Demonstration of Room Temperature Secondary Fluoride Battery System

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Fluoride based secondary battery systems offer the potential for improved consumer and environmental safety. Previous studies have demonstrated intercalation of fluoride ions, F-, into graphite by both chemical and electrochemical means [1]. Other work on high temperature metal-fluoride | metal batteries have demonstrated the potential of secondary fluoride ion battery (FIB) systems over large temperature ranges [2]. This study demonstrates a room temperature lead-fluoride – polyaniline (PANI) secondary battery system.

The performance of FIB systems depends on the formation of a solid-electrolyte interphase (SEI) that selectively conducts fluoride ions at the exclusion of other negative ions. SEI formation in FIB systems, similar to lithium-ion systems, is a function of the decomposition of electrolyte and electrode components [1]. SEI formation can be both instantaneous and grow as function of cycle life. We propose to study the performance of a model room temperature lead-fluoride battery system with additives to study the mechanism of SEI formation. The two additives, (Additive A and Additive B) were chosen in hopes of understanding the polymerization of decomposed electrolyte and electrode components, which form the SEI. Fourier transform infrared absorption spectra (FTIR) was used to study effects of additives on the composition of the SEI.

Coin cells were made to examine the effects of additives in the FIB. The electrolyte used was 1M KPF_6 in acetonitrile (ACN). The anode was PbF_2 70wt%, 20% binder (polyvinylidene difluoride, PVDF) and 10% conducting diluent (super P) while the cathode was PANI 80 wt%, 10 wt% binder (polytetrafluorine, PTFE) and 10 wt% conducting diluent (Super P). Each coin cell with different additives was cycled for 25 cycles on Arbin cycler from 0.01V to 2.9V at a charge/discharge rate of 25μA. The cycling data shows that the addition of additive A had significant improvements in the coin cell performance. Cell components were washed with ACN and dried in vacuum overnight before the FTIR measurements.

All three cells demonstrate cyclability but each cell's discharge capacity decreases to different discharge capacities after 25 cycles (Figure 1). Additive A demonstrated the least %decrease in discharge capacity with increasing cycles. All three cells have an initial increase of discharge capacity, and this may correlate with the formation of the SEI layer that improves cyclability.

FTIR spectra of the cycled coin cells provide insight into the composition of the SEI. The FTIR spectra of the anode material (PbF_2), Figure 2, displays a broad O-H peak around 2700-3200 cm^{-1} for all samples indicative of possible oxygen contamination. Distinctive peaks around 1680-1500 cm^{-1} are associated with alkenes and N-H bond that are found in anodes and cathodes suggest the breakdown of ACN electrolyte. Observed C-F peaks were assigned to the binder material (PVDF) and reacted conducting diluent.

The FTIR spectra for the cathode materials (PANI) displayed common C-F peaks (1150 cm^{-1}) and C-N peak (1250 cm^{-1}). Observed C-F peaks were assigned to the binder material (PTFE) and reacted conducting diluent. The Additive A displayed more pronounced C-N peak and S-H peak (2550 cm^{-1}). The C-N peak is associated with the decomposition of the acetonitrile (ACN) electrolyte. No O-H peaks were observed in any of the cathode samples.

These results suggest that additives can be used to control polymerization of the SEI layer. The absence of significant O-H peaks in the cathode samples indicates that the oxygen is mobile and is preferentially deposited in the SEI of the anode. We attribute the loss in discharge capacity to the SEI composition and growth with cycling.

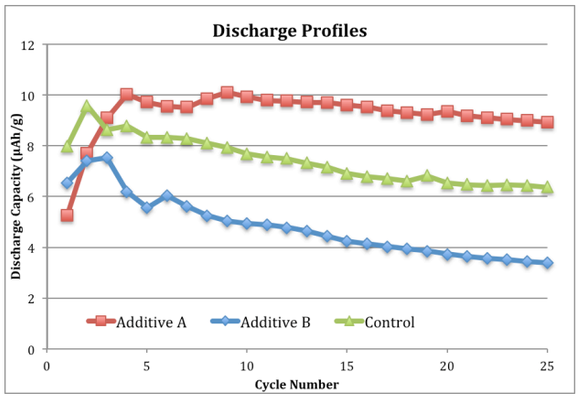

Figure 1. Cycling results of PbF_2/PANI coin cells (control), treated with Additive A and Additive B.

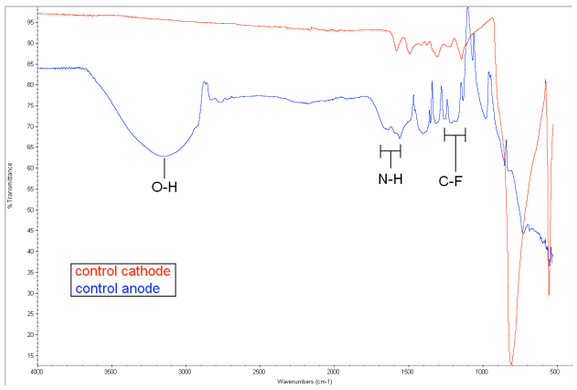

Figure 2. FTIR of cycled anode material (PbF_2) and cycled cathode material (PANI).

References

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2. M. Reddy and M. Fichtner, *J. Mater. Chem.*, 2011, **21**, 17059-17062