The Limited Effect of VC in Graphite/NMC Cells

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Degradation at the electrode surfaces is one of the major reasons behind capacity fade in well-constructed batteries. The effect of electrolyte additives, in particular vinylene carbonate (VC), is studied extensively for different lithium-ion chemistries and is shown to improve cyclic efficiency of some electrodes. We investigate the effect of VC additive in a graphite/NMC333 (lithium-nickel-manganese-cobalt oxide) cell. The addition of VC improves the rate performance, especially, at moderately high rates. A new three-electrode cell design with Li reference electrode was particularly useful in studying the rate performance of each electrode. The rate of side reactions is found to decrease with the addition of VC. Despite these important performance improvements, no significant improvement in the capacity retention is observed. This suggests that the side reactions in graphite/NCM cells consist of two types, (1) repairing cracked solid electrolyte interphase (SEI) on the negative electrode (results in a net consumption of Li from the positive electrode), (2) reforming SEI components that dissolve from the negative electrode and are oxidized at the positive electrode. The VC appears to reduce the second type but have negligible effect on the first. This indicates that cylindrical efficiency measurements are not a reliable indicator of cell cycle life.

Electrode side reactions are one of the major reasons for the loss of performance of Li-ion batteries. The instability of commonly used electrolytes at typical operating potentials results in side reactions, some of which go to solid electrolyte interphase (SEI) formation at electrode surfaces. Using electrolyte additives is one effective way to minimize the rate of chemical degradation. Electrolyte additives also may be used to form a thinner, more compliant oxide SEI, and thus reduce irreversible capacity loss, reduce parasitic reactions, and improve thermal stability of LiPF6 salt against the electrolyte solvents. Zhang et al. nicely summarize different electrolyte additive studies in the literature classifying them by their SEI stabilization mechanism. In lithium ion batteries, electrolyte additives tend to affect two aspects of cell characteristics, namely, cell impedance and side reactions. In the present work the effect of Vinylene carbonate (VC) on both of these parameters was studied. In the first part of this article, the effect of electrolyte additive on the impedance of the individual electrodes using 3-electrode cell is illustrated. The second part correlates the effect of VC on cell side reactions and coulombic efficiency. This study is useful to demonstrate our hypothesis that coulombic efficiency is not a reliable indicator of cell cycle life.

Vinylene carbonate (VC) has been extensively studied as an electrolyte additive and shown to improve battery life in some lithium-ion battery chemistries. Aurbach et al. observed a reduction of the impedance of synthetic graphite flakes, LiNiO2, and LiMn2O4 electrodes against lithium counter electrodes at room temperature as a result of the addition of VC to the solutions. It has been suggested that VC forms thin polymeric films on the positive electrode as well as the negative electrode surfaces, which helps reduce the irreversible capacity loss and the surface impedance of some electrode materials. Ota et al. studied the effect of VC on LiCoO2 electrodes against lithium metal counter electrodes and observed that the cycling efficiency of the cell improved in the presence of VC, especially at room temperature and higher. Itagaki et al. showed that for LiCoO2/Li “half” cells, the presence of VC has a slight influence on the charge transfer resistance at room temperature.

Parasitic reactions in the presence of lithium metal may not be the same as those in cells with other negative electrode materials such as graphite. For this reason, some of the recently published articles use "full" (metal oxide positive electrode, graphite negative electrode) cell configurations to understand parasitic reaction. Wu et al. showed that the presence of VC improves capacity retention with cycling of a LiFePO4/MCMB graphite cell. Burns et al. showed that the addition of VC to the electrolyte improved coulombic efficiency in a commercially wound Li-ion cell with LiCoO2 as the positive electrode and either graphite or Li4Ti5O12 (LTO) as the negative electrode. These articles also reported that capacity slippage (or “marching”) of the charge and discharge endpoints is slowed by the presence of VC.

