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Ionicallly Conductive Polymers:
Application to Solid State Batteries

by

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Paper to be presented at
38th Meeting of International Society for Electrochemistry
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IONICALLY CONDUCTIVE POLYMERS: APPLICATION TO SOLID STATE BATTERIES

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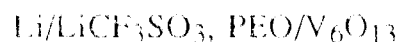
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The use of polymeric ionically conducting electrolyte materials in the fabrication of solid state batteries was proposed approximately ten years ago. Subsequently, a large number of groups have investigated a variety of polymer electrolytes, such as the polyethylene oxide complexes of various lithium salts. Independent efforts were concurrently expended on polymer electrodes, such as polyacetylene, for batteries. The feasibility of batteries of either type has been tested in a variety of research cells, and in some prototype hardware of practical size. Nonetheless, there are at present no commercially available polymer batteries of either type. A stable battery design with the ability to store and to deliver energy efficiently and economically is the prime objective of the development programs in polymeric batteries.

Most of the studies were directed toward secondary batteries with lithium anodes and insertion cathodes. One of the most widely described systems is



(1)

Similar cells with TiS_2 as the cathode, and with LiClO_4 as the salt have shown promise. These cells operate at temperatures near 100 degrees C., and may be cycled up to several hundred times.

The concept of polymer electrolyte batteries need not be restricted to anodes of lithium. For example, sodium, zinc, magnesium and calcium offer some advantages in terms of manufacturability, cost or performance. Little information on these other systems is available. Lithium remains a favored initial choice because of its well known high cell potential and low equivalent weight which yield high values for the theoretical specific energies.

The reactivity of the anodes complicates the manufacturing processes. Dry rooms or inert atmosphere glove boxes have been incorporated for the handling of lithium and sodium. The packaged battery must be hermetically sealed to prevent degradation during storage and operation. The package must withstand the elevated temperatures that have been necessary for permitting adequate ionic mobility within the electrolyte component of the cell. This requirement of high temperature operation also complicates any practical application of these batteries.

Although very specialized high energy batteries such as conceived for the traction or load levelling applications could be designed to incorporate appropriate insulation and thermal management for operation at some constant elevated temperature, the widespread commercial use of solid state batteries will only result if polymer electrolytes of high conductivity are found for the temperature range of approximately -20 to +60 degrees C. Some reports of materials with conductivities of about 10^{-4} S/cm at room temperature are noted but the resistance is increased as the operating temperature is reduced. Also, the polymer structure may be effected by increasing temperatures to result in excessive fluidity of the electrolyte. There remains a need for a mechanically stable polymer electrolyte with high ionic conductivity over the above indicated 80 degree temperature range.

A hermetic battery was designed for a dry room manufactured polymer cell. The cell is based on (I) above, with nickel foil current collectors encapsulated within a hermetic aluminum foil pack that can be heat sealed. The composite cathode element incorporated both

carbon black and the electrolyte. This cell design suffered from internal shorting which was related to the insulation of the electrode terminals and the proximity of the heat sealing zone to the active cell.

The process for preparation of the cathode incorporated the materials V_6O_{13} , Shawinigan Black, polyethylene oxide, lithium salt and acetonitrile. A study of the milling process, process times, particle sizes, surfactants and method of introduction of the lithium salt was initiated. Cathodes were cast from the resultant dispersions and films in the 20-40 micron range were obtained. The electrode loading was typically 1 mAh/cm^2 . The coulombic efficiency of the the cathode was initially about 90% and after a few cycles reached a steady state value of approximately 70% of theoretical (where theoretical corresponds to 8 lithiums per V_6O_{13} unit).

More recent investigations are looking at the performance of sodium and the alkaline earth elements as anodic materials. A sodium cell, analogous to Cell I above, appeared to cycle reversibly with 1 sodium per V_6O_{13} . The initial cell voltage was 2.8 volts when the salt was NaI, and was about 3.2 volts when the salt was $NaCF_3SO_3$. Passivation at the anode was assumed in the latter case, possibly due to the formation of sodium fluoride and oxide layers. In the case of sodium iodide, the reduced cell voltage is consistent with reaction between the iodide electrolyte and the cathode active V_6O_{13} , resulting in formation of iodine. The iodine subsequently may function as the cathode active material.

Further studies are continuing on these cell types to identify the nature of the various degradation reactions. Clearly it points out the need for electrolytes that are compatible with the cathode materials, and cathode materials that, in turn, must interact reversibly with the mobile ionic species.

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