Synergistic Performance of Lithium Difluoro(oxalato)borate and Fluoroethylene Carbonate in Carbonate Electrolytes for Lithium Metal Anodes

Zachary L. Brown
University of Rhode Island

Brett L. Lucht
University of Rhode Island, blucht@uri.edu

Creative Commons License

This work is licensed under a Creative Commons Attribution 4.0 License.

Follow this and additional works at: https://digitalcommons.uri.edu/chm_facpubs

Citation/Publisher Attribution


Available at: http://dx.doi.org/10.1149/2.0181903jes
Synergistic Performance of Lithium Difluoro(oxalato)borate and Fluoroethylene Carbonate in Carbonate Electrolytes for Lithium Metal Anodes

Zachary L. Brown and Brett L. Lucht

Department of Chemistry, University of Rhode Island, Kingston, Rhode Island 02881, USA

There is significant interest in the development of rechargeable high-energy density batteries which utilize lithium metal anodes. Recently, fluoroethylene carbonate (FEC) and lithium difluoro(oxalato)borate (LiDFOB) have been reported to significantly improve the electrochemical performance of lithium metal anodes. This investigation focuses on exploring the synergy between LiDFOB and FEC in carbonate electrolytes for lithium metal anodes. In ethylene carbonate (EC) electrolytes, LiDFOB is optimal when used in high salt concentrations, such as 1.0 M, to improve the electrochemistry of the lithium metal anode in Cu||LiFePO₄ cells. However, in FEC electrolytes, LiDFOB is optimal when used in lower concentrations, such as 0.05–0.10 M. From surface analysis, LiDFOB is observed to favorably react on the surface of lithium metal to improve the performance of the lithium metal anode, in both EC and FEC-based electrolytes. This research demonstrates progress toward developing feasible high-energy density lithium-based batteries.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI:10.1149/2.0181903jes]

The development of energy storage technology is an important topic for facilitating the employment of renewable energy in society. Therefore, current energy storage research is heavily focused on enabling rechargeable high-energy density lithium-based batteries. In particular, permitting reversible electrochemical plating and stripping of the lithium metal anode in carbonate electrolytes can achieve this goal. Unfortunately, the performance of the lithium metal anode in carbonate electrolytes is plagued by unsafe dendrite formation and poor Coulombic efficiency upon cycling. However, recent developments in electrolyte chemistry have improved upon these limitations significantly.

Fluoroethylene carbonate (FEC) containing electrolytes have been reported to improve the performance of lithium metal electrodes via the generation of polymeric species and LiF within the Solid Electrolyte Interphase (SEI), similar to that reported for silicon anodes, which may contribute to the improved cycling performance of lithium metal anodes. Recent work suggests that reduction of FEC generates nano-structured LiF, creating a uniform diffusion field on the lithium metal electrode, leading to uniform plating and stripping. Furthermore, it has been demonstrated that employing FEC in solvent-based electrolyte is optimal for achieving high performance lithium metal anodes.

Lithium difluoro(oxalato)borate (LiDFOB) has also been reported to generate nano-structured LiF for lithium metal electrodes, thereby improving the electrochemical performance of the lithium metal anode. However, the optimal amount of LiDFOB to use in carbonate electrolytes for the lithium metal anode has not been explored. Further, the synergy between FEC and LiDFOB has not been investigated in carbonate electrolytes for the lithium metal anode. Given the reported improvement in plating/stripping of the lithium metal anode with FEC and LiDFOB containing electrolytes, exploring their synergy can assist researchers in developing high performance electrolytes for the lithium metal anode.

Several carbonate electrolyte compositions containing FEC and LiDFOB have been investigated via a combination of electrochemical analysis with Cu||LiFePO₄ cells and ex-situ surface analysis of the cycled electrodes. The in-situ formation of lithium metal and low reactivity of LiFePO₄ in Cu||LiFePO₄ cells ensure that FEC does not react with the electrode surfaces prior to the initial lithium plating cycle, as previously reported. In particular, ex-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and X-ray photoelectron spectroscopy (XPS) were used to confirm the role of LiDFOB in the optimized electrolytes. The analysis reveals that LiDFOB can be used in additive concentrations to work synergistically with FEC co-solvent electrolytes.

