



## **Combining Structure and Power in Battery Materials**

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

**ARL-RP-189**

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| <b>14. ABSTRACT</b><br>This report is a reprint of a paper published in <i>Proceedings of the American Chemical Society Division of Polymeric Materials: Science &amp; Engineering (PMSE Preprints)</i> by the American Chemical Society in Fall 2004.<br>Many current applications demand lighter and stronger structural materials. In addition, more weight efficient power generating devices are needed to support the increasing integration of electronic technology into everyday systems. A multifunctional concept for material development will be presented that combines structural performance with power generation. Such devices would replace inert structural components in common items, such as a vehicle shell, and simultaneously provide supplementary power for light load applications. Particular focus is on the development of polymer electrolyte membranes which exhibit an efficient combination of structural and electrochemical properties. A greater emphasis is placed on structure than is generally seen in the literature. We will present several routes that are underway in our lab to accomplish this goal, including development of fast ion conductive rigid polymers; ion conductive resins or resin scaffolds filled with amorphous polymer; and blending inorganic fibers and fillers with amorphous polymer electrolytes. |                         |                                  |                                              |                                                                   |                                                                    |
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# Combining Structure and Power in Battery Materials

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## INTRODUCTION

Many applications have come to demand lighter and stronger structural materials. In addition, more weight efficient power generating devices are needed to support the increasing integration of electronic technology into everyday systems. We have developed a multifunctional concept for material development that combines structural performance with power generation. Such devices would replace inert structural components in common items, such as a vehicle shell, and simultaneously provide supplementary power for light load applications. The emphasis of our research is twofold. 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.

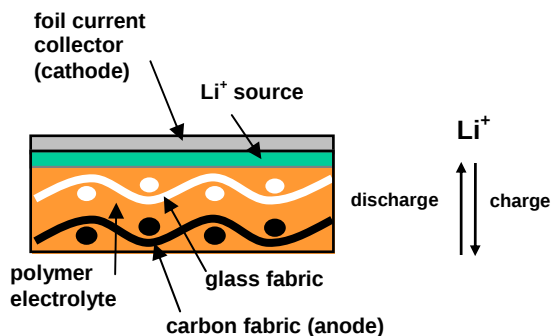
In order to develop an electrolyte membrane as described above, the material must be optimized for both the electrochemical performance and the structural properties. Ion conductive polymers are an ideal medium since they can be modified to exhibit a range of mechanical properties and can be cast into thin films while maintaining acceptable limits of ion diffusion. Significant focus in the literature has been to improve electrochemical performance while maintaining reasonable mechanical properties such that the electrolyte membrane can act as a separator between the electrodes.<sup>1</sup> Less attention has been given to providing enhanced structural properties to the membrane. This is due in part to the dependence of ion diffusion on polymer mobility in solvent-free polymer electrolytes,<sup>2</sup> and to the need for properties conducive to solvent management in gel polymer electrolytes. Interest in flexible membranes for thin film battery devices has also diverted attention from tough, rigid materials towards electrolytes with elastomeric properties.

We are exploring several routes to enhance polymer toughness. The first approach, which will be described in this paper, is to investigate polymer-salt complexes that include reinforcing fibers and fillers. 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.<sup>3</sup> 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.<sup>4</sup> We have seen no exhaustive experiments reported in the literature characterizing mechanical properties for polymer electrolytes with electronically resistive fiber reinforcement.

The second approach involves nanocomposites of conductive, rigid regions with conductive, amorphous regions. Rigid materials include the polymer systems described above as well as resins<sup>5</sup> or glassy polymers<sup>6</sup>. The amorphous regions may include polymer electrolytes with phosphazene<sup>7</sup> or siloxane<sup>8</sup> backbones. Solid materials such as glasses remain too brittle for use monolithically in thin films, while highly amorphous electrolytes tend to be too fluid for use in structural applications. A related approach is development of block copolymers that include highly conductive and highly structural regions.

The third route to structural electrolytes involves rigid solvent-free polymer electrolytes that exhibit fast ion conduction that is decoupled from polymer segmental motions. Decoupled ion transport has been previously described in polymer-in-salt type electrolytes<sup>9</sup> and certain polymerized solvents<sup>10</sup>, although a desirable balance of mechanical properties and conductivity has not been reported.

