In-Situ Detection of Lithium Plating Using High Precision Coulometry

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Plating of metallic lithium on the negative electrode in lithium-ion batteries can dramatically reduce cell lifetime, impact cell safety and must be avoided during normal cell operation. Due to the low efficiency of the lithium plating/stripping process relative to the intercalation/deintercalation of lithium from graphite, small amounts of lithium plating can be detected through high accuracy measurements of coulombic efficiency. In this study, coulombic efficiency versus charging rate was measured at different temperatures and for two cell types. Small changes to the coulombic efficiency during cycling resulting from small amounts of lithium plating during the charging process were detected using a high precision charger. Cells were disassembled and examined to confirm the presence of lithium plating at the rates predicted to cause plating. This work shows how high precision coulometry can be used to maximize the performance of the cell through battery management by varying the maximum charge rate as a function of temperature to avoid lithium plating.

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Lithium-ion batteries are currently used for portable electronics applications (cell phones, laptops, tablets, etc.) because their specific energy and lifetime are adequate for such devices. However, the use of Li-ion batteries for electrified vehicle battery packs requires much longer cycle and calendar life. In addition to the increased demands for longer battery lifetimes, new applications constantly strive to increase energy density and lower recharge time. However, due to the potential for deposition of metallic lithium on the negative electrode at high rates, recharge rates are typically limited by battery management electronics. Studies have been conducted to detect the onset of lithium plating, to measure the plating efficiency and also to see how changes to the cell chemistries impact lithium plating.1,2 One of the clearest ways to detect the presence of lithium plating uses three electrode cells to measure the potential of the negative electrode and measure the state of charge at which it drops below 0 V vs Li/Li+. However this cannot be done in commercial cells without a reference electrode.

Petzl and Danzer3 show that the differential voltage and capacity discharge curves can be used to detect when lithium plating has occurred during a previous high rate charge. When lithium plating has occurred there is a feature in the voltage curve related to the stripping of lithium from the negative electrode due to the difference in potential between stripping of lithium and deintercalating lithium from the negative electrode. Large amounts of lithium plating need to have occurred in order for this feature in the differential capacity or voltage curve to be clearly distinguishable (Figure 3 in reference 3 shows the degree of lithium plating that has occurred for detection in the study). However, even small amounts of lithium plating during cycling of cells can shorten cell lifetime and impact safety and therefore greater sensitivity in detection of lithium plating is required.

Downie et al.4 showed, using isothermal microcalorimetry, that small amounts of lithium plating occurring in Li-ion cells can be detected by measuring the heat signature from the cell with great sensitivity. The efficiency of lithium plating could also be calculated from these measurements and was seen to be around 97 - 98% depending on the graphite active material. Based on this low efficiency of lithium plating/stripping relative to the intercalation/deintercalation process (>99.5%), Downie et al. suggest that when lithium plating occurs during cycling, the coulombic efficiency of the cell will decrease. Based on this premise, lithium plating should be detectable as small changes to the coulombic efficiency of cells cycling at different rates. This implies that the detection limits for lithium plating will be dictated by the precision and accuracy of measurements of the coulombic efficiency. A High Precision Charger5 such as that at Dalhousie University should therefore have a high degree of sensitivity for detecting lithium plating in any cell type under standard cycling conditions.

Experimental

Nominally 220 mAh Li[Ni0.3Mn0.3Co0.4]O2/graphite 402035-size pouch cells (Li-Fun Technology) were studied at various temperatures and charge rates using the Ultra High Precision Charger at Dalhousie University.6 The pouch cells were 40 mm long × 20 mm wide × 3.5 mm thick. The electrode composition in the cells was as follows: Positive electrode - 96.2%:1.8%:2.0% Active Material:Carbon Black:PVDF Binder; Negative electrode 95.4%:1.3%:1.1%:2.2% = Active material:Carbon Black:CMC:SBR. The positive electrode coating had a total thickness of 105 μm, a single side coating thickness of 47.5 μm and was calendared to a density of 3.55 g/cm3. The negative electrode coating had a total thickness of 110 μm, a single side coating thickness of 51 μm and was calendared to a density of 1.55 g/cm3. The positive electrode coating had an areal density of 16 mg/cm2 and the negative electrode had an areal density of 9.5 mg/cm2. The positive electrode dimensions were 200 mm × 26 mm and the negative electrode dimensions were 204 mm × 28 mm. Both electrodes were spiral wound, not stacked, in these pouch cells. The cells were cycled between 2.8 – 4.2 V with charge rates between C/50 and 5C and a discharge rate of C/10. Some cells underwent a two-stage cycling process where the cells were charged at the variable rate to 4.19 V and then the rate was reduced to C/30 and the cell finished charging to 4.2 V. This was done in an attempt to minimize error and noise in the coulombic efficiency measurements. Other cells underwent a single step charge process for comparative purposes.

