Electrolyte Optimization of a Substituted-$LiCo_{1-x}Fe_xPO_4$ Cathode

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Lithium cobalt phosphate ($LiCoPO_4$) is an attractive cathode material due to its high discharge potential (4.8 V vs. Li/Li^+) and specific capacity (167 mAh g^{-1}), resulting in an impressive specific energy of ~802 Wh kg^{-1}. The development of LCP has proven difficult owing to the instability of the electrode and the tendency of the electrolyte to perpetually decompose (oxidize), leading to a highly resistive passivation layer. In this report, a substituted lithium cobalt iron phosphate (s-$LiCo_{1-x}Fe_xPO_4$ or s-LCFP) cathode material was tested with various solvents and additives to find an optimized electrolyte that limits electrode polarization and improves cycle life. The s-LCFP cathode performed best with a 1M $LiPF_6$ solution of EC/EMC (3/7 wt%) with 2% of additive ARL1. Comparing ARL1 to the baseline electrolyte, the fade rate was reduced from 0.014% per cycle to 0.005% per cycle and the shift in charge voltage (due to polarization) was reduced from 39mV to 19mV through 50 cycles.

Introduction

There is a constant drive to improve the specific energy and energy density of the state-of-the-art lithium ion battery. Improvements can be made by either choosing a cathode material that operates at a higher potential or has a higher specific capacity. A promising cathode material that operates at higher potentials is lithium cobalt phosphate ($LiCoPO_4$ or LCP). LCP operates at 4.8V (vs. Li/Li^+) and has a specific capacity of 167 mAh g^{-1}, resulting in a specific energy of ~802 Wh kg^{-1}. Even though Co is often considered an expensive element, LCP is expected to be cheaper than all commercialized Li-ion batteries on the market (due to the improved energy density). Howard et al. estimated the cost of 18650-sized cells and determined that LCP could generate 7.04 Wh $\$^{-1}$ while $LiCoO_2$ (LCO), $LiNi_xCo_yAl_zO_2$ (NCA), and $LiFePO_4$ (LFP) could generate only 6.08, 5.05 and 6.31 Wh $\$^{-1}$, respectively (1). Brutti et al. also estimated the energy cost of 18650-size cells to be 142 \$ kWh^{-1} for LCP while LCO, NCA and LFP were 198, 158 and 158 \$ kWh^{-1}, respectively (2).

Although the economic benefits of LCP are encouraging, the cycling performances of LCP-based batteries have been very poor. One approach for improving the poor cycling performance is through the use of high voltage additives (3-4). This approach, however, does little to stabilize the cathode material itself and is only meant to protect the electrolyte from perpetual oxidation during cycling. Another approach for improved performance with LCP is by Fe-substitution. Our group has previously demonstrated that Fe-substituted LCP ($LiCo_{1-x}Fe_xPO_4$ or LCFP), displays significantly better cycling performance than LCP and is able to cycle in excess of 500 cycles when using an electrolyte with a high voltage additive (5-6). LCP is naturally electronically insulating and thus requires an extended constant voltage (CV) charging step (at 5.0V) to ensure a full charge is obtained. This CV step often leads to irreversible electrolyte decomposition and the formation of a high impedance passivation layer on the cathode surface. The introduction of Fe into the LCP structure, however, improves the bulk ionic and electronic conductivity and requires less CV charging, thus reducing the electrolyte decomposition (7). Substitutions of additional materials into the LCFP structure (i.e., s-LCFP) have further improved the performance of the material, resulting in a higher specific capacity and improved Coulombic efficiency (CE) (8). In this study, the electrolyte was optimized to improve the performance of the s-LCFP cathode. The optimized electrolyte enables an improved cycle life by utilizing an electrolyte additive that promotes a low resistance passivation film on the surface of the cathode that prevents perpetual electrolyte decomposition.

