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The Effect of Electrolyte Additives upon Lithium Plating during Low Temperature Charging of Graphite-LiNiCoAlO₂ Lithium-Ion Three Electrode Cells

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The effects of lithium-ion electrolyte additives in ester-rich low temperature electrolyte blends, including vinylene carbonate (VC), lithium bis(oxalato) borate (LiBOB), lithium difluoro(oxalato)borate (LiDFOB), propane sulfone (PS) and lithium bis (fluorosulfonyl)imide (LiFSI), upon the likelihood of lithium plating are investigated in graphite-LiNiCoAlO₂ three-electrode cells. While metallic lithium is generally absent in lithium-ion cells, certain conditions, particularly charging at low temperature and/or at high rate, can lead to lithium metal plating on the surface rather than intercalating into the carbon anode. Metallic lithium reacts with the electrolyte and forms dendrites upon continuous plating, which can lead to cell shorting and capacity loss. The type of carbon anode, electrolyte, and solid-electrolyte-interphase (SEI) all influence this behavior. SEI stabilizing additives are generally detrimental to low temperature charging performance, however, 0.1 M LiFSI was found to be advantageous to low temperature charging. When charged at a C/5 rate to 4.10 V, lithium plating was evident at ~20 °C higher temperature with VC and LiBOB additives compared to the baseline electrolyte without any additives (plating appears at ~10 °C rather than ~30 °C with the baseline electrolyte). In contrast, the cell containing 0.10 M LiFSI as an additive did not display lithium plating until ~40 °C or 10 °C lower than the baseline cell.

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Despite the fact that Li-ion cells have become ubiquitous since their introduction in the mid-1990s, the phenomenon of metallic lithium plating on the carbon anode, rather than intercalation into its bulk structure during charging at low temperature and/or high charge rates still presents a problem. Lithium plating generally occurs when cells are charged at low temperature, at excessive rates, and/or at high voltage, being more prevalent when it is a combination of these conditions.1–4 Often, the plated Li can have a non-uniform dendritic morphology, which might lead to an internal shorting of the cell. Even without such detrimental failure, the plated lithium can react more readily with the electrolyte, depending upon cell chemistry and cell design, which will lead to increased cell impedance and internal gas generation. Even if the plating is relatively benign, the reaction of the lithium metal with the electrolyte leads to irreversible capacity loss of the cell.5 In designing a Li-ion cell, it is critical that the anode is in excess compared to cathode to minimize the possibility of Li plating. Additionally, for current distribution purposes, the negative electrode needs to be geometrically extended beyond the positive electrode to avoid plating.6 In addition to cell design aspects, most notably being the nature of the anode, the electrolyte and the corresponding solid electrolyte interphase (SEI) layer is recognized as being an important factor that influences lithium plating.1,3,4,6,7 We have previously investigated the influence of the electrolyte type, including the use of additives, upon the propensity of lithium plating under various operation conditions.1,3,4,6,7 In this work, we have extended these studies to investigate the effect of additives upon lithium plating in ester-based low temperature electrolytes.

Plated lithium can be difficult to detect, and a simple method developed by us to detect it is dependent on carefully observing the discharge potential for the presence of a higher voltage plateau associated with oxidation, or stripping, of lithium after subsequently charging the cell under presumed plating conditions.1,3,6,10–13 The reversible potential of lithium is lower than lithiated graphite by ~85 mV, so a higher voltage plateau will be present at the beginning of the discharge, being proportional to the amount of lithium plated during the preceding charge. It is important to discharge the cell at very low rates (C/20 or lower) in order to ensure that the majority of the capacity under the plateau results from lithium stripping and there is not a competition between stripping and de-intercalation.

