Studies of the Effect of High Voltage on the Impedance and Cycling Performance of Li[0.4Mn0.4Co0.2]O2/Graphite Lithium-Ion Pouch Cells

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Li[Ni0.4Mn0.4Co0.2]O2 (NMC442)/graphite pouch cells containing various electrolyte additives, either singly or in combination, were studied using cycling experiments up to 4.4 and 4.5 V coupled with simultaneous electrochemical impedance spectroscopy (EIS) measurements. The impedance of most cells increased dramatically at 4.4 and 4.5 V, but was nearly reversible over one cycle. However, during continued cycling, the impedance of all cells slowly increased at all potentials. Electrolyte additives were found to dramatically affect this behavior. The impacts of adding prop-1-ene-1,3-sultone (PES), vinylene carbonate (VC), triethyl phosphate (TAP), and tris(trimethylsilyl) phosphite (TTSPi) to 1M LiPF6 ethylene carbonate:ethyl methyl carbonate (EC:EMC) electrolyte were studied. PES-containing cells had dramatically lower impedance and better capacity retention than VC and TAP-containing cells during both 4.4 and 4.5 V experiments. When MMDs, DTD and/or TTSPi were added in combination with PES, the performance was improved further. Finally, continuous high charge-discharge cycling was compared to cycling with a 24-hour hold applied at the top of charge at 4.4 V. The high voltage hold led to severe impedance growth which could be partially overcome through the use of optimal additive combinations.

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Lithium-ion (Li-ion) batteries are currently used in phones, laptop computers and, more recently, electric vehicles. It is well known that electrolyte additives can have a dramatic effect on the performance of lithium-ion batteries.1,2 Vinylen carbonate (VC) is perhaps the most famous and widely used additive and has been shown to improve cycle and calendar life of Li-ion cells.3 VC is less effective, however, when used in cells cycling to potentials above 4.2 V or at elevated temperatures.4 Sulfur-containing additives have recently been investigated by several research groups in the hopes of overcoming the temperature sensitivity of VC and extending the usable voltage range of Li-ion cells.5,6

Prop-1-ene-1,3-sultone (PES) has been shown to function as a stable solid electrolyte interphase (SEI)-forming additive that improved coulombic efficiency (CE), reduced charge end point capacity slippage and self-discharge rates.8,9 PES nearly eliminated all gas production during storage at 4.2 V and 60 °C, whereas VC did not.9,10 The work by Xia et al.11 and Nelson et al.12 demonstrated the superiority of PES over VC as an electrolyte additive in NMC/graphite cells. Methylene methane disulfonate (MMDs) has been shown to reduce electrolyte oxidation at the positive electrode and reduce the volume of gas produced, as well as decrease the impedance and rate of parasitic reactions when compared to cells without MMDs.6,11 The additive ethylene carbonate and ethyl methyl carbonate (EC:EMC) electrolyte were studied. PES-containing cells had dramatically lower impedance and better capacity retention than VC and TAP-containing cells during both 4.4 and 4.5 V experiments. When MMDs, DTD and/or TTSPi were added in combination with PES, the performance was improved further. Finally, continuous high charge-discharge cycling was compared to cycling with a 24-hour hold applied at the top of charge at 4.4 V. The high voltage hold led to severe impedance growth which could be partially overcome through the use of optimal additive combinations.

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Despite the apparently stable impedance shown in Figure 1, it is important to measure the impedance at voltages above 3.8 V, and track the changes in impedance over several cycles. Poor performance of certain additives and additive combinations at high voltage may be due to impedance growth. Therefore, it is important to measure the impedance as a function of voltage, time and cycle number. This paper presents studies of the impact of electrolyte additives in NMC442/graphite pouch cells using electrochemical impedance spectroscopy (EIS) measurements coupled with cycling experiments to high voltage. Furthermore, the importance of performing experiments representative of “real-life” Li-ion cell use is demonstrated. Practical applications that use Li-ion batteries often leave the cells at high voltages for extended periods of time after charging. Therefore, studying the effect of extended periods of time at high voltage on the performance and impedance growth of Li-ion cells is imperative.

LiCoO2/graphite cells with upper cutoff potentials of 4.4 V are now common in the marketplace, but NMC/graphite cells that can be charged to 4.4 V are not, since NMC/graphite cells normally do not function well when charged to high potential. For this reason, NMC442/graphite pouch cells, which contain a small amount of Co and a significant amount of Mn, were chosen to be studied. Increasing the voltage range of NMC442, and other NMC grades is important to increase the energy density of cells for EV and other applications.

