Ion transport studies in PEO: NH$_4$I polymer electrolytes with dispersed Al$_2$O$_3$

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Ion conducting polymer electrolyte films having high salt concentrations have been studied. The system studied is PEO: NH$_4$I, dispersed with $\alpha$-Al$_2$O$_3$. Mechanically stable films with NH$_4$I/EO ratio $\geq$ 0.13 have been obtained by dispersal of Al$_2$O$_3$. The films have been characterized using various techniques such as X-ray diffraction (XRD), differential thermal analysis (DTA), polarization and complex impedance spectroscopy. Intercorrelation between polymer matrix crystallite size, conductivity, and $\alpha$-Al$_2$O$_3$ particle size is established.

1. Introduction
Some of the PEO based polymer electrolytes are limited by poor mechanical properties, in spite of their reasonably high electrical conductivity and thereby the possibility of their use in a large number of practical applications. Recently, it has been realised that developing proton (H$^+$) conductors have vast technological applications, particularly in fuel cells and sensors. Some of the reported PEO based proton conductors are, PEO: NH$_4$SCN, PEO: NH$_4$SO$_4$CF$_3$[1], PEO: NH$_4$HSO$_4$[2], PEO: NH$_4$ClO$_4$[3,4], PEO: H$_3$PO$_4$[5], PEO: (NH$_4$)$_2$SO$_4$[6], PEO: NH$_4$I[7].

For most polymer electrolytes the conductivity decreases at higher concentrations due to ion-association. However, Maurya et al.[7] have reported in their studies on the PEO: NH$_4$I system that its conductivity keeps on increasing until 70:30 wt% ratio is reached. Beyond this weight percent ratio (NH$_4$/EO $\geq$ 0.13), the films become mechanically unstable and "glue-like". The motivation of this study was to prepare mechanically stable films (i.e. films which could be handled with ease and were non-sticky) with higher NH$_4$I content in PEO with the hope that a higher conductivity will be obtained. To achieve this goal, we dispersed $\alpha$-Al$_2$O$_3$ in PEO and studied the following:

(i) Differential thermal analysis (DTA) for obtaining phase diagrams.
(ii) X-ray diffraction (XRD) for d-values and crystallite size.
(iii) $\sigma$ versus Al$_2$O$_3$ content for different films.
(iv) $\sigma$ versus Al$_2$O$_3$ particle size.
(v) Correlation between $\sigma$ and polymer matrix crystallite size (i.e. Scherrer length).
(vi) $\sigma$ versus 1/T for different films.

We have found that Al$_2$O$_3$ forms a dispersed phase system with the polymer electrolyte and also affects the crystallinity (and hence the conductivity) of the polymer electrolyte.

2. Experimental procedure
The experimental methods used to obtain and characterize the PEO: NH$_4$I (+ Al$_2$O$_3$) polymer films are given below:

2.1. Film preparation
Polymer films were prepared by the well known solution cast technique. PEO (MW = $6 \times 10^5$) and NH$_4$I were weighed for different NH$_4$/EO ratios (0.034, 0.076, 0.13, 0.20, 0.30) and were dissolved in distilled methanol. To this mixture Al$_2$O$_3$ was added in different weight percentages (1, 5, 10, 15, 20, 30, 40, 50) and the solution was stirred for $\approx$8–10 h at 40°C. The highly viscous solutions thus obtained were poured into polypropylene dishes and the solvent was allowed to evaporate in dry ambient air. These films were then vacuum dried at $\approx$0.013 Pa for 24 h to remove traces of solvent. Aluminium was vacuum coated onto both sides of the films (using masks of known area) to take electrical contacts.

2.2. Complex impedance plots
Complex impedance plots of PEO: NH$_4$I (+ Al$_2$O$_3$) polymer films were obtained using a Solartron (1250 frequency response analyser and 1286 electrochemical interface) coupled to a HP-computer. The measurements were taken in the frequency range 6.5Hz–65 KHz.

