

Transport and dielectric properties of the gel polymer electrolyte system PAN:EC:PC:LiTFSI

Polyacrylonitrile (PAN) based gel polymer electrolytes incorporating lithium(bis)trifluoromethanesulfonate imide ($\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ or LiTFSI) have ionic conductivities high enough to be used as electrolytes in ambient temperature polymer batteries. However, the mechanism of ion transport and the effect of ion pairs and ion-polymer interactions in these electrolytes are still not well understood. High frequency dielectric measurements provide a convenient means to probe the behaviour of ion pairs, and ion-polymer interactions. Ionic conductivity and broad band dielectric relaxation measurements have been performed for the gel polymer electrolyte system PAN/EC/PC/LiTFSI in the frequency range from 1 MHz to 1.8 GHz and from -20 oC to 50 oC. Out of the various PAN/LiTFSI composition ratios studied, the 6:1 composition ratio by weight gives the highest ionic conductivity. The room temperature (25 oC) conductivity of the gel electrolyte with this composition, PAN (15.4%) / EC(41.0%) / PC(41.0 %) / LiTFSI (2.6%) (by weight) is $2.5 \times 10^{-3} \text{ S cm}^{-1}$. The ϵ'' spectra of gel electrolytes with various compositions show the presence of a high frequency peak in the 0.5 GHz region attributed to the α relaxation process and a peak/ shoulder in the 10 MHz region attributed to the ion-pair relaxation. The temperature dependence of the ionic conductivity and the peak ion pair frequency clearly shows that the temperature dependence of the ion pair frequency follows very closely the temperature dependence of the conductivity, where as the α peak frequency does not. This, we believe, is an important observation concerning the mechanism of ion transport in this PAN based gel electrolyte. This suggests that the immediate environment for ion pair relaxation and ionic transport is the same and the Li^+ ion transport probably takes place in the vicinity of the PAN chains and the ion pair relaxation frequency appears to reflect the dynamic environment in which the cations migrate. On the other hand, the coupling of the α relaxation of EC/PC molecules to the ionic conductivity appears to be much weaker.