Experimental

Machine made 220 and 240 mAh NMC442/graphite wound pouch cells balanced for 4.7 V operation were obtained dry (no electrolyte added) from LiFUN Technologies (Zhuzhou City, China). Pouch cells...
were manufactured and vacuum sealed in a dry room in China before shipping to Dalhousie University. After heating to 80°C for 14 hours under vacuum to remove any residual water and then moved into an argon-filled glove box, the pouch cells were filled with 0.90 g of 1M LiPF6 in ethylene carbonate (EC): ethylmethyl carbonate (EMC) (94.0%), 1,3,2-dioxathiolane-2,2-dioxide (DTD, Aldrich, >98%), MMDS (Guangzhou Tinci Co. Ltd, 98.70%), triallyl phosphate (TAP, TCI America, >94.0%), and TTSPi (TCI America, >95%) were added alone or in ternary combinations to the control electrolyte in concentrations of 1 or 2% by weight. Figure 2 shows the chemical structures of the additives studied in this work. Cells were vacuum sealed using a compact vacuum sealer (MTI Corp.) after electrolyte filling.

All cells did a formation cycle at 40 ± 0.1°C, consisting of a 24 hour hold at 1.5 V to ensure adequate electrolyte wetting followed by a C/20 charge to 3.5 V. After this step, cells were transferred into an argon-filled glove box, cut open just below the heat seal to release generated gas and then vacuum sealed again. After degassing, the cells were charged to 4.5 V at C/20 followed by a C/20 discharge to 3.8 V. The temperature boxes used for the measurements presented in this work are stable to ±0.1°C, and are within one degree centigrade of the set temperature.

After formation, these cells were placed in a 40 ± 0.1°C temperature box connected to one of two systems capable of electrochemical impedance spectroscopy measurements coupled with cycling capabilities. The first system consists of a Maccor series 4000 connected to a Maccor FRA model 0356. The second system, built in-house by Greg d’Eon from Dalhousie University, consists of Neware (Shenzhen, China) cyclers connected to computers with Gamry frequency response analyzer (FRA) cards via appropriate computer controlled relays. The relay switching was controlled to connect the cells to the Neware charger or to the Gamry FRA cards as required. Cells underwent charge-discharge cycling by one of two methods, as shown in Figure 3. The time axis is simply provided as a scale, not as the specific time cycles occurred in the experimental method. Cells undergoing method 1 were cycled between 2.8 and 4.4 V at C/5 and 40 ± 0.1°C. Every 12 cycles, the cells underwent an “FRA cycle” consisting of a charge and discharge at C/20 between 2.8 and 4.4 V while the FRA measured the cell impedance every 0.1 V between 3.6 and 4.4 V. After the FRA cycle, the cells were cycled again between 2.8 and 4.4 V at C/5 for 11 cycles, and the protocol was repeated. After approximately 65 cycles, the upper cutoff voltage during cycling and impedance measurements was increased to 4.5 V, and the same 11 cycle-FRA-cycle protocol continued, as shown in Figure 3.

Cells undergoing method 2 were cycled between 2.8 and 4.4 V at C/5 and 40 ± 0.1°C including a 20 or 24 hr hold at 4.4 V. Every 4 cycles, the cells underwent an “FRA cycle” as described in method 1. After the FRA cycle, the cells were cycled again between 2.8 and 4.4 V at C/5 for 3 cycles with a 20 or 24 hr hold at 4.4 V, and the protocol was repeated. Cells were typically removed from testing once they exhibited a dramatic decrease in discharge capacity that did not stabilize.

Gas evolution measurements employing Archimedes principle were done on all cells before and after formation, and after cycling. This was done by weighing the cells in nanopure water with \( \rho = 0.998 \text{ g/ml} \) (20°C), such that the change in mass, \( \Delta m \), is a direct measure of the volume, \( \Delta V \), of gas produced during formation, storage, or cycling as described by \( \Delta V = \Delta m / \rho \). This procedure is discussed in depth by Aiken et al.
the FRA cycle, every 12 cycles, for the cell containing the electrolyte additives as labelled. Partial or missing data for an FRA cycle indicates that the cell was removed from testing at that time. The arrow in panel a) indicates the trend of the data with increasing cycle number, and applies to all panels. Figure 6 has many interesting features. All cells, except the PES211–containing cell, exhibited an increase in resistance as the voltage increased from 3.8 V to 4.4 V and an increased resistance at all voltages as the cycle number increased. When the upper cutoff voltage was increased to 4.5 V, typically at cycle 65, the impedance of all cells increased dramatically, except for the PES211 cell. Most interesting is the reversible nature of the impedance over one cycle. Despite the increase in impedance at 4.4 and 4.5 V, the impedance measured during the subsequent discharge decreased such that the value was nearly identical to the value measured upon charge suggesting dynamic changes to the surface layers on the positive electrode during charge to high voltages which are not understood at this time. All cells exhibited this reversible nature over one cycle. The impedance change for all cells, except PES211, is irreversible, however, over several cycles.

