

# The Effect of Electrolyte Composition on Lithium Plating During Low Temperature Charging of Li-Ion Cells

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In the present work, a number of additives have been investigated for their effect on the charge characteristics of cells containing low temperature, high ester content electrolytes (1.0 M LiPF<sub>6</sub> in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + methyl propionate (MP) 20:20:60 vol % + X additive). These experimental three-electrode cells are composed of graphite anodes, LiNiCoAlO<sub>2</sub> cathodes, and a lithium metal reference electrode. Cells were first subjected to electrochemical characterization at various temperatures, consisting of performing Electrochemical Impedance Spectroscopy (EIS), linear micropolarization and Tafel polarization measurement to determine the kinetic parameters for both the anodes and cathodes. Following electrochemical characterization, the cells were subjected to charging at decreasing temperatures using C/5 rates to 4.10V, with a constant potential C/50 current taper. Analysis of the C/20 discharge following the charge at low temperature revealed either the presence or absence of a high voltage plateau during the initial stages of the discharge. This plateau has been linked to the presence of lithium metal on the anode previously and was used as a measure for the extent of lithium plating in the cell. Differential analysis (dV/dQ) was applied as well to more clearly visualize the position of the high voltage plateau and use the peak position (x-axis) in the dV/dQ plot as a gauge for the amount of plating which took place in the cell on the prior charge. Most additives investigated increased the resistance of the anode and decreased the resistance of the cathode, thereby leading to an overall increase in plating observed at low temperature. One additive, LiFSI, was found to be beneficial during low temperature charging, however studies of electrode kinetics from the cell containing LiFSI did not reveal significant improvements compared to the baseline.

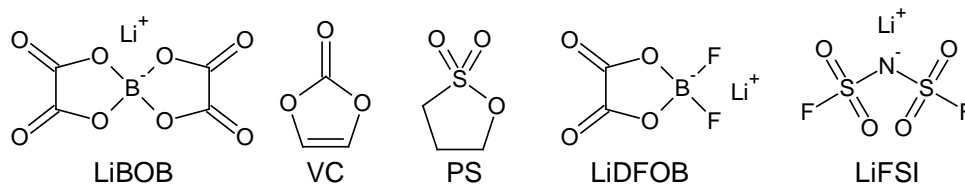
## Introduction

There is considerable interest in the exploration of the icy moons of Jupiter and Saturn, particularly Europa, Enceladus, Ganymede, Titan and Calisto. NASA is currently considering a mission to the surface of Europa, where the average temperature is approximately -170 °C<sup>1</sup> (for comparison, Mars has an average surface temperature of -63 °C). Such extreme temperatures pose serious challenges for batteries which are used either as the primary power source or to store energy from photovoltaics (PVs) or radioisotope thermoelectric generators (RTGs). Additionally, low temperature rechargeable battery

operation is of considerable interest to the automotive and aviation industries, where low temperature performance and decreased lifetime still remain as significant hurdles to overcome.

To enable these potential missions to icy moons, the Electrochemical Technologies Group (ETG) at the Jet Propulsion Laboratory (JPL) has engaged in development of long-life rechargeable batteries for continuous operation at low temperatures.<sup>2-5</sup> All-carbonate based lithium-ion electrolytes, as well as solutions containing ester co-solvents, were evaluated after drawing from experience of developing cell chemistries for past and present missions, including the Mars Exploration Rovers (MER) and the Mars InSight program. One major issue to overcome for a long life low temperature battery is to prevent lithium plating during charging. Here, we study the effects of electrolyte additives on the low temperature charging in three-electrode laboratory cells. Additives, such as vinylene carbonate (VC), are generally added to the electrolyte to form protective films on the electrodes which prolong life at ambient temperatures,<sup>6</sup> however, these protective films can impede lithium intercalation kinetics and cause significant problems during charging at low temperatures. Most additives that were studied lowered cathode film resistance but increased anode SEI resistance, leading to an imbalance between the electrodes. This led to a substantial increase in lithium plating at low temperatures.

In the current work, we have investigated a number of electrolyte compositions using three-electrode experimental cells consisting of graphite carbon anodes, LiNiCoAlO<sub>2</sub> cathodes (electrodes fabricated by Enersys-Quallion, LLC), and lithium reference electrodes, at different temperatures using a combination of tests, including electrochemical impedance spectroscopy (EIS), linear micro-polarization and Tafel polarization. Low temperature cycling was carefully studied by first looking for the presence of a high voltage plateau on the discharge following a charge at low temperature. This high voltage plateau is due to the presence of metallic lithium on the anode, which results in a higher cell voltage due to the lower potential of lithium metal compared to lithium intercalated into graphite.<sup>3,7,8</sup> Differential analysis (dV/dQ) was used as a means to estimate the amount of lithium that was plated during the charge.<sup>9-11</sup> The additives investigated in this study are presented in Figure 1, and included lithium bis(oxalato)borate (LiBOB), vinylene carbonate (VC), 1,3-propanesultone (PS), lithium difluoro(oxalato)borate (LiDFOB) and lithium bis(fluorosulfonyl)imide (LiFSI). Using a previously developed low temperature methyl propionate-based electrolyte core formulation (1.0 M LiPF<sub>6</sub> in EC+EMC+MP 20:20:60 vol%) to which LiFSI was added, we did not observe the presence of lithium plating during charging at -30 °C using C/5 rates and were able to suppress lithium plating to an estimated 11% of the total capacity at -50 °C.



