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Conductivity Behaviour of Nanocomposite Polymer Electrolytes: Role of Fumed Silica and Plasticizer

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Summary: Polymer electrolytes obtained by the complexation of ammonium bifluoride (NH_4HF_2) with polyethylene oxide (PEO) have been studied. The addition of propylene carbonate (PC) results in conductivity enhancement by two orders of magnitude and shows conductivity of 1.4×10^{-4} S/cm at 25 °C, whereas the addition of fumed silica results in conductivity enhancement and show conductivity of 1.19×10^{-5} S/cm at 25 °C. However simultaneous addition of plasticizer (PC) and fumed silica to polymer electrolytes has been found to result in higher conductivity of 1.55×10^{-4} S/cm at 25 °C alongwith better mechanical properties. The complexation of NH_4HF_2 with PEO, formation of ion aggregates and their dissociation with the addition of PC has also been studied by FTIR.

Keywords: conductivity; FTIR; fumed silica; plasticizer; polymer electrolytes

Introduction

The complexation of sodium salts with high molecular weight poly(ethylene oxide) (PEO) and their high ionic conductivity was first reported by Wright and co-workers,[1] whereas the recognition of their potential for applications in solid state batteries was highlighted later by Armand and co-workers.[2] Proton conducting polymer electrolytes, obtained by the complexation of various ammonium salts with PEO, are materials of current research interest due to their potential use in various solid state ionic devices.[3] PEO based polymer electrolytes have been reported to be multiphase systems, with amorphous phase as the high conducting phase.[4] However low conductivity of these electrolytes at moderate temperatures and the mobility of both cations and anions limits their use in different applications. Different approaches viz the addition of plasticizers, insulating phase particles, amorphous polymers, polyelectrolytes etc have been proposed to enhance the conductivity of polymer electrolytes.[5–8]

The addition of plasticizers enhances conductivity of polymer electrolytes by increasing the amorphous content and by dissociating ion aggregates due to an increase in dielectric constant. However it has been accompanied by a decrease in mechanical strength which is due to the softening of polymer electrolytes. The addition of insulating matrix to polymer electrolytes also enhances the conductivity which depends upon the particle size and the concentration of insulating matrix.[9] Although the increase in conductivity in this case is lower as compared to plasticized polymer electrolytes, yet it is accompanied by an improvement in the mechanical properties of electrolytes.[10] The addition of PC and fumed silica simultaneously may be a better approach for an improvement in conductivity and mechanical properties of polymer electrolytes.

In the present work, the effect of the addition of (a) plasticizer, (b) insulating phase particles and (c) both (plasticizer and insulating phase particles) simultaneously on the ionic conductivity of PEO-NH_4HF_2

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polymer electrolytes has been studied. The complexation of NH_4HF_2 with PEO, formation of ion aggregates and their dissociation with the addition of plasticizer has also been studied by FTIR.

Experimental Part

Polyethylene oxide (PEO) (Aldrich, av. mol. wt. $= 5 \times 10^6$), ammonium bifluoride (NH_4HF_2) (CDH), propylene carbonate (PC) (Merck), fumed silica (Aldrich) with average particle size 7 nm have been used as the starting materials for the preparation of polymer electrolytes by solution casting method using methanol as solvent. PEO, NH_4HF_2, PC and fumed silica, taken in stoichiometric ratio were dissolved in methanol and stirred to obtain a homogeneous solution. The solution was then poured in polypropylene dishes and the solvent was allowed to evaporate slowly. Free standing films of polymer electrolytes so obtained were dried and used for further studies. The electrical conductivity and dielectric properties of polymer electrolytes were measured by complex impedance spectroscopy using computer interfaced Hioki 3532-50 LCR HiTester in the 40 Hz–5 MHz frequency range. The conductivity was also measured at different temperatures in the 30–100 °C temperature range by keeping the sample holder containing polymer electrolyte in a temperature controlled furnace.