Figure 6d shows that Rct of the 2% TAP cell that was supposed to be measured at 3.6 V visually shifts to lower voltages during charge and higher voltages during discharge as cycle number increases. This is caused by the increasingly significant relaxation of the cell voltage when the current stops prior to the EIS measurement due to increased cell impedance.

The reversibility in Rct, particularly from 4.5 V to 4.4 V is thought-provoking. Possible explanations for this are 1) resistive surface species are temporarily formed at higher potentials, and return to solution again at lower potentials; or 2) physical and reversible restructuring of the electrodes and/or SEI layers caused by high potential increased the impedance reversibly. The irreversibility in resistance over several cycles, that is, the increase in impedance with increasing cycle number, correlates with discharge capacity fade and is most likely due to SEI growth on both electrodes and electrolyte degradation. Recent work by Petibon et al. using symmetric cells has shown that the reversible impedance increase which occurs at high potential is predominantly due to increases in Rct of the positive electrode. However, the steady increase of impedance over many cycles, as shown in Figure 6, may also involve the negative electrode, due to transfer of oxidation products from the positive to the negative electrode. Further work using symmetric cells made from electrodes of heavily cycled cells is required.

Figure 7a shows the resistance, Rct, as a function of cycle number for the cells as measured at 4.4 V. This further emphasizes the irreversible impedance growth for all cells except PES211. A change in slope occurred around 65 cycles for the 2% PES–containing cell, the FRA cycle, every 12 cycles, for the cell containing the electrolyte additives as labelled. Partial or missing data for an FRA cycle indicates that the cell was removed from testing at that time. The arrow in panel a) indicates the trend of the data with increasing cycle number, and applies to all panels. Figure 6 has many interesting features. All cells, except the PES211–containing cell, exhibited an increase in resistance as the voltage increased from 3.8 V to 4.4 V and an increased resistance at all voltages as the cycle number increased. When the upper cutoff voltage was increased to 4.5 V, typically at cycle 65, the impedance of all cells increased dramatically, except for the PES211 cell. Most interesting is the reversible nature of the impedance over one cycle. Despite the increase in impedance at 4.4 and 4.5 V, the impedance measured during the subsequent discharge decreased such that the value was nearly identical to the value measured upon charge suggesting dynamic changes to the surface layers on the positive electrode during charge to high voltages which are not understood at this time. All cells exhibited this reversible nature over one cycle. The impedance change for all cells, except PES211, is irreversible, however, over several cycles.

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when the upper cutoff voltage was increased to 4.5 V, indicating an increase in parasitic reactions and resistive species formed on the electrodes upon exposure to voltages above 4.4 V. The PES211–containing cell did not exhibit any change in slope, which is consistent with the gradual capacity fade shown in Figure 4. The slope for the 2% TAP-containing cell was constant until 150 cycles when there was an increase in slope, which has been emphasized by the dotted line. This is consistent with the severe discharge capacity fade exhibited by this cell at 150 cycles, as shown in Figure 4. This also indicates that although the impedance of the 2% TAP–containing cell continued to increase with cycle number, it was not immediately affected by the increase in upper cutoff voltage. In addition, the installation of the clamping plates on the TAP-containing cell at cycle 210 did not change the slope of the $R_{ct}$ versus cycle number plot suggesting that any gas evolution in the cell was not affecting $R_{ct}$ strongly.

Figure 7b shows the difference between the average charge and discharge voltage (delta V) as a function of cycle number. A smaller value of delta V means there is smaller polarization and thus smaller discharge voltage (delta V) as a function of cycle number. A smaller change in slope for the 2% TAP-containing cell, as shown in Figure 7b, indicates that although the impedance of the 2% TAP–containing cell continued to increase with cycle number, it was not immediately affected by the increase in upper cutoff voltage. In addition, the installation of the clamping plates on the TAP-containing cell at cycle 210 did not change the slope of the $R_{ct}$ versus cycle number plot suggesting that any gas evolution in the cell was not affecting $R_{ct}$ strongly.