Experimental

Ethylene carbonate (EC), ethyl methyl carbonate (EMC), fluoroethylene carbonate (FEC) and dimethyl carbonate (DMC) were purchased from BASF and used as received (< 15ppm H_2O). Lithium hexafluorophosphate ($LiPF_6$, Morita Chemical) was used as received. Tris-hexafluoro-isopropyl phosphate (HFiP) was obtained from Argonne National Lab (ANL) and sublimed prior to use (9). The electrolyte mixtures were prepared in an argon-filled glove-box (O_2 < 10ppm, dew point < -70°C). Two baseline electrolytes were considered for this test, the standard baseline (STD, 1M $LiPF_6$ in 3:7 wt% EC:EMC) and an FEC-based standard (FEC-STD, 1M $LiPF_6$ in 1:4 wt% FEC/DMC). The additives (HFiP and ARL1) were added to the STD (2 % by weight).

The substituted lithium iron cobalt phosphate (s-LCFP) cathode contained 76% active LCFP, 10% binder (Kynar 761), 7% Super P-Li (Timcal), 3% CNT (Cheaptubes), and 4% carbon black (Alfa Aesar). Lithium metal (negative electrode) was purchased from FMC Lithium and stored in a desiccator in the dry room (dew point < -60°C). Electrochemical testing was performed with 2032 coin cells with Al-clad cans (Hohsen) on the positive side with cathodes and lithium anodes measuring 1/2” and 9/16”, respectively, and a ceramic coated polyethylene separator (Asahi). Charge-discharge cycling and dQ/dV data was collected using a Maccor Series 4000 battery cycler at C/10 for a single formation cycle, then C/3 for the remaining cycles. The cells were galvanostatically charged to 5.0 V (vs. Li/Li^+), held at 5.0 V until the current < C/20 (CV step), then discharged to 3.6 V. All testing was performed at 25°C.

Results

Cycle Life/Fade Rate Analysis

Neat LCP, with a discharge voltage of 4.8V, is highly oxidizing toward electrolytes and has not been demonstrated to cycle well to date. Even with high voltage electrolytes (Figure 1), neat LCP fades very rapidly due to severe impedance buildup on the cathode and thus substantial cell polarization. The iron-substituted LCFP, shown in Figure 1, displays markedly better cycling performance due to less electrolyte decomposition. The addition of a high-voltage additive (HFiP) further improved the performance of the LCFP cathode. To further improve the performance of the LCFP cathode, the electrode was substituted with various materials (Figure 1). The s-LCFP displays significant improvements in cycling performance over LCP and both a capacity and efficiency improvement of LCFP (8).

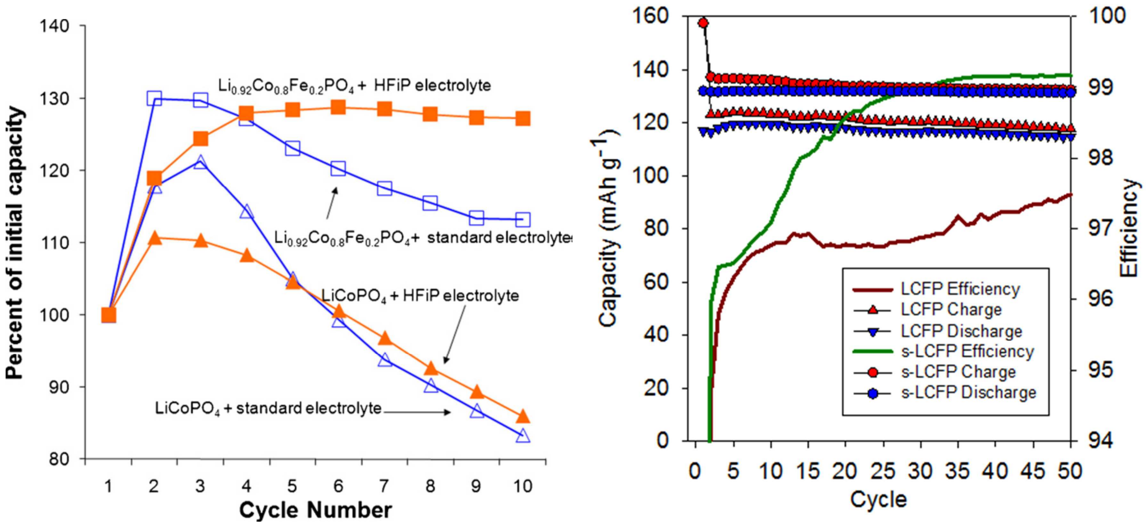

Figure 1. Cycle life/fade rate of (a) LCP and LCFP with and without HFiP (5) and (b) substituted LCFP cathode with STD electrolyte.