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

## Experimental

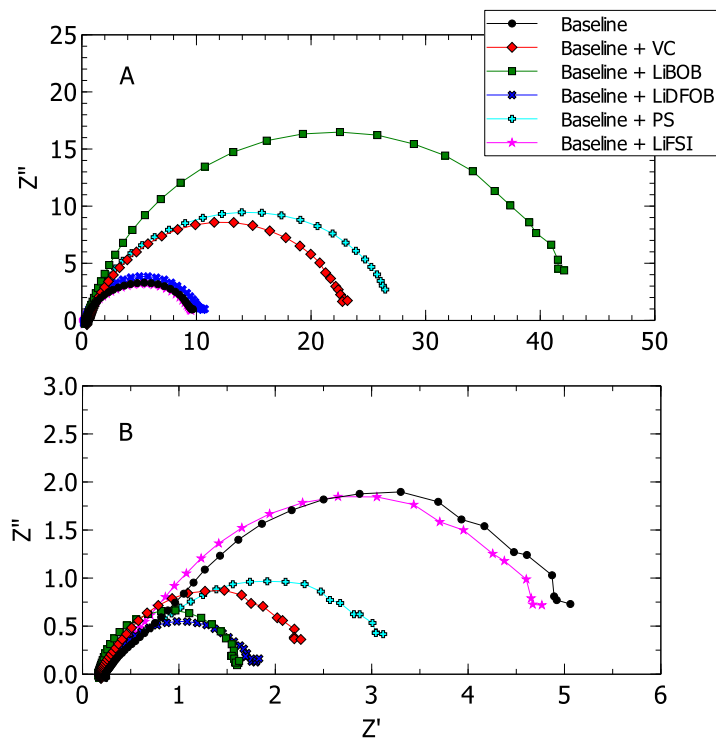
Cells were assembled with graphite carbon anodes, LiNiCoAlO<sub>2</sub> (NCA) cathodes (electrodes fabricated by Enersys-Quallion, LLC), and lithium reference electrodes. Tonen-Setella 20 μm porous polyethylene separator was used for the spiral wound cells which were placed inside glass cell housings equipped with O-ring seals. The electrolyte solutions of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and methyl propionate (MP) containing LiPF<sub>6</sub> salt in the desired concentration, were purchased from Novolyte, Inc. and contained less than 50 ppm of water. Additional LiPF<sub>6</sub> and LiBOB were also procured from Novolyte, Inc. Lithium (LiDFOB) were synthesized and purified by Prof. Henderson's group at the North Carolina State University. Vinylene carbonate (99%, with 80 ppm BHT as stabilizer) and 1,3-propane sultone (≥99%) were obtained from Sigma-Aldrich. Lithium bis(fluorosulfonyl)imide was obtained from Boulder Ionics, Inc.

Electrochemical measurements on the three-electrode cells, such as electrochemical impedance spectroscopy (EIS), Tafel polarization and linear-micro polarization, were performed using a Princeton Applied Research VersaSTAT with a built in frequency response analyzer. Charge-discharge measurements and cycling tests were performed with an Arbin battery. Cells were formed at +23 °C by cycling between 4.10 V and 2.75 V using C/20 charge and discharge rates (5.4 mA), with a C/50 current taper on the charge steps. For low temperature performance, cells were initially charged to 4.10 V at room temperature and then cooled to the desired temperature for at least 4 hours prior to discharge. The cells were then discharged at C/20 to 2.75 V followed by a 15-minute rest and then charging to 4.10 V at a C/5 rate with a C/50 taper. After another 15-minute rest, the cells were again discharged to 2.75 V and this cycling regime was repeated two more times for a total of 4 discharges and 3 charges at low temperature. Temperature was maintained by a Tenny environmental chamber at ±1 °C.

