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PMMA-based polymer gel electrolytes containing NH_4PF_6: Role of molecular weight of polymer

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Abstract

The effect of the molecular weight of polymethylmethacrylate (PMMA) on the conductivity and viscosity behavior of proton conducting polymer gel electrolytes containing ammonium hexafluorophosphate (NH_4PF_6) in propylene carbonate (PC) has been studied. The addition of PMMA having molecular weights: 15,000; 120,000; 350,000; 996,000 results in an increase in conductivity and gels with conductivity higher than the corresponding liquid electrolytes have been obtained. The maxima observed in the variation of conductivity with PMMA concentration shifts towards higher concentrations of PMMA with an increase in the molecular weight of PMMA. The increase in conductivity with PMMA addition also depends upon the molecular weight of PMMA and has been found to be more for gels containing PMMA with lowest molecular weight (15,000). The increase in conductivity at low concentrations of PMMA is due to an increase in free ion concentration with the dissociation of ion aggregates, whereas the decrease in conductivity at higher concentrations of PMMA, is due to the exponential increase in viscosity, which lowers mobility and as a result conductivity decreases. These gels show high value of conductivity ($\sim 10^{-2}$ S/cm at 25 °C) which does not vary with time and shows only a small increase over the 20–100 °C temperature range and is desirable for their potential use in applications.

Keywords: Molecular weight; Viscosity; Polymer gel electrolytes; Free ion concentration; Conductivity

1. Introduction

Polymer gel electrolytes belong to the salt–solvent–polymer hybrid system and are generally prepared by immobilizing the salt solution with a suitable polymer matrix and solvent is retained in these electrolytes, which also helps in the conduction process [1,2]. Although initial work on these electrolytes mainly concentrated on lithium ion conducting gels due to their use in lithium batteries, yet proton conducting polymer gel electrolytes are also receiving attention due to their potential use in various devices [3–6]. Polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polyvinylidene fluoride (PVdF), polyvinylidene fluoride-*co*-hexafluoropropylene (PVdF-HFP), polyethylene oxide (PEO), etc. are some of the commonly used polymers in the synthesis of polymer gel electrolytes. The addition of different polymers increases the viscosity (η) of the electrolytes which lowers mobility ($\mu = q/6\pi r\eta$, where μ is the carrier mobility, q the carrier charge and r is the radius of the carrier ions) and as a result, a decrease in conductivity ($\sigma = nq\mu$, where σ is the ionic conductivity and n is the concentration of charge carriers) is generally observed [7,8]. The viscosity of the electrolytes will also depend upon the average molecular weight of the polymer used and polymers with different molecular weights may affect the conductivity behavior of gel electrolytes differently [9]. Although the role of different polymers on the conductivity modification of polymer gel electrolytes has been discussed, yet the effect of different molecular weight of the polymer is not generally taken into account [10–13]. The comparison of conductivity and other results reported by different workers on the same system, sometimes become difficult due to the different molecular weight of the polymer used in their study. Thus the effect of using the same polymer but having different molecular weights on the viscosity and conductivity behavior of polymer gel electrolytes will be an interesting study and is the subject for the present investigation.

In the present study, polymethylmethacrylate (PMMA) with average molecular weights: 15,000; 120,000; 350,000; 996,000 has been used in the synthesis of polymer gel electrolytes and the

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effect of the molecular weight of polymer on the conductivity and viscosity behavior of proton conducting polymer gel electrolytes containing NH_4PF_6 in PC has been studied. The change in viscosity of the electrolytes with the addition of polymer having different molecular weights has been monitored by viscosity measurements. The variation of conductivity with the concentration of salt, concentration and molecular weight of polymer, temperature and time has also been investigated.

2. Experimental procedure

PMMA (Aldrich, M_w = 15,000, 120,000, 350,000 and 996,000), NH_4PF_6 (Aldrich), propylene carbonate (PC) (Merck) were used as the starting materials. Polymer gel electrolytes containing PMMA with different molecular weights in the 1 M solution of NH_4PF_6 in PC were prepared by the method described in earlier publications [8,14]. The conductivity of electrolytes was measured by complex impedance spectroscopy using HP 4284A precision LCR meter with a cell having platinum electrodes. Impedance/admittance plots were drawn and conductivity was calculated by using the relation $\sigma = Gl/A$, where G is the conductance to be determined from the impedance/admittance plots, l the distance between the electrodes and A is the area of cross section of each electrode. The viscosity of the electrolytes was measured by Fungi lab rotating viscometer (Visco Basic L) using a small sample adapter assembly.