Various electrolyte mixtures and additives were tested in order to optimize the electrolyte for improved cycle life (Figure 2). The baseline STD electrolyte had an initial (3rd cycle) and final (100th cycle) capacity of 131.6 and 129.9 mAh g^{-1}, respectively, resulting in an overall fade of 1.42%, or a fade rate of 0.0147% per cycle. The FEC-STD electrolyte had a much higher initial capacity of 138.6 mAh g^{-1}, but faded 8.89% (0.0916% per cycle) to a final capacity of 126.3 mAh g^{-1}. Although the capacity increase is beneficial in short cycle life applications, the reduced fade rate means the FEC-STD would reach 80% capacity retention after ~200 cycles compared with ~1400 cycles for the baseline STD. Due to poor fade rate of the FEC-STD, HFiP and ARL1 additives were added to the baseline STD only to investigate any improvements to the fade rate. The STD electrolyte with 2% HFiP displayed the highest initial capacity of 139.7 mAh g^{-1} with a final capacity of 134.5 mAh g^{-1}. The fade of the HFiP electrolyte, however, was 3.69% with a fade rate of 0.0381% per cycle, roughly double the fade rate of the STD electrolyte which would result in a fade to 80% capacity retention after ~500 cycles. The STD electrolyte with 2% ARL1 displayed the lowest initial capacity of 129.4 mAh g^{-1}, but had the best fade rate (0.49%, 0.0051% per cycle) with a final capacity of 128.8 mAh g^{-1}. With a fade rate of ~0.005% per cycle, the ARL1-based electrolyte could theoretically be cycled over 4,000 cycles and still maintain 80% capacity retention.

