Effects of Electrolyte Additives and Solvents on Unwanted Lithium Plating in Lithium-Ion Cells

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Unwanted lithium plating on the graphite anode of lithium ion batteries can reduce the cycle life and safety of lithium ion batteries. Increased charging rates, lower temperatures, thicker electrodes, lower Li-ion diffusion constant and larger graphite particles all increase the propensity for unwanted lithium plating. In this work, a variety of electrolyte additives and electrolytes, which extend lifetime during low rate cycling, were used in Li[Ni0.5Mn0.5Co1]O2/graphite (NMC111/graphite) pouch cells subjected to high rate charging at 20°C. It was found that additives and electrolytes which increased the negative electrode area-specific resistance, \( R_{\text{negative}} \), decreased the onset current, \( I_u \), for unwanted lithium plating. Here, the processes of ion desolvation, electron and ion transport through the solid electrolyte interface and contact resistance are lumped into the \( R_{\text{negative}} \). Under conditions where \( R_{\text{negative}} \) is the dominant factor determining when unwanted Li plating occurs, the onset current for lithium plating could be well predicted by the expression: 

\[
I_u = 0.080 \times V_{S/R_{\text{negative}}},
\]

where \( S \) is the geometric electrode surface area. \( R_{\text{negative}} \) is easily determined using negative electrode coin-type symmetric cells. This simple rule-of-thumb relation will help guide researchers seeking to select electrolyte additives that simultaneously increase lifetime and also allow fast charging.

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Unwanted lithium plating can occur in Li-ion cells at high charge rates due to the close working potential of the graphite anode to metallic lithium. If the lithium ions and corresponding electrons cannot intercalate within the graphite particles fast enough, then metallic lithium can deposit on the surface of the graphite anode. Unwanted lithium plating is one mechanism that can limit the lifetime of lithium-ion cells. Even worse, plated Li can form dendrites which may pierce the separator and affect the safety of lithium-ion cells.\(^{1,2}\)

The propensity for unwanted lithium plating depends on many factors such as electrolyte components, \(^5\) cell design (e.g., anode/cathode ratios, thickness and porosity of the graphite anode), \(^5\) cell history and age (e.g., thickening of the negative electrode solid electrolyte interphase (SEI)\(^6\) and harsh charging conditions (e.g., high charge rates, low temperature and overcharge).\(^6-8\) Among these factors, the electrolyte used in lithium-ion cells not only determines the ionic conductivity but also plays a significant role in determining the properties of the SEI films.\(^9,10\) Therefore, the electrolyte components (i.e., Li salt, solvents and additives) can strongly affect unwanted lithium plating.

The choice of appropriate electrolyte additives is an efficient and simple way to improve the lifetime of Li-ion batteries by modifying the SEI properties.\(^11\) Vinylecne carbonate (VC) has been commonly used as an additive for forming a robust negative electrode SEI and has been shown to improve the cycle life and calendar life of Li-ion cells.\(^12-14\) Ethylene sulfite (ES) was reported to form a protective SEI film on the negative electrode.\(^15-17\) Ternary additives of 2% propene sultone (PES), 1% ethylene sulfate (DTD) and 1% tri-(trimethylsilyl)-phosphate (TTPS) (called PES211) improved the cycle and calendar life of NMC/graphite Li-ion cells under normal (i.e., 4.2 V) and high voltage (i.e., 4.4 V) operation.\(^18-20\) The additive triallyl phosphate (TAP) is reported to improve the high-voltage performance.\(^21\)

Many electrolyte additives have been proposed and shown in the literature to improve cell performance and lifetime. However, in the literature, the effects of these additives on low-temperature performance and on unwanted lithium plating are seldom considered or studied. Only a few papers regarding to the impact of additives on unwanted lithium plating could be found. Smart and Ratnakumar\(^3\) found that when VC was used in Li-ion cells the propensity for unwanted lithium plating increased due to the high resistive surface films formed by VC on the graphite negative electrode. SEI film modifiers with less resistive SEI-films such as FEC\(^22\) and allyl sulfide (AS)\(^23\) have been reported to reduce the propensity for unwanted lithium plating. Therefore, the effects of different additives on unwanted lithium plating are very important to explore when developing electrolyte additives for commercial applications.

