December 1, 1997

Mr. Anthony N. Ogunnaike
U.S. Department of Energy
Office of Headquarters Procurement Services
1000 Independence Avenue, S.W.
Washington, D.C. 20585

Dear Mr. Ogunnaike:

The following is my final report for the Department of Energy grant DE-FG01-94CE15581, "Develop Safe, Low-Cost Method of Manufacturing Rechargeable, High Conductivity Lithium Batteries."

Purpose and Background

The development of new energy storage systems is a crucial step for progress toward the electric or hybrid electric car, long-life batteries for portable computers, and for large-scale power storage from solar cells, wind and tidal generating systems.

The focus of much of this work is the rechargeable lithium battery, because of its high energy density, and the use of solid polymer electrolytes (SPE's) for ease of fabrication and lightness of weight. The classical solid polymer electrolyte is based on the use of salts such as lithium triflate dissolved in poly(ethylene oxide) (PEO) or poly(propylene oxide). This specific polymer electrolyte has severe limitations. Poly(ethylene oxide) is a microcrystalline polymer at 25°C, and ion migration occurs only in the 20-30% of the material that is amorphous. Useable conductivities (10^{-5} S/cm) can be achieved only when the material is heated above 80°C.

Two approaches to generate higher electrolyte conductivities at ambient temperatures are being developed. In the first, organic solvents are added to the polymer to plasticize it and dissolve the microcrystallites. This increases the conductivity but raises the possibility of fires if the battery casing ruptures during high charge or discharge conditions or when the device is punctured by impact. The alternative is to design new polymers that are good solid electrolyte media but which are completely amorphous and have low glass transition temperatures.

Such a polymer is MEEP (1) (poly[bis(methoxyethoxy)phosphazene]), first synthesized in our laboratories.

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MEEP gives conductivities at 25°C that are two to three orders of magnitude higher than comparable systems based on PEO. However, the incorporation of MEEP into thin film batteries was frustrated by the viscous, liquid-like character of this polymer which allows the electrodes to make electrical contact when pressure is applied to the battery. It was found that the crosslinking of MEEP provided dimensional stability and did not lower the conductivity.

Objectives of this Program

The main objective was to develop crosslinking methods for MEEP which could be used on a mass production scale to produce thin film rechargeable lithium batteries. A further objective was to assemble working energy storage devices to investigate the feasibility that this system could be developed commercially.

Results

The crosslinking of MEEP in the presence of dissolved lithium triflate was accomplished by two methods. In the first, the polymer electrolyte was exposed to approximately 2 Mrad of gamma rays from a ⁶⁰Co source. This procedure yielded a conductive polymer film with sufficient dimensional stability that thin films provided a good, permanent separation between the two electrodes of a thin film lithium battery. The ionic conductivity of the solid polymer electrolyte was not affected by the crosslinking process.

The second method involved exposure of MEEP/lithium triflate films to ultraviolet light in the presence of a photosensitizer such as benzophenone. This process also had no effect on the conductivity.

The choice of one method or another depended on engineering considerations. The fabrication of thin film rechargeable lithium batteries requires the use of two different electrodes per cell--a thin sheet of lithium metal (the anode) and an intercalation cathode such as titanium disulfide or manganese dioxide. Most of our work was accomplished with the use of titanium disulfide. A major source of the weakness (and failure) of batteries of this type is the poor electrical contact between the titanium disulfide and the polymer electrolyte. We addressed this problem through the incorporation of powdered graphite into the cathode layer, with the components cemented together by MEEP, which forms a continuum with the main electrolyte layer.

Crosslinking by ultraviolet light, while convenient, precludes exposure of the polymer from the titanium disulfide side, since this would shield the bulk of the polymer from the radiation. Hence, the use of UV-crosslinking required exposure from the electrolyte side group before the anode was positioned, followed by completion of the sandwich by placement of a thin sheet of lithium. All this

was accomplished in an inert atmosphere glove box.

Gamma rays can be used to crosslink the MEEP in preformed sandwich structures, but limits exist to the size of the batteries that can be processed in this way in the laboratory. However, in a continuous battery assembly production line, this method would be preferred.

Prototype batteries were assembled (see appended photograph). These varied in size from two inches square to 12 inches square. They were shielded from atmospheric moisture by polyethylene film enclosures. Seven different prototype batteries were constructed in both flat and "rolled carpet" configurations. They yielded approximately 2.8 volts with a current level of millamperes. Charge-discharge cycles were carried out to assess the long-term use stability and storage stability. The storage stability appeared to be longer than 12 months, provided oxygen, nitrogen, and moisture were excluded. The charge-discharge cycling began to deteriorate after about 20 cycles. Analysis of the electrode-electrolyte interface suggested that the fault lay in the intercalation cathode material and not at the MEEP/lithium interface.

Conclusions

Further work needs to be carried out to improve the fabrication and structure of these batteries. Newer, better analogues of MEEP are now available which either do not require radiation crosslinking in order to form stable laminates or require far less radiation treatment. However, MEEP itself will almost certainly be needed for adhesion within the cathode and to the anode. Alternative intercalation cathode materials need to be investigated. It seems clear that continuous, thin film battery assembly is now possible for these systems.

From a manufacturing point of view, a recently-formed company (Phosphazene Custom Synthesis, "PCS," in State College, Pennsylvania) has begun commercial production of the starting materials needed to produce MEEP and its analogues on a commercial scale. It is anticipated that this will stimulate commercial development of these batteries.

We very much appreciate the financial support from the Department of Energy that made this work possible.

Sincerely yours,

Harry R. Allcock
Evan Pugh Professor of Chemistry

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