The presence of VC is also reported to improve the charge transfer resistance of a LiCoO2/graphite cell. Though several articles have observed a change in the cell/electrode impedance or change in SEI film morphology and composition in the presence of VC, it was surprising that not a single article could be found reporting the direct effect of VC on rate performance of a full cell. In the present article, the effect of VC on the rate performance of a NMC/graphite cell is described. The experiments used our in-house designed three-electrode coin cell. The three-electrode coin cell design allows for the monitoring of the voltage of both electrodes independently. It is shown that the presence of VC improves the cell rate performance at moderately high rates. Many of the full-cell studies in the literature report improvement in the coulombic efficiency of the cell due to presence of electrolyte additives, electrode coatings, artificial SEIs, etc. However, whether improved coulombic efficiency always represents an improvement in cycle life is still an unanswered question. In the present article, the term coulombic efficiency is explained in a full cell context. Contrary to some findings in the literature, the data presented below show that cells with different coulombic efficiencies can have the same capacity fade rate. This demonstrates that coulombic efficiency is not a reliable indicator of cycle life.

Experimental

Electrode preparation.— The electrode materials were NMC111 (Applied Materials Inc.) and CGP-8 graphic carbon (Conoco Phillips). Battery grade acetylene black (AB) (Denka Singapore Private Limited), Polyvinylidene difluoride (PVDF) no. 1100 (Kureha, Japan), Anhydrous N-methylpyrrolidone (NMP) (Sigma–Aldrich) were used as conducting carbon, binder and solvent for electrode fabrication. A slurry casting method developed in our lab was used to prepare all of the electrodes. The method involved a slurry mixing process which was done in a glove box with argon atmosphere (Vacuum Atmospheres Co (VAC)). The mixture was blended together using a Polytron PT 30–35 homogenizer at 2500 rpm until
uniform (about 2 hours). The positive electrodes were prepared with NMC (92.8 wt%) acetylene black (AB)(3.2 wt%) as a conducting additive and polyvinylidenedifluoride (PVDF) (4.0 wt%) binder well mixed in the N-methyl pyrrolidone (NMP) solvent. The slurry was cast on the aluminum current collector with an adjustable height doctor-blade. The negative electrodes were prepared with graphite CGPG-8 (8 wt%) mixed with AB (3 wt%) and PVDF (8 wt%) in NMP solvent. This slurry was coated onto a copper current collector with the doctor-blade. Different loading densities (1 mAh/cm² to 3 mAh/cm²) of electrodes were cast by varying the height of the doctor-blade. After the NMP evaporated, the dried electrodes were calendared to approximately 37% porosity using a roll press (Innovative Machine Corp.). The calendared electrodes were then punched into 1.27 cm and 1.43 cm diameter disks for positive (NMC) and negative (graphite), electrodes, respectively. The initial ratio of negative electrode capacity to positive electrode capacity was 1.3 based on the amount of active material on each entire electrode and reversible capacities of 330 mAh/g for graphite and 185 mAh/g for NMC between 2 and 4.4V vs Li. The punched electrodes were dried under vacuum at 130 °C for 15 h and then transferred into an argon atmosphere glove box.

Two and three-electrode cell assembly.— Standard ethylene carbonate-diethylene carbonate (EC-DEC) (1:1 vol/vol) with 1 M LiPF₆ (Daikin Industries, Japan) was prepared as the baseline electrolyte. 1 wt% solution of vinylene carbonate (VC) (97% purity, Sigma Aldrich) in the baseline electrolyte was also prepared. 90 µL of electrolyte was used in the cell assembly. In case of cell with VC electrolyte additive, total VC content is calculated to be about 8.5 wt% of the total graphite contain in the cell. 2325-type coin cells (National Research Council Canada) and custom-made 3-electrode cells (Figure 1) were assembled in an argon atmosphere glove-box (Vacuum Atmospheres Co.) with less than 0.1 ppm of oxygen and moisture. Lithium foil (FMC Inc) was used for the reference electrode. Porous polypropylene separator Celgard 2400 (Celgard LLC) was used between the electrodes.

Figure 1 shows the cell design for the custom-made 3-electrode cell. The reference electrode was placed behind the positive electrode in a modified 2325 coin cell can. Celgard 2400 separator was used to avoid contact between the lithium reference electrode and the back of the positive electrode. The separator was soaked with electrolyte solution to maintain an ionic path to the reference electrode for the measurements.

