Lithium Tetrafluoroborate-Based Ester Electrolyte Formulations to Improve the Operating Temperature Range in NCM 622 || Graphite Li-Ion Batteries

Chamithri Jayawardana,[§] Nuwanthi D. Rodrigo,[§] Munaiah Yeddala, Bo Nan, Leah Rynearson, Chunsheng Wang, and Brett L. Lucht*



ester electrolyte containing 1% LiTMSP delivers the highest reversible capacity at low temperature $(-20 \, ^{\circ}C)$, while the roomtemperature performance is significantly improved compared to that of the base ester-based electrolyte (LiBF₄-MA) and almost comparable to that of the standard carbonate-based electrolyte. The improved electrochemical performance for 1% LiTMSP at -20 $^{\circ}C$ is due to the lower charge transfer resistance as supported by electrochemical impedance spectroscopy, and improved roomtemperature performance can be ascribed to the generation of a stable phosphate-rich SEI on the graphite surface as revealed by Xray photoelectron spectroscopy.

KEYWORDS: ester electrolytes, low-temperature electrolytes, lithium tetrafluoroborate, lithium bis(trimethylsilyl) phosphate, lithium-ion batteries, solid electrolyte interphase

INTRODUCTION

Lithium-ion batteries (LIBs) are an important electrochemical energy storage technology due to their high energy density $(\sim 300 \text{ W h kg}^{-1})$.¹ Since LIBs are utilized in a wide range of applications including consumer electronics, grid-scale energy storage, power tools, and electric vehicles, operation over a wide range of operating temperatures without loss of energy density is critical.² Current LIBs only produce a fraction of the room-temperature energy when operated at temperatures below 0 °C, and the cause for poor energy density is attributed to several factors including reduced ionic mobility in the bulk electrolyte and increased resistance at the interfaces.^{3,4} Since the electrolyte composition controls Li⁺ mobility and the composition and conductivity of the solid electrolyte interphase (SEI), optimization of the electrolyte formulation is a common method for improving the low-temperature performance of LIBs.⁵⁻⁷

Most of the previous approaches toward improving the lowtemperature performance of LIBs were focused on the development of liquid electrolytes with lower freezing points; this includes lowering the amount of ethylene carbonate (EC) in the electrolyte and/or using eutectic electrolyte systems or adding low-freezing-point diluents.^{8–10} Introducing lowmelting point/low-viscosity co-solvents such as esters has been widely elxpored.^{11–15} However, most esters are not capable of forming a stable SEI on the graphite surface.^{16,17} Recent discoveries also found that the competition between the ion–ion interaction and ion–solvent interaction plays an important role in low-temperature LIB performance.^{9,18} However, most of the previous research focused on the modification of the solvents, and lithium hexafluorophosphate

Received: January 30, 2023 Accepted: April 21, 2023 Published: May 1, 2023







Figure 1. Charge–discharge cycling performance of NCM 622 || graphite cells with 3 salts in the MA–FEC solvent system and the STD electrolyte at (a) -20 and (b) 25 °C.

(LiPF₆) was kept as the primary salt. The impact of the salt on the low-temperature performance has not been investigated in detail. A recent report focused on the effects of replacing LiPF₆ with LiBF₄ or lithium difluoro(oxalato)borate (LiDFOB) in novel ester-based electrolyte formulations, and the incorporation of either LiBF₄ or LiDFOB resulted in superior cycling performance compared to the conventional carbonate-based electrolyte or the ester-based electrolyte with LiPF₆.¹⁹ A detailed investigation of the source of superior cycling performance observed with LiBF₄ and LiDFOB salts in esterbased electrolyte systems under low-temperature conditions has been conducted.

The room-temperature cycling performance of LiPF₆-based electrolyte formulations (both the carbonate and ester) outperformed that of LiBF₄ or LiDFOB in ester-based formulations. The differences in cycling performance have been attributed to different requirements of the electrolyte at different operating temperatures.²⁰ At low temperatures, reduced ionic transport properties and significant charge-transfer polarization limit cell performance, while room-temperature cycling performance is limited by the composition and the stability of the SEI on the graphite anode.^{4,21,22} Therefore, improvement in the room-temperature cycling performance of the novel ester-based formulation with LiBF₄ salt has been expanded by introducing additives that have been reported to form a stable SEI on graphite anodes.^{23–26}

In this work, a novel methyl acetate (MA)-based electrolyte was selected due to its promising liquidus range and potential applications in low-temperature LIBs. The effects of three lithium salts, LiBF₄, LiPF₆, and lithium bis(oxalato)borate (LiBOB), were first investigated, and then, three different electrolyte additives, lithium bis(oxalato)borate (LiBOB), lithium difluorophosphate (LiF₂PO₂), and lithium bis(trimethylsilyl) phosphate (LiTMSP), were investigated with the ester-based electrolyte formulation, aiming to specifically address the poor SEI properties and improve the low-temperature and room-temperature battery performance. The surface films generated in the presence of the novel electrolyte formulations were studied via ex situ surface analysis to

understand the effect of additives on the cycling performance at each temperature.