Plated lithium can also be observed using destructive analysis,6,14,15 by using specially designed cells which permit the direct observation of lithium metal during cell cycling,16,17 or measuring the thickness of the cell during cycling.18 The analysis presented here non-destructive, where lithium plating is inferred from observation of the discharge following a charge where plating occurred. Since lithium ions which have been intercalated into graphite are ~85 mV higher in potential than metallic lithium, the cell voltage will be ~85 mV higher during discharge if lithium stripping is taking place rather than de-intercalation. This method relies on the lithium metal stripping reaction, and thus is unable to detect the presence of lithium metal that may be electrically insulated from the anode. Lithium that has become insulated from the anode should present itself in the form of low coulombic efficiency since there are no other significant competing degradation pathways at low temperature11 and may also result in increased gas generation from its reaction with electrolyte. The effects of lithium plating are partially mitigated by discharging the cell soon after finishing the charging step to minimize the lithium-induced reactions with electrolytes as well as reducing its harmful effects on cycling. In our previous studies,3,4,6 we observed the presence of this “voltage plateau” in both prototype Li-ion cells and experimental three-electrode cells where the cell voltage remained noticeably high during the initial discharge stage before falling back to the expected overpotential associated with de-intercalation following the stripping of plated lithium metal, while Fan and Tan13 observed similar effects in commercial 18650-size lithium-ion cells. Petzl and Danzer10 used differential analysis of the discharge curve to aid in the quantitative determination of the precise amount of lithium that was stripped during discharge.

In previous work, we have demonstrated that lithium-ion cells containing electrolyte blends containing ester co-solvents deliver improved performance at low temperatures,3,19–21 which has also been reported by other groups using similar approaches.22–24 For this study, the solvents ethylene carbonate (EC), ethyl methyl carbonate (EMC), and methyl propionate (MP) were combined in a 20:20:60 volume ratio with 1.0 M lithium hexafluorophosphate (LiPF₆) to...
produce an electrolyte base suitable for low temperature operation. Additives were then incorporated into this electrolyte base in either 0.1 M or 2% quantities for solids and liquids, respectively. Vinylene carbonate (VC), lithium bis(oxalato)borate (LiBOB), lithium difluoro(oxalato)borate (LiDFOB), 1,3-propane sultone (PS) and lithium bis(fluorosulfonyl)imide (LiFSI) were examined due to their chemical diversity (structure and decomposition products, Fig. 1) and interest as anode SEI or cathode electrolyte interphase (CEI)-stabilizing additives. Cells were fabricated using LiNiCoAlO$_2$ (NCA) cathodes and graphite anodes.

**Experimental**

Electrolytes were prepared by combining battery grade 1.0 M LiPF$_6$ in EC + EMC (50:50 vol%) from BASF with anhydrous MP obtained from Aldrich (stored over molecular sieves and determined to have less than 5 ppm of water by Karl-Fisher test) and battery grade LiPF$_6$ from Novolyte/Ferro to prepare the 1.0 M LiPF$_6$ in EC + EMC + MP (20:20:60 vol%) electrolyte which was used as the baseline formulation in this study. Additives were then added to the stock solution to achieve 2% concentration by volume for VC and PS and 0.1 M by mass for LiBOB, LiDFOB and LiFSI. The LiBOB used was obtained from Novolyte Industries, Inc., LiDFOB was synthesized by Prof. Henderson’s group at University of North Carolina, and LiFSI was purchased from Boulder Ionics, Inc.

Experimental three-electrode glass cells of 100–120 mAh capacity were fabricated using graphite carbon anodes and LiNiCoAlO$_2$ (NCA) cathodes, both of which were provided by Enersys/Quallion, LCC, and Tonen polyethylene separator material. The carbon electrodes were coated with active material on both sides of the substrate, and the dimensions were 155 × 42 mm for an active material area of approximately 130 cm$^2$. The NCA electrodes were also double sided and were cut to 140 × 40 mm with an active material area of approximately 112 cm$^2$, (with a loading of ~5 mg cm$^{-2}$). A lithium metal reference electrode was also included in the wound cell so that the individual electrode potentials could be monitored. The jelly-roll wound cells were placed inside O-ring sealed glass cells.

Electrochemical measurements were performed on a Princeton Applied Research VersaSTAT with a built-in frequency response analyzer. All cells were fully charged at ambient temperature prior to low temperature characterization, to serve as a comparison in discharge performance. The cells were characterized in Tenney environmental chambers (−1 °C) to maintain the desired temperature.

