SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF SOME SOLID POLYMER ELECTROLYTES BASED ON POLY(ETHYLENE OXIDE), PEO

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In recent decades, a considerable interest has been focussed on polymer electrolyte materials, prepared by complexing suitable polymers with selected metal salts to give electrolyte membranes of interest for the development of electrochemical devices. 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 density rechargeable batteries. Polymer electrolytes suitable for secondary lithium batteries are thoroughly studied in order to achieve better performance in terms of high ionic conductivity at room temperature and stability against lithium electrodes. However, one major problem of PEO based electrolytes is that the conductivity assumes practically acceptable values only at high temperatures around 100 °C.

The objective of the present work is to study the characteristics of PEO based solid polymer electrolytes. This thesis focuses on enhancement of ionic conductivity and ionic transport mechanisms in these electrolytes. Efforts have been made to increase the ambient temperature conductivity by decreasing the crystallinity and increasing the segmental mobility of the polymer by the incorporation of salts and plasticizers into PEO. The two systems, PEO-$LiCF_3SO_3$ and PEO-$LiN(CF_3SO_2)_2$, have been chosen for this work. Low molecular weight PEGM (M_w = 400), EC and PC were used as conventional plasticizers. Furthermore, nano-composite electrolytes i.e. plasticized polymer-salt electrolytes with an

added ceramic filler of small particle size, such as Al2O3, has been found to enhance ionic conductivity.

The addition of finely dispersed non-miscible particles in a polymer electrolyte generally enhances the ion conductivity. PPFEMO (M_w = 4000) was introduced as a new type of plasticizer for PEO based polymer electrolytes. There are, up to now, no other examples of mixing this type of electrolyte with non-miscible liquids except with the PEO based electrolytes with PPFEMO systems presented here. The system PEO-LiX, with the addition of PPFEMO is a bi-phase stable emulsion. The micro-droplets present in the emulsion prevent or retard the crystallisation of the electrolyte when it is cooled from the melting temperature to ambient temperature. The ion conductivity below the melting point temperature maintains stable values as long as the re-crystallisation is prevented. The characteristics of the electrolytes were investigated by Complex Impedance Spectroscopy, Complex Dielectric Spectroscopy, Differential Scanning Calorimetry and tranference number measurements. The temperature dependence of the conductivity was studied in 8detail for all materials. Dielectric properties, dynamical mechanical properties, glass transition temperature and degree of crystallinity of these materials were also discussed in detail.

For the systems, PEO-$LiCF_3SO_3$, PEO-$LiN(CF_3SO_2)_2$, PEO-$LiN(CF_3SO_2)_2$-EC/PC and PEO-$LiN(CF_3SO_2)_2$-PPFEMO, the dielectric measurements reveal two peaks in the imaginary part of the dielectric function, a high frequency peak in the GHz region attributed to the α- process of the pure polymer, and a lower frequency 'ion-pair' peak in the MHz region, the intensity whose is found to be dependent upon the concentration of the salt present in the polymer-salt complex. Considerable amounts of ion pairs were present in both plasticized and unplastisized polymer electrolytes and if the relaxation frequency can be taken as a probe of the local flexibility of the polymer chain it can be concluded that the conductivity increases in parallel to the increases in the local flexibility of the polymer segments.