Figure 8 shows the voltage-capacity curve for the TAP and PES211-containing cells for cycles 10, 160, and 260. This figure emphasizes the difference in delta V between these two cells as shown in Figure 7b. Figure 8a shows that the polarization of the TAP-containing cell increases significantly with cycle number. Figure 8b shows that the polarization of the PES211-containing cell is smaller and increases slightly with cycle number.

Figure 9 shows a comparison of the discharge capacity (top panels) and $R_{ct}$ as a function of voltage (bottom panels) for NMC442/graphite cells containing PES211. Figure 9a shows the discharge capacity as a function of cycle number for cells containing PES211 undergoing testing using method 1 (continuous cycling) and method 2 (cycling with a 24 hr hold at 4.4 V). Despite the excellent capacity retention of the PES211–containing cell during continuous cycling, the hold at high voltage leads to severe discharge capacity fade. This effect is also seen in Figure 9b, which shows the discharge capacity as a function of time. The discharge capacity of the cell undergoing testing using method 2 exhibited a brief drop in discharge capacity and then recovered at ~25 cycles in Figure 9a and 1000 hours in Figure 9b. This was caused by a temporary increase in voltage polarization during these cycles presumably due to jelly roll deformation caused by some gas generation. Figure 9c shows $R_{ct}$ as a function of cycle number for the PES211–containing cell undergoing method 2 testing. The arrow in panel c) indicates the trend of the data with increasing cycle number for panels c) and d). This cell exhibited severe impedance growth over 50 cycles (~1700 hours). Interestingly, the impedance was reversible over one cycle, similarly to Figure 6, while the impedance was irreversible over several cycles. Figure 9d shows $R_{ct}$ as a function of voltage for the PES211–containing cell undergoing method 1. This cell had very low impedance at all voltages and all 285 cycles (~3000 hours). Figure 9 dramatically demonstrates that holding cells
at high potentials for extended periods (as might be expected in real-life charging situations in portable electronics, for example) leads to severe impedance growth issues, at least with PES211 electrolyte and presumably with the other electrolytes described in Figures 4 and 6, which should be worse than PES211.

The paper by Wang et al. shows that the coulombic efficiency of cells with 2% PES + 1% DTD + 1% TTSPi is larger (better) than those of cells with 2% PES + 1% MMDS + 1% TTSPi, so it was decided to try replacing MMDS with DTD in studies of cells cycled according to method 2.

Figure 7. (a) The combination of charge transfer resistance (both positive and negative electrodes) and resistance due to motion of ions through the SEI layers (both positive and negative electrodes), Rct, measured at 4.4 V and (b) the difference between the average charge and discharge voltage, delta V, both as a function of cycle number for cells (indicated in the legend) undergoing method 1 testing. The closed star indicates when the corresponding cell was clamped.

Figure 8. The voltage-capacity curve for cycles 10, 160 and 260 for the 220 mAh cells containing (a) TAP and (b) PES211.

Figure 9. The discharge capacity for cells containing PES211 undergoing cycling tests and FRA measurements according to method 1 and method 2 as a function of (a) cycle number and (b) time. The combination of charge transfer resistance (both positive and negative electrodes) and resistance due to motion of ions through the SEI layers (both positive and negative electrodes), Rct, as a function of voltage measured during every FRA cycle for (c) the cell undergoing method 2 and (d) the cell undergoing method 1 testing. The arrow in panel c) indicates the trend of the data with increasing cycle number for panel c) and d).

Figure 10 shows the discharge capacity for NMC422/graphite pouch cells with 240 mAh capacity undergoing experimental method 2 as a function of time and cycle number. Every 3 cycles there is a cycle with visibly lower capacity due to the FRA cycle. The cells containing DTD have better capacity retention than the cell containing MMDS in agreement with expectations based on earlier work. The clamped cell containing 2% PES + 1% DTD + 1% TTSPi has significantly

Figure 10. The discharge capacity as a function of cycle number for cells undergoing cycling tests and FRA measurements according to method 2 at 40°C. The legend indicates the electrolyte additive sets incorporated in the cells.
containing the same additive combination have almost the same $R_{ct}$ as we have defined it, but may change the overall cell impedance by improving contact resistances.