Co-solvents can improve the ionic conductivity of electrolytes at low temperatures. Ternary or quaternary carbonate-based electrolytes with low EC-content and co-solvents having low melting points and low viscosities have exhibited improved low temperature performance. Among these co-solvents, optimized proportions of the ester-based components such as methyl propanoate (MP), ethyl propionate (EP) and methyl acetate (MA) have been reported to provide good low temperature performance including better charge rate capability.\(^24,25\) In cases where electrodes are thick or highly compressed, the addition of such co-solvents can also reduce the propensity for unwanted lithium plating at high charge rates even at higher temperatures.

In this work, effects of electrolyte additives and electrolyte solvents on unwanted lithium plating were studied using NMC111/graphite pouch cells. All electrolyte additives were added as weight fractions compared to the weight of the rest of the electrolyte. The electrolyte additives included 1%, 2% and 3% TAP, fractions, x, of the ternary additive blend, xPES211 (x = 0.25, 0.5, 0.75, 1), 2% VC, 2% VC + 1% trimethylsilyl methanesulfonate (TMSMS) and 2% VC + 1% ES. Different proportions of MP were also studied as co-solvent in EC:EMC (3:7) electrolyte. Charge-discharge cycling at 20°C using different charge rates was used to determine the onset current for unwanted lithium plating. Electrochemical impedance spectroscopy (EIS) measurements were used on the full pouch cells, negative electrode symmetric cells and positive electrode symmetric cells to investigate how the resistances of the electrodes affect unwanted lithium plating.

Experimental

1 M LiPF\(_6\) (BASF, purity 99.94%) in EC:EMC (3:7 wt% ratio, BASE, purity 99.99%) was used as control electrolyte. To this electrolyte, TAP (TCI, purity > 94.0%) was added as an additive at 1, 2 or 3 wt%. Fractions, x, of PES211 (x = 0.25, 0.5, 0.75 or 1) were also used as electrolyte additives (PES: Lianchuang Medicinal Chemistry Co., Ltd., China, purity 98.20%; TTPS: TCI America, purity > 95%);
Table I. Detailed information about the electrode materials in each of the NMC111/graphite pouch cells. Each pouch cell contained 0.9 g of electrolyte. The cells were balanced for 4.4 V operation, but only used to 4.1 V.

| Electrode composition | Positive electrode | Negative electrode |
|-----------------------|--------------------|---------------------|
|                       | 96.2% NMC111+1.8% carbon Black+2.0% PVDF Binder | 95.4% graphite+1.3% carbon black+1.1%carboxymethyl cellulose+2.2% styrene butadiene rubber |
| Areal loading (mg/cm²) | 16 (on each side) | 9.5 (on each side) |
| Surface area (cm²) | 90.7 | 102.2 |
| Mass (g) | 1.37 | 0.72 |
| Electrode density (not including foil) g/cm³ | 3.2 to 3.3 | 1.55 to 1.60 |
| Size of active particles (µm) | 10. ± 2 | 20. ± 5 |

DTD: Sigma Aldrich, purity 98%. For example, in xPES211 with x = 0.25 (i.e. 0.25PES211) the electrolyte additive is 0.5% PES + 0.25% TTPSi + 0.25% DTD. The additive combinations: 2 wt% VC (purity > 99.8%, BASF); 2 wt% VC + 1 wt% TMSMS (TMSMS: Shenzhen Capchem Technology Co. Ltd., China) and 2 wt% VC + 1 wt% ES (ES: Aldrich, purity 99.0%) added to the control electrolyte were also studied.

To study the effects of methyl propanoate (MP: BASF, purity 99.99%) as a co-solvent on unwanted lithium plating, xMP (x = 0.1, 0.2, 0.4, 0.6 (weight fraction)) was added to (1-x) EC:EMC (3:7) with PES211 as the electrolyte additive combination. The lithium salt in this study was always 1 M LiPF₆.