2.3. X-ray diffraction
XRD patterns of the polymer films were taken on a Rigaku Rotaflex unit with scan speed of 2° min$^{-1}$. The size of the PEO crystallites ($L$) have been calculated using the Scherrer formula, given as

$$L = \frac{0.9\lambda}{B\cos\theta_B}$$

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2.4. Differential thermal analysis

Differential thermal analysis (DTA) of the PEO: NH₄I ( + Al₂O₃) films was carried out with a Linseis's unit (Model 2045). The measurements were done from room temperature (~ 30 °C) to 200 °C at a heating rate of 5 °C min⁻¹.

2.5. Ionic transference number

Wagner's polarization method was used to find out the total ionic transference number. The polarization was performed by applying a d.c. bias of 200 mV and the current was measured by a Keithley source measure unit (Model 236).

3. Results and discussion

The structural and ion transport studies carried out on the PEO: NH₄I ( + Al₂O₃) systems are given below.

3.1. Differential thermal analysis (DTA)

DTA is reported by Maurya et al. [7] for PEO: NH₄I for different NH₂/EO ratios but with no alumina. Here, we wanted to study the effect (if any) caused in the phase diagram of PEO: NH₄I on the dispersal of Al₂O₃. Therefore, DTA was carried out for PEO: NH₄I films with NH₄⁺/EO = 0.13 with 0, 10, 20, 30, 40 and 50 wt% of Al₂O₃. The results are shown in Fig. 1. A comparison of all the DTA curves shows that the dispersal of Al₂O₃ introduces only the following minor changes:

(a) The PEO: NH₄I complex T_m “peak” corresponding to melting of PEO in the crystalline phase, at 66 °C for a sample with no Al₂O₃, shifts slightly to the lower temperature side by ≤ 3 °C as Al₂O₃ content is increased.

(b) The broad peak at ~ 86 °C in 0% Al₂O₃ film (identified as T_m for the crystalline complex of PEO, abbreviated as (PEO)cc) splits into two peaks. The split peak (at ~ 78 °C) on the lower side of the original peak (at 86 °C) shows a similar shift to T_m (66 °C) given above with the addition of Al₂O₃. The other split peak is tentatively assigned to (PEO)cc,Al₂O₃ assuming that the Al₂O₃ dispersal affects the energetics of (PEO)cc by distorting the PEO helical chain.

Fig. 2 is the phase diagram of the PEO: NH₄I polymer film (NH₄⁺/EO = 0.13) based on DTA curves for different weight percentages of Al₂O₃ given in Fig. 1. In this figure, Region I is marked by the coexistence of PEO in the crystalline form (PEO)cc, PEO in the crystalline complex form (PEO)cc, and PEO crystalline complex distorted due to Al₂O₃ (PEO)cc,Al₂O₃, Region II contains the (PEO)cc and (PEO)cc,Al₂O₃, Region III has only the (PEO)cc,Al₂O₃, Region IV is the liquidus phase.

3.2. X-Ray diffraction

In PEO: NH₄I films without Al₂O₃, it is observed that for NH₂/EO ratio equal to 0.13, there are no well-defined peaks. Instead there are a few overlapping peaks indicative of a low degree of crystallinity. Fig. 3 gives the XRD patterns of PEO: NH₄I films (with NH₄⁺/EO = 0.13) with 0, 10, 20 and 50 wt% of Al₂O₃. From these figures it is obvious that an addition of Al₂O₃ increases the crystallinity in the otherwise low crystallinity films. From this figure it is also clear that the addition of Al₂O₃ modifies the lattice, changing the “d” and 20 values. The shifts in “d” and 20 values are given in Table I. It may be remarked here that the enhancement in the crystallinity (and changes in “d-values”) are likely to affect the conductivity of these films (actually found by us and discussed later). Further, it should also be noted that Al₂O₃ is forming a dispersed phase with PEO.