Figure 11 shows $R_{ct}$ as a function of voltage for the cells undergoing method 2. Each panel shows the resistance measured during each charge and discharge of the FRA cycle, every 4 cycles, for the cell containing the electrolyte additives as labelled. The arrow in panel a) indicates the trend of the data with increasing cycle number, and applies to all panels. Each panel has a different number of cycles shown. The DTD-containing cells have smaller impedance than the MMDS-containing cell, which is consistent with the capacity fade results shown in Figure 10. The clamped cell and the unclamped cell containing the same additive combination have almost the same $R_{ct}$ for the same cycle number which is expected. However, the capacity fade in Figure 10 for these two cells is very different. The reasons for this will be addressed in the next paragraph. The cell containing 1% PES + 2% DTD + 2% TTSPi had the smallest impedance at all voltages and at all cycles, suggesting that this additive combination is superior in maintaining stable films on the electrode particle surfaces.

Figure 12a shows the resistance, $R_{ct}$, as a function of cycle number for the cells undergoing method 2 as measured at 4.4 V. All cells exhibited impedance growth. The cell containing 1% PES + 2% DTD + 2% TTSPi had low impedance growth until cycle 40 when the slope changed in Figure 12a. This is consistent with the discharge capacity fade shown in Figure 10. Figure 12b shows the difference between the average charge and discharge voltage (delta V) as a function of cycle number. The MMDS-containing cell exhibited a sharp increase in delta V after 20 cycles, while the slope of its $R_{ct}$ versus cycle number stayed constant. The unclamped cell containing 2% PES + 1% DTD + 1% TTSPi exhibited a slight increase in delta V after 35 cycles while the clamped cell did not. This may explain the difference in capacity fade shown in Figure 10. Furthermore, the clamped cell containing 2% PES + 1% DTD + 1% TTSPi and the cell containing 1% PES + 2% DTD + 2% TTSPi show an increase in delta V after 60 cycles, which is consistent with the capacity fade shown in Figure 10 and the increase in $R_{ct}$ at all voltages shown in Figure 11 for these two cells.

Figure 13 shows the volume of gas evolved in all cells studied during formation (top panel) and during cycling (bottom panel). Cells undergoing method 2 produced more gas during cycling compared to cells undergoing method 1. Figure 14 shows the volume of gas evolved during FRA testing as a function of delta V. The delta V shown is from the last cycle, and the gas was measured when the cell was removed from testing after the last cycle. It appears to us that one must consider several factors in the impedance growth: changes in $R_{ct}$; changes in solution resistance which were difficult to measure and changes to stack pressure as evidenced by gassing. The cell with 2% PES + 1% MMDS + 1% TTSPi generated significant gas and had large delta V. Perhaps a decrease in stack pressure due to this gassing contributed to the increase in delta V. The cell with 2% VC cycled using method 1 only underwent 47 cycles so did not develop a large delta V nor a large amount of gas, although it did show a significant increase in $R_{ct}$. The cell with 2% TAP cycled using method 1 underwent 353 cycles and did develop a very large $R_{ct}$ even in the absence of gassing suggesting that for TAP, the increase in $R_{ct}$ is responsible for the capacity fade. The cells with PES + DTD + TTSPi all had delta V near 0.15 V, consistent with similar values of $R_{ct}$ shown in Figure 12, even though some had up to 0.2 ml of gas generated (10% volume expansion). The results of Figure 14 are summarized in Table 1, which also lists the number of cycles before the cell was removed. The cycle number given indicates when the gas evolution measurements were taken.
Four 240 mAh cells undergoing method 2 testing and one 220 mAh cell undergoing method 1 testing were opened in an argon-filled glove box while at 4.4 V, after they were removed from testing at various cycle numbers. Table II shows photographs of the positive electrode, separator and negative electrode of each cell, as labelled in the first row. The 220 mAh cell undergoing method 1 testing containing PES211 had Li plating on the negative electrode, which is also evidenced by the dark spots on the separator. All 240 mAh cells undergoing method 2 testing showed evidence of Li plating, reflected by dark spots covering the entire separator. The cell containing the same additive combination that was clamped during testing had only a small amount of Li plating and the separator was free of dark spots. However, the entire separator had a brown color, instead of the white color seen in the unclamped cell. Clamping clearly has a significant effect on the amount of Li plating observed in the cells. The cell containing 2% PES + 1% DTD + 1% TTSPi, which exhibited the lowest R_{ct} of all cells, had Li plating on the negative electrode. The separator was also light brown in color. Finally, the cell containing 1% PES + 2% MMDS + 2% TTSPi showed severe Li plating on the negative electrode and the separator was covered with dark spots. This is consistent with the poor capacity retention (shown in Figure 10) and the severe impedance growth in this cell (shown in Figure 11).

