Using Triethyl Phosphate to Increase the Solubility of LiNO$_3$ in Carbonate Electrolytes for Improving the Performance of the Lithium Metal Anode

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Zachary L. Brown et al 2019 J. Electrochem. Soc. 166 A2523. https://doi-org.uri.idm.oclc.org/10.1149/2.0991912jes

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To cite this article: Zachary L. Brown et al 2019 J. Electrochem. Soc. 166 A2523

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Using Triethyl Phosphate to Increase the Solubility of LiNO₃ in Carbonate Electrolytes for Improving the Performance of the Lithium Metal Anode

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The investigation of novel electrolytes for lithium metal anodes has been conducted. Incorporation of LiNO₃ into lithium difluoro(oxalato)borate (LiDFOB) in ethylene carbonate (EC) and dimethyl carbonate (DMC) electrolytes results in a significant improvement in capacity retention and Coulombic efficiency. While the solubility of LiNO₃ is very low in common carbonate solvents (~0.03 M), the use of triethyl phosphate (TEP) significantly increases the solubility of LiNO₃ and improves the capacity retention and Coulombic efficiency of lithium metal anodes. Ex-situ surface analysis of the cycled electrodes suggests that incorporation of LiNO₃ results in nitrogen containing species (NO₃⁻, NO₂⁻, and N₃⁻) in the solid electrolyte interphase (SEI) which is likely responsible for the performance enhancement.

The performance of lithium metal electrodes cycled with lithium difluoro(oxalato)borate (LiDFOB), lithium nitrate (LiNO₃) and triethyl phosphate (TEP)-containing carbonate electrolytes has been investigated with Cu||LiFePO₄ cells. The in-situ formation of lithium metal and low reactivity of LiFePO₄ in Cu||LiFePO₄ cells ensure that the electrolyte components do not react with the electrode surfaces prior to the initial lithium plating cycle, as previously reported. The LiNO₃ additive was observed to improve the cycling performance of Cu||LiFePO₄ cells with carbonate electrolytes. Further, TEP was observed to increase the solubility of LiNO₃ in carbonate electrolytes, leading to significant improvement of the cycling performance of Cu||LiFePO₄ cells. By analyzing the surface of lithium metal plated with the investigated electrolytes with X-ray Photoelectron Spectroscopy (XPS), it is suggested that the improved cycling performance derives from LiNO₃ decomposing to modify the SEI of the lithium metal anode.

Experimental Electrochemistry.—Electrochemical characterization was performed using Cu||LiFePO₄ 2032 coin cells. The Cu||LiFePO₄ cells were assembled with a Cu metal foil negative electrode (15 mm diameter, MTI Corporation), two Celgard 2400 separators (19 mm diameter), and a LiFePO₄ positive electrode (91% active material, 13.7 mm diameter, 83 μm thickness, 12 mg/cm² loading, MTI corporation), the other 9% of the composite electrode is composed of conductive carbon and PVDF coated on aluminum. The Cu||LiFePO₄ and Li||Li cells were prepared with 40 μL/cm² of electrolyte. Electrolytes investigated include 1.0 M LiDFOB in ethylene carbonate: dimethyl carbonate (16.8:83.2, volume:volume, EC:DMC, LiDFOB EC electrolyte), 1.0 M LiDFOB in EC:DMC with saturated LiNO₃ (estimated 0.03 M LiNO₃ in 16.8:83.2, EC:DMC, LiDFOB LiNO₃ EC electrolyte), 1.0 M LiDFOB in triethyl phosphate (TEP):EC:DMC (8.4:8.4:83.2, by volume, LiDFOB TEP:EC electrolyte), and 1.0 M LiDFOB in TEP:EC:DMC with saturated LiNO₃ (estimated 0.2 M in 8.4:8.4:83.2, by volume, LiDFOB LiNO₃ TEP:EC electrolyte). The LiDFOB, EC, and DMC electrolyte components were battery grade and supplied from Gotion Inc. The LiNO₃ (99.99%, trace metals basis) and TEP (≥99.8%, dried over molecular sieves) were purchased from Sigma-Aldrich. The copper metal foil was sonicated with isopropanol (2 × 2 minutes), punched to the specified diameter, and dried at 110°C overnight under vacuum prior to cell assembly. The LiFePO₄ electrodes were punched to the specified diameter, and dried at 110°C overnight under vacuum prior to cell assembly. The cycling procedure consisted of plating Li metal at 0.1 mA/cm² (approx. C/20 rate,
where C represents the theoretical capacity of LiFePO₄ with subsequent stripping and plating at 0.4 mA/cm² (approx. C/4 rate), within a voltage window of 2.0 – 4.0 V, using an Arbin BT2000 battery cycler at 25°C. There was a rest period of one hour between cell construction and the beginning of the electrochemical protocol.