Results and Discussion

The conductivity of polymer electrolytes having composition PEO-NH_4HF_2 was measured at different concentrations of salt and the conductivity of PEO ($\sim 10^{-9}$ S/cm) increases by three orders of magnitude ($\sim 10^{-6}$ S/cm) with the addition of salt and reaches a maximum value of 5.96×10^{-6} S/cm at 25 °C for electrolytes containing 10 wt% NH_4HF_2 (Figure 1). The addition of salt provides free mobile ions upon dissociation, which take part in the conduction process and as a result conductivity increases.

However the conductivity decreases at higher salt concentrations, which could be

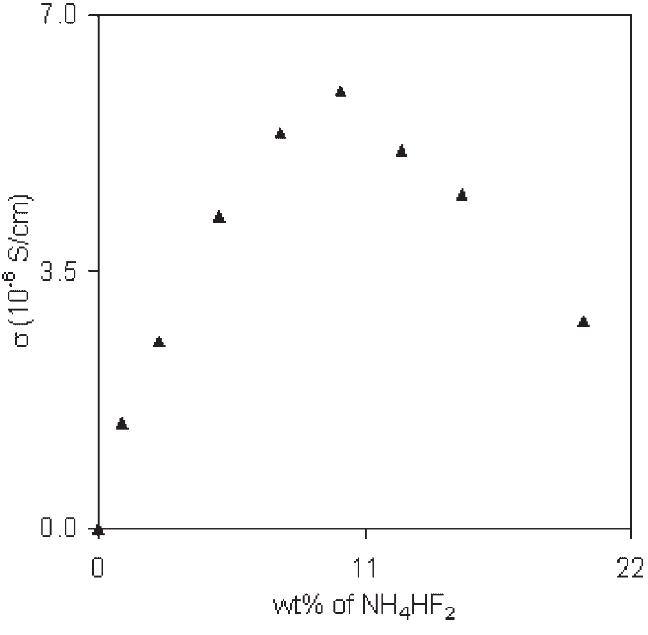

Figure 1.
Conductivity of PEO-NH_4HF_2 polymer electrolytes as a function of NH_4HF_2 concentration.

due to the formation of ion aggregates, which generally do not take part in the conduction process.[11] The complexation of NH_4HF_2 with PEO was studied by FTIR spectroscopy and spectra for some samples in selected regions is given (Figure 2).

From Figure 2, it has been observed that:

(i) shifting in N–H stretching vibrations of NH_4^+ from 3182 cm^{-1} to 3270 cm^{-1} and H–N–H bending vibrations from 1380 to 1368 cm^{-1}[12] takes place. These shifts in the position of N–H related peaks show the complexation of NH_4HF_2 with PEO.

(ii) some changes in the position of peaks in the 1500–800 cm^{-1} region occurs due to the scissoring, wagging, twisting and rocking modes of methylene group in PEO.[13] The peak at 722 cm^{-1} (due to HF_2^- anions)[14] also shifts to 740 cm^{-1}.

(iii) the peaks at 767 cm^{-1} and 1390 cm^{-1} (for samples containing higher concentrations of salt) are due to the presence of ion aggregates.

The addition of PC ($\varepsilon = 64.4$) to polymer electrolytes results in conductivity enhancement by two orders of magnitude and plasticized polymer electrolytes containing 42 wt% PC show conductivity of 1.4×10^{-4} S/cm at 25 °C (Figure 3). The increase in conductivity is due to the high dielectric constant of plasticizer which helps in enhancing the dissociation of salt and ion aggregates present in these electrolytes, in addition to increasing the amorphous content. The increase in dielectric constant with the addition of PC has also been studied (inset of Figure 3). The increase in amorphous content with the concentration of plasticizer has been studied by XRD studies (Figure 4). Well defined peaks observed for