**Pouch cells.**—The pouch cells used in this study were Li[Ni₀.₃₄Mn₀.₃₄Co₀.₃₄]O₂ (NMC111)/graphite cells with a capacity of 220 mAh balanced for 4.4 V operation. Cells were manufactured by Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000) and vacuum sealed again in an argon-filled glove box. After this step, the electrode stack (about 0.5 atm. pressure) and push small amounts of gas that may be produced during cycling to the edge of the pouch. The pouch cells were cycled with external clamps to maintain pressure on the electrode stack (about 0.5 atm. pressure) and push small amounts of gas that may be produced during cycling to the edge of the pouch.

**Results and Discussion**

Figure 1a shows the chemical structure of the additives used. Figures 1b, 1c and 1d show the differential capacity (dQ/dV) vs. cell voltage of NMC111/graphite pouch cells filled with control electrolyte and with control electrolyte in combination with 1% – 3% TAP, xPES211 (x = 0.25, 0.5, 0.75 and 1), 2% VC, 2% VC + 1% TMSMS or 2% VC + 1% ES during formation (first charge to 3.5 V). The dQ/dV plot indicates the potential(s) at which the solvents or additives reduce on the graphite anode. Figure 1b shows that cells with control electrolyte show a characteristic peak at around 2.90 V (graphite potential around 0.65 V ± 0.1 V vs. Li/Li⁺) which is associated with the reduction of EC on the surface of graphite. With the addition of TAP, a new peak appeared at a cell voltage of about 2.70 V (graphite potential around
Figure 1. (a) Chemical structure of the different electrolyte additives used in this work and (b)-(d) differential capacity (dQ/dV) versus cell voltage during the first (formation cycle) charge to 3.5 V for NMC111/graphite pouch cells with different types and concentrations of additives as indicated. The first charge was made at C/20 and at 40 °C.

0.85 V ± 0.1 V vs. Li/Li⁺ in addition to the reduction peak of EC at 2.90 V, indicating that the peak at 2.70 V corresponds to the reduction of TAP partially suppressed the reduction of EC.

Figure 1c shows that with the addition of xPES211, a new peak appeared at around 2.40 V (graphite potential around 1.15 V ± 0.1 V vs. Li/Li⁺) corresponding to the preferential reduction of PES. Similar to TAP, as the amount of xPES211 increased, the capacity associated with the reduction of PES111 increased. When x ≥ 0.5 in xPES211, xPES211 passivated the graphite effectively and the reduction of EC (2.90 V) was almost fully suppressed.

Figure 1d shows that the reduction of 2% VC occurred at a cell voltage around 2.7 V which fully suppressed the reduction of EC. Cells with 2% VC + 1% TMSMS show a reduction peak at around 2.8 V, while adding TMSMS alone to control electrolyte showed no extra reduction peaks apart from the reduction of EC on the graphite electrode. Therefore, the reduction peak of 2% VC + 1% TMSMS at 2.8 V is probably related to the reduction of VC.Figure 1d shows that reduction peak in cells with 2% VC + 1% ES at about 2.5 V is different from the reduction of VC alone. This peak is caused by the reduction of ES or by the combined reduction of ES and VC.

Figure 2 shows the Nyquist plots for NMC111/graphite pouch cells with different electrolyte additives measured at 3.80 V and 10 °C after cell formation. Figures 2a and 2b show that the addition of TAP and xPES211 (0 ≤ x ≤ 1) increased cell impedance (diameter of “semicircle” increases) and this impedance increased with increasing content of TAP or xPES211 (0 ≤ x ≤ 1). This result correlates well with the CEC plot vs. V results shown in Figures 1b and 1c. Figures 1b and 1c show that when more TAP or xPES211 were added, more reduction reactions of TAP or PES occurred, and Figure 2 shows that more resistive SEI films were formed. Figure 2c shows that the addition of 2% VC alone increases the impedance while the addition of 2% VC in combination with 1% ES or 1% TMSMS lowers cell impedance. Figure 2d shows a summary of the resistances, Rct, of NMC111/graphite pouch cells calculated from Figures 2a, 2b and 2c.
during cycling decreases the cell capacity. This increased polarization is mainly caused by the increased R_\text{ct} of the negative electrode which will be confirmed by symmetric cell experiments below, thus the increased polarization forces the potential of the negative electrode below 0 V vs. Li/Li^+ to induce unwanted lithium plating. For cells with control + 3% TAP, \Delta V increases faster during cycling at C/3 suggesting that unwanted lithium plating causes impedance growth for control + 3% TAP, presumably by blocking the surface of the negative electrode. Figures 3d and 3e show that \Delta V of cells with control electrolyte increases with cycle number much faster than cells with control + 1% TAP which suggests that other parasitic reactions still occur in cells with control electrolyte during long-term cycling even though cells with the control electrolyte show no unwanted lithium plating. The slow increase of \Delta V with cycle number for cells with TAP at low charge rates where no unwanted lithium plating occurs may be due continual reduction of TAP at an appreciable rate after the formation cycle.