Rate performance and cell impedance testing.— The three-electrode design described above and shown in Figure 1 was used to understand the effects of the presence of VC on overall cell impedance and the rate performance of the individual electrodes. Two sets of full cells were fabricated with the same electrode loading. There were four cells in each set. In one set of cells, baseline electrolyte was used, and the other set was assembled with 1 wt% VC added to the electrolyte. After formation cycles, both sets of cells were charged to 50% state of charge (SOC) (based on capacity between 4.2 and 2.0 V ) and held overnight at open circuit. The cell voltage at 50% SOC was relatively flat and thus this SOC and the open circuit period assures minimal variation in cell voltage during the EIS study. A current controlled AC impedance study was performed using frequencies of 100 kHz to 20 mHz for the cells with and without 1 wt% VC. The cell voltage was observed to be ca. 3.67 V during the impedance test. The ohmic portion of the impedance is calculated from the high frequency intercept at the x-axis.

During rate performance testing, the cells were charged at the relatively low rate of C/10 to minimize the effect of impedance while charging. They were then discharged at rates of C/10, C/2, 1C, 2C and 5C to a lower limit of 2V. Two cycles were performed at each rate of discharge to confirm the rate performance.

Cycling performance tests.— Electrochemical cycling to measure current efficiency, capacity fade, and marching was carried out in standard (two-electrode) coin cells. Two sets of graphite-NMC full cells (with 4 cells in each set) were fabricated with equivalent electrode loadings. In one set of cells, baseline electrolyte was used, in the other set the baseline electrolyte with 1 wt% VC additive was used. After formation, the cells were cycled at C/2 from 4.2 to 2.0 V with a fifteen minutes rest period after every charge and discharge. Cell capacity was measured every 40 cycles at the slower C/10 rate to reduce the effect of impedance on the measurement.

Cell cycling protocol.— The cells were cycled with a Biologic VMP3 potentiostat at constant current (CC) on charge and discharge. Typically, 7 to 10 formation cycles were performed at a rate of C/10 between 4.4 and 4.6 V and 2.0 V.

Results and Discussion

Cell impedance measurements.— EIS measurements in 3-electrode cells were used to study the change in cell impedance due to addition of VC additive just after formation cycling. The Nyquist plot of the full cell impedance of both cells is shown in Figure 2. In the Nyquist plot, the high frequency intercept of the horizontal axis represents the ohmic resistance of the cell, and the medium-frequency minimum in the imaginary resistance component represents the ohmic

![Figure 1. Schematic diagram of 3-electrode cell with lithium reference arrangement.](image1)

![Figure 2. EIS study for the full cells, with and without 1 wt% electrolyte additive in the baseline electrolyte.](image2)
Figure 3. a. Rate test data capacity vs discharge C rate plots for cells with and without 1 wt% VC electrolyte additive in the baseline electrolyte. b. A plot of normalized instantaneous resistance of the cells with and without VC additive at different SOC. The resistances are normalized with the respective cell resistances at 90% SOC. The instantaneous resistances are measured after 1 second of a 1C charge pulse. The data show that the presence of VC decreases the instantaneous cell resistance at lower SOCs.

