Fluorinated Battery Electrolytes for Wide Operating Temperature Range

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Abstract: Li-ion technology has advanced significantly over the past decade; however, traditional electrolytes based on volatile and flammable organic solvents limit performance under extreme conditions such as high/low temperatures, high voltage, and under fast charge conditions. Koura has developed fluorinated materials for use as solvents / additives in Li-ion battery electrolytes that provide multiple performance advantages. In this paper we highlight the performance of select Koura's fluorinated electrolyte materials in expanding the operating temperature range of graphite-anode/NMC811-cathode pouch cells. Our tests confirm that while conventional ester-based electrolytes can improve low temperature performance of Li-ion cells, the high-temperature stability is quite poor. In contrast, fluorinated solvents not only improve low-temperature performance, but also enable excellent high temperature performance stability.

Keywords: electrolyte; Lithium Ion; solvent; LIB; low temperature; rate; transport; high temperature; thermal stability; oxidation; reduction; impedance; safety; solvation; LiPF₆; Lithium; SEI; solid electrolyte interphase; energy storage; NMC; graphite; gassing; DOE; battery; cell; molecule; electrochemical; electrochemistry; fluorine; anode; cathode; cycling;

Introduction

Li-ion batteries used in Defense applications have to operate under a wide range of operating temperatures. The operating temperature range of Li-ion batteries is dictated by the electrolyte used. In general, electrolytes that enable improved low temperature performance of Li-ion batteries are not stable at higher temperatures or when used with higher voltage cathode materials. For example, methyl acetate, methyl butyrate, and methyl propionate solvents are often used to enhance the low-temperature performance of Li-ion cells. However, these solvents result in poor performance at elevated temperatures. In this paper, we discuss how fluorinated solvents and additives can provide adequate low temperature performance without compromising elevated temperature performance.

Fluorinated Electrolyte Materials

Koura is a fully integrated fluorine technology company with a global footprint that spans mining of fluorine-based minerals to the production of hydrogen fluoride, aluminum fluoride, refrigerants, and medical propellants. We have an emerging business in fluorine-based battery materials. We aim to localize the supply chain for key fluorinated materials used in Li-ion batteries today. In addition, we are developing advanced fluorine-based battery materials.

A focus area for our development is fluorinated solvents and additives for use in Li-ion battery electrolytes. Fluorinated electrolyte components are known to provide multiple benefits to Li-ion battery performance including: improving the safety profile, enabling the use of silicon-based anodes, enabling the use of Mn-rich cathode materials, etc. Koura is leveraging expertise in fluorine chemistry to develop and produce a wide range of fluorinated molecules that have the potential to further enhance Li-ion performance. We have synthesized more than 25 different fluorinated molecules and characterized their physico-chemical properties and electrochemical stability. Rate performance and cycle life were characterized in NMC811/graphite pouch cells across a range of temperatures from -20 °C to 45 °C and charging conditions from C/2 to 4C.

In this paper we highlight two fluorinated molecules – a fluorinated dioxalane (KDC-403) and a fluorinated cyclic carbonate (KDC-301) – that have the potential to expand the operating temperature window of Li-ion cells. We compare the performance of these molecules to commercial ester solvents that have been shown to improve low temperature performance but are also known to not be stable at higher operating temperatures. We present and discuss physico-chemical property as well as electrochemical measurements over a wide temperature range.

Results and Discussion

Bulk Electrolyte Properties: Li^+ *Transport*: Bulk conductivity and viscosity are commonly cited physical properties in the design of optimized electrolytes for low temperature¹ and fast charge² applications. In this study, the low temperature conductivity and viscosity of several electrolytes containing Koura solvents (KDC-301, KDC-403) were compared to a carbonate-only baseline (EC/DEC/EMC – 1/1/1 by volume) and three low temperature optimized electrolytes containing low viscosity ester solvents (methyl acetate – MA, methyl propionate – MP, methyl butyrate – MB). All co-solvents added at 20% by volume. All electrolytes contain 1M LiPF₆.

Referring to Figure 1 – top, the ester electrolytes provide the highest bulk conductivity compared to the carbonate control and Koura electrolytes. Overall, methyl propionate (MP) provided the highest conductivity and KDC-301 provided the lowest conductivity. For bulk viscosity (Figure 1 – bottom), a similar trend emerges where the ester-based electrolytes provide the lowest low temperature viscosity while KDC-403 shows lower viscosity compared to the carbonate-only baseline. KDC-301 has the highest viscosity.

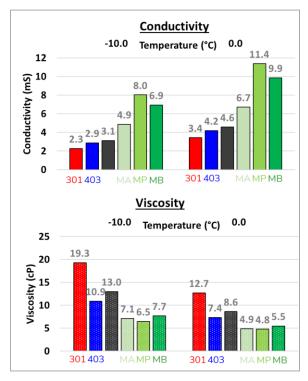


Figure 1. Bulk electrolyte conductivity and viscosity at low temperature (0°C, -10°C).

