



Integrating Structure with Power in Battery Materials

by James F. Snyder, Robert H. Carter, and Eric D. Wetzel

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*A reprint from the Proceedings of the 2004 Army Science Conference,
Orlando, Florida, 29 November – 2 December 2004.*

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14. ABSTRACT This report is a reprint from the <i>Proceedings of the 2004 Army Science Conference</i> at Orlando, Florida, in 2004. We have developed a multifunctional material concept that combines structural performance with power generation. Such devices would replace inert structural components in U.S. Army systems, such as a ground vehicle body or a soldier's helmet, and simultaneously provide supplementary power for light load applications. The emphasis of our research is two-fold. We are developing structural polymer electrolytes that exhibit desirable ion conductivity, and we are researching augmentation of overall mechanical properties in polymer based power generating devices.					
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INTEGRATING STRUCTURE WITH POWER IN BATTERY MATERIALS

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1. Abstract

We have developed a multifunctional material concept that combines structural performance with power generation. Such devices would replace inert structural components in U.S. Army systems, such as a ground vehicle body or a soldier's helmet, and simultaneously provide supplementary power for light load applications. The emphasis of our research is two-fold. We are developing structural polymer electrolytes that exhibit desirable ion conductivity, and we are researching augmentation of overall mechanical properties in polymer based power generating devices.

2. Background

Many Army applications require lightweight structural materials. In addition, more weight efficient power generating devices are needed to support the increasing integration of electronic technology into military systems. Current generation batteries add significant bulk and weight to the overall load of the soldier. Much of the remaining load is comprised of inert constituents that provide only structural functionality. Lightweight supplemental battery devices that are seamlessly integrated into existing structural components, simultaneously providing power and carrying static loads, would reduce dependence on traditional batteries and make the Future Force Warrior more agile and survivable. In order to develop such a multifunctional battery, the electrolyte material must be optimized for both the electrochemical performance and the structural properties. Ion conductive polymers are an ideal medium since they can be modified to exhibit a range of mechanical properties and can be cast into thin films while maintaining acceptable limits of ion diffusion.

3. Toughened Electrolytes

3.1 Approach

We are currently exploring two primary routes to enhance polymer electrolyte stiffness and toughness. The first method concentrates on the polymer chemistry, and specifically on developing thermoset resins (Vondrak et al., 1999). Thermoset resins may be

synthesized from monomers with a wide range of functionality and often provide for convenient handling prior to cure. We have chosen to focus our study on resins that include oligo (oxyethylene) units owing to the known ion conductive properties of poly (ethylene oxide), PEO, and the ease with which lithium salts may be dissolved into PEO oligomers. The desired balance between mechanical and electrochemical properties has led us to research partially crosslinked polymer electrolyte matrices that combine monofunctional and difunctional resin monomers, as well as interpenetrating networks of difunctional resins and linear PEO. Table 1 lists some of the polymer materials currently under scrutiny. Ethoxylated bisphenol-A diacrylates are considered as a crosslinking agent owing to the variable number of ion-coordinating ethylene oxide units, indicated in parentheses, which are evenly distributed on either side of the central rigid bisphenol unit. Lithium trifluoromethane-sulfonate (triflate) is used as the lithium salt owing in part to its thermal and electrochemical stability.

The second route of polymer electrolyte development utilizes the reinforcing properties of ceramic fillers and fibers and is also summarized on Table 1. Ceramic fillers have been demonstrated to boost the mechanical and interfacial properties of polymer electrolytes as well as improve the conductivity, the latter owing in part to the plasticizing effect of small particles (Scrosati et al., 2001). Much less attention has been devoted to optimizing the combined effects on structure and ion diffusion through the addition of electrically resistive fibers, although nanoscale alumina whiskers have been shown to have a positive effect on mechanical and electrochemical properties while also preventing microscale cracks (Wen et al., 2002).

Testing of the materials represented by Table 1 involves quantifying the ionic conductivity and mechanical properties of each sample. Indentation techniques have been chosen as a quick test to give a qualitative measurement of the elastic modulus of the material. The samples with the best combination of stiffness and lithium ion conductivity are downselected and subjected to dynamic mechanical analysis (DMA) to give a more quantitative measurement of the elastic properties.

Table 1.