Resistance performance.—With the three electrode cell, the effect of the presence of VC additive on overall rate performance assessed. Figure 3a shows the discharge capacity as a function of rate. Both sets of cells have similar discharge capacities at the C/10 rate. However, the cells with 1% VC electrolyte additive tend to retain more capacity at moderate discharge rates (ca. 2C). These observations are highly reproducible, and are repeated for cells with different electrode loadings. In this particular example, the large drop in the capacity of both sets of cells at 5C is generally attributed to liquid phase ion transport becoming rate-limiting. This drop in the discharge capacity between 2C and 5C is characteristic of the thickness of electrodes and is observed in thinner electrode cells when discharged at higher C-rates. VC affects the surface resistances which can be observed from the moderate discharge rate (2C) data. The improved rate performance with VC at moderately high rates in spite of the similar full cell impedance of the two sets of cells at 50% SOC suggests that an impedance measurement at a mid to high state of charge is not a reliable indicator of capacity achieved by completely discharging the cell. Pulse current data (Figure 3b) did indicate that, at lower SOCs, cells with VC have lower impedance than cells without VC. The resistances plotted in Figure 3b are the ‘1sec resistances’ of cells calculated based on 1C charge pulse data. These resistances are normalized to the cell resistance at 90% SOC of the respective cells. From Figure 3b, we observe that, for a cell with the baseline electrolyte, cell resistance increases at SOCs below 50% SOC. In the presence of VC, the cell resistance at lower SOCs does not show an increase relative to that at high SOCs. Since the impedance at the lower SOCs has a larger impact on accessible discharge capacity than the impedance at higher SOCs, it is possible that impedance is playing a role at moderate rates even though it is not reflected in the impedance data taken at moderate depths of discharge, e.g., 50% DOD. To better capture this aspect of cell performance, EIS should be taken at low SOCs. At very high discharge rates the cells become limited by a different mechanism - the mass transfer of lithium ions in the electrolyte. Consequently, transport in the electrolyte is apparently unaffected by VC as the cells with and without VC show similar capacities at very high discharge rates.

Figure 4. a. Positive electrode voltage profiles vs Li reference electrode at different discharge rates for a cell with baseline electrolyte (blue), and a cell with 1% VC electrolyte additive (red). b. Negative electrode voltage (vs Li) profiles at different discharge rates of a cell with baseline electrolyte, and a cell with 1% VC electrolyte additive.
is clearly limited by the capacity of the negative electrode due to the sharp turn-up of the voltage of the negative electrode. The capacity of the cell without VC appears to be limited more by the capacity of the positive electrode: it is just about full of Li as the negative electrode is just about to be exhausted of Li.

At 2C both electrodes in the cell with VC deliver significantly more capacity than they do in the cell without VC before the cell voltage drops off as it becomes positive electrode limited. The cell without the VC shows much less capacity and is equally limited by both electrodes. Combining this data with the EIS data at 50% SOC suggests that somewhere between 50% and 10% SOC (as determined at the C/10 rate) the surface impedance of the both electrodes is significantly higher without VC.

At 5C, the salt concentration in the positive electrodes of both cells is being driven to zero to nearly the same extent, although the negative electrode in the cell with no VC is clearly limiting the discharge capacity. The data also show that at 2 and 5C, the negative electrode profile in a cell with VC remains much lower than in the cell without VC especially near the capacity at which the discharge limit is reached. This indicates higher impedance in the negative electrode profile in a cell with VC near the capacity at which the discharge limit is reached. This indicates higher impedance in the negative electrode in absence of VC.

The marching of both the charge and discharge endpoints as shown in Figure 5 can only occur if there are simultaneous side reactions on both electrodes during cell cycling. For example, the shift of the charge end point to the right with each cycle indicates an oxidation side reaction on the positive electrode which allows the cell charge to continue to higher cumulative capacity than if only lithium deintercalation were occurring on each and every charge.

That the negative electrode must also be undergoing a side reaction during cell cycling is evident from the marching of the discharge limit. The discharge limit is controlled by the rise in negative electrode voltage as its store of intercalated lithium is depleted. The discharge limit shifts to the right with each cycle because on discharge there is insufficient intercalated lithium to supply all of the electrons that were absorbed in the negative electrode during the previous cell charge. This lithium deficiency occurs because reductive side reactions other than reversible lithium intercalation (such as the side reactions which form the SEI layer) occur on the negative electrode during cycling.

Electrochemical cells cycle at less than 100% coulombic efficiency because of these side reactions. In other words, more electrical charge (mAh) is consumed during cell charge than is recovered during cell discharge. Thus the cumulative charge (or capacity) consumed by the cell grows during ongoing cycling. This capacity consumption of a cell can be visualized in a plot of the “cumulative capacity” consumed since the first cycle, of the charge and discharge endpoints of each cycle and plotted versus cycle number or versus time. In Figure 6 these cycling endpoints are plotted versus time for two cells. The two cells are as identical as possible except that one has 1 wt% VC added to the electrolyte. The plot clearly shows that the charge and discharge endpoints shift or “march” to higher capacity with each cycle; to the right in Figure 5. Such marching of charge and discharge endpoints has been previously observed and is attributed to side reactions on each electrode.