It is our opinion that the lithium plating occurs in these cells for two reasons. First, when gassing occurs and stack pressure is lost, there may be some regions of the negative electrode with a poor ionic path connecting them to the positive electrode. Those regions will accept less lithium (no plating) and other regions will accept more lithium during charge leading to plating near the top of charge. The clamped cell showed little, if any, evidence for Li plating, consistent with this model. Secondly, the impact of electrolyte oxidation during the extended exposure to high potentials is most likely also responsible for lithium plating. Oxidation products migrate to the negative electrode where they form a surface film that eventually blocks the negative electrode porosity and leads to Li plating on the surface during charge.¹
Table I. Summary of the gas evolution and delta V (both measured after the last cycle) for the cells shown in Figure 14.

| Additive Combination * = cell clamped during testing | Method | Maximum upper potential reached during testing (V) | Cycle number when removed from testing | Gas evolution during FRA cycling (ml) | Delta V (V) |
|--------------------------------------------------------|--------|--------------------------------------------------|--------------------------------------|-------------------------------------|------------|
| 2% VC                                                  | 1      | 4.4                                              | 47                                   | 0.01936                             | 0.130036   |
| 2% PES                                                 | 1      | 4.5                                              | 135                                  | 0.13515                             | 0.217773   |
| PES211                                                 | 1      | 4.5                                              | 285                                  | 0.34912                             | 0.25291    |
| 2% TAP                                                 | 1      | 4.5                                              | 361                                  | 0.07206                             | 0.392692   |
| 2% PES + 1% DTD + 1% TTSPi                             | 2      | 4.4                                              | 41                                   | 0.1717                              | 0.12       |
| 2% PES + 1% DTD + 1% TTSPi∗                            | 2      | 4.4                                              | 66                                   | 0.10249                             | 0.145      |
| 1% PES + 2% DTD + 2% TTSPi                             | 2      | 4.4                                              | 66                                   | 0.22898                             | 0.14       |
| 1% PES + 2% MMDS + 2% TTSPi                            | 2      | 4.4                                              | 42                                   | 0.36385                             | 0.24       |

Table II. Photos of the positive electrode, separator, and negative electrode for select cells.

| Additive Combination | Method | NMC442 220 mAh | NMC442 240 mAh | NMC442 240 mAh | NMC442 240 mAh |
|----------------------|--------|----------------|----------------|----------------|----------------|
| 2% PES + 1% MMDS + 1% TTSPi | Method 1 | 1              | 2              | 2              | 2              |
| 2% PES + 1% DTD + 1% TTSPi | Method 2 | 1              | 2              | 2              | 2              |
| 1% PES + 2% DTD + 2% TTSPi | Method 2 | 1              | 2              | 2              | 2              |

Conclusions

The effectiveness of electrolyte additives during high voltage charge-discharge testing of NMC(442)/graphite cells at 40°C was studied through the use of impedance measurements coupled with cycling experiments. The additive combination of 2% PES + 1% MMDS + 1% TTSPi is superior to VC alone and to PES alone when undergoing continuous cycling in terms of capacity retention and impedance growth. However, the effect of a high voltage hold for an extended period of time is detrimental to cell performance due to severe impedance growth. When DTD was used to replace MMDS, severe impedance growth was delayed dramatically and capacity retention was dramatically improved. In particular, cells containing 1% PES + 2% DTD + 2% TTSPi have excellent capacity retention and virtually no impedance change during one cycle and over several cycles. However, some gassing in the cells occurred as did lithium
plating. Clamping cells with one of the better additive combinations (2% PES + 1% DTD + 1% TTSPi) eliminated lithium plating but did not dramatically affect the changes in \( R_\text{ct} \) compared to cells with the same additives that were not clamped and that did show lithium plating.

Automated impedance measurements coupled with cycling experiments give valuable information about the effectiveness of additives and additive combinations over a range of voltages and as a function of time and cycle number. One of the most important things learned from this study is that the performance of NMC442/graphite cells tested to 4.4 and 4.5 V can be dramatically improved using electrolyte additives but that the improvements reported here are probably not enough to enable 4.4 and 4.5 V products to be made. Surface science studies are required to learn how these improved additive sets cause the benefits that they do.

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