Figures 4a, 4b and 4c show the discharge capacity versus cycle number for NMC111/graphite pouch cells containing different concentrations of xPES211 (x = 0.25, 0.5, 0.75, 1) tested with different C-rates: C/3 (4a); C/2 (4b) and 1 C (4c) during cycling to 4.1 V at 20 °C. One C/20 cycle was also made before and after the testing at higher C-rates. Figures 4a, 4b and 4c show that with increased concentrations of xPES211, the discharge capacity is reduced especially during high rate cycling. Rapid capacity fade and unwanted lithium plating occur at C/2 for cells with xPES211 (x = 1) while unwanted lithium plating occurs at 1 C for cells with xPES211 (x = 0.5 or 0.75). Cells with xPES211 (x = 0.25) have about the same capacity retention as cells incorporating control electrolyte when cycling at C/3 and C/2 but their capacity retention is slightly better at 1 C (see next paragraph).

Figures 4d, 4e and 4f show \Delta V versus cycle number for NMC111/graphite pouch cells corresponding to Figures 4a, 4b and 4c, respectively. Figure 4d shows that the \Delta V is stable for cells with xPES211 (0 ≤ x ≤ 1) during cycling at C/3. Figure 4e shows that the \Delta V does not increase much during cycling even though rapid capacity fade and unwanted lithium plating occur for xPES211 (x = 1) during cycling at C/2. Figures 4d, 4e and 4f show that \Delta V of cells with control electrolyte increases slightly faster during C/3, C/2 and 1 C cycling compared with cells containing xPES211 (x = 0.25) at the same charge rate. This result suggests that cells with control electrolyte without additives have more parasitic reactions and a small amount of xPES211 (x = 0.25) reduces impedance growth during long-term cycling even at 1 C. Figure 4f shows that during cycling at 1 C, \Delta V increases significantly for cells with xPES211 (x ≥ 0.5) which is probably associated with unwanted lithium plating.

Figures 5a, 5b and 5c show the discharge capacity versus cycle number for NMC111/graphite pouch cells containing control electrolyte with 2% VC, 2% VC + 1% TMSMS or 2% VC + 1% ES tested with different C-rates: C/2 (5a); 1 C (5b) and 1.5 C (5c) during cycling to 4.1 V at 20 °C. Figure 5a shows that there is no much difference between cells with the different additives during cycling at C/2 and this is supported by similar \Delta V versus cycle number graphs in Figure 5d. Figure 5c shows that during cycling at 1.5 C, cells with control + 2% VC have the worst performance while the combination of 2% VC with 1% ES improves cycling performance at 1.5 C. However the performance is not as good as cells with control electrolyte. Figures 5d, 5e and 5f show \Delta V vs. cycle number for the NMC111/graphite pouch cells described in Figures 5a, 5b and 5c, respectively. Figure 5e shows that during cycling at 1 C, cells with control + 2% VC + 1% ES have the most stable \Delta V vs. cycle number which is consistent with the good cycling performance in Figure 5b. This means that the combination of VC and ES can reduce cell impedance and capacity loss during high rate cycling at 20 °C compared to cells containing VC alone. Figure 5f shows that cells with 2% VC and 2% VC + 1% TMSMS have higher polarization which is consistent with the bad performance during 1.5 C cycling shown in Figure 5c.