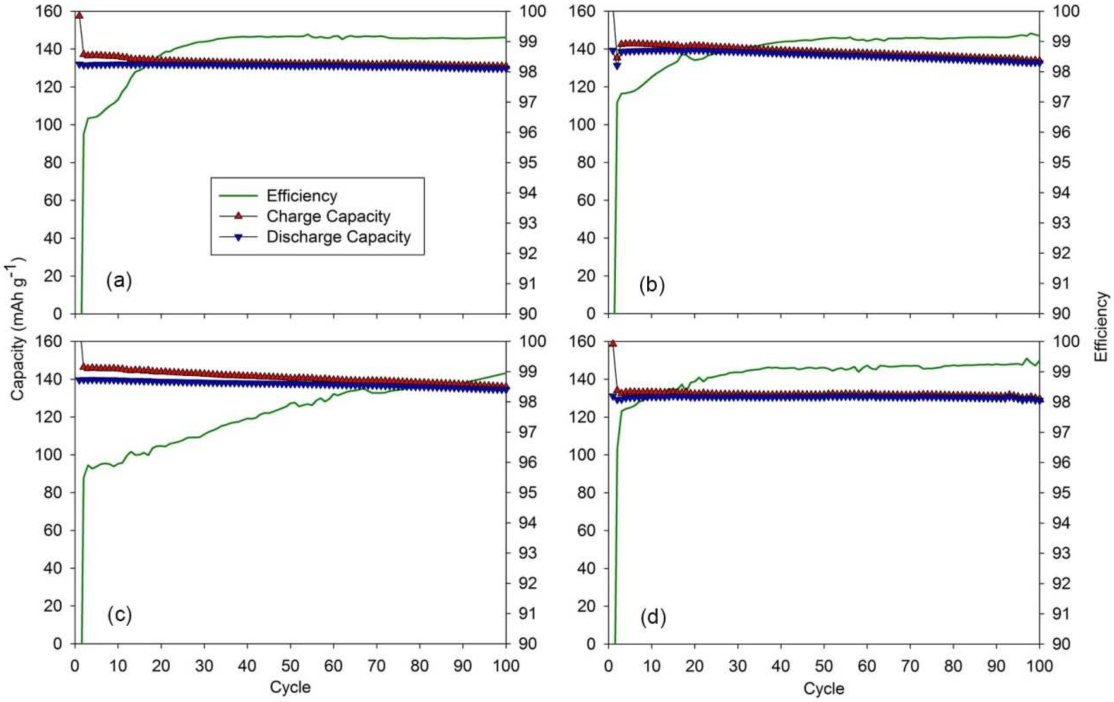

Figure 2. Capacity and efficiency of s-LCFP/Li half cells with (a) STD, (b) FEC-STD, (c) STD+2% HFiP and (d) STD + 2% ARL1

The CE is highly important when analyzing the performance of the electrode and electrolyte materials as the dissolution of transition metals from the cathode and decomposition of the electrolyte are irreversible processes that will result in a decreased cycling efficiency. The first cycle efficiency is important as this typically indicates the irreversible decomposition of the electrolyte to form a passivation layer on the electrode surfaces. The first cycle CE of the electrolytes were 83.8%, 85.1%, 82.1% and 82.7% for the STD, FEC-STD, STD+HFiP and STD+ARL1 electrolytes, respectively. The electrolyte containing the high-voltage additives had a lower first cycle efficiency due to the additive decomposition to form a passivation layer. The efficiency of the STD+ARL1 electrolyte increased immediately to 97.8% by the 4th cycle, while the other cells were 96.5%, 97.2% and 95.8% for the STD, FEC-STD and STD+HFiP electrolytes, respectively. The final efficiency of the cells were 99.1%, 99.1%, 98.9% and 99.4% for the STD, FEC-STD, STD+HFiP and STD+ARL1 electrolytes, respectively. The CE values indicate that the STD+ARL1 electrolyte forms a highly stable passivation layer in the first few cycles that promotes a stable cycling with a very small fade rate.

Cell Polarization

To further investigate the electrolyte stability with the s-LCFP cathode, dQ/dV plots were made with the first 50 cycles plotted (Figure 3). The first cycle of each cell shows an oxidation peak at ~4.5 V, attributed to the irreversible oxidation of the electrolyte in which a passivation layer is formed (Figure 1 insets). After the formation cycle, the cells are cycled and their oxidation/reduction peak position is indicative of the stability of the system; stable cycling without significant polarization/impedance buildup would yield a dQ/dV plot with perfectly overlapping redox peaks. The baseline STD electrolyte begins to polarize after a few cycles and from cycles 2-50 the charging voltage has shifted 39mV while the discharge voltage has shifted 36mV. The FEC-STD electrolyte had a voltage shift of 36mV and 48 mV and the STD+HFiP electrolyte had a voltage shift of 31 mV and 27 mV for the charge and discharge, respectively. In contrast with these electrolytes, the STD+ARL1 dQ/dV plot indicates only a 19mV shift in the charging voltage and a 22mV shift in the discharge voltage. These results agree with the cycling/fade rate analysis and suggest the presence of ARL1 forms a stable, low impedance passivation layer that limits cell polarization and improves the cycle life of the s-LCFP cathode.