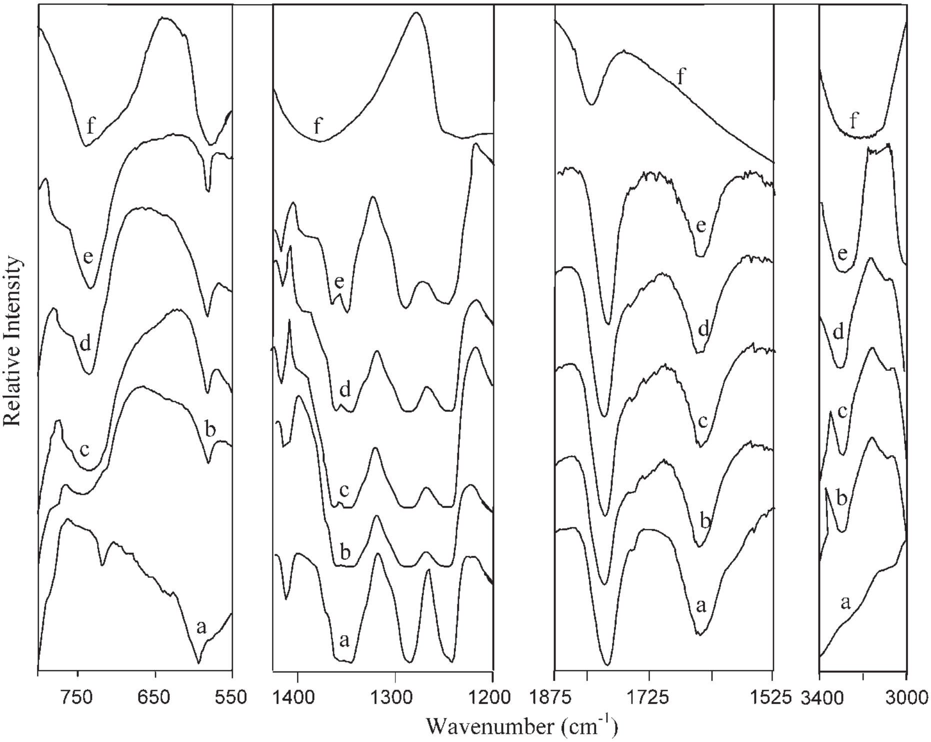

Figure 2.

FTIR spectra of (a) PEO, PEO-NH_4HF_2 polymer electrolytes containing 1 wt% (b), 2.5 wt% (c), 5 wt% (d), 10 wt% NH_4HF_2 (e) and (f) NH_4HF_2 in different regions.

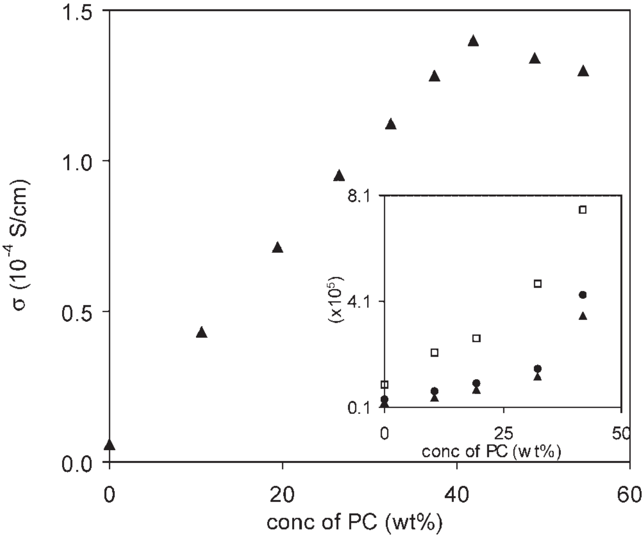

Figure 3.

Conductivity of PEO-10 wt% NH_4HF_2 polymer electrolytes as a function of PC concentration. Inset shows variation of dielectric constant vs PC concentration for PEO - 10 wt% NH_4HF_2 -x(wt%) PC at 100 Hz (□), 600 Hz (●) and 1 KHz (▲) at 25 °C.

PEO-NH_4HF_2 polymer electrolytes show the presence of crystalline phase. The broadening of the peaks with the addition of PC indicates that an increase in amorphous content of polymer electrolytes takes place with the addition of plasticizer.