**Effects of co-solvent MP on Li plating.**—Figure 6a shows dQ/dV vs. cell voltage for NMC111/graphite pouch cells filled with {xMP + (1-x)EC:EMC(3:7)} + PES211 (x = 0, 0.1, 0.2, 0.4, 0.6). Figure 6a shows that MP does not influence graphite passivation and the reduction peak at 2.4 V corresponds to the reduction of PES. Figure 6b shows the electrochemical impedance spectra for cells with different contents of MP measured at 3.8 V and 10.0 °C after formation. Adding MP as a co-solvent decreases the diameter of the semi-circle but the impedance growth during cycling is not as good as cells with control electrolyte.

Figure 6c shows the conductivity of electrolytes with different contents of MP as co-solvent. As the amount of MP increases, the conductivity of the electrolyte increases since MP has a lower viscosity and lower melting point than the other solvents.\(^{34}\)
Figure 4. (a)-(c) The discharge capacity and (d)-(f) the corresponding ΔV vs. cycle number for NMC111/graphite pouch cells cycled at C/3 (a, d), C/2 (b, e) and 1 C (c, f) at 20 ± 0.1 °C with different concentrations of the electrolyte additive combination, xPES211 (0 ≤ x ≤ 1).

Figure 5. (a)-(c) The discharge capacity and (d)-(f) the corresponding ΔV vs. cycle number for NMC111/graphite pouch cells cycled at C/2 (a, d), 1 C (b, e) and 1.5 C (c, f) at 20 ± 0.1 °C with different electrolyte additive combinations: 2% VC, 2% VC + 1% TMSMS or 2% VC + 1% ES.
Figure 7 shows the capacity versus cycle number and ΔV versus cycle number of NMC111/graphite cells with 1 M LiPF6 in EC:EMC (3:7) + PES211 (x = 0, 0.2, 0.4, 0.6) electrolyte after cell formation and (c) the ionic conductivity versus temperature of electrolytes with different proportions of MP in EC:EMC (3:7).

Comparison of Figures 7 and 8 shows nearly the same capacity loss as cells with control electrolyte even at 1.5 C, although adding MP increases the electrolyte ionic conductivity, the high cell resistance caused by the PES211 electrolyte additives is still primarily responsible for the poor high rate cycling caused by unwanted lithium plating.

Figure 8 shows the overall capacity loss measured by the C/20 cycles before and after the high rate cycling at 20°C. Two cells were measured for each charge rate and the error bars represent the range of the data from the pair cells cycling at the same current and the same electrolyte. The blue shaded area in Figure 8 indicates a capacity loss less than 5% where no unwanted Li plating occurs. Capacity loss less than 5% occurs at small charge rates (e.g. C/3) and is probably caused by the growth and repair of the negative electrode SEI during cycling. The larger capacity loss above the shaded area in Figure 8 indicates where unwanted lithium plating occurs as lithium plating accelerates capacity loss. Figures 8a and 8b show that higher contents of TAP or xPES211 cause rapid capacity loss and unwanted lithium plating at lower currents. This result can be explained by the cell impedance shown in Figure 2 and the values of ΔV shown in Figures 3 and 4. The propensity for unwanted lithium plating increases with increased cell resistance when xPES211 or TAP is added to the electrolyte. Figure 8c shows that cells containing VC and ES have nearly the same capacity loss as cells with control electrolyte even at 1.5 C.
Figure 8. The capacity loss measured from the C/20 cycles before and after high rate cycling at 20°C for cells with: (a) different contents of TAP; (b) different contents of xPES211 (0 ≤ x ≤ 1); (c) the additives of 2% VC, 2% VC + 1% TMSMS or 2% VC +1% ES and (d) different amounts of MP, in 1M LiPF6 xMP + (1−x) EC:EMC (3:7) + PES211 (x = 0, 0.1, 0.2, 0.4, 0.6) electrolyte. The error bars show the difference between the two “brother” cells, consistent with Figure 2c which shows that ES lowers the resistance of cells containing VC. Figure 8d shows that the MP co-solvent helps to lower capacity fade and reduce the likelihood of unwanted Li plating at C/2 while rapid capacity loss and unwanted Li plating still occur at 1 C for cells with MP co-solvent and PES211.