Cells were all dried under vacuum at 100 °C overnight before being transferred into an argon-filled glove box, vacuum filled with 0.9 g of 1 M LiPF6 ethylene carbonate/ethyl methyl carbonate (EC:EMC 3:7 wt, BASF) + 2% Vinylene Carbonate (VC) (BASF, 99.97%) electrolyte and sealed (MTI Corporation, MSK-115A). Cells were formed with a 1.5 V hold for 24 hours followed by a charge to 3.5 V at 40 °C and a C/20 rate. After charging to 3.5 V, the cells were taken back inside an argon-filled glove box, cut open to release any gas generated and resealed. The cells then were put at their respective temperatures and the first charge to 4.2 V was completed along with the first discharge at C/20 before beginning to cycle at various charge rates. After cycling, cells were disassembled within an argon-filled glove box at ~50% state of charge to look for lithium plating.
Nominal 3.4 Ah Panasonic 18650 (Li[NCA]O₂/graphite) cells, obtained from Orbtronics, were also studied at different charge rates. The positive electrode dimensions were 660 mm × 59 mm and the negative electrode dimensions were 710 mm × 60 mm. Both electrodes were coated on both sides except for small area of the negative electrode (final 25 mm on one side and 70 mm on the other). All cells were studied at 25 °C and cycled between 2.8 and 4.2 V at charge rates of C/10, C/5, C/3, C/2 or 1C and a discharge rate of C/10 on the High Precision Charger at Dalhousie University. A class “A” resistance temperature detector (RTD) (US Sensor, PPG101A1) was attached to the cells to measure variations in cell temperature at high rates. After cycling, cells were discharged to 0 V (to ensure safety while opening) and opened to look for evidence of lithium plating on the negative electrode.

**Results and Discussion**

Figure 1 shows the anticipated dependence of coulombic efficiency on charge rate as a schematic. Smith et al. characterized the coulombic efficiency as a function of rate and temperature for low rate cycling and showed that the coulombic efficiency departed further from 1.0000 when cycled at a slower rate (due to a longer time during each cycle for parasitic reactions to degrade the cell) or a higher temperature (due to the increased rates of parasitic reactions with increased temperature). However, after time normalizing the efficiency to account for cycling at different rates it was found that the cells exhibited the same coulombic inefficiency per hour (CIE/h) implying that all cells were degrading at the same rate with time despite the cycling rates being different. In further work, Smith et al. confirmed these short term measurements by showing that cells cycled at C/24, C/48 and C/96 under otherwise the same conditions (elevated temperature and voltage limits) all failed after about 14 months of cycling even though there were large differences in the number of cycles before failure due to the different cycling rates.

The results of these previous studies are captured in the bottom panel of Figure 1 in the red curves labelled as “Time dependent CE”. However, these curves imply that as the cycle rate becomes very rapid the coulombic efficiency should become almost exactly 1.0000 because there is minimal time per cycle for parasitic reactions to occur and degrade the cell. Therefore this work cannot represent the full spectrum of charge rates because it does not include any cycle dependent failure mechanism such as lithium plating that only occurs at higher cycling rates and should decrease the coulombic efficiency. The blue curves in the bottom panel of Figure 1 show that as the cycle rate becomes very high lithium plating will occur and will cause the coulombic efficiency to deviate from 1.0000. The onset of lithium plating will be impacted by temperature. If a cell is cycled at higher temperature it will improve the kinetics within the cell and therefore lithium plating will not occur until higher charge rates are applied. Therefore the impacts of both the time dependent and charge rate dependent effects on coulombic efficiency can be combined (by summing the inefficiencies from each component at a given rate) to give the “hump” shaped curves for coulombic efficiency versus rate (that shift to higher rates with increased temperature) shown in Figure 1.

