Solid Ion-Conductive Polymers

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Many materials, ranging from covalent solids such as the β-aluminas [$(Na_2O)_x \cdot 11Al_2O_3$] [1] to soft ionic crystals such as AgI [2], act as solid electrolytes in which the ion conductivity, σ, is much greater than that of typical ionic solids such as NaCl. These solid electrolytes exhibit conductivities in the range (10^{-6} to 10^{-1} S cm^{-1}) comparable to dilute ionic aqueous solutions [3]. The need for softer more compliant solid electrolytes has resulted in polymer-salt complexes being among the most recent solid electrolytes to be investigated [4]. The properties of polymer electrolytes such as their good adherence to electrodes and their ability to be cast as thin films are attractive for their use in high energy density batteries [15]. Other potential applications are as electrochromic displays and electrochemical transistors [16].

Two of the most studied solid polymer electrolytes are the linear polymer, poly-(ethylene oxide) [PEO] , and the comb polymer, methoxyethoxyethoxy poly(phosphazene) [MEEP], complexed with alkali metal salts (Figure 1) [5]. The formation of the metal salt complexes is usually accomplished by dissolving or suspending both the salt and the host polymer in a common solvent (usually acetonitrile or methanol) and then removing the solvent, producing the solvent-free polymer electrolyte in either bulk or thin films [6].

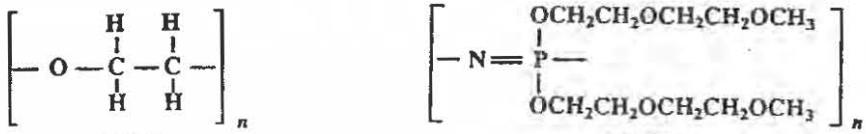

Figure 1

The polymer-cation interaction has been established by vibrational spectroscopy as a cation in an etherial cage. Far-IR and Raman spectroscopic studies show bands at about 400 and 860-870 cm^{-1} respectively. These bands are similar to the bands assigned to crown ether alkali metal salt complexes [7]. The ion pairing between the cation and polyatomic anions has also been established from such vibrational spectroscopy. It was found that strong ion pairing leads to low ion conduction [4].

In the characterization of the electrical properties of a solid electrolyte the most useful information is the conductivity of the bulk electrolyte. The conductivity of the polymer electrolytes occurs by the migration of ions from one polymer segment to another. Impedance spectroscopy [8] revealed that the ion conductivity increased dramatically above the polymer's glass transition temperature, T_g [9].

The temperature dependance of the conductivity can be described in terms of the chain segment mobility of the polymer host [10]. Central to such discussions is the Williams-Landel-Ferry (WLF) relationship [11] which relates the polymer chain viscosity to the glass transition temperature. The WLF relationship is an empirical generalization which has lead to theoretical models that describe ion transport in polymers such as the free volume model [12], excess entropy model [13], and ultimately the dynamic percolation model. The latter is a microscopic model that describes the cationic motion in terms of "jumps" which correspond to a complete exchange of one ligand (Figure 2) [14].

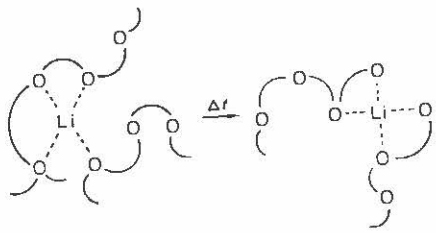

Figure 2

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