XPS.—XPS measurements were acquired with a K-alpha Thermo system using Al Ka radiation (hv = 1486.6 eV) under ultra-high vacuum (<1 × 10⁻¹² atm) and a measured spot size of 400 μm in diameter. Lithium metal was deposited onto Cu foil according to the first charge procedure outlined in the electrochemistry section (charge to 4.0 V at C/20 rate), and held at rest for approximately 4 hours to ensure cell equilibration before disassembly. Electrodes were washed with 4 × 500 μL battery grade DMC and dried under vacuum for 10 minutes, then overnight in the argon glovebox. The samples were transferred from the argon glovebox in an air-free transfer case, while sealed under vacuum. The binding energy was corrected based on the F1s spectrum, assigning LiF to 685 eV.

Results

The stripping capacity vs. cycle number and Coulombic efficiency vs. cycle number are provided in Figures 1A and 1B, respectively, for the electrolytes investigated. For this investigation, a baseline carbonate electrolyte, 1 M lithium difluoro(oxalate)borate (LiDFOB) dissolved in ethylene carbonate (EC): dimethyl carbonate (DMC) has been selected (LiDFOB EC electrolyte, see electrolyte abbreviations in experimental section). The cell containing the LiDFOB EC electrolyte achieves over 25 cycles before dropping below 20% initial capacity (Fig. 1A) and a first cycle Coulombic efficiency of 89% (Fig. 1B) is observed for the lithium metal anode, as previously reported. Upon saturating the LiDFOB EC electrolyte with LiNO₃ (LiDFOB LiNO₃ EC electrolyte) the Coulombic efficiencies are further improved to 98% after 10 cycles (Fig. 1B) along with an improvement in cycle lifetime. Furthermore, employing TEP to increase the solubility of LiNO₃ in the electrolyte to ~0.2 M (LiDFOB LiNO₃ TEP:EC) leads
Figure 3. C1s, O1s, F1s, and B1s spectra of lithium metal plated on the first cycle with the investigated electrolytes.
to further improved performance, with efficiencies reaching up to 99% after 15 cycles (Fig. 1B) and cycling for over 65 cycles before the capacity drops below 20% of the initial capacity (Fig. 1A). The LiDFOB TEP:EC electrolyte without LiNO₃ has very poor performance compared to the other electrolytes investigated with a first cycle Coulombic efficiency of 62% (Fig. 1B) and lasting only 13 cycles before capacity drops below 20% of the initial capacity (Fig. 1A). Therefore, the improved performance for the LiDFOB LiNO₃ TEP:EC electrolyte is due to the increased concentration of LiNO₃ in the electrolyte, and not the presence of TEP. The improved performance observed with the LiDFOB LiNO₃ TEP:EC electrolyte is further illustrated in Figure 1C, with the sum of reversibly cycled lithium over the first 100 cycles reaching over 4250 mAh/g, almost twice the amount observed for the next best performing LiDFOB LiNO₃ EC electrolyte. It is worth noting the sum of reversibly cycled lithium for the LiDFOB LiNO₃ TEP:EC electrolyte surpasses the previously reported performance for FEC electrolytes.° Finally, the first cycle galvanostatic cycling profile (Fig. 1D) eludes to the dramatic decrease in cycling performance for the LiDFOB TEP:EC electrolyte. Specifically, a decrease in discharge voltage is observed upon stripping lithium for the LiDFOB TEP:EC electrolyte, in comparison to the other electrolytes, suggesting a more resistive SEI is formed on the lithium metal anode with the LiDFOB TEP:EC electrolyte. The electrochemistry of these electrolytes was also characterized in Li||Li symmetric cells, shown in Figure 2. The cycling performance of cells with LiDFOB EC, LiDFOB TEP:EC and LiDFOB LiNO₃ EC electrolyte are similar. The high reactivity of lithium metal in electrodes makes it challenging to resolve the minor changes in electrolyte performance, as electrolyte components are likely consumed at a higher rate than in the lower reactivity Cu||LiFePO₄ cells. However, it is clear that the LiDFOB LiNO₃ TEP:EC has the best performance, with cycle lifetime almost twice that observed for the other electrolytes, consistent with the improvement observed in Cu||LiFePO₄ cells (Figure 1C). These observations confirm that increasing the concentration of LiNO₃ via dissolution in a good solvent such as TEP improves the cycling performance of the lithium metal anode.