Charge/discharge measurements were performed on an Arbin battery cycler (BT-2042). The charge and discharge cycling was typically performed using current densities of 0.33 mA cm$^{-2}$, corresponding to a C/5 rate. The cells were charged using constant current to 4.10 V, followed by a tapered charge period at constant potential until the current tapers to a C/50 rate, and discharged to 2.75 V, with 15 min rest periods between the charge/discharge steps. Prior to low temperature discharge and charge characterization, the cells were soaked at the desired temperature for at least five hours. The cells were initially charged at room temperature prior to low temperature characterization, to serve as a comparison in discharge performance. The cells were characterized in Tenney environmental chambers (+/− 1 °C) to maintain the desired temperature.

**Results and Discussion**

**Electrochemical impedance spectroscopy (EIS).**—After performing initial formation cycling at 23 °C, which consisted of completing five cycles over the voltage range of 2.75 V to 4.10 V using C/5 rates, the cells were subjected to EIS characterization at a number of temperatures. EIS was performed on each electrode separately as well as on the full cell, which is possible due to the use of a reference electrode (lithium metal) in the cell. EIS analysis of the cells at 23 °C, −20 °C, −30 °C, and −40 °C confirmed that VC, PS and LiBOB produced more resistive SEI layers on the anode than baseline electrolyte (without additives) and those with LiDFOB and LiFSI. Since the trends are similar at all tested temperatures and we are primarily focused on low temperature performance, Fig. 2 plots the results from impedance analysis at −30 °C for the (a) graphite anodes and (b) LiNiCoAlO$_2$ cathodes as a function of electrolyte additives.

![Chemical structures of the investigated additives.](image1)

**Figure 1.** Chemical structures of the investigated additives.

![Electrochemical Impedance Spectroscopy (EIS) measurements at −30 °C for the (a) graphite anodes and (b) LiNiCoAlO$_2$ cathodes as a function of electrolyte additives.](image2)

**Figure 2.** Electrochemical Impedance Spectroscopy (EIS) measurements at −30 °C for the (a) graphite anodes and (b) LiNiCoAlO$_2$ cathodes as a function of electrolyte additives.
to the baseline electrolyte. For cells with LiBOB, VC, and PS, the anode film resistance is much higher than that of the cathode, a trend observed across the range of temperature evaluated. Thus, the measured full cell impedance at low temperatures is dominated by the anode impedance. The addition of LiDFOB led to the formation of low resistance films on both electrodes, so it displayed the overall lowest full cell impedance compared to the other cells containing the other electrolytes. LiFSI as an additive showed almost no effect on the EIS spectrum of the anode or cathode compared to the baseline electrolyte.

**Linear polarization measurements.**—The results from DC linear polarization measurements that were performed on the three-electrode cells at +23, −20, −30 and −40 °C for the anodes and cathodes at −30 °C are presented in Figs 3a and 3b, respectively, and the resistance calculated from the slope presented at all temperatures in Fig. 4. These measurements were performed on fully charged cells (charged at a constant current of C/5 to 4.10 V, then held at a constant voltage of 4.10 V until the current tapered to C/50 (CC-CV charging)) directly following formation (5 cycles at C/5 rate, 23 °C) and enable one to determine the polarization resistance of the electrodes from the slopes of the linear plots that are produced under potentiodynamic conditions using slow scan rates (0.02 mV sec$^{-1}$) and measured over +/- 10 mV from the initial equilibrium potential. The trends observed with respect to electrolyte type generally mirror the findings from the EIS study. Figure 4a reveals that LiBOB (2.33 to 296 Ω) and VC (1.85 to 132 Ω) produce steeper slopes and thus highly resistive films on the anode from +23 to −40 °C, while Fig. 4b demonstrates that the electrolytes without additives have steeper slopes and thus higher cathode film resistance. The electrolyte with LiBOB produces the lowest polarization resistance on the cathode at −30 °C (2.42 Ω), while simultaneously producing the highest polarization resistance on the anode (117 Ω). The baseline electrolyte is more balanced between the cathode and anode at −30 °C, with 7.33 Ω and 15.8 Ω polarization resistance, respectively. Once again, LiDFOB produces films with low resistance on both the cathode and the anode. Adding LiFSI to the baseline electrolyte slightly reduces the polarization resistance on the cathode (6.92 Ω), while slightly increasing that of the anode (15.9 Ω).

