Li-ion batteries are widely used in portable consumer electronics such as laptops, cellphones, and tablets where energy density and battery life-time are of key importance. Recently, electric vehicles powered by Li-ion battery packs have begun to increase in market share, but the calendar life of the battery pack must be improved substantially if this trend is to continue, in part so that automakers can offer competitive warranties on their products. It is therefore desirable to develop methods for testing the calendar and/or cycle life of Li-ion batteries that can produce results within shorter amounts of time.

A good indicator of the relative calendar life of a battery is its coulombic efficiency (CE). In combination with measurements of cell internal resistance, high accuracy CE experiments offer a rapid way to predict the relative lifetimes of many potential cell chemistries or designs. The CE is, in general, a time-dependent quantity that is expected to increase with time as the solid-electrolyte interphase (SEI) layers on the negative and positive electrodes mature and their growth slows. For example, Figure 1 shows data collected by Harlow et al. that shows CE initially trending both up and down for automotive size (35 Ah) Li-ion cells that were either fresh, aged for 1 year or aged for 2 years. To compare cells of various chemistries it is therefore important to select the time at which the CE is measured judiciously. However, several studies have observed anomalous transient CE behavior, especially in cells with previous histories of testing or usage.

When identical dry Li-ion batteries are filled with different electrolyte solutions, those with higher coulombic efficiency (CE) normally have a longer life-time, provided the batteries have the same test history (storage time and temperature, cycling protocol etc.). Accurate CE measurements can therefore be used to rapidly rank cells according to their life-time without relying on tests that are many years long. The CE of Li-ion cells normally increases with time since SEI layers thicken and parasitic reactions between electrodes and electrolyte, which cause the departure of the CE from unity, slow down. However, in some cases, the CE of Li-ion cells has been observed to be greater than unity and decrease during early charge-discharge cycling, which is unexpected. This anomalous behavior is shown here to be caused by the impact of lithium atoms stored in the negative electrode “overhang”, the small portion of the negative electrode that extends past the positive electrode in commercial Li-ion cells. Storage protocols are discussed that allow CE to more rapidly stabilize with time or cycle number.

During extended periods of storage at high states of charge, Li atoms within the graphite negative electrode can diffuse (as ions in the electrolyte and electrons within the solid phases) into the overhang region. As will be shown, the storage and release of Li atoms from the overhang region leads to the anomalous behavior observed in the CE measurements in Figures 1 and 2.

Fortunately, transport phenomena of Li species within the graphite anode are relatively easy to observe, thanks to a unique property of lithiated graphite. Figure 3 shows approximately where the visible color transitions occur along the voltage-capacity curve of the lithiated graphite electrode, where the picture inset was adapted from a paper by Harris et al. By observing the color changes of the graphite as it is lithiated through three staged phases of LiC6 intercalation, the Li content at various points along the overhang can be roughly approximated. As a Li-ion cell is charged, graphite turns from black, to dark blue, to red at LiC12, and then to gold at LiC6.

The mechanism by which the overhang causes anomalous CE is introduced here and subsequently demonstrated experimentally. Figure 4 shows a schematic of the diffusion of Li into the negative electrode overhang in the context of a pouch cell. The positive electrode, separator, and negative electrode are depicted for a jelly roll that has been spread flat, or for a stacked cell, with size differences exaggerated for clarity. Inset 4a illustrates the case where a cell is charged to the upper cut-off voltage. The negative electrode region that is covered directly by positive electrode is gold-coloured immediately after charging is complete. At this point, lithium atoms move toward areas of lower concentration in the overhang, coloured black.

In this report, high precision coulometry as well as post-mortem optical observation was used to show that the anode electrode overhang is the source of a “memory effect” that results in anomalous transient CEs.

Experimental

Nominally identical, machine-made Li-ion pouch cells (~220 mAh capacity from 2.8–4.2 V) were obtained from Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District,
Zhuzhou City, Hunan Province, PRC, 412000). These cells will be referred to as Li-fun pouch cells throughout this paper. All cells had Li[Ni0.5Mn0.3Co0.2]O2 (NMC 111) positive electrodes and graphite negative electrodes. Details of the electrodes are provided in Table I. Both electrodes were coated on both sides, except for small regions on one side at the end of the foils. Unless otherwise noted all cells were placed in temperature chambers controlled at 40 ± 0.1 °C for the electrochemical testing/storage tests completed.