## Results and Discussion

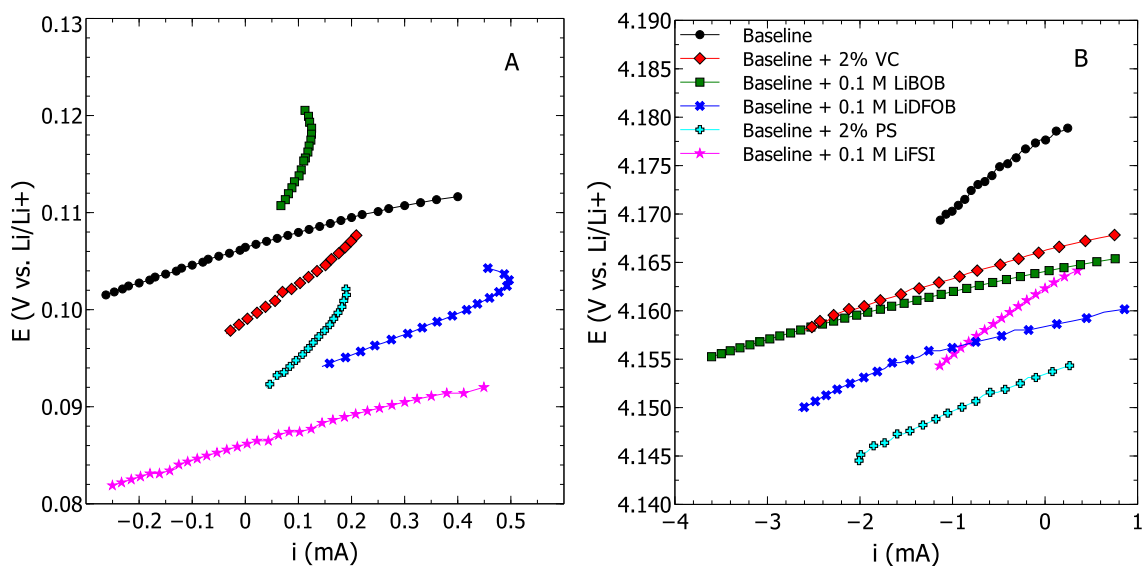
After undergoing formation, EIS analysis commenced at temperatures ranging from +23 to -40 °C. All temperatures below 0 °C displayed similar trends, so Figure 2 has results from -30 °C as a representative temperature. The baseline electrolyte (1.0 M LiPF<sub>6</sub> in EC+EMC+MP 20:20:60 vol. %) along with the electrolytes containing LiFSI and LiDFOB display the lowest film and/or charge transfer resistance on the anode (Fig. 2A), while the cells containing LiBOB and LiDFOB display the lowest film/charge transfer resistance on the cathode (Fig. 2B). Cells containing VC and PS improve the film/charge transfer on the cathode compared to the baseline, but significantly increase resistance of the film/charge transfer on the anode. The cell containing LiBOB displayed the highest resistance film/charge transfer on the anode, which is consistent with our previous findings with other chemistries.<sup>2</sup> The baseline and LiFSI containing cells had the worst cathode film/charge transfer, however, the anode scale is ~10X greater than that of the cathode. The cell containing LiDFOB had the lowest overall lowest film and charge transfer resistances, resulting in the most preferred kinetics for both the anode and cathode. Given these results, the cell containing LiBOB is expected to have the most severe lithium plating because the anode kinetics are significantly reduced and the cathode kinetics are significantly improved. This leads to a situation where there is very little polarization on the cathode during charging and significant polarization on the anode, therefore leading to increased plating

because lithium can only plate on the anode when the potential is significantly negative (vs.  $\text{Li}^+/\text{Li}$ ).



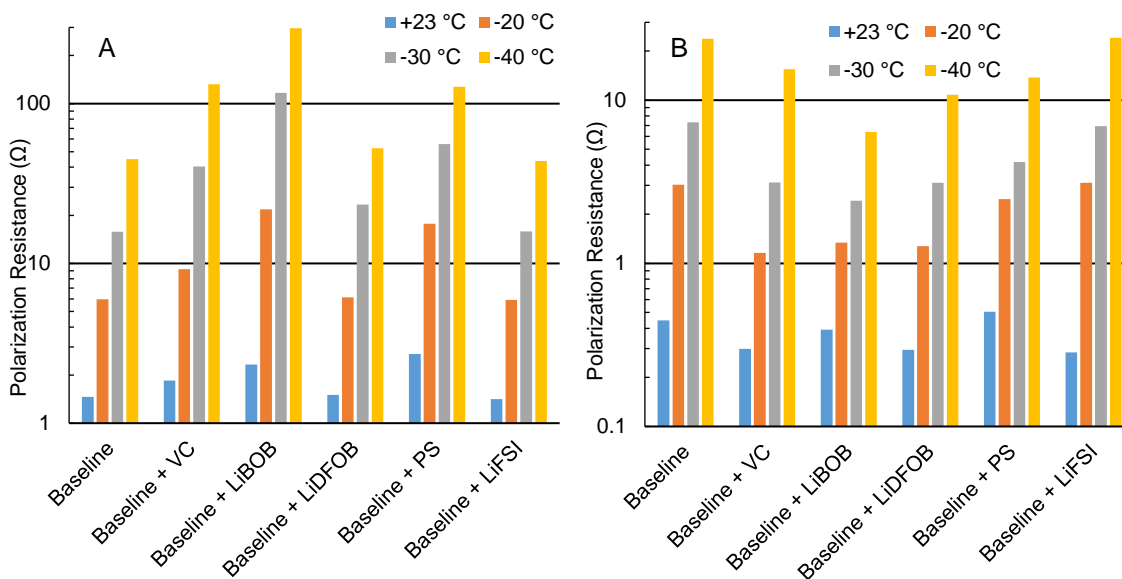
**Figure 2.** Electrochemical Impedance Spectroscopy (EIS) measurements at  $-30\text{ }^{\circ}\text{C}$  for the (A) graphite anodes and (B)  $\text{LiNiCoAlO}_2$  cathodes with the baseline electrolyte  $1.0\text{ M LiPF}_6$  in EC+EMC+MP (20:20:60 vol. %) and formulations containing various additives.