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discharge endpoints of both cells shift (march) to higher capacity with each cycle. After every 40 cycles of C/2 cycling, the capacity of the cells was measured with 2 cycles at C/10. These points in Figure 6 provide distinctly observable charge and discharge endpoints.

Effect of VC on marching.— The data in Figure 6 show that in the cell with 1% VC additive, the charge and discharge endpoints march more slowly. A decrease in marching rate of the charge end point could be caused by a decrease in rate of side reactions at the positive electrode, an increase in cell impedance, or an increase in rate of active material loss. A decrease in marching rate of the discharge end point could be caused by a decrease in side reaction rates at the negative electrode, a decrease in cell impedance, or by a decrease in rate of active material loss in the negative electrode. A simultaneous increase and decrease in cell impedance due to the presence of VC is not sensible and can be ruled out as a means by which VC causes the observed decrease in marching. However, a change in impedance occurred over time both in cells with and without VC as discussed below. All the three possible mechanisms causing charge/discharge endpoints to march, namely, (i) loss of active host material, (ii) cell impedance rise and (iii) side reactions are discussed in next few paragraphs in relation to the cells with and without VC.

To check for negative electrode active material loss during cycling, we plot the differential voltage versus the state of charge (dV/dQ vs SOC) of cells with and without VC. The dV/dQ vs SOC curve of a full cell shows peaks related to phase changes in the graphite electrode (the voltage curve of the positive electrode varies smoothly with SOC, thus no distinct peaks as a result of sudden phase changes). This is demonstrated in Figure 7. In Figure 7a, the dV/dQ curve for a graphite-lithium half-cell contains the same peaks that are associated with phase changes in the graphite electrode as lithium is removed from it. None of these peaks are associated with the lithium electrode because its voltage is constant at all SOC. The dV/dQ curve of the lithiation of LiNi0.3Mn0.3Co0.3O2 (NMC) in a Lithium-NMC half cell (Figure 7b) monotonously increases with increasing degree of delithiation, so there is more subtle information about the degree of lithiation of the NMC electrode in the dV/dQ curve. Thus, all the prominent peaks in the dV/dQ curve data of the graphite-NMC cell (Figure 7c) are due to phase changes in the negative electrode graphite as a function of the extent of lithiation. Cycle 4 in Figure 7c is chosen for illustrative purposes and similar phenomena can be observed for any cycle. For visual clarity in the figure, the differential voltage curve for the 4th cycle discharge is shifted in the vertical axis by adding a constant 0.3 V/mAh. Readers are recommended to read Deshpande et al.3 to understand differential voltage curves in detail.

In Figure 8, we plot the differential voltage versus the capacity of the cell for various cycle numbers for the cells with and without 1 wt% VC. Though the dV/dQ curves for the baseline electrolyte march further to the right, the distance between the dV/dQ peaks (Δx₁ and Δx₂) remains constant over many cycles confirming insignificant loss of negative electrode capacity. Thus, a comparison of the dV/dQ curves for the cells with and without VC indicates that the additive causes no difference in negative electrode material loss rate. Thus negative electrode material loss does not account for the slower marching rates in the presence of VC.

Loss of active material from the positive electrode as a result of particle isolation or trapped Li in the oxide would result in a reduction in the rate of marching to the right of the charge end point when
positive electrode limited. It is difficult to confirm positive electrode active material loss during cycling in the same way as with the negative electrode as there are no distinct humps in the d\(V/\text{d}Q\) curve coming from the positive electrode (it behaves as a single-phase material with regard to lithium intercalation). However, steady active material loss in the positive electrode could eventually result in the cell being discharge-limited based on the positive electrode. A change from negative electrode-limited to positive electrode-limited on discharge would result in a loss of the humps in the d\(V/\text{d}Q\) attributed to the negative electrode at the end of discharge. It would also result in a change in the trajectory in the discharge end point as the mechanism for marching would shift from the marching of the negative electrode to the marching of the positive electrode. Since none of these indicators are apparent after the 1700 hours of cycling, as shown in Figure 6, it is not likely that the reduction of the rate of marching of the charge end point in the VC cell was due to an acceleration of active material loss in the positive electrode.