EXPERIMENTAL SECTION

Graphite (91.83% active material, 2% conductive carbon, 6% polyvinylidene difluoride (PVdF) binder, and 0.17% oxalic acid, active material loading, 6.38 mg cm⁻²) and LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (NCM622; 90% active material, 5% conductive carbon, and 5% PVdF binder, active material loading, 9.78 mg cm⁻²) single side-coated electrodes were obtained from Cell Analysis, Modeling and Prototyping (CAMP) facility, Argonne National Laboratory, with an n/p ratio of 1.22. Battery grade LiPF₆, lithium tetrafluoroborate (LiBF₄), LiDFOB, fluoroethylene carbonate (FEC), LiBOB, and LiF₂PO₂ were supplied by BASF (Germany), and electrolyte grade using the procedure as previously described with a very high purity of over 99% based on ¹H NMR spectroscopy.²⁶ All electrodes and reagents were stored in an Ar-filled glovebox (M-Braun with a \leq 0.1 ppm moisture level), and the reagents were used as received.

Cell Construction. 2032-type coin cells were assembled inside an Argon glovebox (with a ≤ 0.1 ppm moisture level). The coin cells consisted of two electrodes (NCM622 13.7 mm and graphite 15 mm), three separators (two 2325 Celgard separators, 19 and 15 mm, and one Whatman GF/D glass microfiber separator, 15.6 mm), and 100 μ L of the electrolyte. The standard electrolyte used in this study was 1 M LiPF₆ in EC: ethylmethyl carbonate (3:7, v/v) denoted STD was obtained from Gotion Inc. Other electrolyte formulations investigated include 1 M LiPF₆ in MA/FEC (90:10 vol %) (LiPF₆-MA), 1 M LiBF₄ in MA/FEC (90:10 vol %) (LiBF₄-MA; base), and 1 M LiDFOB in MA/FEC (90:10 vol %) (LiDFOB-MA), and LiBOB, LiF₂PO₂, and LiTMSP were added to the base (LiBF₄-MA) electrolyte formulation in a 1 weight percent (wt %).

Electrochemical Testing. After the cells were constructed, a 6 h wetting period was allowed before initiating cycling. Galvanostatic charge/discharge cycling was performed in a high-precision Arbin LBT21084 battery cycler between 3 and 4.2 V. For formation cycling, NCM622 || graphite full cells were galvanostatically cycled for 5 cycles at a rate of C/20 for the first cycle, C/10 for the next two cycles, and C/5 for an additional two cycles at 25 °C. After formation cycling cells, cells were transferred to a temperature chamber (Tenney environmental test chamber) at $-20 (\pm 1)$ °C for low-temperature cycling. After a 6 h equilibration period, the cells were cycled for 50 or 100 cycles, at a charge rate of 0.2C and a discharge rate of 0.3C at

-20 °C. Another set of cells were built for low-temperature rate testing (-20 °C), which included a total of 15 cycles (0.1C/0.1C, 0.2C/0.2C, 0.3C/0.3C, 0.5C/0.5C, and 0.1C/0.1C for three cycles at each rate). A third set of cells were built, for room-temperature (25 °C) cycling; after formation cycling, these cells were cycled for 100 cycles at a rate of 0.5C in a Fisherbrand Isotemp oven. Cells were built in triplicate for each electrolyte formulation to confirm reproducibility, and representative data was provided (cell to cell variation is less than 3%).

Electrochemical impedance spectroscopy (EIS) measurements were acquired with a BioLogic Multichannel potentiostat/galvanostat (model: VSP). The impedance spectra were obtained between 20 MHz and 300 kHz with an AC amplitude of 10 mV at -20 °C after cells were cycled for 50 cycles at the same temperature. Impedance measurements were taken in the fully charged state of the cells.

lonic Conductivity Measurements. The ionic conductivity of the electrolytes was measured at different temperatures: 20, 10, 0, -10, and -20 °C. The electrolytes were first prepared in an Ar-filled glovebox with $O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm. Then, 1.5 mL of the prepared electrolyte solution was sealed in a plastic tube with the same diameter as the ionic conductivity probe. Tape was used to seal the connection part to ensure the airtight environment of the electrolytes. After this, the electrolytes were transferred into a TPS Tenney Junior environmental chamber (control tolerance ± 1 °C) and held at the desired temperature for 1 h before EIS (Gamry EIS measurements station). The ionic conductivity at different temperatures was calculated by converting the impedance to the ionic conductivity based on the impedance of a standard NaCl solution with a known ionic conductivity.