The dissociation of ion aggregates with the addition of PC has also been studied by

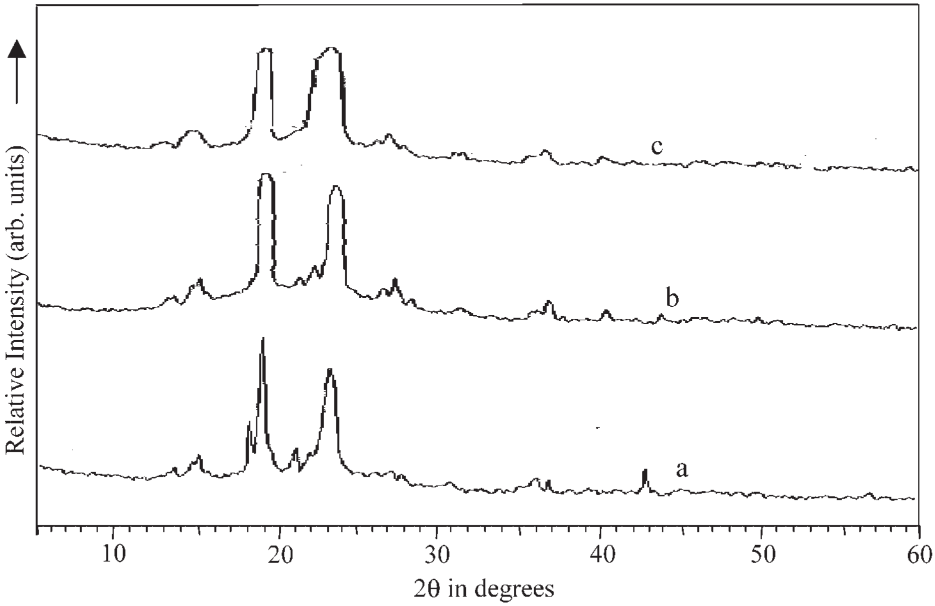

Figure 4.

XRD pattern of PEO- NH_4HF_2 polymer electrolytes containing (a) 0 wt%, (b) 20 wt% and (c) 42 wt% PC.

