

EJ7.

ENHANCEMENT OF THE MECHANICAL PROPERTIES OF PLASTICIZED SOLID POLYMER ELECTROLYTES

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In recent decades, substantial interest has been devoted to polymer materials, which in combination with suitable metal salts give electrolyte membranes of interest for the development of electrochemical devices. The various types of polymer electrolytes can be easily fabricated into flexible thin films with large surface areas where the ions are free to move and can conduct electricity as in conventional liquid electrolytes. The most classic example is the combination of poly(ethylene oxide), PEO, and lithium salts (LiX), which in fact are being explored for the development of high-energy rechargeable batteries. Other promising technological applications of polymer electrolytes are electrochromic devices, room temperature fuel cells, electrochemical gas sensors and photo electrochemical solar cells.

In PEO - Li salt complexes, the ionic conductivity has been shown to be significantly higher in amorphous regions. The formation of crystallites in PEO systems has prevented their use as electrolyte at room temperature. Out of the methods available for enhancing the ionic conductivity, plasticization has the advantages that a variety of plasticizers can be chosen. Furthermore, film preparation of these materials is a simple process and the cost is relatively low. Plasticizers, which have a high relative permittivity such as propylene carbonate (PC), and ethylene carbonate (EC) may also enhance the dissociation of ion pairs of the salt. The amount of the plasticizers added to each polymer has a specific upper limit since the plasticizers influence the structure of the polymer thus reducing the mechanical stability. In order to exceed this limit while keeping good mechanical stability various additives are being attempted. The additions of inert fillers such as SiO₂, Al₂O₃ have also been attempted to improve the mechanical integrity.

In this work, a new method of producing highly conductive polymer electrolytes incorporating both, the plasticizers as well as inert fillers was developed by us to obtain conductivities of the order $3.0 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. It was based on addition of inert ceramics powder, α -alumina (Al₂O₃ - grain size 0.3 μ) to a plasticized polymer matrix LiCF₃SO₃[0.5PEO + 0.5EC]₉. Plasticized polymer electrolyte films were prepared by solvent casting method. The thermal properties of the electrolytes were evaluated from DSC measurements. Complex impedance spectroscopy in the frequency region 5Hz -13MHz and in the temperature range -20 °C to 100 °C gave information on the ionic conductivity and dielectric relaxations. A stable amorphous phase was formed after addition of alumina particles to the polymer and the conductivity values of the composite plasticized electrolyte ranged from 10^{-5} to $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ over the temperature range 27-110 °C. The conductivity vs temperature behavior was found to be of VTF type for all the complexes over the entire temperature range. The highest conductivity, at 108 °C, $2.57 \times 10^{-3} \text{ S cm}^{-1}$ was obtained for the sample LiCF₃SO₃[0.5PEO + 0.5EC]₉ +5 wt.% Al₂O₃ and the dielectric results of this sample indicated that the logarithm of peak frequency of the dielectric relaxation also follows the same VTF shaped $\log(\sigma)$ curve.