Ex Situ Analysis of the Electrode. At different stages of cycling, fully discharged cells were disassembled in an argon glovebox, and electrodes were extracted for ex situ surface analysis. Harvested electrodes were washed with 700 μ L of dimethyl carbonate 3 times to remove any residual electrolyte. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical compositions of the surface films generated on the electrodes at different stages of cycling with different electrolyte formulations. The washed electrodes were dried in the argon glovebox antechamber overnight and using a vacuum-sealed transfer module transferred to a Thermo Scientific K-alpha spectrometer without air exposure. The binding energy was corrected based on the C 1s spectrum, assigning the C–C/C–H peak to 284.8 eV. The pass energy and X-ray spot size were 50 eV and 400 μ m, respectively.

RESULTS AND DISCUSSION

The charge-discharge cycling performance of NCM622 || graphite cells with the alternative lithium salts along with the STD electrolyte at low temperature $(-20 \ ^{\circ}C)$ and room temperature (25 °C) is given in Figure 1a,b, respectively. For low-temperature cycling, all three MA/FEC-based solvent systems reveal higher reversible capacities than the carbonatebased STD electrolyte system. At low temperature, among the three MA-based formulations investigated, the formulation containing $LiBF_4$ gives the best cycling performance with an average capacity of 99.9 mA h g⁻¹ over 50 cycles. Both LiDFOB and LiPF₆ in MA have better cycling performance at -20 °C compared to the STD electrolyte. However, at room temperature, the STD electrolyte outperforms all three salts in the MA-based electrolyte system as depicted in Figure 1b. When comparing the three Li salts in MA/FEC-based formulations, only the formulation containing LiPF₆ has comparable reversible capacities (133 mA h g^{-1}) to the STD (141 mA h g^{-1}). Despite the lower initial capacity, both LiBF₄ and LiDFOB electrolytes, as previously reported, have good capacity retention after 100 cycles, retaining 84 and 94% of their initial capacities, respectively.¹

To understand the influences of the three different salts in the MA-based electrolyte formulations on battery performance, ionic conductivities of the electrolyte systems were measured at different temperatures and are given in Figure 2. The ionic



Figure 2. Ionic conductivities of the three salts in the MA-FEC solvent system and the STD electrolyte measured at different temperatures.

conductivity of the LiPF₆-MA electrolyte (17.01 mS cm⁻¹) is higher than that of the other two MA-based electrolyte formulations which have ionic conductivities of 10.70 (LiBF₄-MA) and 12.04 mS cm⁻¹ (LiDFOB-MA) at 25 °C. This can be attributed to the low dissociation energy of LiPF₆ due to the larger size of the PF_6^- anion which is known to form solvent-solvated ion pairs.^{27,28} Considering the two formulations with $LiPF_6$ as the salt, the ester formulation has a much higher ionic conductivity compared to the carbonate at 25 °C (17.01 vs 7.23 mS cm⁻¹). This implies that solvents influence the ion transport properties through different intramolecular interactions and through properties related to melting points, viscosity, etc.²⁸ Previous reports suggest that LiPF₆ in carbonate-based electrolytes has a much higher ionic conductivity than $LiBF_4$ and that LiDFOB has an ionic conductivity in between that of $LiPF_6$ and $LiBF_4$.²⁹ BF_4 - is known to strongly coordinate with Li⁺, resulting in more contact ion pairs.²⁷ However, in the novel ester-based electrolyte system, when the temperature decreases, the ionic conductivity change of the LiPF₆-MA electrolyte is greatest and the change in that of the LiBF₄-MA electrolyte is the smallest, though the relative dimension of the ionic conductivity does not change. Overall, a clear trend in higher ionic conductivity for all three Li salts in ester-based electrolytes was observed compared to the STD electrolyte over the temperature range of 20 to -20 °C. The improved low-temperature performance observed with the ester-based electrolytes compared to the STD carbonate electrolyte is related to the increased ionic conductivity of the electrolyte formulations containing esters.¹⁹

The log σ versus 1000/T plots for the four electrolytes are provided in Figure S1 supporting Arrhenius behavior for all electrolytes and that there are no phase transformations within the -20-25 °C temperature range measured. Our previous results showed that the LiBF₄-MA electrolyte has a much



Figure 3. (a) Equivalent circuit used for interpreting the EIS spectra. R_s = solution resistance, $R_{SEI/CEI}$ = SEI/CEI layer resistance, R_{anode} = anode resistance, $R_{cathode}$ = cathode resistance, and CPE = constant phase elements representing capacitance on each interface. (b) Solution resistance values obtained by fitting the spectra. (c) Nyquist plots of the 3 salts in MA-FEC electrolyte formulations and the STD electrolyte taken in the fully charged state after 50 cycles at -20 °C.



Figure 4. Charge–discharge cycling performance of NCM 622 \parallel graphite cells with STD; LiBF₄-MA (base); and base with 1% LiBOB, 1% LiF₂PO₂, and 1% LiTMSP electrolyte formulations at (a) –20 and (b) 25 °C.

higher reversible capacity and lower cell polarization than the LiPF₆-MA or LiDFOB-MA electrolyte despite the lower conductivity at -20 °C.¹⁹ This suggests that the ionic conductivity of the electrolyte may not be the limiting factor determining low-temperature performance.