Figure 2 shows the voltage curves measured during two-stage charge cycling at 30 °C for different charge rates. It is clear that at higher rates there is a larger polarization in the voltage curve due to the impedance within the cell. Two-stage charges were conducted in an attempt to minimize the inaccuracies in the coulombic efficiency by ensuring that the cells were not slightly overcharged at high rates due to timing resolution of the equipment. However, when cycling at very high rates much more time is spent in the second, slow-rate stage of charging which causes the cell to have a higher average charge voltage than during a single stage charge. This difference in average charge voltage caused by the two-stage charge will lower the coulombic efficiency as the cell will degrade faster with a higher average voltage. Therefore cells at intermediate rates were also cycled with single-stage charges in order to ensure that any decrease from expected coulombic efficiency at high rates comes from lithium plating and not from differences in the average voltage of the cells. At very high charge rates there is massive “slippage” of the voltage curves to higher capacity as a consequence of the inefficiency of lithium plating/stripping which leads to capacity loss within those cells.

Figure 3 shows the cycling data (versus time) collected on the High Precision Charger for cells cycled at 30 °C with the two-stage charge process at different rates. Figure 3a shows that until charge rates of 2C and higher there is minimal difference between the capacity loss (fade) rates of the cells. However, there are clear differences in the coulombic efficiencies of the cells cycling at different rates. The coulombic efficiency however must be time normalized to compare cells that are entirely in the time dependent regime and those that have rate dependencies and therefore are plating/stripping lithium. Figure 3c shows the CIE/h where all cells at low rates fall on the same curve indicating they are in a purely time dependent degradation regime which agrees well with the previous work from Smith et al. However, when charging at 1C or higher the CIE/h becomes worse than those cells in the time dependent regime indicating the occurrence of lithium plating. Based on the work of Smith et al. it was shown that normally parasitic reactions are predominantly time dependent and cycle independent (note: parasitic reactions on Si negative electrodes (which are not in the cells tested here) are expected to be strongly cycle dependent due to the large volume changes during each cycle) so therefore the increase in CIE/h must be attributed to lithium plating as it is a cycle dependent degradation mode. As the rate is increased the CIE/h gets worse as the amount of lithium plating/stripping increases. Therefore from this data it can be seen when cells leave the time dependent regime and lithium plating occurs resulting in an increase in the degradation rate of the cells. The cells charged at a 5C rate lessen their capacity loss rate around 200 hours (near 170 mAh of remaining capacity) which is likely due to the large difference in electrode slippage of the negative electrode relative to the positive electrode such that when the cell is reaching the upper cutoff potential of 4.2 V, the state of charge of the graphite is significantly less than in the early cycles (hence the lower full cell capacity). Therefore because the graphite is not being charged to as high an electrode state of charge, the voltage curve of the graphite no longer reaches 0 V vs Li/Li⁺ to initiate lithium plating even with the same overpotential from the high current.
Figure 2. Voltage versus capacity curves for pouch cells under test at 30°C during cycling with a two-step charge process from C/50 to 5C charge rates (a-h).

Figure 3. Capacity (a), coulombic efficiency (b) and coulombic inefficiency per hour (CIE/h) (c) versus time for pouch cells cycling at 30°C during cycling with a two-step charge process from C/50 to 5C charge rates.

Figure 4 shows the results for fade (a), coulombic efficiency (b) and CIE/h (c) as a function of charge rate at different temperatures. All data from cycling with both single- and two-stage charge steps are shown. Coulombic efficiency and CIE/h are taken as an average over the final ~50 hours of cycling while fade is taken as a linear fit to the capacity versus time data over that same final ~50 hours. Figure 4c shows that the CIE/h for cells cycled at lower rates at a given temperature is a constant. At lower temperature this constant is smaller as the degradation rate is less than at higher temperature due to the slower rate of parasitic reactions. However, as the rate is increased, the CIE/h begins to deviate from the low-rate constant value and becomes larger (worse). This leads to “kinks” in the CIE/h versus rate curves where CIE/h is constant during the time dependent regime and then increases with rate during the charge rate dependent regime (where lithium plating occurs). The “kinks” indicate the charge rate at which lithium plating begins at that temperature. These results in CIE/h are exactly as expected and generate the anticipated “hump” shaped CE versus rate curves that shift to the right with increasing temperature. There are measurable differences in the fade rates (especially when the efficiency becomes very poor at high rates) but the difference in fade rates is so small that there is much easier to resolve the onset of plating by examining the CIE/h.