An increase in cell impedance could slow the marching of the charge end point without affecting the discharge end point, as the discharge end point is strongly controlled by the thermodynamics of the negative electrode as it becomes fully delithiated. However, the likelihood that the addition of VC caused an increase in the resistance of the positive electrode slowing the marching of the charge end point and simultaneously a decrease in the marching of the negative electrode as a result of slower side reactions that result in exactly the same overall rate of capacity fade of the cell with and without VC is difficult to accept. An alternative and more palatable conclusion is the decrease in the rates of marching of both the charge and discharge endpoints, shown in Figure 6, is due to a decrease in side reaction rates on both electrodes in the presence of VC. The slope of each line in Figure 6 is the marching rate in units of current per unit electrode area. The electrode area used is the overlapping area of the electrodes, which is equal to the smaller (positive electrode) electrode area. The presence of VC clearly decreases the marching rate of both electrodes. However, the difference between the marching rates of each cell’s electrodes (13 \(\mu\text{A/cm}^2\)), which is the cell’s capacity fade, is unchanged by VC. That both the marching rates of the charge and discharge endpoints are decreased by the presence of VC while the difference between these marching rates (i.e., the capacity fade) remains unchanged by VC suggests that there are two kinds reactions happening at the negative electrode, one which is suppressed in the presence of VC, and another which is not, and is responsible for the capacity fade.

What could these two types of reactions be? Irreversible, ongoing SEI formation causes capacity fade, but if some fraction of the SEI dissolves and is reformed on the negative electrode with the same number of electrons with which it was formed, that fraction of the SEI formation would not contribute to capacity fade as this would cause the electrodes to march at the same rate. This hypothesis is in agreement with the previous experimental evidence of SEI dissolution on graphite and silicon.\(^{20-22}\) The constant rate of capacity fade of the cell suggests an additional process that requires the same amount of SEI reformation is needed each cycle whether VC is present or not, perhaps in the repair of cracks formed in the SEI caused by negative electrode swelling during cell charge. That the overall marching of both electrodes without VC is greater than the cell with VC suggests that either a reversible shuttle between the electrodes or the products of the negative electrode reduction that migrate to the positive electrode are simply hindered in their transport across the cell. In summary, it appears that two processes are at work: 1) the cracking and repair of the negative electrode SEI which results in the reformation of SEI, a net rate of capacity fade, that is unaffected by the presence of VC, and 2) a side reaction on the positive electrode that originates from products formed on the negative electrode from dissolution of the SEI or were formed during the formation process whose formation or transport across the cell is inhibited by the addition of VC.

Coulombic efficiency.— Coulombic efficiency is the ratio of the discharge capacity \(Q_d\) of a particular cycle to the charge capacity \(Q_c\) of the cell.
The coulombic efficiency could measure 100% only when there is no marching of the negative electrode in a negative-electrode-limited cell. The efficiency is completely independent of the marching of the positive electrode.

**Capacity fade.**—If charge and discharge endpoints have the same marching rate (i.e., $\frac{d\theta}{dT} = \frac{d\theta}{dN}$) then the cell does not experience capacity fade. If the discharge end point moves faster than the charge endpoint (i.e., $\frac{d\theta}{dT} > \frac{d\theta}{dN}$) as it does in the cycling data shown in Figure 6, the capacity of the cell fades.