Three cells were filled with 0.90 g ± 1% of electrolyte, containing LiPF6 salt (BASF, 99.99% pure) in a solution of 3:7 (by volume) ethylene carbonate:ethyl-methyl carbonate (BASF, less than 20 ppm water), with additives vinylene carbonate (VC, 2% by weight), methylene methanedisulfonate (MMDS, 1% by weight), and tris(trimethylsilyl) phosphate (TTSPIm, 1% by weight). The details of the additives used are described in.6 After vacuum sealing, the cells were held at 1.5 V for 24 hours, charged to 4.2 V at 10 mA and then de-gassed and vacuum sealed again at the top of charge. After formation and a single discharge (10 mA to 2.8 V), cells were charged to and then held at constant potentials of 3.5 V, 3.7 V, or 4.2 V, corresponding to states of charge (SOC) of approximately 20%, 50%, or 100%, for a period of 100 hours. Subsequently, these cells were cycled at 10 mA (approximately 20 hour discharge) between 2.8 V and 4.2 V, while CE was monitored using the ultra high precision charger at Dalhousie University.7,8

A more detailed study was also completed with 12 more nominally identical Li-Fun pouch cells. In order to mitigate the impact of solid-electrolyte interphase formation on CE, all 12 cells were aged by storing at 4.2 V after formation (open circuit conditions) for 500. After aging, 2 cells were then discharged and stored open-circuit at each of 3.56 V, 3.66 V, 3.70 V, 3.76 V, 3.95 V, and 4.20 V, corresponding to SOC’s of 20%, 40%, 50%, 60%, 80%, and 100%, for 500 hours more. Finally, all cells were cycled at 10 mA (C/22) between 2.8 V and 4.2 V, while CE was accurately measured for each charge-discharge cycle.

In parallel, six more nominally identical Li-Fun pouch cells were used for post-mortem optical observations of Li diffusion in the overhang. After formation, the first three of these cells were stored at a nominal voltage of 4.2 V at room temperature (23 ± 3 °C). After allowing diffusion to proceed for periods of 50, 150 or 850 hours (± 10%), each cell was disassembled in an argon-filled glove box, and photos were taken of the negative electrode. In order to speed up diffusion in the final cell, a 400 hour potential hold step at 4.2 V and 40. ± 0.1 °C was included as part of the 850 hours of total diffusion time. Figure 7 shows the photographs of these cells which will be described later. The second group of three cells were stored at a nominal voltage of 4.2 V. The cell pictured in Figure 8a was stored for 400 hours at the top of charge before disassembly. The cell pictured in Figure 8b was stored for 380 hours at the top of charge, discharged to 3.66 V at 110 mA (C/2), left open circuit and then disassembled after 2 hours. The cell pictured in Figure 8c was stored for 340 hours at 4.2 V, discharged to 2.8 V at 80 mA (C/2.5) and disassembled after 18.5 hours. All cells were disassembled in an argon-filled glove box.

Figure 1. Coulombic efficiency versus cycle number for fresh (black triangles), one year aged (blue diamonds), and two year aged (red circles) NMC442/graphite cells cycled at C/20 at 25 °C. Adapted from reference 3.

Figure 2. Coulombic efficiency versus cycle number for wound prismatic LiCoO2/graphite cells. Left and right panels describe cells with different cathode surface areas and cycled at different temperatures. Adapted from reference 4.

Figure 3. Photograph of graphite anode color as it moves through 3 phases of Li-C intercalation. Anode voltage-capacity curve (for a 3.2 mAh coin half-cell) shown above shows the approximate correlation between color and state of charge. Adapted from reference 5.
Results and Discussion

With the intent of systematically attaining anomalous CEs versus time or cycle number similar to those previously reported [Figures 1 and 2], three nominally identical cells were prepared and stored at different states of charge (SOC) for 100 hours. The length of time was chosen to reduce the total length of the experiment, yet still to yield detectable differences in CE due to lithium diffusion into the overhang. Figure 5 shows the CEs of the three cells plotted versus time measured from the end of the storage phase. There is a considerable difference in CE during the first cycle, and then the CEs converge to the same limit after ∼700 hours of cycling. In particular, the cell stored at 100% SOC temporarily exhibits a CE > 1.0000, which can be explained by including the contribution of the lithium stored in the overhang, that had diffused there from the active region during storage.