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



**Figure 1.** Schematic of a lithium-polymer battery employing carbon fiber and glass fabric as structural reinforcement.

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 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.

## EXPERIMENTAL

**Materials.** All reagents were used as received without further purification. Poly(ethylene glycol) was purchased from Aldrich. Lithium trifluoromethane sulfonate (lithium triflate) was purchased from Alpha Aesar. Woven E-glass fiber was supplied by Hexcel Schwebel. The fiber mesh was either used intact or cut into 1-10mm random length unwoven fibers. Solid glass spheres of E-glass, Spherglass product 3000E, were supplied by Potters Industries Inc.

**Method.** Polymer-salt complexes were prepared by heating 10 g of poly(ethylene glycol), MW 2000, to 100 °C under vacuum until the resulting liquid was visibly degassed, evident by a cessation in gas evolution by bubbling. The flask was then backfilled with air and 3 g of lithium salt, or 0.165 g of reinforcement, were added. The mixture was stirred then melt-cast into rubber molds. In the case of woven fiber mesh reinforcement, the mesh was cut to the dimensions of the mold and molten PEG was poured around it such that the mesh was completely enveloped by polymer. The samples were further heated at 100 °C for 24 hours under vacuum and then allowed to slowly cool to room temperature within the oven. Contact with air was minimized at all times.

## DISCUSSION

The studies reported here provide a baseline through which to gauge the utility of using various mechanical reinforcements in polymer electrolytes. Poly(ethylene glycol) (PEG) 2000 was chosen as a starting point for this study owing to its ease of handling, particularly above the melting point at 60°C. We have also starting using PEO 200,000 in similar studies. Bulk PEO is about 60% crystalline and 40% amorphous at room temperature. It is the amorphous regions in PEO and PEG that are suitable for long-range ion diffusion.

Table 1 provides the composition for several of the samples. Glass was chosen as the initial structural material owing to its known reinforcing abilities. Since E-glass is not an appreciable ion conductor, it is expected that any change in ion diffusion by the introduction of glass will be due to changes in polymer morphology or to regions of glassy barriers. It is known that very small ceramic beads help to reduce regional polymer crystallinity and therefore to improve ion conductivity. Limited data suggests that nanoscopic fibers may play a similar role. Electrochemical tests are underway on samples 1-6.

**Table 1. Poly(ethylene glycol) 2000 Prepared With Mechanical Reinforcement**

| Sample | Salt        | Reinforcement        |
|--------|-------------|----------------------|
| 1      | None        | None                 |
| 2      | None        | Glass fiber, woven   |
| 3      | None        | Glass fiber, chopped |
| 4      | None        | Glass beads          |
| 5      | Li Triflate | None                 |
| 6      | Li Triflate | Glass fiber, woven   |

While the fillers employed in Table 1 have unknown effects on ion diffusion, the mechanical properties are expected to improve from that of neat PEG or PEG + Li triflate. This was found to be the case such that samples 2-4 are noticeably more resistant to fracture than sample 1. Visual inspection indicates that the most fracture resistant salt-free sample is sample 3, in which cut fibers were evenly distributed through the polymer matrix. Sample 2 was also found to be very fracture resistant around the woven fiber, but inhomogenous fiber distribution resulted in weaker mechanical properties elsewhere. Introducing glass beads in sample 4 was found to reduce brittleness of the polymer as well, although to a lesser degree than by introduction of fibers. Mechanical analyses are underway to quantify the results. In addition, extensive sample development is currently underway within each of the categories defined by Table 1 in an effort to define the range with which mechanical properties may be enhanced without significant detriment to ion conductivity. The mechanical properties associated with each sample are expected to improve as long-range order of the filler improves, and as homogeneity of the filler through the polymer improves.

### CONCLUSIONS

The demands on current lithium-polymer battery materials increasingly involve desirable mechanical properties as well as electrochemical properties. These demands require it to exhibit combined structural and electrochemical properties.

The samples and data reported here comprise a baseline from which we are studying the effects that fibers and particles have on structure and ion diffusion in an effort to optimize both properties for a given material. It is expected that reduced filler diameter, limited filler content, increased filler homogeneity within the polymer matrix, and higher dielectric filler material will optimize the effects on ion diffusion. Filler homogeneity and better processing are also expected to aid mechanical properties.

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