The C1s, O1s, F1s, and B1s spectra of lithium metal plated with the investigated electrolytes are plotted in Figure 3. In general, these spectra are dominated by the decomposition products of LiDFOB. For example, in the C1s spectra, peaks are observed at 289.1 eV (C=O), and 286.6 eV (C-O), with the greatest relative intensity observed for lithium plated from the baseline LiDFOB EC electrolyte, suggesting the formation of oxalate species, consistent with previous work.° Lower intensities for these peaks are observed for lithium plated with the other electrolytes, suggesting that LiDFOB reduction is inhibited when LiNO₃ or TEP is present in the electrolyte. The same trend is apparent in the O1s spectra, where a broad peak at ~532.5 eV (mixture of C=O/C-O) is most intense for lithium plated with the baseline LiDFOB EC electrolyte.° As observed in the F1s spectra, LiF (685.0 eV) is the dominant product for lithium plated with each electrolyte, consistent with previous results. The LiF intensity is weakest for lithium plated with the baseline LiDFOB electrolyte, as it likely has the thickest layer of oxalate species on the upper surface of the SEI.° Finally, a broad peak is observed at ~193.0 eV in the B1s spectra for lithium plated with each electrolyte, consistent with LiDFOB decomposition.° The N1s and P2p spectra for lithium metal plated with the investigated electrolytes are plotted in Figure 4. Lithium plated with the electrolytes containing LiNO₃ contain the expected decomposition products including NO₂⁻ (~407.5 eV), NO₃⁻ (~402.0 eV), and N³⁻ (~400.0 eV) as observed in the N1s spectra.° These products are not observed for lithium plated with the LiDFOB TEP:EC electrolyte. These observations suggest the incorporation of LiNO₃ decomposition products in the SEI are beneficial for improving the performance of the lithium metal anode. Further, there is a broad peak observed at ~135.0 eV in the P2p spectra for lithium plated with both electrolytes containing TEP, consistent with reduction of TEP. There appears to be a significant amount of TEP decomposition for the LiDFOB TEP:EC electrolyte, suggesting that TEP decomposition is detrimental to the cycling performance of the lithium metal anode, since these cells have the poorest cycling performance. Apparently, saturating TEP with LiNO₃ can overcome the negative impact of TEP on the cycling performance of the lithium metal anode, perhaps through a similar mechanism as described for concentrated lithium bis(flourosulfonyl)amide/trimethyl phosphate electrolytes cycled with graphite anodes.° The improved performance may be due to synergistic reactions of LiNO₃ and TEP to generate SEI products similar to that of the LiPON solid state electrolyte.° However, the increased concentration of LiNO₃ in the electrolyte does not significantly change the composition of the SEI for the lithium metal anode compared to electrolytes with lower concentrations of LiNO₃. It is likely that LiNO₃ is continuously consumed during cycling and the increased concentration of LiNO₃ provides a larger supply of LiNO₃, increasing the number of cycles that generate an SEI rich in LiNO₃ decomposition products. Similar results have been reported with FEC electrolytes and silicon based anode materials.° Furthermore, recent
work has demonstrated that LiNO₃ and TEP containing electrolytes can be used in high voltage lithium metal batteries. However, a more detailed investigation is required to explore these mechanisms. In general, LiNO₃ appears to preferentially react on the surface of lithium metal, modifying the SEI, and thereby improving the cycling performance of the lithium metal anode.

Conclusions

Developing carbonate electrolytes for the lithium metal anode is important for enabling high-energy lithium batteries. Employing phosphate solvents to increase the solubility of beneficial additives, such as LiNO₃, can improve the electrochemical performance of the lithium metal anode significantly. For example, by adding a saturated solution of LiNO₃ in TEP to a LiDFOB-based carbonate electrolyte, it was possible to cycle more than double the amount of lithium than was achieved with the original LiDFOB-based carbonate electrolyte. This observation motivates researchers to pursue various new solvents, compatible with carbonate solvents, to increase solubility of desired additives that are sparingly soluble in pure carbonate solvents.

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