Linear micropolarization (LP) is a potential sweep technique that polarizes the cell  $+5\text{ mV}$  above the open circuit voltage (OCV) of the electrode being measured to  $-5\text{ mV}$  below OCV in  $0.3\text{ mV}$  steps with 30 seconds for each step. This technique gives a DC resistance measurement to complement the AC resistance measurement result derived from the EIS measurements. Figure 3 provides representative plots at  $-30\text{ }^{\circ}\text{C}$ , since the trends are conserved throughout the investigated low temperature range investigated. The findings are similar to that of the EIS measurements, indicating that VC, LiBOB and PS increase the polarization resistance on the anode (Fig. 3A) while decreasing the resistance on the cathode (Fig. 3B). Interestingly, LiDFOB appears to increase the anode polarization resistance slightly compared to the baseline and LiFSI containing cells (Fig. 3A), whereas little change in the film and charge transfer resistance were observed with the EIS measurements (Fig. 2A). The cathode polarization resistance was observed to similar for cells containing the baseline electrolyte and LiFSI (Fig. 3B).



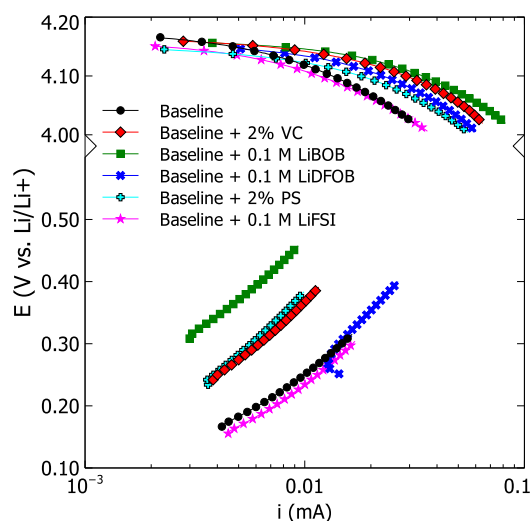
**Figure 3.** Linear micro-polarization measurements performed at  $-30\text{ }^{\circ}\text{C}$  on the (A) graphite anodes and (B)  $\text{LiNiCoAlO}_2$  cathodes of three-electrode cells possessing various electrolytes with and without additives.

The calculated resistance values derived from the LP measurements at  $+23$ ,  $-20$ ,  $-30$ , and  $-40\text{ }^{\circ}\text{C}$  are presented in Figure 4 for comparison across multiple electrolyte formulations and temperatures. A log scale is used on both plots to improve legibility, however, the scales are offset by one order of magnitude because the anodes (particularly those of cells with additives) are more resistive than the cathodes at low temperature. Comparison across the range of temperatures reveal that resistance increases relatively uniformly as temperature drops. The cell with LiDFOB is among the best performers on both the anode and cathode.