To understand the LiBF₄-MA electrolyte's superior performance at -20 °C cycling, the effect of the salt on cell impedance was examined using EIS (Figure 3). It has been reported that the cell impedance, particularly charge transfer impedance $(R_{\rm CT})$, varies significantly with the state of charge of the cell.³⁰ Therefore, the impedance of the cells was measured in a fully charged state. Full-cell impedance spectra typically consist of bulk electrolyte resistance ($R_{\rm s}$; which reflects the conductivity of the electrolyte, separator, and the electrode), solid-state interface layer resistance ($R_{\rm SEI/CEI}$; represented by a semicircle at high frequency), and faradaic charge transfer resistance



Figure 5. F 1s (left), P 2p (center), and B 1s (right) XPS spectra of the graphite anodes after 5 formation cycles at 25 °C with different electrolyte formulations.

 $(R_{\rm CT};$ by a semicircle at medium frequency). Figure 3a represents the equivalent circuit of the full-cell impedance spectra fitted to obtain the R_s values for the 4 electrolyte formulations. LiPF₆-MA has the lowest solution resistance, while the STD electrolyte-containing cells have the highest. The R_s values shown in Figure 3b calculated from the Nyquist plot (Figure 3c) correlate well with the conductivity data shown in Figure 2. Nyquist plots reveal that the STD electrolyte has the highest $R_{\rm CT}$ value after low-temperature cycling, while the cells containing the LiBF₄-MA electrolyte have the lowest. Charge transfer impedance includes multiple reaction-dependent steps related to Li⁺ charge transfer. Multiple reports have identified desolvation of solvated Li⁺ as the limiting step in this process which determines the lowtemperature performance.^{4,7,31} Therefore, it can be concluded that while ionic conductivity of the electrolyte is a major component affecting the low-temperature performance, the charge transfer process is a key factor that limits low-temperature performance of the Lithium ion battery; thus, the superior low-temperature performance of the $LiBF_4$ -MA electrolyte can be attributed to the lower charge transfer kinetics.

As discussed in Figure 1b, the room-temperature cycling performance of the ester-based electrolyte formulations has lower capacities compared to that of the STD electrolyte despite having good capacity retention. Previously, it was suggested that the inferior performance at room temperature could be due to the instability of the SEI on the graphite anode (despite having higher ionic conductivities compared to the STD electrolyte at RT; Figure 2) and that FEC alone may not be sufficient to form a protective SEI resulting in continuous decomposition of the salt and MA.¹⁹ Since the LiBF₄-MA



Figure 6. F 1s (left), P 2p (center), and B 1s (right) XPS spectra of the graphite anodes after 50 cycles at 25 °C with different electrolyte formulations.

electrolyte formulation provided the best capacities at -20 °C, a further investigation has been conducted to improve roomtemperature performance in LiBF₄-MA electrolyte-containing cells without compromising low-temperature performance. Thus, the LiBF₄-MA electrolyte formulation was modified by introducing electrolyte additives to generate a more stable SEI on the anode surface. Long-term cycling of the LiBF₄-MA electrolyte containing various electrolyte additives at low temperature (-20 °C) and room temperature (25 °C) is provided in Figure 4a,b, respectively. Cells with ester-based electrolyte formulations have superior performance compared to the STD electrolyte formulations for cells cycled at low temperature (-20 °C). Cells containing the STD electrolyte have an average capacity of ~72 mA h g⁻¹ after 100 cycles, whereas LiBF₄-MA, the base electrolyte (blue), has an average capacity of ~99 mA h g⁻¹. Incorporation of 1% LiBOB (gray) and 1% LiF₂PO₂ (orange) results in a slight decrease in the overall capacity of the cells at low temperature, while addition of 1% LiTMSP (green) improves the low-temperature capacity resulting in the highest average capacity of ~105 mA h g⁻¹ over 100 cycles. Low-temperature rate performance (-20 °C) along with initial formation cycling capacities of NCM622 ||

graphite cells of the different electrolytes is provided in Figure S2. At higher rates, the capacity of cells cycled with the STD electrolyte is significantly decreased compared to that of the cells cycled with the ester electrolyte formulation. Incorporation of 1% LiTMSP or 1% LiF_2PO_2 into the base ester formulation results in significant improvements in the capacities at high rates.

Cells cycled with the STD electrolyte still have the highest initial capacity and capacity retention (~132 mA h g⁻¹ average capacity over the 100 cycles) at room temperature (Figure 4b), but incorporation of additives significantly improves the performance of ester-based formulations compared to that of the base ester electrolyte formulation (LiBF₄-MA), which has an average capacity of ~97 mA h g⁻¹ and a capacity retention of only 84%. Cells containing 1% of added LiTMSP, which has the highest initial capacity of 129 mA h g⁻¹, have a significant increase in the capacity retention with 91% of the initial capacity after 100 cycles. Addition of 1% LiBOB and 1% LiF₂PO₂ results in slightly lower initial capacities of ~122 and 120 mA h g⁻¹⁻⁻, respectively, but incorporation of these additives provides better capacity retention (94.3 and 94.6%, respectively) after 100 cycles.

