LITHIUM AND SODIUM POLYMER ELECTROLYTE BATTERIES

FINAL REPORT
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James McBreen

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**DEPARTMENT OF APPLIED SCIENCE
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INTRODUCTION

The BNL/Moltech CRADA was focused on the processing, construction and characterization of the components and cells of lithium polymer batteries and sodium polymer batteries. Component work included cathodes based on organic and inorganic active materials, ion conducting polymer films and new lithium salts. Moltech processed components, and assemble and tested cells. BNL facilities were used by Moltech personnel to characterize components and test cells. Component characterization included conductivity measurements, electrochemical characterization, thermal analysis and the use of various spectroscopies. Cell testing involved mostly cycling, performance tests and teardown analysis. Most of the work was on polymer cathode materials, polymer electrolytes and salts and additives for polymer electrolytes.

MATERIALS AND COMPONENT EVALUATION

A. Cathode Development

Poly(carbon disulfide) cathodes: Poly(carbon disulfide) (PCS), a high charge density cathode material, was synthesized at BNL. The material was evaluated at Moltech in rechargeable lithium cells. The results were very promising. An excess of 200 deep cycles was achieved. Typical charge/discharge curves are shown in Figure 1.

Poly(carbon disulfide) was also studied by cyclic voltammetry using glassy carbon and platinum macro- and microdisk electrodes. The charge transfer kinetics was significantly faster at glassy carbon electrodes than at Pt electrodes. The results were in good agreement with battery testing data.

Poly(carbon disulfide) is a complex material of unknown structure. In an effort to elucidate aspects of the electrode mechanism, a model compound poly(ethyleneglycol dixanthate) was also

prepared at BNL and evaluated at Moltech. The results indicated that in the model compound each $(CS_2)_2$ unit acts independently whereas in PCS they do not.

The compound [1,2] dithiolo [4-3-c]-1,2-dithiole-3,6-dithione was also evaluated as a cathode in polymer electrolyte lithium cells. Typical cycling results are shown in Figure 2.

Modified Manganese dioxides: Several manganese dioxide cathodes were prepared with additions of other transition metal oxides. The most promising results were obtained with the composition 90% MnO_2 -10% Cr_2O_3 . The additions of chromium oxides enhanced the reversibility and high rate capability of the electrodes.

Cathode binders: A cathode binding material, oxymethylene linked poly(oxyethylene) was synthesized at BNL. Tests at Moltech showed promising results. This material was also used as a polymer matrix for new lithium salts described below.

B. Electrolyte Development

Siloxane based electrolytes: In their battery tests, Moltech has used an electrolyte, poly(methylsiloxane) grafted with heptaethylene glycol monomethyl ether side chains. This electrolyte, which has a conductivity of $\sim 10^{-4}$ S/cm at 25°C, was developed at BNL. During the year Moltech and BNL collaborated on methods to further improve the conductivity of polymer electrolytes.

Modified carbonate plasticizers: Moltech evaluated several new modified carbonate plasticizers that were developed at BNL. One of these new type of plasticizer is a modified carbonate (MC3) made by attaching three ethylene oxide units to the 4-position of ethylene carbonate, has been synthesized. The ionic conductivity of a polymer electrolyte using this type of plasticizer in a poly(ethylene oxide) (PEO)- $LiCF_3SO_3$ complex was been studied. Adding 50% of this plasticizer by weight of PEO to the PEO- $LiCF_3SO_3$ complex, yielded an ionic conductivity of 5×10^{-5} S/cm at 25°C, which is two orders of magnitude higher than that found for a PEO- $LiCF_3SO_3$ electrolyte

without a plasticizer, and one order of magnitude higher than that found when using propylene carbonate (PC) as a plasticizer. The temperature dependence of the conductivity and thermal analysis results indicate that this new plasticizer increases the ionic conductivity throughout the entire complex system, whereas conventional plasticizers, like PC, simply create a high conductivity pathway through the plasticizer itself. The new plasticizer also enhances the ion pair dissociation which in turn improves the ionic conductivity.

Fluorinated sulfonate aromatic lithium salts: A series of new fluorinated sulfonate aromatic lithium salts were synthesized at BNL. The anions were designed to delocalize the negative charge over conjugated electronic structures so as to promote ion dissociation. The anions were 2,4 - bis(trifluoromethylsulfonyl) pyrrole, 2,5 -bis(trifluoromethylsulfonyl) pyrrole, 2,4,6 - tris(trifluoromethylsulfonyl) phenol, and p-trifluoromethylsulfonyl phenol. Cyclic voltammetry revealed that all these salts had a potential stability window close to 5 V vs. lithium, with the bis-substituted pyrrole salts having a slightly smaller potential window than the phenolate salts. All salts had good conductivity in THF with the tri-substituted phenolate showing the highest conductivity.

Figure 1. Charge discharge curves for a lithium polymer electrolyte cell with a poly(carbon disulfide) cathode. Cycle numbers are indicated on the Figure.

Figure 2. Charge discharge curves for a lithium polymer electrolyte cell with a [1,2] dithiolo [4-3-c]-1,2-dithiolo-3,6-dithione cathode. Cycle numbers are indicated on the Figure.