The data in Figure 10a show that the capacity of cells with and without VC both fade at nearly identical rates, by about 0.4 mAh, or 25% in 400 cycles. A rise in internal resistance during cycling would contribute to capacity fade. To determine the contribution of resistance rise to capacity fade, the difference between the average cell voltage during charge and the average cell voltage during discharge are plotted, as shown in Figure 10b. That voltage difference rose by about 30 mV in 400 cycles. Roughly half of that voltage difference rise occurs during charge. Since the slope of the discharge curve near the end of discharge is very steep, a 15 mV drop in voltage due to impedance rise has an insignificant effect on the discharge capacity. However, the slope of the charging curve near the end of charge is about 0.53 V per mAh, so a rise in the charge voltage of 15 mV brings the cell voltage to the 4.4 V limit 0.028 mAh “sooner”, which accounts for about 7% of the 0.4 mAh total capacity fade. Thus 93% of the capacity fade is not due to resistance rise or to active material loss, but to the difference between the marching rates at each electrode, which in turn is caused by side reactions.

**Capacity retention.**—It is mathematically convenient here to consider capacity fade (CF) in the form of capacity “retention” (CR):

$$CR = 1 - CF$$

Capacity retention of the nth cycle is the ratio of discharge capacity of a cycle to the discharge capacity of the previous cycle:

$$CR_n = \frac{Q_{d_n}}{Q_{d_{n-1}}}$$

Using equalities in equation 3 we can rewrite the capacity retention as:

$$CR_n = \frac{Q_{d_n} - \frac{d\theta}{dT}}{Q_{d_{n-1}} - \frac{d\theta}{dT}} = \frac{Q_{c_n} - \frac{d\theta}{dT}}{Q_{c_{n-1}} - \frac{d\theta}{dT}}$$

From equation 4, it is evident that capacity retention is dependent on marching of both charge and discharge endpoints. Also from equation 4, if $\frac{d\theta}{dN} > \frac{d\theta}{dT}$ then $CR_n < 1$. Thus if the discharge end point marches faster than the charge end point, the capacity retention is less than 1. If both the electrodes are marching at the same rate, i.e.,

$$if \frac{d\theta}{dN} = \frac{d\theta}{dT} \rightarrow CR_n = 1,$$

the capacity retention of the cell can reach 100%, regardless of the rate of marching of either electrode, even though the coulombic efficiency, being solely a function of $\frac{d\theta}{dT}$, could be much less than 100%. Thus, coulombic efficiency is not necessarily a predictor of capacity retention.

Since the decay rate of both of the cells is similar (Figure 10a) we can conclude that the % capacity retention of both the cells is very similar. As discussed above, these cells differed in coulombic efficiency. Thus, though the presence of VC markedly improved the coulombic efficiency, it did not alter the capacity retention significantly. These long-term cycling data, which are reproduced with six cells, three with and three without VC as an electrolyte additive, contradict published claims that coulombic efficiency is a reliable predictor of cycle life, at least in the short term. If the side reactions result in loss of solvent, salt, or both, it is possible that in the long term, the rate of the side reactions will show up as catastrophic failure as the ability

![Figure 9. Coulombic efficiency vs cycle number of cells with baseline electrolyte (blue circles) and with 1 wt% VC dissolved in baseline electrolyte (red circles).](Image 38x549 to 280x716)
to transport ions across the cell is lost. If, however, the side reactions are a result of a reversible chemistry that transports back and forth across the cell either in a reduced or oxidized form, the rate of the side reaction would have little impact on the life of the cell.

**Side reactions and lithium depletion.** — As explained above, side reactions occur during charge as well as discharge. The total rate of side reactions (RSR) in capacity per cycle is

\[ RSR = \frac{dC}{dN} + \frac{dD}{dN} \]  

When cell impedance is not limiting and if there is no electrode material isolation (as discussed earlier with reference to Figure 8) the capacity loss during cycling may be assigned to the loss of cycleable lithium or lithium “inventory” due to side reactions. This is the amount of lithium that moves between the electrodes during cycling. It does not include the lithium in the electrolyte. The rate of loss of lithium inventory (RLLI) is the difference between the marching rates of the discharge and charge endpoints.

\[ RLLI = \frac{dD}{dN} - \frac{dC}{dN} \]  

In Figure 11, we plot marching of the charge (blue circles) and discharge (red circles) endpoints against cycle number of a cell with no electrolyte additive. This cell is formed between 4.2 and 2.0 V voltage limits at for 10 cycles at C/10 rate. The cell is cycled at the C/2 rate between the same voltage limits. As before, the capacity of the cell was checked at the slower charge discharge rate C/10 after every 40 cycles. In Figure 11 we also plot the capacity of the cell versus cycle number (black circles, the difference between the blue and red circles).