The polarization resistance values that were derived from the DC linear polarization measurements or the graphite anodes and LiNiCoAlO$_2$ cathodes in contact with the various electrolytes at 23 °C, −20 °C, −30 °C, and −40 °C are illustrated in Fig. 4. The large difference in polarization resistance between the electrodes at 23 °C and −40 °C necessitates the use of a log scale for the y-axis.

![Figure 3. Linear polarization measurements performed at −30 °C for the (a) graphite anodes and (b) LiNiCoAlO$_2$ cathodes.](image)

![Figure 4. Polarization resistance of (a) the graphite anodes and (b) LiNiCoAlO$_2$ cathodes at +23, −20, −30, and −40 °C.](image)
LiNiCoAlO₂ cathodes, the addition of LiBOB and VC to the baseline trend of decreasing exchange currents was observed at the anodes: implying that it possesses the most sluggish lithium de-intercalation measured was from the cell containing the LiBOB additive, lowest limiting current observed at > PS 0 °C, the anode is significantly more resistive than the cathode, and thus is polarized more than the cathode during charge and discharge at these low temperatures. As illustrated in Fig. 5b, the lowest limiting current observed at ∼30 °C of the graphite anodes measured was from the cell containing the LiBOB additive, implying that it possesses the most sluggish lithium de-intercalation kinetics of all the samples investigated. In summary, the following trend of decreasing exchange currents was observed at the anodes: Baseline + LiDFOB > Baseline + LiFSI > Baseline + PS > Baseline + VC > Baseline + LiBOB. With regard to the LiNiCoAlO₂ cathodes, the addition of LiBOB and VC to the electrolyte resulted in the highest intercalation kinetics. Of particular note is the fact that the lithium kinetics are dramatically higher at the anode than at the cathode in many cases at low temperature, with the anode polarized to negative potentials (vs lithium metal) when charging due to sluggish intercalation kinetics. These trends are substantiated by the electrical charge/discharge cycling performed on the cells at low temperatures, as discussed below.

**Low temperature charging characteristics.**—To look for clear evidence for lithium plating on the anode, the cells were charged to 4.1 V at C/5 rate with a C/50 taper (CC-CV charging) at room temperature (23 °C), cooled to low temperature (−20 °C, −30 °C, or −40 °C), discharged at C/20, and then cycled three times at low temperature with a C/5 rate charge to C/50 taper followed by a C/20 discharge (Fig. 6). The cells with all the electrolyte formulations spent a significant amount of time with the anode polarized below 0 V vs Li⁺/Li⁺ where lithium plating might take place. Figure 7 plots the cell, cathode, and anode potentials during charging at −20 °C for the baseline electrolyte, which has low anode polarization resistance. Despite polarizing the anode to −100 mV vs Li⁺/Li⁺ (which suggests that lithium plating may occur depending upon the degree of overpotential involved), no high-voltage plateau (indicating lithium plating) is evident for the baseline cell at −20 °C from the discharge curves, as shown in Fig. 8. There is decreased capacity (~7%) when charging at −20 °C, but there is no evidence (in the form of a plateau during discharge or reduced coulombic efficiency) for lithium plating based on this discharge curve. This may be due to the dominance of ohmic polarization, which is common to both intercalation and plating. However it is possible that lithium plating took place in the cell and the lithium metal was subsequently intercalated into the graphite anode and was not observed in the charge/discharge voltage profiles.

By contrast, Fig. 9 plots the cell, cathode, and anode potentials during CC-CV charge at −30 °C with 1.0 M LiPF₆ EC + EMC + MP (20:20:60) + 0.1 M LiBOB as an electrolyte. Comparison with Fig. 7 shows that the anode clearly spends much more time polarized below 0 V vs Li⁺/Li⁺, and gets as low as −180 mV before slowly coming back up to −120 mV during the taper.