 Li^+ transference number (t₊) is utilized to evaluate Li^+ transport and represents the fraction of the current carried by Li^+ (vs PF₆⁻), calculated by comparing the diffusion coefficients of Li^+ and PF₆⁻. In general, higher t₊ is better (1 is ideal). The Li^+ conductivity is estimated by multiplying the bulk conductivity by the Li^+ transference number.

Figure 2 summarizes the Li⁺ transport parameters for the electrolytes investigated in this study. KDC-403 and methyl butyrate (MB) show the highest Li⁺ transference number at 25°C; however, the ester solvents show significantly higher Li⁺ conductivity. Overall, methyl propionate (MP) provides the highest Li⁺ conductivity.

Based upon the bulk transport data summarized in Figure 1 and Figure 2, we would expect the ester electrolytes should provide the best low temperature performance (specifically methyl propionate), KDC-403 should perform slightly better than the control, and KDC-301 should provide the worst low temperature performance. However, as discussed below, cell performance does not always follow this expectation.

Electrochemical Performance

Low Temperature Performance in Gr/NMC81 pouch cells: Low temperature rate capability performance was evaluated in Gr/NMC811 pouch cells (~ 230 mAh, 4.3V - 2.75V) by measuring the C/2 and 2C discharge capacity at 0°C and -20°C after charging at C/2. Both charge and discharge were conducted at low temperature. All co-solvents were added at 20% by volume to an EC/DEC/EMC (1/1/1, %v) control with 1M LiPF₆.

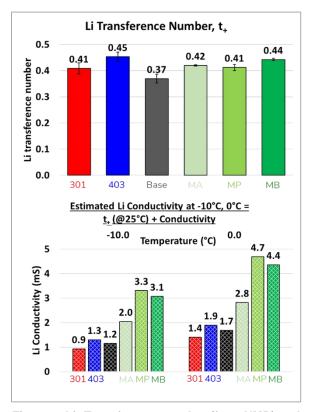


Figure 2. Li⁺ Transference number (from NMR) and estimated Li⁺ conductivity (at low temperature).

Figure 3 summarizes the discharge capacity at C/2 and 2C measured after 3 cycles at 0°C, and -20°C for the Koura solvent-based electrolytes compared to the carbonate control and ester electrolytes. At C/2, both the Koura electrolytes provide higher discharge capacity compared to the carbonate control while the ester co-solvents do not improve control performance. At 2C, the Koura solvents show distinct behavior. KDC-301 significantly reduces 2C discharge capacity compared to the control at all tested temperatures while KDC-403 provides similar or improved capacity compared to the control at all temperatures. The ester co-solvents provide improved 2C capacity at -10°C and -20°C.

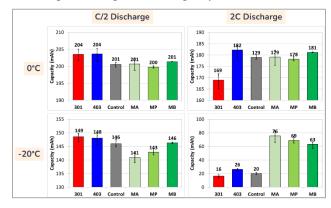


Figure 3. C/2 and 2C Rate Capability at Low Temperature

0°C cycling stability was conducted at C/2 charge and discharge after the low temperature rate capability test.

Figure 4 summarizes the discharge capacity for the 1st cycle and 100th cycle at 0°C. The capacity loss during cycling is shown in red. As expected, based upon the C/2 discharge capacity at 0°C (Figure 3), the Koura electrolytes provide the highest initial 0°C discharge capacity. After 100 cycles, KDC-403 also shows the lowest capacity loss (2.5% vs. \geq 4% for the control and ester solvents).

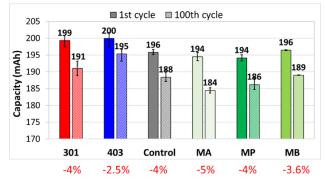


Figure 4. 0°C Cycling Stability in 4.3V Gr/NMC811 cells

In summary, the low temperature testing conducted in 4.3V Gr/NMC811 cells does not strictly follow the trend expected based upon the bulk properties. For example, the ester cosolvents provide consistently higher conductivity and lower viscosity than the control, but only provide improved LT rate capacity at 2C and -20°C. Otherwise, the ester electrolytes are similar to or worse than control. Similarly, while KDC-301 should be consistently worse than the control based upon bulk properties, it provides improved C/2 LT discharge capacity and only significantly underperforms the control at higher rates (2C, 0°C). The KDC-403 solvent shows the best agreement with the expected performance based upon bulk properties as 20% KDC-403 always provides similar or better capacity than the control during the LT rate test (0°C and -20°C) and 0°C cycling. Therefore, despite a significant decrease in 2C capacity at -20°C, the KDC-403 co-solvent provides the most comprehensive low temperature improvement compared to the control for LT rate capability and cycling stability.

Full Cell Impedance as a function of Temperature: To understand the origin of the comprehensive KDC-403 LT benefit, the full cell impedance was measured at multiple temperatures (30° C, 0° C, -20° C) and summarized in Figure 5. The 20% KDC-403 electrolyte has lower impedance at all temperatures while the ester electrolytes show higher impedance, especially at -20° C (+ 50-90%).

Comparison of the impedance, discharge capacity, and conductivity at each temperature allows the identification of the characteristics driving performance, specifically impedance vs. bulk properties. At 0°C, lower impedance results in lower capacity indicating that impedance drives performance. The same is true for C/2 capacity at -20°C. However, at 2C and -20°C, impedance does not clearly correlate with capacity while bulk conductivity does.