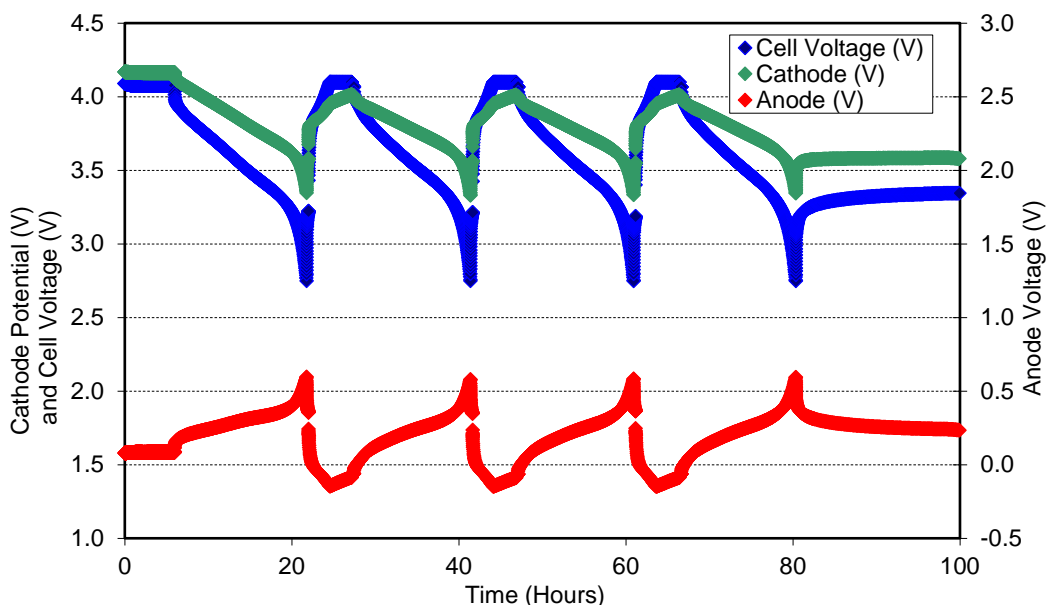
**Figure 4.** Polarization resistance of (A) the graphite anodes and (B)  $\text{LiNiCoAlO}_2$  cathodes at  $+23$ ,  $-20$ ,  $-30$ , and  $-40\text{ }^{\circ}\text{C}$  of three-electrode cells possessing various electrolytes with and without additives.

Tafel measurements were conducted on both the anodes and the cathodes of graphite-LiNiCoAlO<sub>2</sub> cells by slowly scanning 155 mV from the electrode OCV in the discharge direction at 0.2 mV/sec. The results obtained at -30 °C are presented in Figure 5. The conclusions remain consistent with the findings observed with the LP measurements: VC, LiBOB and PS improve the lithium cathode kinetics and reduce the lithium kinetics at the anode. In terms of the cathode kinetics, the cells containing the baseline electrolyte and the LiFSI-containing electrolyte deliver similar performance, with the cell containing LiDFOB displaying slightly better kinetics. Whereas, all three of these electrolytes lead to comparable performance on the anode. With both the cathode and the anode on the same (broken) axis, Figure 5 helps to illustrate how much more resistive the anodes are than the cathodes. From Figure 5, it is clear that any charging done at low temperature on cells with more resistive anodes (such as LiBOB) will produce significant polarization on the anode.



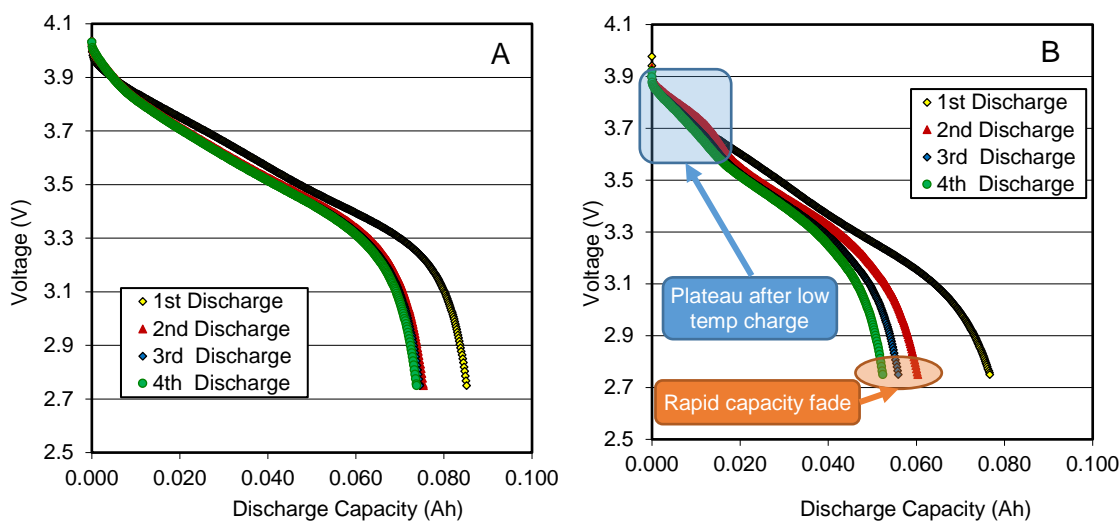
**Figure 5.** Tafel polarization measurements of the graphite anodes and LiNiCoAlO<sub>2</sub> cathodes at -30 °C of three-electrode cells possessing various electrolytes with and without additives.