Given the significant negative polarization on the anode during charging, it is perhaps unsurprising to see evidence of a plateau indicating indirect evidence of lithium plating in the discharge curve after charging at −30 °C in Fig. 10. Cycling at low temperature led to severe capacity loss (~95% coulombic efficiency vs >98% at room temperature), and also a decrease in the amount of plating, similar to what was observed by Petzel et al.¹⁰ Petzel et al. hypothesize that lithium plating causes an imbalance between the electrodes in the cell and leads to a situation where the anode does not reach the charge state necessary for plating to occur. Figure 10b demonstrates that decreased plating was observed in our cells as

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**Figure 5.** Tafel polarization measurements of the graphite anodes (bottom) and LiNiCoAlO₂ cathodes (top) at −20 (A) and −30 (B) °C.
well, with a significantly more pronounced voltage plateau early in the 2nd discharge compared to the 3rd and 4th discharge after charging at low temperature. All tested electrolytes displayed a similar pattern, where the first discharge following charging at low temperature displayed a much more obvious voltage plateau compared to subsequent cycles.

Since the difference in the discharge curve between a cell with obvious plating and a cell without any plating is quite subtle, differential capacity analysis was used, similar to what has been described by Legrand et al.,

Liu et al.,

and Petzl et al.

The data presented here is from three-electrode cells, however, so the differential capacity analysis is based exclusively on the anode, rather than the full cell. Figure 11 plots the differential of the anode voltage (dV) vs the differential of the charge (dQ) during a C/20 discharge after CC-CV charging at $-20 \, ^\circ\text{C}$, $-30 \, ^\circ\text{C}$, and $-40 \, ^\circ\text{C}$. The baseline electrolyte without additives produced only a slight shoulder towards the beginning of the discharge (left side of graph) at $-20 \, ^\circ\text{C}$ and $-30 \, ^\circ\text{C}$, whereas electrolytes with additives...
produced definitive peaks, indicating the transition between lithium stripping and de-intercalation. Although the lithium stripping and de-intercalation reaction may overlap to some degree during the initial discharge, at low discharge rates (C/20) it is unlikely that a significant portion of the capacity comes from de-intercalation given the sluggish de-intercalation kinetics of the graphite anode, therefore the capacity measured during the high voltage plateau was attributed exclusively to lithium metal. These peaks shift to later (i.e., lower states of charge) in the discharge when going from −20 °C to −30 °C, indicating that more lithium was plated during the charge at lower temperature. The peaks shifted back to higher SOC in the discharge going from −30 °C to −40 °C for cells containing LiBOB and VC, however, indicating that less lithium was plated on the cells at −40 °C than at −30 °C. The capacity of the cells was severely reduced at −40 °C as well. However, analysis on a percentage basis in Fig. 12 indicates that there was still less
lithium plated in these cells at −40 °C than at −30 °C. The cell containing LiDFOB produced more plating at −40 °C than at −50 °C, indicating that there may be a preferential temperature where conditions lead to increased plating compared to lower temperature. The cell with LiFSI showed the least evidence for lithium plating, with only a very small peak appearing at −40 °C, while simultaneously exhibiting the highest capacity (53% of room temperature capacity, or 57 mAh out of 107 mAh) at −40 °C. This is the only cell tested where an additive outperformed the baseline electrolyte at low temperature. The height of the peaks also increases at lower temperature, indicating a more abrupt change between lithium stripping and de-intercalation. The peak height could be indicative of the amount of de-intercalation occurring simultaneously during lithium stripping, with a sharp peak indicating that stripping occurred almost exclusively, while a broad peak would indicate that de-intercalation and stripping were occurring simultaneously to some extent.