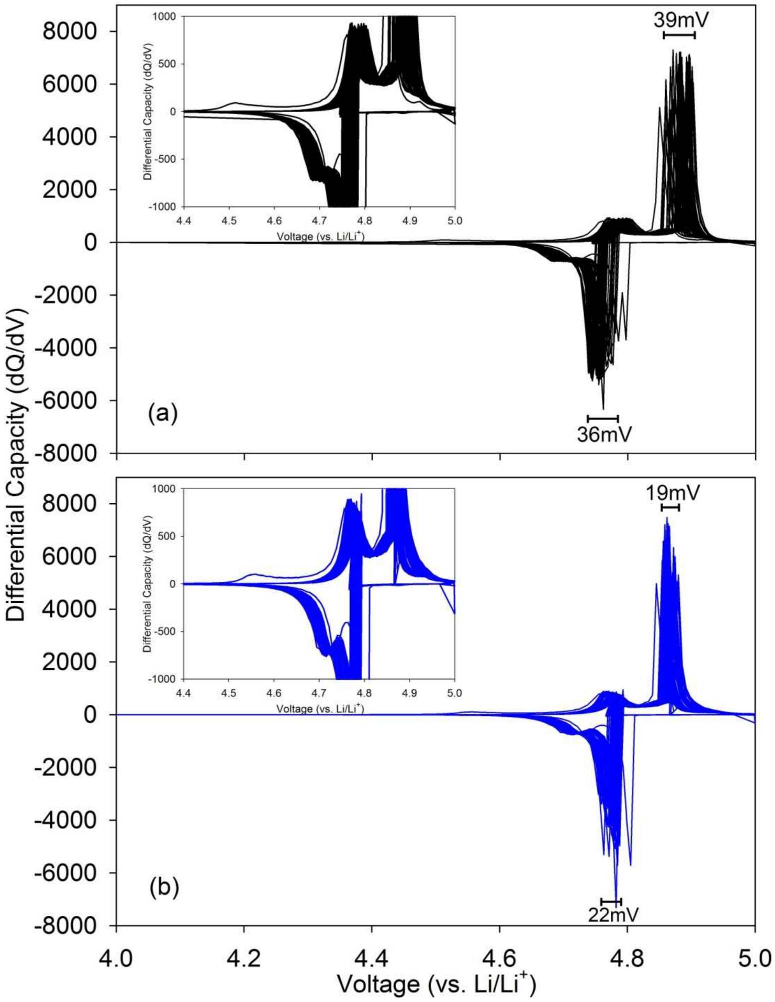

Figure 3. Differential capacity (dQ/dV) plot of (a) the STD electrolyte and (b) the STD-ARL1 electrolyte. Insets show passivation layer formation (first cycle dQ/dV).

Conclusions

The performance of LCP and LCFP cathodes has been drastically improved recently through various substitutions of the transition metals. In order to utilize the s-LCFP in a battery, the electrolyte must be optimized in order to form a protective passivation layer that improves the cycle life and fade rate while minimizing the passivation layer impedance and thus reducing the cell polarization. While the STD electrolyte performs well with an initial capacity of 131.6 mAh g^{-1} and a fade rate of 0.0147% per cycle, the addition of 2% ARL1 additive improves the fade rate to only 0.0051% per cycle with a comparable initial capacity of 129.4 mAh g^{-1}. Although the FEC-STD and STD+HFiP displayed a higher initial capacity (138.6 mAh g^{-1} and 139.7 mAh g^{-1}, respectively), their fade rate was larger than the STD electrolyte (0.0916% and 0.0381% per cycle, respectively). The CE of the cells suggests they all form relatively stable passivation layers that enable long-term cycling with a final cell efficiency of 99.1%, 99.1%, 98.9% and 99.4% for the STD, FEC-STD, STD+HFiP and STD+ARL1, respectively.

The differential capacity indicates that the passivation layer that forms on the cathode for the STD, FEC-STD and STD+HFiP cells are more resistive; therefore, the cells tend to polarize more. The charge and discharge voltage of the STD+ARL1 cell shifted 19mV and 22 mV, respectively, while the other cells shifted 39mV, 36mV and 31mV for the charge and 36mV, 48mV and 27mV for the discharge (STD, FEC-STD and STD+HFiP, respectively). The reduced impedance of the STD+ARL1 passivation layer leads to the improved fade rate of the cell and enables the long term cycling of the s-LCFP cathode. Although the FEC-STD did not perform the best, the s-LCFP material is compatible with FEC at high potentials and thus may be used with Si-containing anodes (which rely heavily on FEC for surface stabilization) for higher specific energy cells.

Acknowledgments

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