Crosslinking Agent (Diacrylate)	PEO/PEG Matrix		Salt	Filler Reinforcement	
	Comb (Monoacrylate)	Linear		Fiber	Particle
PEG 600	PEO 350 Acrylate	PEO 200k	LiOTf	Glass, Silica	Silica
Ethox. (30) Bis-A	PEO 550 Acrylate	PEO 1,000k		Alumina	Alumina

3.2 Experimental

Chemicals were handled in a glove box under dry nitrogen. Lithium triflate was purchased from Sigma Aldrich Chemical Company and dried for 12 hours under vacuum at 180 °C. Monomer samples, received from Sartomer Company, Inc., were mixed thoroughly with the appropriate amount of lithium triflate in a glass vial. Dissolution of the salt was aided by briefly heating the vial up to 80 °C. 1.5 wt% initiator (Trigonox) and 1 wt% dimethylaniline were stirred into the vial at room temperature. The resulting solution was poured into a pellet shaped rubber mold and heated under nitrogen to 80 °C for 12 hours, followed by 100 °C for 1 hour, and then allowed to cool to room temperature. The cured pellets were painted on both sides with quick drying silver paint and further heated to 80 °C under vacuum for 12 hours to remove residual solvent and water.

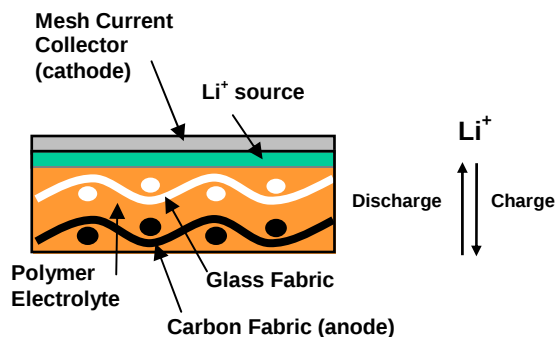
Conductivity values were calculated from data collected through impedance spectroscopy. It was found that conductivity was optimized at 6-9 wt% salt for the resins in Table 1. Ethoxalated (30) bisphenol-A has the highest conductivity of Sartomer's difunctional resins, with a maximum of 2×10^{-6} S/cm at 9 wt% salt. Conductivity values 20 times higher were measured for PEG 550 acrylate, which is very soft. Blends of monofunctional and difunctional monomers are being developed to create materials with both high conductivity and robust mechanical properties. Elastic modulus values for initial blend formulations, as measured by indentation, have been 0.1-0.01 GPa.

Limited studies have also been conducted using silica particles as additives. Addition of 10% silica has been found to have a five-fold increase in modulus with an accompanying 75% reduction in conductivity. Addition of 20% silica has a ten-fold increase in modulus. Further experimentation is underway.

4. Battery Design

In addition to developing electrolyte materials, our research focuses on improving the overall structural properties in power source devices. In particular, we are designing configurations to optimize the overall structural efficiency of battery devices that may replace inert structural components. Figure 1 shows a generic representation of how this might be accomplished using a

carbon fiber anode. In this structure, the polymer electrolyte serves as the matrix phase in the structural composite. This design requires the electrolyte to possess both good mechanical properties, to enable load transfer to the reinforcing fibers and metal mesh, and good ionic conductivity, for acceptable power density. The carbon fiber reinforcement serves multiple purposes. As an anode material, it intercalates the lithium ions and conducts electrons out of the cell. As a reinforcement material, the high stiffness and strength of the carbon fibers greatly enhances the structural capacity of the composite. A layer of glass fabric is also included in the design, to ensure electrical isolation of the anode and cathode, improve mechanical properties, and possibly enhance the ion conductivity of the electrolyte.

**Figure 1.**

5. References

- [1] Vondrak, J., Sedlarikova, M., Reiter, J., and Hodal T., 1999: Polymer gel electrolytes for electrochromic devices, *Electrochim. Acta*, **44**, 3067-3073.
- [2] Scrosati, B., Croce, F. and Panero, S., 2001: Progress in lithium polymer battery R&D, *J. Power Sources*, **100** (1-2), 93-100.
- [3] Wen, Z., Wu, M., Itoh, T., Kubo, M., Lin, Z., and Yamamoto, O., 2002: Effects of alumina whisker in (PEO)(8)-LiClO₄-based composite polymer electrolytes, *Solid State Ionics*, **148**, 185-191.

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