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, MTI corporation), the other 9% of the composite electrode is composed of conductive carbon and PVDF coated on aluminum. The cells were prepared with 60 μL of electrolyte. Electrolytes investigated included (1-x) M LiPF₆ + x M LiDFOB in ethylene carbonate: dimethyl carbonate (1:4g, EC:DMC) solvent and (1-x) M LiPF₆ + x M LiDFOB in fluoroethylene carbonate: dimethyl carbonate (1:4g, FEC:DMC) solvent. The compositions studied consist of 1.0 M LiPF₆, 1.0 M LiPF₆, 0.95 M LiPF₆ + 0.05 M LiDFOB (0.05 M LiDFOB EC electrolyte), 0.90 M LiPF₆ + 0.10 M LiDFOB (0.10 M LiDFOB EC electrolyte), 0.50 M LiPF₆ + 0.50 M LiDFOB (0.50 M LiDFOB EC electrolyte), and 1.0 M LiDFOB (1.0 M LiDFOB EC electrolyte). Comparable compositions studied in FEC:DMC electrolytes are abbreviated as 1.0 M LiPF₆, FEC electrolyte, 0.05 M LiDFOB FEC electrolyte, 0.1 M LiDFOB FEC electrolyte, 0.5 M LiDFOB FEC electrolyte, and 1.0 M LiDFOB FEC electrolyte. 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.

DRIFTS.—IR spectra of lithium metal electrodes were acquired with a Bruker Tensor 27 spectrometer equipped with an UPlR
Diffuse Reflectance accessory (Pike Technologies) and LaDTG detector. 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 20 minutes, then stored overnight in an argon-filled glove box. The electrodes were transferred from an argon glove box to a nitrogen-filled glove box in a sealed Nalgene vial and measured immediately with DRIFTS. There is no evidence for reaction of the lithium metal anodes with N₂ during the timeframe of the analysis. The spectra were acquired in the nitrogen glove box with a resolution of 4 cm⁻¹ and 32 scans.

**XPS.**—XPS measurements were acquired with a K-alpha Thermo system using Al Kα 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 glove box. The samples were transferred from the argon glove box 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 concentration of Li⁺ is maintained at 1.0 M for all electrolytes investigated, emphasizing the influence of the PF₆⁻ and DFOB⁻ anions on electrochemical performance. The stripping capacity vs. cycle number, Coulombic efficiency vs. cycle number and sum of reversibly cycled lithium for Cu||LiFePO₄ cells after 50 cycles for the EC:DMC electrolytes investigated are provided in Figures 1A, 1B, and 1C, respectively. The stripping capacity of the cells containing the 1.0 M LiPF₆ EC electrolyte (see electrolyte abbreviations in experimental section) is extremely poor, with no significant reversible capacity upon cycling (Fig. 1A), as evidenced by the low initial Coulombic efficiency of 15%. In general, the cycling performance is improved as the concentration of LiDFOB is increased in the electrolyte, with the 1.0 M LiDFOB EC electrolyte having the best performance, achieving 30 cycles before the cell drops below 20% of the initial capacity (Fig. 1A). This trend is evident in Fig. 1B, with initial efficiencies of 52%, 69%, 87%, and 89% for the 0.05 M LiDFOB EC, 0.10 M LiDFOB EC, 0.50 M LiDFOB EC, and 1.0 M LiDFOB electrolytes, respectively. The improvement in electrochemical performance is further illustrated by the sum of the stripping capacities (reversibly cycled lithium) over 100 cycles, which increases with increasing LiDFOB content in the electrolyte (Fig. 1C). With EC-containing electrolytes, it is optimal to use LiDFOB as the pure salt instead of as an additive, supporting previous investigations of LiDFOB electrolytes.

