Fluorescence Studies for the Local Viscosity Measurements in Polyacrylonitrile(PAN)-based Polymer Gel Electrolytes

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A fluorescence probe sensitive to the local viscosity was used to study the conduction property of the polymer gel electrolytes, polyacrylonitrile(PAN)/ propylene carbonate(PC) + ethylene carbonate(EC) in 1:3 volume ratio/LiClO₄. conductivity of the gel electrolytes was in the range of 10^{-2} - 10^{-3} S/cm, of which value is much higher than those for the conventional polymer electrolytes such as PEO/Li salts. Conductivity profile of the polymer gel electrolytes, according to the LiClO₄ concentration ([LiClO₄]/[PC + EC] = 0.05 - 0.11), looked similar to that of the liquid electrolytes of the same composition. Also, the Arrhenius activation energies of the gel electrolytes (10-15 kJ/mole) were rather closer to those (5 kJ/mole) of the liquid electrolytes than those for the unplasticized polymer electrolytes (a few tens to However, the observed local viscosities of the gel electrolytes hundreds kJ/mol). were higher than those of the liquid electrolytes by a factor of 20, while the conductivity was smaller by a factor of 2 - 9, suggesting that the inverse relationship between the local viscosity and the conductivity does not hold in this system. This is contradictory to the earlier report that ion conduction in polymer gel electrolytes is completely decoupled from the segmental motions of the polymer matrix. FT-IR spectra of the gel electrolytes showed that the CN groups in PAN interact with Li⁺ ions, which causes an increase in the local viscosity through a cross-linking effect. In short, the conduction property of the gel electrolytes looked similar to that of the liquid electrolytes in several ways. However, the cross-linking effect in the gel electrolytes causes the inverse relationship invalid and consequently the observed conductivity and activation energy values are somewhat different to those for the liquid electrolytes of the same composition.