This comparison explains why KDC-403 can improve LT performance compared to both the control (expected based upon bulk properties) and ester electrolytes (not expected based upon bulk properties). The 20% KDC-403 electrolyte provides favorable interfacial properties that are key driving factors under specific LT conditions (all rates at moderate temperature, all temperatures at moderate rate). In contrast, the ester co-solvents excel under test conditions that exploit bulk properties and struggle under impedance-driven test conditions (likely due to the known instability of the esters³).

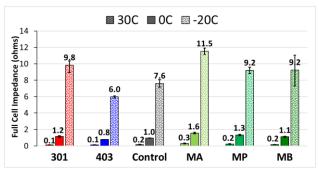


Figure 5: Impedance as a function of temperature.

High Temperature (HT) Performance in 4.3V Gr/NMC81: Cycling Stability at 45°C: To determine the best electrolyte formulation for wide operating range, HT stability was assessed by measuring cycle life at 45°C in Graphite/NMC811 pouch cells (~ 230 mAh, 4.3V - 2.75V). for the fluorinated solvents and compared to the carbonate control and ester-based electrolytes. Figure 6 shows the 45°C cycle life for representative cells and summarizes the discharge capacity for the 1st and 300th cycles.

Overall, both Koura electrolytes provide superior 45°C cycling stability. As expected, the low molecular weight ester solvents (MA, MP) show significantly lower 45°C capacity retention due to their established instability³. The highest molecular weight ester (MB) has lower initial 45°C capacity compared to the control with a moderate cycling improvement after 300 cycles.

Comparison of the 45°C capacity retention to the impedance before and after cycling (Figure 7) shows a clear correlation between increased cycling stability and lower impedance. KDC-403 provides the lowest impedance before and after 45°C cycling with significantly less impedance growth compared to the low molecular weight ester electrolytes.

Nyquist impedance plots (Figure 8) for selected electrolytes provide insight into the source of impedance differences. In general, the 1st and 2nd semi-circles are associated with anode and cathode impedance, respectively. KDC-403 shows significantly reduced anode impedance with similar cathode impedance while MA shows similar anode impedance as the control with significantly increased cathode impedance. In separate measurements, we found that the SEI on the graphite anode was thinner with KDC-403-based electrolyte compared to control electrolyte further supporting the impedance measurements in Figure 8.

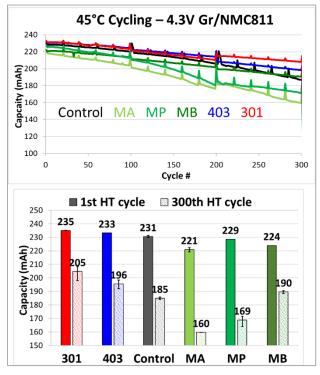


Figure 6: 45°C Cycling Stability in 4.3V Gr/NMC811 cells.

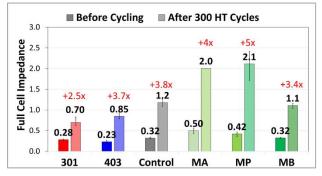


Figure 7: Full cell impedance before and after 45°C cycling.

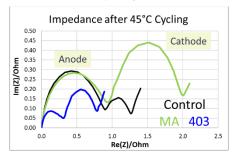


Figure 8: Nyquist plots for select electrolytes after 45°C cycling.

Gas generation during 45°C cycling is another indicator of instability of the electrolyte and/or electrode surface layers. Figure 9 shows the total gas generated during 45°C cycling (cycling data in Figure 7). Like the impedance data, there is a correlation between higher capacity retention and reduced

gas generation. Overall, KDC-403 generates the least gas during 45°C cycling although both Koura electrolytes provide a benefit.

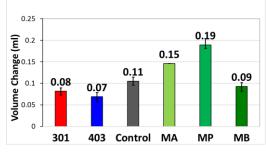


Figure 9: Gas generation during 45°C cycling.

Conclusions

In this study, the wide operating temperature performance of two fluorinated Koura materials was compared to a carbonate control and several low-temperature optimized ester electrolytes. Bulk Li⁺ transport properties at low temperature (0°C, -10°C) predict that the ester co-solvents should significantly improve low temperature performance while KDC-403 should be similar to the control. However, full cell impedance measurements at low temperature show that KDC-403 provides the lowest interfacial impedance of all electrolytes tested.

Low temperature rate and cycling stability show that KDC-403 improves performance of the carbonate control when impedance is the primary factor driving capacity (all rates at 0°C, C/2 at -20°C, cycling stability at 0°C) while the ester co-solvents improve control performance where bulk properties drive capacity (2C at -20°C). 45°C cycling stability studies highlight the instability of the low molecular weight ester co-solvents with both Koura electrolytes providing superior 45°C cycling, lower impedance, and lower gas generation.

This study highlights the importance of favorable interfacial properties (i.e., lower full cell impedance, lower impedance growth during cell testing) in addition to bulk Li+ transport properties when optimizing an electrolyte for wide temperature operation.

Acknowledgements

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