Figure 9 shows the pictures of negative electrodes extracted from pouch cells after cycling at different C-rates for cells with 0% to 3% TAP. These photos are consistent with the capacity loss versus C-rate shown in Figure 8. Figure 8 shows that the cells with control electrolyte begin to lose large amounts of capacity during cycling at 1.5 C and Figure 9b shows that unwanted lithium plating was observed on the graphite surface after testing at 1.5 C while no unwanted lithium plating was observed after testing at 1 C as shown in Figure 9a. (Note: The photographs were taken through a glove box window and unwanted lithium plating may not be clearly shown in the pictures, however, lithium plating on the graphite surface was clear to the naked eye.) Figures 9c and 9d show that for cells with 1% TAP, no unwanted lithium plating occurred on the negative electrode after cycling at C/2 while unwanted lithium plating was observed after cycling at 1 C, consistent with Figure 8a. Figures 9e and 9f show that more white areas (i.e. lithium plating) were observed on the graphite electrode for cells with 3% TAP than for cells with 2% TAP (Figure 9e). This is consistent with the more severe capacity loss at C/3 for cells with 3% TAP than for cells with 2% TAP as shown in Figure 8a. The post-mortem analysis further confirms that capacity loss during high rate cycling at ambient temperature and modest upper cutoff potential (i.e. 4.1 V) can be used as a detection method for unwanted lithium plating since other parasitic reactions are negligible by comparison.

Figures 10a to 10d show the resistance, Rct, (diameter of the semicircle in the Nyquist plot) after formation and after 20°C cycling at C/3, C/2, 1 C and 1.5 C for cells containing (10a) different concentrations of TAP, (10b) different concentrations of PES211 (i.e. xPES211 (with x = 0, 0.25, 0.5, 0.75, 1.0)), (10c) 2% VC, 2% VC with 1% TMSMS or with 1% ES and (10d) {xMP + (1−x) EC:EMC (3:7)} + PES211 (x = 0, 0.1, 0.2, 0.4, 0.6). The impedance spectra were measured at 3.8 V and at 10.0°C in all cases. The complete impedance spectra of the NMC111/graphite pouch cells are given in Figures S1, S2, S3 and S4 in the supporting information.

Figure 10a shows that Rct decreases after cell cycling except for cells with 2% TAP after 1 C cycling. The impedance growth for cells
with 2%TAP after 1 C cycling might be caused by the large amount of unwanted lithium plating. Figure 10b shows that \( R_{\text{ct}} \) decreases for cells with xPES211 (0 \( \leq x \leq 1 \)) after cycling at different charge rates even though unwanted lithium plating occurs at high charge rates. Figure 10c shows that \( R_{\text{ct}} \) increases for cells with 2% VC and 2% VC + 1% TMSMS after cycling at 1.5 C while the \( R_{\text{ct}} \) of cells with control and control + 2% VC + 1% ES changed little even after cycling at 1.5 C. Figure 10d shows that \( R_{\text{ct}} \) increases after 1 C cycling for cells with MP co-solvent and the addition of PES211. This is probably caused by the increased impedance of the negative electrode after unwanted lithium plating. Generally, \( R_{\text{ct}} \) decreases for cells with xPES211 (0 \( \leq x \leq 1 \)) after cycling at different charge rates even though unwanted lithium plating occurs at high charge rates.

Figure 11 shows the area-specific Nyquist plots of the reassembled full coin cells, positive electrode symmetric cells and negative electrode symmetric cells constructed from parent NMC111/graphite pouch cells initially filled with control electrolyte plus 0%, 1%, 2% and 3% TAP. These full and symmetric coin cells were made from the pouch cells after the C/3 cycles at 20 C (Figure 3a). Figures 11a, 11b and 11c show the EIS spectra from full cells and symmetric cells reconstructed from NMC111/graphite pouch cells initially filled with control electrolyte plus 0%, 1%, 2% and 3% TAP. These full and symmetric coin cells were made from the pouch cells after the C/3 cycles at 20 C (Figure 3a). Figures 11a, 11b and 11c show that xPES211 dramatically increases the impedance of the negative electrode as x increases while it decreases the positive electrode impedance.
Figures 11g, 11h, and 11i show that with the addition of 2% VC, the increased impedance of the negative electrode exceeds the reduced impedance of the positive electrode, thus the full cell impedance is higher than for cells with control electrolyte. Cells with 2% VC + 1% TMSMS and 2% VC + 1% ES have nearly the same negative electrode impedance and are convenient in the search for additives that simultaneously promote long lifetime and high charge rates – one can evaluate the negative electrode impedances as cells with control electrolyte and additives with high negative electrode impedance such as the combination of 2% VC and 1% ES.