Figure 5 shows the negative electrode (at ~50% state of charge, opened in an argon-filled glove box) of cells after cycling at different rates. These images confirm the experimental observations of the onset of lithium plating made from coulombic efficiency. At 12°C, the “kink” in the CIE/h curve occurs between C/5 and C/2 which implies that the cell charged at C/5 should not show lithium plating while the cell charged at C/2 should show small amounts and then the higher
Figure 4. A summary of fade (a), coulombic efficiency (b) and coulombic inefficiency per hour (CIE/h) (c) versus charge rate for all pouch cells at different temperatures and rates using both the single and two-stage charge process.

Figure 5. Photograph of the negative electrode after cycling for cells cycled at different rates and 12°C (a) and 50°C (b) to examine for confirmation of the occurrence of lithium plating.

Figure 6 shows the voltage curves at various charge rates (as indicated in the panels) for the 3.4 Ah NCA/graphite 18650 cells. At higher rates, as expected, there is an increase in the polarization of the voltage curve due to the internal impedance of the cells. Figure 7 shows the differential voltage (dashed curves on the right axis) and cell temperature (solid curve on the left axis) as a function of state of charge of the cells at different charge rates. During low rate charge
study, the coulombic efficiency versus rate takes the shape of an asymmetric “hump” which corresponds to the CIE/hour being roughly constant at low rates until lithium plating occurs. From Figure 9, lithium plating was predicted to start occurring at a 1C charge rate for the 18650 cells, and it may have occurred slightly even at C/2. Figure 10 shows photographs of the negative electrode of each of the 18650 cells after being opened in the fully discharged state. Due to opening the cells at the fully discharged state, no metallic lithium was observed on the negative electrode the way it was in the pouch cells. However, the cell charged at 1C rate does show clear differences in the color and texture of the negative electrode which may be evidence of areas on which lithium plating/striping had occurred during cycling. (Note: Again the picture may not be clear but there were clear differences evident to the naked eye.) Therefore these results remain consistent

Figure 7. Cell temperature profiles (left axis) and differential voltage (right axis) versus normalized capacity for 18650 cells cycling at different rates.

Figure 8 shows the C/10 discharge capacity (bottom) and normalized capacity (top) versus time number for the NCA/graphite 18650 cells cycled at different charge rates. While the capacity loss rates at C/10 through C/2 show minimal difference, the loss rate for the cell charged at 1C is notably higher due to the inefficiency of lithium plating relative to the intercalation/deintercalation process. The cell charged at 1C was removed before the other cells due to the indication of lithium plating and concerns over safety surrounding potentially large amounts of lithium plating within a high capacity cell. There are small differences in the capacity loss rates between cells likely from variability in manufacturing.

Figure 9 shows the coulombic efficiency (a) and CIE/hour (b) as a function of rate for the 18650 cells. Insets are shown in both panels to expand the scale for the lower rate cells which do not show indications of lithium plating. Consistent with the results seen in the pouch cell
with the study in the pouch cells but the rate at which the onset of lithium plating occurs is different due to temperature and differences in the electrode and cell design.

**Conclusions**

The effect of high charge rates was studied in both pouch-style and commercial 18650 cells to detect subtle signals indicating the onset of lithium plating, in-situ, from changes in the coulombic efficiency. Results between both sets of experiments shows the same predicted trend where the coulombic efficiency as a function of rate is time dependent until the onset of lithium plating which causes the efficiency to decrease. The use of a High Precision Charger such as the one at Dalhousie University allows for accurate measurements of the coulombic efficiency to detect these small amounts of lithium plating. As the cycling temperature is increased, the low rate cycling becomes less efficient due to increased parasitic reaction rates but the onset of lithium plating is not detected until higher charge rates due to the improved intercalation kinetics and diffusion at the negative electrode. This type of work highlights how high precision coulometry can be very useful for application specific testing to optimize the conditions for extending cycle life under which battery packs are managed depending on the temperature. In addition, the information in Figure 4 should be measured for cells used in long-term applications after several years of testing to determine how cycling and aging affect the onset of Li-plating.

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