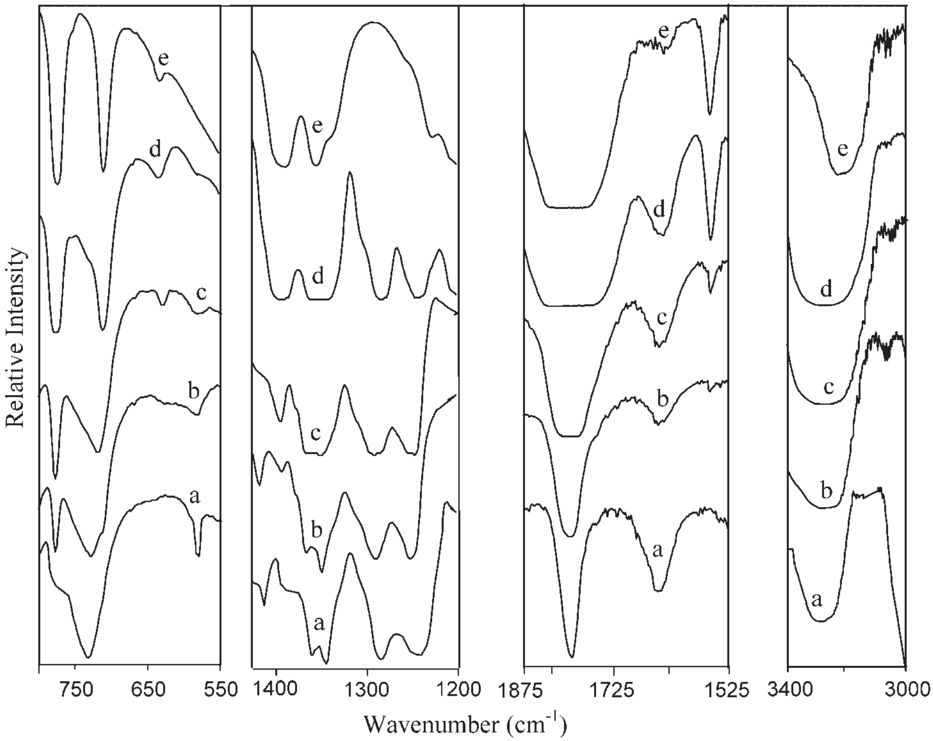

Figure 5.
FTIR spectra of (a) PEO-10 wt% NH_4HF_2 polymer electrolytes containing 11 wt% (b), 20 wt% (c), 42 wt% (d) PC and of (e) PC in different regions.

FTIR and some representative spectra are given (Figure 5).

From Figure 5, it has been observed that:

(i) broadening of the peaks at 3270 cm^{-1} (N–H stretching vibrations) and 1368 cm^{-1} (due to H–N–H bending) indicate that NH_4^+ ions are bounded with the carbonyl oxygen of PC.
(ii) shifting of the peak at 740 cm^{-1} to 711 cm^{-1} is due to the peak of PC at 711 cm^{-1} (due to symmetric ring deformation and ring breathing).[15]
(iii) formation of new peaks at 777 cm^{-1} (ring deformation), 1395 cm^{-1} (C–H bending and CH_3 bending), 1556 cm^{-1} (C–H bending) is due to the presence of PC[15] alongwith the disappearence of peak at 1413 cm^{-1}.
(iv) broadening of the peak at 1796 cm^{-1} due to its overlap with the peak of PC at 1800 cm^{-1} (C=O stretching vibration)[15] indicates the interaction of NH_4^+ with C=O stretching mode of PC.
(v) disappearence of peaks at 767 and 1390 cm^{-1} (due to ion aggregates) with the addition of PC. This indicates the dissociation of ion aggregates present at higher concentrations of salt with the addition of plasticizer, which results in an increase in free ion concentration and hence conductivity. The above FTIR results are in close agreement with the conductivity results of these polymer electrolytes.

The addition of fumed silica to polymer electrolytes (PEO-NH_4HF_2) also results in conductivity enhancement and nanocomposite polymer electrolytes containing 3 wt% fumed silica show conductivity of 1.19×10^{-5} S/cm at 25 °C (Figure 6(a)).

Although the increase in conductivity in this case is relatively low, yet it has been accompanied by an improvement in the