Figure 12a shows a strong correlation between the negative electrode resistance, $R_{\text{negative}}$, and the onset current for unwanted lithium plating. $R_{\text{negative}}$ is read from the Nyquist plots shown in Figures 11b, 11e, and 11h. Here, the processes of ion desolvation, electron and ion transport through the solid electrolyte interphase (collectively called charge transfer resistance here), current collector/active particle contact resistance and the resistance of Li$^+$ ion diffusion in the pores of the negative electrode are lumped into $R_{\text{negative}}$. The effects of the contact resistance and resistance of Li$^+$ ion diffusion in the pores of the negative electrode are seen as the small high frequency shoulder in these spectra. The charge transfer resistance (the diameter of mid-frequency semi-circle) dominates $R_{\text{negative}}$ which means changes in $R_{\text{negative}}$ are mainly determined by the charge transfer resistance of the negative electrode. $R_{\text{negative}}$ in Figure 12a was obtained from symmetric negative electrodes of disassembled pouch cells directly after formation and $R_{\text{negative}}$ in Figure 12b was obtained from symmetric negative electrodes of disassembled pouch cells after 20°C cycling (shown in Figure 11). Detailed Nyquist plots of symmetric cells with different electrolytes are shown in Figures S5 and S6 and the cycling performance at 20°C of NMC111/graphite cells using pyridine boron trifluoride (PBF) as an additive is shown in Figure S7 in the supporting information.

Figure 12 shows that there is a general negative correlation between the magnitude of the negative electrode resistance and the onset current for unwanted Li plating for all cells. Cells with control electrolyte have lower $R_{\text{negative}}$, thus are less likely to have unwanted lithium plating. Electrolyte additives that lead to low negative electrode impedance such as the combination of 2% VC and 1% ES promote high charge currents before unwanted lithium plating while additives with high negative electrode impedance such as high concentrations of TAP or PBF are more likely to lead to unwanted lithium plating. Therefore, cells with additives of that yield lower $R_{\text{negative}}$ are expected to have higher onset currents for unwanted lithium plating. Figures 12a and 12b show that the correlation between high $R_{\text{negative}}$ and small onset current for lithium plating is observed if $R_{\text{negative}}$ is measured directly after formation or after cycling. This is very convenient in the search for additives that simultaneously promote long lifetime and high charge rates – one can evaluate the negative electrode charge transfer impedance in symmetric cells made right after formation. Figures 12a and 12b show that the negative electrode resistance is generally slightly lower when measured after cycling compared to
the same electrodes measured just after formation. This suggests that the SEI in these electrolytes matures somewhat over time during the cycling of the cells.

A simple model can be used to explain the results in Figures 12a and 12b. Figure S8a shows that the potential of the stage 1–2 plateau of Li,C6 measured at C/20 and 40 C is about 0.080 V higher than Li/Li+⁰. Lithium plating will occur thermodynamically when the negative electrode potential is below 0 V vs. Li/Li⁰⁺. Therefore, it is assumed that unwanted lithium plating can begin when the negative electrode overpotential is about 0.080 V. Figure S8b shows a section of the graphite negative electrode having area, S, and thickness, L. The negative electrode resistance, R, is obtained by dividing the negative electrode area specific resistance, Rnegative, (obtained from the Nyquist plots in Figures 11b, 11e and 11h) by the active surface area of the negative electrode. In the case where the negative electrode resistance, R, dominates the contributions to the overpotential, η, then

\[ \eta = 1/R \]

where I is the cell current. If η ≥ 0.080 V, one expects unwanted lithium plating to occur. Therefore the onset current for unwanted lithium plating, Iₜ, is given by

\[ Iₜ ≥ 0.080 V / R = 0.080 V \times S / R_{negative}. \]  