Investigation of low temperature charging characteristics was performed by first charging to 4.10 V at room temperature, then cooling the cell down and discharging at C/20, followed by 3 cycles at low temperature (C/5 charge to 4.10 V, C/50 taper, C/20 discharge) as illustrated in Figure 6.



**Figure 6.** Cathode, cell, and anode potential curves for 1.0 M LiPF<sub>6</sub> EC+EMC+MP (20:20:60) cell at -30 °C. The cell was charged at room temp first, then discharged at C/20 at -30°C, followed by C/5 charge to 4.1 V with a C/50 taper, repeated three times.

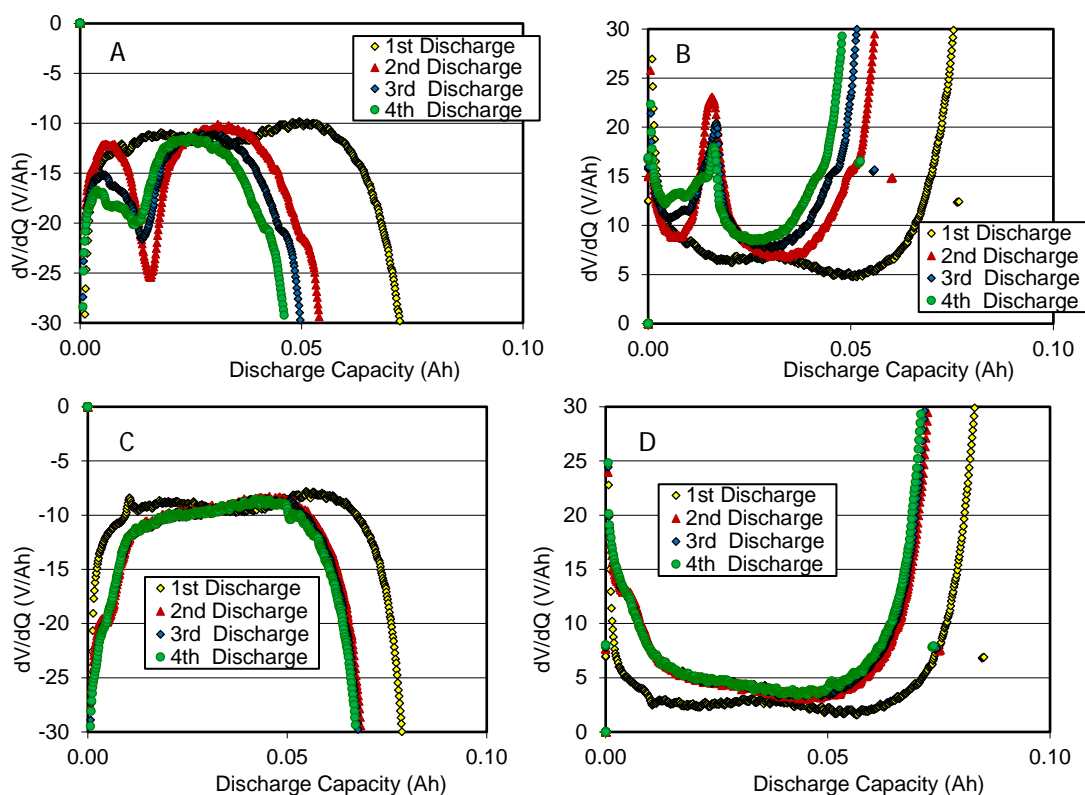
Overlaying the discharges from the testing described in Figure 6 reveals the presence of high voltage plateaus in the early part of discharge (Figure 7). The baseline cell (Fig. 7A) shows very little perturbation in the early part of the discharge, whereas there is a noticeable higher voltage plateau for the LiBOB-containing cell (Fig. 7B), which corresponds to the lithium stripping reaction which is more facile than the lithium de-intercalation process from the carbon anode. In addition to the increased voltage (relative to the 1<sup>st</sup> discharge), the cell with LiBOB also experienced severe capacity fade over the course of three cycles at -30 °C which was corroborated by poor coulombic efficiency (~95%).



**Figure 7.** -30 °C discharges for (A) baseline cell and (B) LiBOB containing cell.

Analysis of the high voltage plateau was aided by taking the derivative ( $dV/dQ$ ) of the discharges as reported by others previously.<sup>9-13</sup> Derivative plots in Figure 8 clearly