Figure 12 re-plots data from Fig. 11 in terms of percentage of discharge capacity at each temperature arising from lithium plating. These values were obtained by determining the capacity at which the peak appears in the dV/dQ plot and then dividing that by the total capacity given at that temperature. Figure 12 reveals that there is an “optimal” lithium plating temperature at which a large percentage of the available lithium is stored temporarily as lithium metal. Counterintuitively, lower temperatures do not always produce more lithium plating. There are several possible explanations for
this, one of which being that as the electrolyte becomes more viscous, even lithium plating becomes more challenging at lower temperatures. Additionally, the duration of charging at high current becomes shorter at lower temperatures, because the cell spends much more time in the taper mode at lower current. It may also be possible for the lithium plated on the surface of the anode to be intercalated during the long taper or the rest following the charge,\textsuperscript{10,11} thus decreasing the amount of plated lithium that is detected during the subsequent discharge. The rest time after charging was kept constant throughout all the testing at 15 min, however the taper time changes depending on conditions. The variability of the taper time changes the amount of time that the anode is below 0 V vs Li/Li\textsuperscript{+}. For example, the anode of the cell with LiBOB spent 4.4 hours below 0 V vs Li/Li\textsuperscript{+} at \(-20^\circ C\), 5.1 hours at \(-30^\circ C\), and 4 hours at \(-40^\circ C\). From Fig. 12, 14% of the discharge capacity of the LiBOB cell was derived from plated lithium at \(-20^\circ C\), 27% at \(-30^\circ C\), and 12% at \(-40^\circ C\). This trend closely matches the trend for time spent below 0 V vs Li/Li\textsuperscript{+}, indicating that there may be a correlation.

### Conclusions

We have shown that the propensity of lithium plating at the anode during low temperature charging may be minimized by a judicious selection of electrolyte composition, and especially the electrolyte additives that control Li intercalation kinetics at the anode and cathode. We have shown that it is possible to reduce lithium plating during charging at low temperature using LiFSI electrolyte additive, which showed better low temperature performance than the baseline electrolyte, despite having similar electrode kinetics. The majority of additives tested effectively reduced CEI film resistance at the cathode, but either increased resistance at the anode, which led to more lithium plating during low temperature charging than the cell with the baseline electrolyte. The addition of LiFSI to the baseline electrolyte (1.0 M LiPF\textsubscript{6} in EC + EMC + MP (20:20:60 v/v)) resulted in reduced lithium plating at low temperature. At \(-40^\circ C\), an estimated 8% of the discharge capacity resulted from stripped lithium in the electrolyte with LiFSI, compared to 14% in the baseline electrolyte. At \(-30^\circ C\), no observed lithium plating was detected in the cell containing the electrolyte with LiFSI, while 7% was plated in the baseline electrolyte. At \(-50^\circ C\), an estimated 11% of the charge capacity was attributed to plated lithium for the LiFSI-containing electrolyte, which compares well to the baseline electrolyte at \(-40^\circ C\). Overall, it appears that the addition of LiFSI has resulted in the ability to charge the cell at lower temperatures without introducing lithium plating, i.e., by lowering the Li plating temperature approximately 10 °C when charging at a C/5 rate. LiFSI also maintained 53% of its room temperature capacity (107 mAh for both cells) during C/5 charging at \(-40^\circ C\) compared to 42% for the baseline cell, which is impressive considering that the baseline cell already has a low temperature optimized electrolyte. Conversely, adding VC or LiBOB to the baseline electrolyte resulted in increasing the Li plating temperatures by 10 or even 20 °C compared to the baseline cell. Adding LiDFOB to the electrolyte produced positive results when considering the kinetics of the electrodes at low temperatures, but yielded the highest proportion of lithium plating observed in this study: 28% at \(-40^\circ C\). This poor result is likely due to the improved cathode kinetics with the LiDFOB additive, which would shift the anode potentials to lower values during charge.

By combining the kinetics at low temperatures for Li intercalation into graphite anodes in electrolyte solutions with different additives with the low temperature plating analysis, it becomes apparent that additives like LiBOB, PS and VC cause an increase in lithium plating because they increase the resistance of the anode and cathode. However, we have shown that the Li plating temperature can be significantly altered by judicious selection of electrolyte composition, and the electrolyte additive(s) used. A judicious selection of electrolyte composition and additives is necessary for low temperature Li plating.

### Figure 11

Differential capacity plots for the first C/20 discharge of cells following charge at low temperature containing the baseline electrolyte (1.0 M EC + EMC + MP (20:20:60 v/v)) alone or with additives at (a) \(-20^\circ C\), (b) \(-30^\circ C\) and (c) \(-40^\circ C\).
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Figure 12. Estimated lithium stripped during discharge as a percentage of discharge capacity at specified temperature for the baseline electrolyte (1.0 M LiPF6 EC + EMC + MP (20:20:60 v/v)) alone or with additives.