To understand how the incorporation of the different additives leads to improved low- and room-temperature cycling performance, XPS was conducted on the graphite anodes of the cells after formation cycling (Figures 5 and S3), roomtemperature (25 °C) cycling (Figures 6 and S4), and -20 °C cycling (Figure S5). As depicted in Figure 5, surface films generated with the STD electrolyte after formation cycling appear to differ from the surface film derived from ester-containing electrolytes.^{32,33} The anode surface films generated from the ester-containing electrolytes contain peaks characteristic of boron-containing species (B-F at 192 eV).³⁴ Moreover, additional differences are observed for the esterbased electrolyte formulations which contain different electrolyte additives. Compared to the electrolytes containing additives, increased intensities for O 1s [C-O/C=O at 533 eV (Figure S3)], F 1s (LiF at 685 eV), and B 1s (B-O at 192 eV, B-F at 193 eV) spectra observed for the base ester electrolyte (LiBF₄-MA) suggest that more decomposition of the LiBF₄ salt has occurred to form a thicker SEI in the absence of additives. A thinner SEI was observed with the different electrolytes containing additives as suggested by reduced peak intensities for C 1s, O 1s (Figure S3), and F 1s (LiF at 685 eV, $\text{Li}_{x}\text{PF}_{y}O_{z}$ at 687 eV). In addition, significant differences in surface film composition were observed for electrolytes containing 1% LiTMSP or 1% LiBOB. A phosphate-rich SEI (134 eV) is observed with added 1% LiTMSP, while an SEI rich in oxalatoborates (B-O and B-F at 192/193 eV) is observed for electrolytes containing 1% LiBOB.^{24,34} Similar to the electrolyte containing LiTMSP, the surface film generated from the 1% LiF₂PO₂ electrolyte consists of an inorganic-rich SEI which primarily consists of LiF and $Li_x PF_y O_z$ and boron-containing decomposition products from $BF_4^{-23,34}$.

After low-temperature cycling at -20 °C (Figure S5), there are only small changes to the chemical composition of the anode surface film derived with STD, base ester (LiBF₄-MA), 1% LiBOB, 1% LiF₂PO₂, and 1% LiTMSP electrolytes suggesting minimal SEI evolution between formation and low-temperature cycling. This is evident from relatively similar peak intensities and shapes observed with the elemental spectra for the same electrolyte compositions after formation cycling and after low-temperature cycling.

However, upon cycling at 25 °C for 50 cycles, the chemical composition of surface films on the graphite electrodes with the base ester (LiBF₄-MA), 1% LiBOB, and 1% LiF₂PO₂ electrolytes (Figures 6 and S4) has changed significantly generating thicker surface films. For the base electrolyte (LiBF₄-MA) and the 1% LiBOB electrolyte, increased intensities for peaks characteristic of O-species [C-O, C=O at 533 eV (Figure S4)], LiF (685 eV), and boron species (133 eV) suggest more decomposition products on the graphite electrode.^{34,35} The SEI generated from the base electrolyte is primarily composed of the reduction products of LiBF₄ and FEC, while the SEI generated from the 1% LiBOB-containing electrolyte is dominated by LiBOB reduction products.³ Similarly, when electrolytes containing 1% LiF₂PO₂ are utilized, the SEI is dominated by the decomposition products of LiF₂PO₂ as supported by increased intensities for LiF (685 eV) and $\text{Li}_x PF_v O_z$ (687 eV in F 1s and 136 eV in P 2p).²³ Alternatively, a lower LiF to $Li_x PF_y O_z$ ratio in the F 1s spectrum and increased intensities in O 1s spectra [C-O, C=O at 533 eV (Figure S4)] for the STD electrolyte suggest that the carbonate solvent decomposition is more dominant compared to salt decomposition as the SEI changes during room-temperature cycling.³⁵ However, minimal changes to the surface composition upon extended cycling are observed for cells cycled with 1% LiTMPS suggesting less evolution of the SEI over a wide operating temperature.²

To understand how the different surface films formed with the additives affect the cell impedance, EIS measurements were performed at -20 °C in a fully charged state after cells were cycled at low temperature (-20 °C) for 50 cycles, and the Nyquist plots are presented in Figure 7. $R_{\rm CT}$ values are consistent with the low-temperature cycling performance illustrated in Figure 4a. Addition of 1% LiTMSP results in generation of lower $R_{\rm CT}$ compared to its base electrolyte (LiBF₄-MA), and this further confirms that $R_{\rm CT}$ of the cell is the major limiting factor determining the low-temperature cycling performance of the cells.^{4,30}



Figure 7. Nyquist plots of NCM 622 || graphite cells with STD; LiBF₄-MA (base); and base with 1% LiBOB, 1% LiF₂PO₂, and 1% LiTMSP electrolyte systems, measured in the fully charged state after 50 cycles at -20 °C.