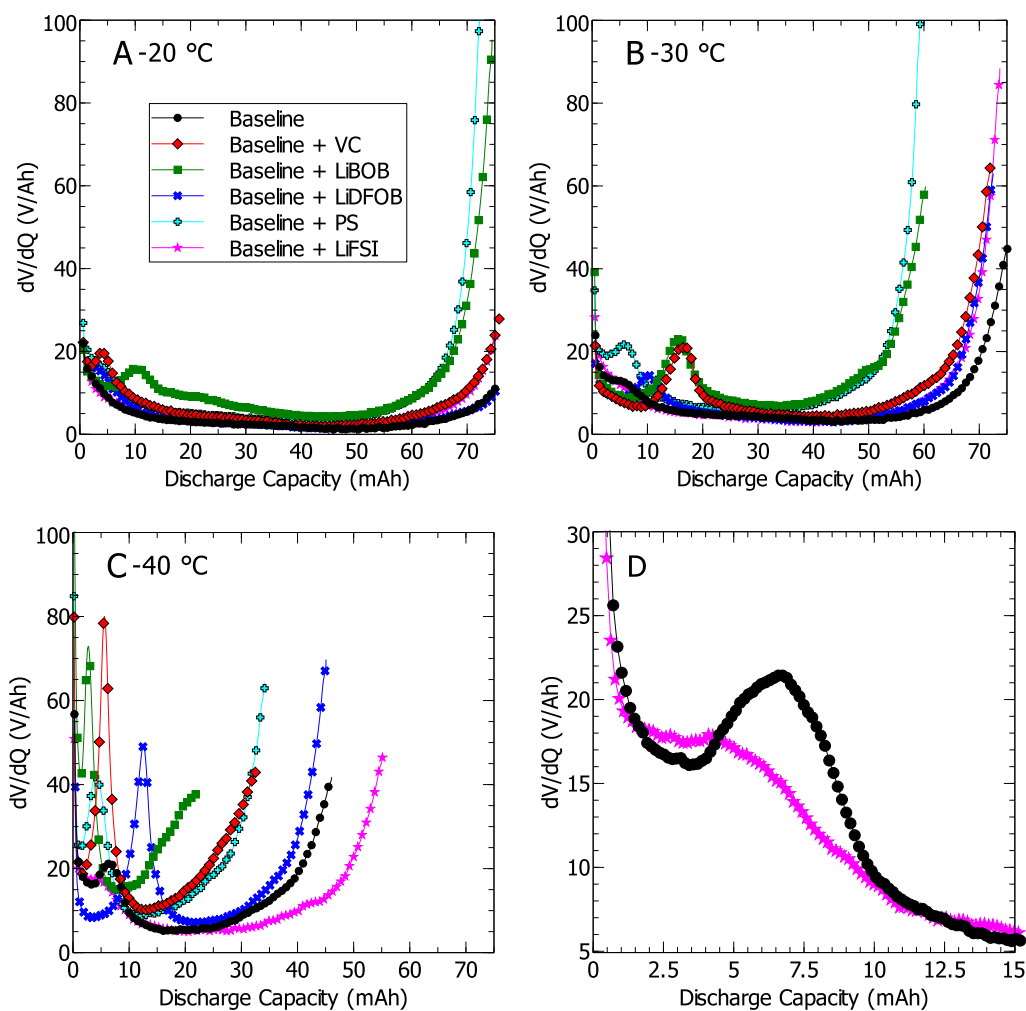
show the presence of additional peaks for the cell containing the LiBOB additive (Fig. 8A and 8B) and the absence of peaks for the baseline cell (Fig. 8C and 8D) at  $-30\text{ }^{\circ}\text{C}$ . The x-axis position of the peak correlates with the transition between the stripping reaction and the de-intercalation reaction on discharge.<sup>11</sup> Although there is likely some overlap in the early discharge when lithium ions start to de-intercalate even though lithium metal is still present, it is likely a minor reaction because: (i) lithium stripping is more facile than de-intercalation, (ii) at low temperature, the relative kinetics favor stripping lithium more strongly than at ambient temperature, (iii) the discharge is performed very slowly (C/20 rate), and (iv) the discharge is conducted directly after the charge at low temperature. Since these conditions are met, it is anticipated that the majority of the capacity recovered before the peak in the  $dV/dQ$  plot can be attributed to the stripping of lithium metal.



**Figure 8.** Derivative ( $dV/dQ$ ) plots at  $-30\text{ }^{\circ}\text{C}$  for (A) the full LiBOB-containing cell, (B) the anode of the LiBOB-containing cell, (C) the full baseline cell and (D) the anode of the baseline cell.