For this cell the total marching of the charge end point after 612 cycles is

\[ (qC_{612} - qC_1) = 0.914 \text{ mAh/cm}^2 \]

Total marching of the discharge end point is

\[ (qD_{612} - qD_1) = 1.813 \text{ mAh/cm}^2 \].

The capacity fade (and the loss of lithium inventory) is the difference between the total capacity shift of the charge and discharge endpoints: 0.90 mAh/cm².

Note that as defined above, the RSR is greater than RLLI. If the residual side reactions are electrolyte reactions which consume lithium salt at the rate ERR,

\[ ERR = RSR - RLLI = 2\frac{dC}{dN} \]  

In a simple model we take the salt depletion reactions to have a two electron, single electrode transfer mechanism. During cell charge:

**Negative electrode reaction:**

\[ S + 2e^- + 2LiPF_6 \rightarrow SLi_2 + 2PF_6^- \]

**Positive electrode reaction:**

\[ S + 2PF_6^- \rightarrow S(PF_6)_2 + 2e^- \]

or

\[ SLi_2 \rightarrow S' + 2(e^- + Li^+) \]

**Total reaction:**

\[ 2S + 2LiPF_6 \rightarrow SLi_2 + S(PF_6)_2 \]  

(reversible when \( S = S' \), or non-reversible)
in 612 cycles would be

\[ Total \text{ electrolyte reaction} = \int_0^{N} (ER) dN = \int_0^{612} \frac{\partial q_c}{\partial N} dN = (q_{c,12} - q_{c,1}) \]

\[ = 0.914 \text{ mAh} = 3.29 \text{ C} \]

\[ Total \text{ lithium lost} = \frac{3.29 \text{ C}}{96500} \times 3.41 \times 10^{-5} \text{ mol} = 9 \times 10^{-5} \text{ mol} \]

We use 90 microliters of 1 M LiPF6 salt solution as electrolyte. Hence during the electrolyte reactions resulting in marching of electrodes.19

Another possibility is that the electrolyte reaction products ELi and/or EPF6 are soluble and migrate to the opposite electrode and there the reactions are either reversed or result in loss of solvent. In the case of reversible reactions, electrolyte salt and solvent are not consumed in this overall reaction “shuttle”. Shuttle reactions would not lead to capacity loss. As discussed previously, addition of VC suppresses reactions that cause the marching of the cycling endpoints. That VC does this without affecting capacity retention suggests that it inhibits shuttle reactions while leaving the side reactions that cause capacity fade unchanged.

Conclusions

The presence of VC improves the rate performance of the cell at moderately high rates. This was in spite of the fact that the full cell impedance at 50% SOC was unaffected by VC additive. With the three-electrode cell, the voltage profiles of the individual electrodes could be measured. The reduction of impedance in the graphite electrode was evident in the negative electrode voltage profiles of cells containing VC.

For graphite/NMC cells, the presence of 1% VC slows the marching of cycle endpoints and improves coulombic efficiency significantly. However, there is no significant impact on capacity fade. This suggests that there are two kinds of side reactions occurring, both of which cause marching at both electrodes, but only one of which is slowed by VC. The type of side reaction which is slowed by VC reduces coulombic efficiency. It may consume electrolyte and/or salt irreversibly, or may not (a shuttle reaction). The other type of side reaction is responsible for 93% of the capacity fade in these cells, does consume lithium inventory, and is not slowed by VC. It is believed that this fraction of the side reaction occurs at the same rate in cells with and without VC and may be the result of negative electrode SEI repair, the SEI having been fractured during cycling. SEI is known to have high fracture tendency in the electrodes due to electrode volume expansion.23 VC appears to have no effect on this process. The remaining 7% of capacity fade is due to cell resistance rise during cycling and occurred to the same extent in cells with or without VC when cycled at moderate rates. That VC increased coulombic efficiency without reducing capacity fade shows that coulombic efficiency is not a reliable indicator of battery cycle life.

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