the jelly roll.

Recall that RVC is $\frac{1}{2} \Delta V$, zeroed to an initial cycle. The practice of zeroing means that information about the magnitude of the cell impedance is lost, but trends in impedance growth become more obvious. Li et al. in Figure 9 show that cells containing higher amounts of MA as co-solvent have lower $\Delta V$ when cells are fresh. Impedance growth quickly becomes important in cells cycling to 4.3 V with no DTD. The bottom row of Figure 5 shows that cells follow two groupings: the crosses, cells without DTD, follow a steeper slope than the triangles, cells with 1DTD. The authors were very surprised that a 1% change in electrolyte (adding DTD) should have a larger impact on suppressing impedance growth than changing up to 40% of the solvents in the electrolyte! There is little difference in impedance growth rates for different amounts of MA up to 400 cycles to 4.3 V or 800 cycles to 4.2 V. After 400 or 800 cycles, higher MA content begins...
to show faster impedance growth (black > red > blue). Many cells reach RVC = 70–80 mV at 80% original capacity.

Table 1 summarizes cycles to lithium deposition for all of the chemistries in Figure 5. Columns with the entry “2000+” have not shown evidence of lithium deposition up to 2000 cycles and are still on test. When chemistries cycle to the same upper cutoff voltage, cycles to rollover follows the order: FEC_40MA, FEC_20MA, FEC-DTD_40MA, FEC, FEC-DTD_20MA, and FEC-DTD where the latter have increased longevity.

Figure 6 shows SVC with standard long term cycling metrics, capacity and ΔV. Both high rate (C/3 CCCV) and low rate (C/20 CC, every 50 cycles) cycles are shown. The low rate, constant-current cycles show very similar trends to high rate cycles in all three metrics. Shift voltage change shows a sharp increase at 1100 and 1200 cycles for FEC and FEC-DTD_20MA respectively. The increase is attributed to lithium-metal deposition (rapid loss of lithium inventory). These cycle counts are indicated with a dashed line. Both cells show slow, smooth capacity loss, and a near-linear increase in ΔV after 300 cycles. There is small curvature before shift voltage increases sharply. Shift voltage change clearly identifies the mechanism of failure (lithium deposition) and the cycle count where lithium deposition begins. The standard metrics cannot identify either the mechanism or the cycle count where failure begins. This demonstrates the importance of the SVC method.

Conclusions

Analysis of the shift voltage change was introduced as an analysis technique suitable for a wide variety of applications and cells. Asymmetries between the average voltages during charge and discharge were used to make inferences about the lithium inventory of a cell while it was in operation. The sharp increase in shift voltage change was shown to be useful in very precisely identifying the onset of unwanted lithium deposition. Common degradation metrics including capacity loss and ΔV have no obvious feature to indicate lithium deposition has begun. Higher RVC does not necessarily indicate earlier lithium deposition. Shift voltage change suggested that the FEC-DTD-MA matrix of cells studied at 20°C, C/3 CCCV cycling will likely all rollover for reasons related to lithium deposition. Higher MA concentrations lead to shorter lifetime, but the lifetime penalty can be mitigated by the addition of 1% DTD.

This technique opens many new questions. Future work should address the question of why the SVC initially has a negative slope for all cells presented in this work. Future work should investigate the effect of different temperatures, and different electrode materials. Effort should be spent investigating if all cells that show lithium deposition show sharply increasing SVC, or if the cells studied in this matrix were a special case.

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