Figure 6 shows data for the same cells, but in terms of charge and discharge capacities rather than CE. As the cell (previously stored at 100% SOC) cycles, the difference between the average concentration of lithium over a cycle in the active region and the average concentration of lithium in the overhang results in a concentration gradient and a net diffusion of lithium from the overhang back into the active region. During a charge, this influx of lithium reduces the externally measured charge capacity. During discharge, it inflates the externally measured discharge capacity. These two effects together cause an apparent CE > 1 as long as the diffusion rate remains sufficiently high. Conversely, for the cell stored at 20% SOC, the overhang is depleted of lithium relative to the average lithium concentration in the anode active region over a cycle. As lithium is accepted into the overhang, the charge capacity is increased and the discharge capacity is reduced, resulting in a CE < 0.99 during the early cycles.

Over time, lithium diffusion between the overhang and the active region reduces the concentration gradient that existed due to diffusion during storage. In the limit of this process, the average concentration of lithium in the active region and the average concentration of lithium in the overhang, both considered over a full cycle, are equal. After this point, no further net diffusion occurs, and the CEs of the three cells are measured to be approximately equal, as in Figure 5 after ∼700 hours of cycling.

Table I. Electrode details.

|                        | Positive Electrode | Negative Electrode |
|------------------------|--------------------|--------------------|
| Material               | Li[Ni0.3Mn0.3Co0.4]O2 (NMC 111) | Graphite |
| Composition            | 96.2% : 1.8% : 2.0% | 95.4% : 1.3% : 1.1% : |
| Active Material        | 2.2% Active material : | |
| Carbon Black : PVDF    | Carbon Black : CMC : | SBR |
| Binder                 | 105 μm             | 110 μm             |
| Electrode              | 3.55 g/cm³         | 1.55 g/cm³         |
| Thickness              | 200 mm × 26 mm     | 204 mm × 28 mm     |

Figure 5. CE versus cycle number of newly-formed NMC pouch cells after being held for 100 hr at various SOC at 40°C.

Figure 6. Charge and discharge capacities versus cycle number of newly-formed NMC pouch cells held for 100 hr at various SOC at 40°C. These results are for the same cells as in Figure 5.
In order to prove the hypothesis presented above, visual observations of lithium diffusion into the overhang region were made. Figure 7 shows photos (taken through the glove box window) of the graphite negative electrodes of cells disassembled at different times. These three NMC/graphite cells were first stored at 4.2 V, which was taken to be the top of charge in this context. After periods of 50, 150, and 860 hours, each pouch cell was disassembled in order to observe the progress of diffusion. Figure 7a shows that even after 2 days of diffusion there is still a region of overhang with low lithium content in the overhang, as indicated by the thin strip of blue-black on either edge of the overhang. After 150 hours, most of the overhang is near 50% SOC, indicated by the red color in Figure 7b. Figure 7c shows that even after 860 hours, the overhang has not yet reached equilibrium with the active region of the negative electrode.

Figure 8 shows photos of the opposite process to that depicted in Figure 7, where lithium from the overhang diffuses back into the anode active region. After storage at TOC for 380 hours, the cell was discharged and quickly disassembled in an effort to observe the negative electrode overhang at a much higher state of lithiation than the active area. Figure 8a shows the initial state of the cells before discharge. Figure 8b shows that even after only 2 hours at 3.66 V (~40% SOC), no gold-coloured graphite remains in the overhang region, except for a small strip in the extremity of the negative electrode. However, a thin strip of red indicates that the overhang is at ~50% SOC while the active region is dark blue since it has not been fully de-lithiated (these are not artifacts of color balancing). In Figure 8c, the entire anode is black, demonstrating all the lithium has diffused out of the overhang in less than 19 hours at 2.8 V.

Figure 9 shows the CE of eleven cells during cycling after 300 hours of open-circuit storage at six different nominal SOCs: 20%, 40%, 50%, 60%, 80%, and 100%. In contrast to the three cells introduced before, these cells have undergone an aging procedure where they were first stored at 4.2 V for 500 hours before the 300 hour storage periods at different SOC. As a result, these cells are expected to have a thicker layer of negative electrode SEI, and a slower rate of further SEI growth. With this assumption, the CE change from cycle to cycle for a particular cell, and also the CE difference between cells stored at different SOCs, can be considered to be small. Any difference in CE should be principally due to different degrees of lithiation of the overhang as a result of the SOC during storage.