Figure 12c shows the calculated onset current for Li plating, Iₜ, given by Equation 1 for tests conducted at both 10 C and 20 C. For example, Rnegative of a negative electrode symmetric cell with control electrolyte is 34.8 Ω cm² measured at 10 C as shown in Figure S6 in the supporting information. The active negative electrode surface area in the pouch cell is 90.74 cm². This yields Iₜ = 0.080 V/(34.8 Ω cm²) × 90.74 cm² = 208.6 mA. Therefore, the calculated onset current for unwanted Li plating is predicted to be about 208.6 mA (0.95 C) for cells with control electrolyte at 10 C. Figure 12c compares the onset current for unwanted lithium plating from high rate cycling experiments and post mortem analysis to the predictions of Equation 1. The EIS measurements on negative/negative symmetric cells (shown in Figure S9) used for the data points in Figure 12c were made at the same temperature as the determination of the onset current for unwanted Li plating and it appears that data collected at both 10 and 20 C fall onto the same universal curve.

It is unfortunate that the data shown in Figures 12a and 12b are for measurements of Rnegative at 10 C and for the onset current for unwanted Li plating at 20 C. When these experiments began EIS spectra were taken always at 10 C in order to amplify differences between cells with different electrolyte additives. It is then realized later, based on the trends in Figures 12a and 12b, that a simple relation like Equation 1 might describe the data. The temperature dependence of Rnegative for the negative electrodes with SEI layers formed in different electrolytes is unknown and should be characterized. This is most likely why the points in Figures 12a and 12b do not fall closer to a single trend line. The dashed line in Figure 12a is simply a graph of the function: B/Rnegative with B = 64.34 Ω cm² to show that data in Figure 12a approximately follows the trend of Equation 1. Figure 12d shows the predicted values for the onset currents for unwanted lithium plating at 10 C calculated using the values of Rnegative measured at 10 C using Equation 1. Figure 12d also shows the measured values of the onset currents for unwanted lithium plating at 20 C plotted versus Rnegative measured at 10 C. Figure 12d suggests the onset currents for unwanted lithium plating at 10 C will be about 30% to 50% of the values at 20 C.

It is important to stress that the overpotentials due to lithium diffusion in the graphite and lithium-ion diffusion in the electrolyte have not been considered in the simple model that yields Equation 1. The goal of this work was to explore how electrolyte additives, which affect the SEI layers, affect the onset current for lithium plating. Obviously, when very large graphite particles or very thick electrodes are used, these factors must be taken into account.

Conclusions

The impacts of negative electrode impedance and electrolyte ionic conductivity on unwanted lithium plating were investigated with 20 C high rate cycling, EIS measurements and symmetric cells. Unwanted lithium plating was the main mechanism for rapid capacity loss with cycle number at high charge rates in this study. The negative electrode SEI and its impedance were changed by adding different types and different amounts of electrolyte additives including TAP, xPES211 (0 ≤ x ≤ 1), VC, VC + TMSMS and VC + ES to 1 M LiPF6 EC:EMC(3:7) electrolyte. The additives used and the amount added all strongly affected cell impedance and unwanted lithium plating. Symmetric cells showed that higher concentrations of TAP or xPES211 increased the resistance of the negative electrode, which decreased the onset current for unwanted lithium plating. Cells with both the additives VC and ES had lower negative electrode impedance and higher onset currents for unwanted lithium plating. Therefore, additives that promote low negative electrode charge transfer resistance are good for low-temperatures and high rate charging. Such additives must be carefully selected so that the lifetime of Li-ion cells is not compromised.

A simple model was proposed for estimating the onset current, Iₜ, for unwanted lithium plating. Based on this model, Iₜ = 0.080 V x S/Rnegative, where S is the electrode surface area and Rnegative is the area specific negative electrode resistance measured as the diameter of the “semicircle” in the Nyquist plot of a negative electrode symmetric cell. The predictions of the model agreed very well with the trends observed in experiment.
Researchers hoping to find electrolytes and electrolyte additives that simultaneously promote long lifetime and high charge rates can simply measure the impedance spectrum of a negative electrode symmetric cell made from negative electrodes harvested after formation and then use the simple model to estimate $I_u$. Obviously, other measurements, such as high precision coulometry, are required to estimate the impact of electrolytes and electrolyte additives on cell lifetime.

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