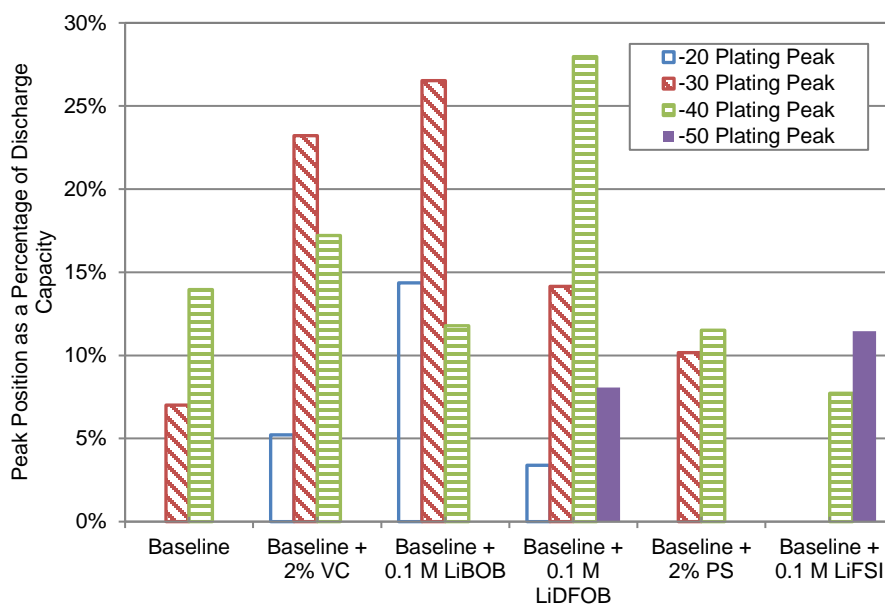
Derivative plots of the anodes at  $-20$ ,  $-30$  and  $-40\text{ }^{\circ}\text{C}$  are presented in Figure 9, with special attention given to the baseline and the LiFSI containing electrolyte at  $-40\text{ }^{\circ}\text{C}$  in Figure 9D. No plating was observed for the baseline cell or the cell containing LiFSI until  $-40\text{ }^{\circ}\text{C}$ . Cells containing VC and LiBOB clearly show evidence for plating starting at  $-20\text{ }^{\circ}\text{C}$ , while the cells containing PS and LiDFOB show evidence for plating at  $-30\text{ }^{\circ}\text{C}$ . At  $-40\text{ }^{\circ}\text{C}$ , the baseline appeared to have a much more significant peak than the cell containing LiFSI (Fig. 9D). Despite the observation of favorable electrode kinetics, the cell containing LiDFOB performed significantly worse than the baseline cell. Although the cell containing LiFSI showed very similar kinetics to the baseline cell, it performed significantly better during low temperature charging, both in terms of avoiding plating and in charge and discharge capacity at  $-40\text{ }^{\circ}\text{C}$ .





**Figure 9.** Derivative plots for C/20 discharges of cells charged at low temperature at (A) -20 °C, (B) -30 °C, (C) -40 °C and (D) magnification of the Fig. 9C highlighting the difference between baseline and LiFSI cells

Assuming that the majority of the capacity delivered before the peak in Fig. 9 is due to stripped lithium,<sup>11</sup> comparisons can be made between the electrolyte formulations at various temperatures as plotted in bar graph form in Figure 10. The two electrolytes which produced the highest amount of plating were LiDFOB at -40 °C (28 %) and LiBOB at -30 °C (27 %). It is not surprising to see that LiBOB produced so much plating, given that it was observed to have the lowest cathode impedance while simultaneously increasing the anode impedance most significantly. In contrast, LiDFOB generally resulted in good kinetics on both electrodes. The cell containing LiFSI performed the best in terms of the least amount of lithium plating at low temperature, being comparable to the baseline cell at 10 °C lower in temperature. LiFSI also maintained the highest discharge capacity at -40 °C, with >50 % of its room temperature capacity being available when charging at C/5.



**Figure 10.** Estimated lithium stripped as a percentage of discharge capacity at -20, -30, -40 and -50 °C

### Conclusion

Additives can have major implications for low temperature performance, particularly lithium plating, which is a major concern for lithium ion cells operated at low temperature. Using the semi-quantitative, non-destructive technique described here, it is possible to determine if lithium metal was plated in a lithium ion cell. By simply charging the cell under conditions where plating might occur and then quickly discharging the cell at low rate, one can observe the discharge curve for evidence of a high-voltage plateau. This high-voltage plateau corresponds to lithium metal being present in the cell and differential analysis aids in visualizing the point where the cell transitions from stripping lithium metal to de-intercalation.

Most additives (such as LiBOB, VC, PS, and LiDFOB) used in cells were observed to increase the likelihood of lithium plating. However, LiFSI was the lone exception, producing surface films on par with the baseline electrolyte and resisting plating at low temperature. Despite excellent electrode kinetic data, LiDFOB did not produce good results during low temperature charging, which significantly increased plating compared to the baseline. Due to the similarity between the anodes of the cell with LiDFOB and the baseline, it appears that improving the lithium kinetics at the cathode can increase the likelihood of lithium plating. These findings emphasize that the relative electrode kinetics are important to consider when assessing the likelihood of lithium plating, rather than the influence of an additive on only one electrode of a system.

### Acknowledgments

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