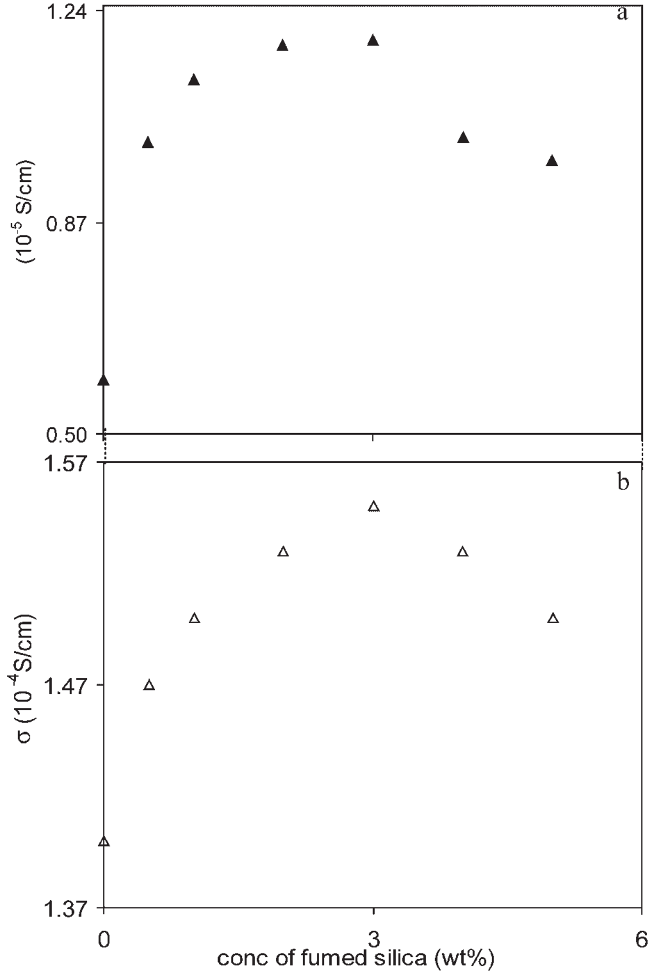

Figure 6.
Conductivity of (a) PEO-NH_4HF_2 and (b) PEO-NH_4HF_2-PC polymer electrolytes as a function of fumed silica concentration.

mechanical strength (visual observations only, no measurements) of polymer electrolytes. However the simultaneous addition of plasticizer (PC) and fumed silica to PEO-NH_4HF_2 polymer electrolytes has been found to result in electrolytes with higher conductivity of 1.55×10^{-4} S/cm at 25 °C (Figure 6(b)) alongwith better mechanical properties.

The variation of conductivity for different polymer electrolytes containing PC, fumed silica and both PC and fumed silica with temperature has also been studied in the 20–100 °C temperature range (Figure 7). It has been observed that the conductivity of polymer electrolytes containing PC is higher than those of unplasticized polymer electrolytes and polymer electrolytes containing fumed silica only. The conductivity of PEO-NH_4HF_2 increases by one order of magnitude at the temperature corresponding to melting temperature ($T_m = 65$ °C) of PEO and is generally explained to be due to a transition from the semicrystalline to the amorphous phase, which is reported to be the high conducting phase[4] in these polymer electrolytes. In the case of polymer electrolytes containing plasticizer, the conductivity does not show any change at T_m and curved

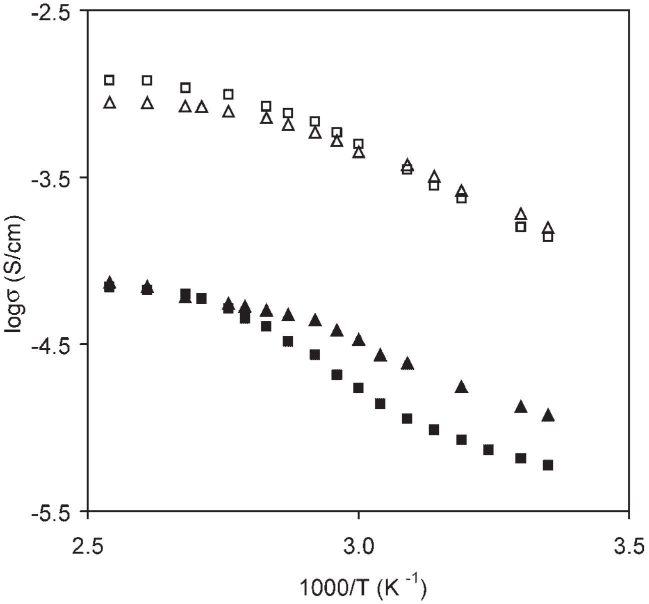

Figure 7.
Variation of log conductivity with reciprocal temperature for PEO-NH_4HF_2 (■), PEO-NH_4HF_2-fumed silica (▲), PEO-NH_4HF_2-PC (□) and PEO-NH_4HF_2-PC-fumed silica (△) polymer electrolytes.

behaviour observed between log conductivity and reciprocal temperature suggests the amorphous nature of these electrolytes. However polymer electrolytes containing both PC and fumed silica show highest conductivity alongwith better mechanical strength and only a small change in conductivity has been observed over the 20 °C–100 °C temperature range which is also suitable for applications.

Conclusions

Polymer electrolytes containing plasticizer (PC) show higher conductivity whereas nanocomposite polymer electrolytes containing fumed silica possess better mechanical strength. However polymer electrolytes containing both PC and fumed silica simultaneously show higher conductivity as well as better mechanical strength.

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