The stripping capacity vs. cycle number, Coulombic efficiency vs. cycle number and sum of reversibly cycled lithium for Cu||LiFePO₄ cells after 100 cycles for the FEC:DMC electrolytes investigated are provided in Figures 2A, 2B, and 2C, respectively. The 1.0 M LiPF₆ FEC electrolyte, out performs all EC electrolytes described above, achieving 40 cycles before the cells drop below 20% of the initial capacity and higher efficiencies stabilizing around 98% (Figs. 2A, 2B), consistent with previous work. This is also evident in Figure 2C, since the figure of the range of reversibly cycled lithium exceeds the best EC electrolyte by more than 1000 mA h/g. Upon addition of LiDFOB to the electrolyte, there are minor improvements in Coulombic efficiency, extending the lifetime of the cell for more cycles (Figs. 2A, 2B). This observation suggests that, upon incorporation of LiDFOB into the electrolyte, parasitic reactions of the lithium metal electrode with the electrolyte are mitigated. The optimal concentration of LiDFOB required is lower for the FEC electrolytes, with the 0.05 M LiDFOB FEC and 0.10 M LiDFOB FEC electrolytes having slightly better electrochemical performance. This trend is also clear for the sum of reversibly cycled lithium (Fig. 2C). Therefore, incorporation of LiDFOB in additive concentrations to FEC based electrolytes improves performance synergistically with FEC to improve the cycling performance of the lithium metal anode.

The DRIFTS spectra of the lithium electrode after the first plating cycle of lithium from 1.0 M LiPF₆, EC, 1.0 M LiDFOB EC, 1.0 M LiPF₆ FEC, and 0.10 M LiDFOB FEC electrolytes are provided in Figure 3. The peak at 1573 cm⁻¹ is an artifact peak of the DRIFTS spectrum of the lithium electrode. The DRIFTS spectra of the lithium electrode plated with 1.0 M LiPF₆, EC, and 1.0 M LiPF₆ FEC after the first plating cycle contains major peaks assigned to lithium carbonate (Li₂CO₃; 1510, 1460 cm⁻¹) and lithium alkyl carbonates (ROCO₂Li; 1690 cm⁻¹), as
Figure 2. The stripping capacity vs. cycle number (A), Coulombic efficiency vs. cycle number (B), and sum of reversibly cycled lithium (C) for FEC:DMC electrolytes in Cu||LiFePO₄ cells after 100 cycles.

Figure 3. DRIFTS of lithium metal plated with the investigated electrolytes.
Figure 4. C1s, O1s, and F1s spectra of lithium metal plated with the investigated electrolytes.
are observed at 193.4 eV and ~191.5 eV in the B1s spectra for lithium plated from 1.0 M LiDFOB EC and 0.10 M LiDFOB FEC electrolytes, respectively. It should be noted that intensity from the P2s peak overlaps with B1s peak. However, the intensity of the P2p peak at ~135.2 eV, characteristic of LiPF₆ and Li₅PF₆O₇, is similar for both the 1.0 M LiPF₆ FEC and 0.10 M LiDFOB FEC electrolytes, yet the intensity and peak position of the peaks the B1s spectra are different supporting the presence of boron decomposition products on the surface of lithium metal plated from the 0.10 M LiDFOB FEC electrolyte. The shift in binding energy suggests that the boron containing species in the SEI differ in structure, but it is unclear at this time how the structures may differ. In addition, as expected the concentration of B is lower for the lithium plated with a lower concentration of LiDFOB. Overall, LiDFOB improves the electrochemical performance of the cells via modification of the SEI, confirming the synergistic behavior of LiDFOB and FEC for lithium metal electrodes.

Conclusions

The concentration of LiDFOB was varied in carbonate electrolytes to optimize the performance of the lithium metal anode in Cu||LiFePO₄ cells. In EC electrolytes, LiDFOB is optimal in higher concentrations (1.0 M), as the bulk salt. However, in FEC electrolytes, LiDFOB is optimal when used in lower concentrations, 0.05–0.10 M. Ex-situ surface analysis suggests that LiDFOB reacts on the surface of lithium metal to generate a more stable SEI improving the performance of lithium metal anodes in both EC and FEC-based electrolytes. Therefore, LiDFOB and FEC can be used in the electrolyte synergistically to optimize the performance of the lithium metal anode. This research demonstrates progress toward feasible high-energy density lithium-based batteries.

Acknowledgment

The authors thank BASF SE Electrochemistry Research Network for financial support.

ORCID

Zachary L. Brown <https://orcid.org/0000-0003-0772-3159>
Brett L. Lucht <https://orcid.org/0000-0002-4660-0840>

References