CONCLUSIONS

From the 3 salts investigated in MA-FEC-based electrolyte formulations, 1 M LiBF₄ in MA/FEC has the best lowtemperature performance (reversible capacities of ~100 mA h g^{-1}) despite having lower bulk ionic conductivity at low temperature. EIS results suggest that the improved lowtemperature performance likely results from lower $R_{\rm CT}$ in LiBF₄-MA-containing cells which leads to lower cell polarization, as previously reported.¹⁹ While the LiBF₄-MAcontaining cells have excellent low-temperature cycling performance compared to the other three formulations, room-temperature capacities are inferior to those of the other two salts. It was hypothesized that the improved lowtemperature performance of ester formulations could be coming from the improved physiochemical properties (improved bulk conductivity, lower R_{CT}), but these properties are unlikely to be the most important factors determining room-temperature performance. Stable room-temperature cycling performance is dominated by the formation of a stable SEI on the graphite electrode. The hypothesis has been investigated via the incorporation of four different electrolyte additives that have been reported to improve both low- and room-temperature cycling performance, for the LiBF₄-MA formulation. Incorporation of all the additives results in improved low-temperature and room-temperature performance compared to the base formulation (1 M LiBF₄-MA), while the electrolyte containing 1% LiTMSP has the best overall performance. XPS analysis of the graphite surface reveals a generation of a phosphate-rich SEI, which has been previously reported to improve the cycling performance of the cell.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.3c00261.

Arrhenius plots of ionic conductivities, low-temperature rate test, and XPS spectra of graphite electrodes after room-temperature cycling (PDF)

AUTHOR INFORMATION

Corresponding Author

Brett L. Lucht – Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, United States; orcid.org/0000-0002-4660-0840; Email: blucht@ uri.edu

Authors

- Chamithri Jayawardana Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, United States
- Nuwanthi D. Rodrigo Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, United States; © orcid.org/0000-0003-4312-9536
- Munaiah Yeddala Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, United States
- **Bo Nan** Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States
- Leah Rynearson Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, United States

Chunsheng Wang – Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States; orcid.org/0000-0002-8626-6381

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.3c00261

Author Contributions

[§]C.J. and N.D.R. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Vehicle Technology Office of the U.S. DOE, through Applied Battery Research for Transportation (ABRT) program under contract no. DE-SC0012704.

REFERENCES

(1) Trahey, L.; Brushett, F. R.; Balsara, N. P.; Ceder, G.; Cheng, L.; Chiang, Y. M.; Hahn, N. T.; Ingram, B. J.; Minteer, S. D.; Moore, J. S.; Mueller, K. T.; Nazar, L. F.; Persson, K. A.; Siegel, D. J.; Xu, K.; Zavadil, K. R.; Srinivasan, V.; Crabtree, G. W. Energy Storage Emerging: A Perspective from the Joint Center for Energy Storage Research. *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 12550–12557.

(2) Manthiram, A. An Outlook on Lithium Ion Battery Technology. ACS Cent. Sci. 2017, 3, 1063–1069.

(3) Hou, J.; Yang, M.; Wang, D.; Zhang, J. Fundamentals and Challenges of Lithium Ion Batteries at Temperatures between -40 and 60 °C. *Adv. Energy Mater.* **2020**, *10*, 1904152.

(4) Jow, R.; Zhang, S. S.; Xu, K.; Allen, J. Electrolytes for Low Temperature Operations of Li-Ion Batteries. *ECS Trans.* **2007**, *3*, 51–58.

(5) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104*, 4303–4418.

(6) Xu, K. Electrolytes and Interphases in Li-Ion Batteries and Beyond. *Chem. Rev.* 2014, 114, 11503-11618.

(7) Hubble, D.; Brown, D. E.; Zhao, Y.; Fang, C.; Lau, J.; McCloskey, B. D.; Liu, G. Liquid Electrolyte Development for Low-Temperature Lithium-Ion Batteries. *Energy Environ. Sci.* **2022**, *15*, 550–578.

(8) Zhang, X.; Zou, L.; Xu, Y.; Cao, X.; Engelhard, M. H.; Matthews, B. E.; Zhong, L.; Wu, H.; Jia, H.; Ren, X.; Gao, P.; Chen, Z.; Qin, Y.; Kompella, C.; Arey, B. W.; Li, J.; Wang, D.; Wang, C.; Zhang, J. G.; Xu, W. Advanced Electrolytes for Fast-Charging High-Voltage Lithium-Ion Batteries in Wide-Temperature Range. *Adv. Energy Mater.* **2020**, *10*, 2000368.