Figure 9 also shows the non-linear relationship between storage SOC and initial CE after storage. Rather than a symmetric distribution of CEs about the asymptote, the CEs for 40%, 50%, and 60%, and for 80% and 100% respectively, are grouped quite close together, and there is a wide gap between 60% and 80%. This is a result of the voltage-capacity curve of the graphite negative shown in Figure 3. Figure 3 shows that the voltage of the graphite negative electrode between ~70% and ~100% SOC is relatively constant, which results in only a small driving force for diffusion to proceed further than 70% SOC. Likewise, 40% and 50% SOC occupy positions on the same negative electrode voltage plateau, so diffusion is expected to proceed to a similar extent for cells stored at 50% SOC as for cells stored at 40% SOC. Cells stored at different SOC with large differences in CE are separated by steep negative electrode voltage gradients that encourage rapid diffusion along those sections of the graphite voltage-capacity curve. This effect also accounts for the fact, seen in Figure 7c, that after 860 hours at 100% SOC, the overhang had not yet come to equilibrium with the active region, yet it did so after just 19 hours at 0% SOC (Figure 8c). At 0% SOC the voltage-capacity curve of graphite is extremely steep encouraging rapid diffusion. The impact of voltage gradient on overhang behavior implies that the effect of the negative electrode overhang may be accentuated when using materials with sloping voltages such as Si or Sn based materials.

Figure 9 demonstrates that the impact of cell storage on the lithiation level of the overhang region can be used to advantage in highly accurate measurements of CE. The key to speeding the measurements is to store cells at the midpoint of the window in which they will be charge-discharge cycled prior to the commencement of cycling. This will ensure that the overhang region has the average amount of lithium that the graphite negative will hold and thus, no net long-term diffusion of Li into or out of the overhang will occur. The resultant CE will be very stable with cycle number as illustrated by the CE versus time curves in Figure 9 for the cells stored at 50 and 60% SOC.

Figure 10 shows the charge and discharge capacities for selected cells stored at different states of charge. For the cell stored at 100% SOC, while the discharge capacity slowly falls beneath the charge capacity, both charge and discharge move to higher capacity, for at least 400 hours of cycling. The cell stored at 60% experiences the same steady growth in capacity, albeit at a slower rate. This effect can also be attributed to the excess Li, compared to the average amount over a cycle, slowly diffusing out of the overhang. As the amount of Li locked up in the overhang decreases over time, the amount of Li in the cell increases, and so does the capacity. The cells stored at 60% SOC have much less Li stored in the overhang than those stored at 100% SOC, so the capacity only rises by a small amount compared to the cells stored at 100% SOC.
Conclusions

The negative electrode overhang is a source or sink for lithium atoms to emerge from or enter into during charge-discharge cycling that takes place after storage. If storage takes place at a high state of charge (near 100%), then the overhang becomes more and more filled with lithium as the storage time increases. Then, during subsequent cycling, lithium in the overhang slowly diffuses out, causing the cell capacity to start low and increase slightly in the initial cycles, and the CE to start at large values (can be greater than 1.0000) and decrease. By contrast, if storage takes place at a low state of charge (near 20%), then the overhang becomes less and less filled with lithium as the storage time increases. Then, during subsequent cycling, lithium slowly diffuses into the overhang region, causing the cell capacity to start high and decrease slightly in the initial cycles, and the CE to start at small values (can be less than 0.99) and increase. In the end, as Figure 9 shows, eventually (and this can take almost 1000 hours!) the CE of cells initially stored at high or low SOC reach close to the same values.

It is extremely important that practitioners of high accuracy CE measurements appreciate the effects of the negative electrode overhang. We hope that this simple study will aid such researchers. In addition, it will be important to make more quantitative studies of this effect. Synchrotron radiation diffraction studies of the overhang region in operating pouch cells using a tiny diameter X-ray beam (approx. 0.1 mm) would be very useful. Since the diffraction pattern of lithiated graphite changes with lithium content, it should be “easy” to determine the lithium content versus position in the overhang region by moving the cell with respect to the X-ray beam and recording diffraction patterns as a function of position and time. It is our goal to do such studies.

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