3. Results and discussion

3.1. Liquid electrolytes

The conductivity of liquid electrolytes used in the preparation of polymer gel electrolytes and containing different concentrations of NH_4PF_6 in PC was measured as a function of salt concentration and is given in Fig. 1. The conductivity of the solvent (~10^{-6} S/cm) increases by four orders of magnitude to 10^{-2} S/cm with the addition of NH_4PF_6. The increase in conductivity is very steep at low concentrations of salt, but does not show much change at higher concentrations of salt and reaches a saturation value. The salt upon dissociation provides free ions for conduction, but at higher concentrations of salt, ion aggregates are also formed due to the presence of a large number of ions, which do not contribute to the conduction process and as a result conductivity does not increase at the same rate as observed at low salt concentrations [15,16]. The addition of salt also results in a small increase in viscosity of the electrolytes, which shall lower mobility and hence conductivity also but in the present case, the increase in viscosity with the addition of salt from 3.82 to 5.15 mPa s for liquid electrolytes containing 1 M NH_4PF_6 in PC is very small and this may affect the conductivity only marginally. The saturation in the value of conductivity at higher salt concentrations as observed in Fig. 1 may be due to the formation of ion aggregates which do not contribute to conductivity. Thus ion aggregates are present in these liquid electrolytes at higher concentrations of NH_4PF_6 in PC.

3.2. Gel electrolytes

The variation of conductivity and viscosity with PMMA concentration for polymer gel electrolytes containing PMMA with average molecular weight 350,000 in the 1 M solution of NH_4PF_6 in PC is given in Fig. 2. The conductivity of polymer gel electrolytes has been observed to increase with the addition of PMMA, reaches a maximum value of 4.16×10^{-2} S/cm at 3 wt.% PMMA and then decreases to a value of 2.85×10^{-2} S/cm at 10 wt.% PMMA. The presence of maxima is generally indicative of the simultaneous presence of two competing processes, which in the present case are free ion concentration at low PMMA concentrations and viscosity at high PMMA concentrations [17]. The increase in free ion concentration at low PMMA concentration is due to the dissociation of ion aggregates with the addition of polymer [14]. The viscosity of gel electrolytes is very small at low concentrations of PMMA but increases sharply at higher concentrations of PMMA. The large value of viscosity (η) at higher concentra-

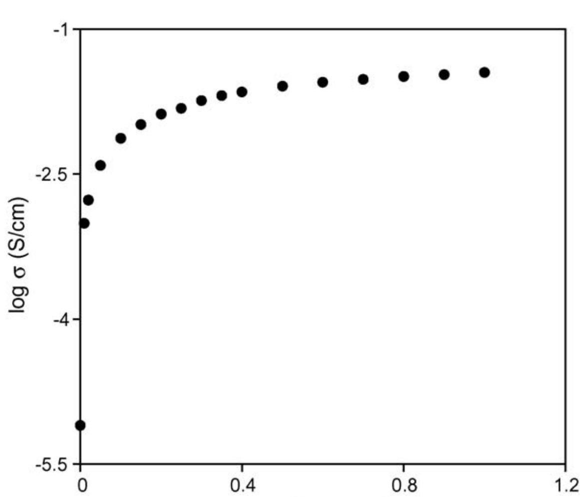

Fig. 1. Variation of conductivity (σ) of liquid electrolytes (PC–NH_4PF_6) with the concentration of NH_4PF_6 in PC.

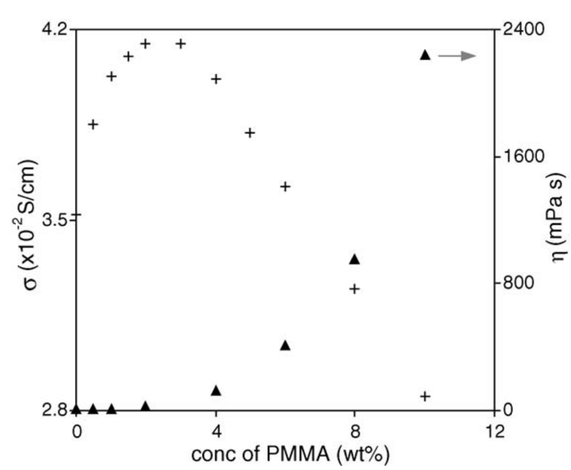

Fig. 2. Dependence of conductivity (+) and viscosity (▲) with PMMA (average molecular weight = 350,000) concentration for polymer gel electrolytes containing 1 M NH_4PF_6 in PC.