(9) Nan, B.; Chen, L.; Rodrigo, N. D.; Borodin, O.; Piao, N.; Xia, J.; Pollard, T.; Hou, S.; Zhang, J.; Ji, X.; Xu, J.; Zhang, X.; Ma, L.; He, X.; Liu, S.; Wan, H.; Hu, E.; Zhang, W.; Xu, K.; Yang, X. Q.; Lucht, B.; Wang, C. Enhancing Li+ Transport in NMC811llGraphite Lithium-Ion Batteries at Low Temperatures by Using Low-Polarity-Solvent Electrolytes. *Angew. Chem., Int. Ed.* **2022**, *61*, No. e202205967.

(10) Cho, Y. G.; Kim, Y. S.; Sung, D. G.; Seo, M. S.; Song, H. K. Nitrile-Assistant Eutectic Electrolytes for Cryogenic Operation of Lithium Ion Batteries at Fast Charges and Discharges. *Energy Environ. Sci.* **2014**, *7*, 1737–1743.

(11) Sazhin, S. V.; Khimchenko, M. Y.; Tritenichenko, Y. N.; Lim, H. S. Performance of Li-Ion Cells with New Electrolytes Conceived for Low-Temperature Applications. *J. Power Sources* **2000**, *87*, 112–117.

(12) Smart, M. C.; Ratnakumar, B. v.; Surampudi, S. Use of Organic Esters as Cosolvents in Electrolytes for Lithium-Ion Batteries with Improved Low Temperature Performance. *J. Electrochem. Soc.* 2002, 149, A361.

www.acsaem.org

(13) Smart, M. C.; Ratnakumar, B. V.; Chin, K. B.; Whitcanack, L. D. Lithium-Ion Electrolytes Containing Ester Cosolvents for Improved Low Temperature Performance. *J. Electrochem. Soc.* **2010**, *157*, A1361.

(14) Smith, K. A.; Smart, M. C.; Prakash, G. K. S.; Ratnakumar, B. V. Electrolytes Containing Fluorinated Ester Co-Solvents for Low-Temperature Li-Ion Cells. *ECS Trans.* **2008**, *11*, 91–98.

(15) Smart, M. C.; Ratnakumar, B. v.; Whitcanack, L. D.; Chin, K. B.; Surampudi, S.; Croft, H.; Tice, D.; Staniewicz, R. Improved Low-Temperature Performance of Lithium-Ion Cells with Quaternary Carbonate-Based Electrolytes. *J. Power Sources* **2003**, *119–121*, 349–358.

(16) Cho, Y. G.; Li, M.; Holoubek, J.; Li, W.; Yin, Y.; Meng, Y. S.; Chen, Z. Enabling the Low-Temperature Cycling of NMCllGraphite Pouch Cells with an Ester-Based Electrolyte. *ACS Energy Lett.* **2021**, *6*, 2016–2023.

(17) Li, J.; Li, H.; Ma, X.; Stone, W.; Glazier, S.; Logan, E.; Tonita, E. M.; Gering, K. L.; Dahn, J. R. Methyl Acetate as a Co-Solvent in NMC532/Graphite Cells. *J. Electrochem. Soc.* **2018**, *165*, A1027–A1037.

(18) Wang, Z.; Sun, Z.; Shi, Y.; Qi, F.; Gao, X.; Yang, H.; Cheng, H. M.; Li, F. Ion-Dipole Chemistry Drives Rapid Evolution of Li Ions Solvation Sheath in Low-Temperature Li Batteries. *Adv. Energy Mater.* **2021**, *11*, 2100935.

(19) Rodrigo, N. D.; Jayawardana, C.; Rynearson, L.; Hu, E.; Yang, X.-Q.; Lucht, B. L. Use of Ethylene Carbonate Free Ester Solvent Systems with Alternative Lithium Salts for Improved Low-Temperature Performance in NCM622-Graphite Li-Ion Batteries. *J. Electrochem. Soc.* **2022**, *169*, 110504.

(20) Smart, M. C.; Ratnakumar, B. v.; Whitcanack, L. D.; Smith, K. A.; Santee, S.; Gitzendanner, R.; Yevoli, V. Li-Ion Electrolytes Containing Ester Co-Solvents for Wide Operating Temperature Range. *ECS Trans.* **2008**, *11*, 99–108.

(21) Zhang, S. S.; Xu, K.; Jow, T. R. The Low Temperature Performance of Li-Ion Batteries. *J. Power Sources* **2003**, *115*, 137–140. (22) Smart, M. C.; Lucht, B. L.; Dalavi, S.; Krause, F. C.; Ratnakumar, B. v. The Effect of Additives upon the Performance of MCMB/LiNi_xCo_{1-x}O₂ Li-Ion Cells Containing Methyl Butyrate-Based Wide Operating Temperature Range Electrolytes. *J. Electrochem. Soc.* **2012**, *159*, A739–A751.

(23) Yang, B.; Zhang, H.; Yu, L.; Fan, W. Z.; Huang, D. Lithium Difluorophosphate as an Additive to Improve the Low Temperature Performance of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2/Graphite$ Cells. *Electrochim. Acta* **2016**, 221, 107–114.

(24) Kim, J.; Adiraju, V. A. K.; Chae, O. B.; Lucht, B. L. Lithium Bis(Trimethylsilyl) Phosphate as an Electrolyte Additive to Improve the Low-Temperature Performance for $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2/Graphite$ Cells. J. Electrochem. Soc. **2021**, 168, 080538.

(25) Chen, Z.; Qin, Y.; Liu, J.; Amine, K. Lithium Difluoro-(Oxalato)Borate as Additive to Improve the Thermal Stability of Lithiated Graphite. *Electrochem. Solid-State Lett.* **2009**, *12*, A69–A72.

(26) Kim, J.; Adiraju, V. A. K.; Rodrigo, N.; Hoffmann, J.; Payne, M.; Lucht, B. L. Lithium Bis(Trimethylsilyl) Phosphate as a Novel Bifunctional Additive for High-Voltage $\text{LiNi}_{1.5}\text{Mn}_{0.5}\text{O}_4/\text{Graphite}$ Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 22351–22360.

(27) Chapman, N.; Borodin, O.; Yoon, T.; Nguyen, C. C.; Lucht, B. L. Spectroscopic and Density Functional Theory Characterization of Common Lithium Salt Solvates in Carbonate Electrolytes for Lithium Batteries. *J. Phys. Chem. C* **2017**, *121*, 2135–2148.

(28) Seo, D. M.; Reininger, S.; Kutcher, M.; Redmond, K.; Euler, W. B.; Lucht, B. L. Role of Mixed Solvation and Ion Pairing in the Solution Structure of Lithium Ion Battery Electrolytes. *J. Phys. Chem.* C **2015**, *119*, 14038–14046.

(29) Zhang, T.; Porcher, W.; Paillard, E. Towards Practical Sulfolane Based Electrolytes: Choice of Li Salt for Graphite Electrode Operation. *J. Power Sources* **2018**, 395, 212–220. (30) Zhang, S. S.; Xu, K.; Jow, T. R. Electrochemical Impedance Study on the Low Temperature of Li-Ion Batteries. *Electrochim. Acta* **2004**, *49*, 1057–1061.

(31) Li, Q.; Lu, D.; Zheng, J.; Jiao, S.; Luo, L.; Wang, C. M.; Xu, K.; Zhang, J. G.; Xu, W. Li⁺-Desolvation Dictating Lithium-Ion Battery's Low-Temperature Performances. *ACS Appl. Mater. Interfaces* **2017**, *9*, 42761–42768.

(32) Nie, M.; Abraham, D. P.; Seo, D. M.; Chen, Y.; Bose, A.; Lucht, B. L. Role of Solution Structure in Solid Electrolyte Interphase Formation on Graphite with LiPF₆ in Propylene Carbonate. *J. Phys. Chem. C* **2013**, *117*, 25381–25389.

(33) Rodrigo, N. D.; Jayawardana, C.; Lucht, B. L. Investigation of the Electrode-Electrolyte Interphase in Ester-Based Electrolytes in NCM523/Graphite Cells. J. Electrochem. Soc. **2022**, 169, 030519.

(34) Nie, M.; Lucht, B. L. Role of Lithium Salt on Solid Electrolyte Interface (SEI) Formation and Structure in Lithium Ion Batteries. *J. Electrochem. Soc.* **2014**, *161*, A1001–A1006.

(35) Heiskanen, S. K.; Kim, J.; Lucht, B. L. Generation and Evolution of the Solid Electrolyte Interphase of Lithium-Ion Batteries. *Joule* **2019**, *3*, 2322–2333.

Recommended by ACS

Effect of Fluoroethylene Carbonate Electrolyte Additives on the Electrochemical Performance of Nickel-Rich NCM Ternary Cathodes

Shengxian She, Yongjun Wu, et al. JUNE 23, 2023 ACS APPLIED ENERGY MATERIALS

READ 🗹

Suppression of Dehydrofluorination Reactions of a Li_{0.33}La_{0.557}TiO₃-Nanofiber-Dispersed Poly(vinylidene fluoride-co-hexafluoropropylene) Electrolyte for Quasi-So...

Purna Chandra Rath, Jeng-Kuei Chang, et al. MARCH 15, 2023

MARCH 15, 2025	
ACS APPLIED MATERIALS & INTERFACES	READ 🗹

Understanding the Improved Fast Charging Performance of Graphite Anodes with a Fluoroethylene Carbonate Additive by In Situ NMR and EPR

Shinuo Kang, Bingwen Hu, et al.	
JULY 05, 2023	
ACS APPLIED ENERGY MATERIALS	READ 🗹

Optimal Blend between Carbonate Solvents and Fluoroethylene Carbonate for High-Voltage and High-Safety Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂ Lithium-Ion Cells

Dongxu Ouyang, Zhirong Wang, et al. JANUARY 19, 2023 ACS APPLIED ENERGY MATERIALS

READ 🗹

Get More Suggestions >