



Investigation of XRD and Transport Properties of (PEO+KNO₃+Nano Al₂O₃) Composite Polymer Electrolyte

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Abstract

(PEO+KNO₃+Nano Al₂O₃) based Composite Polymer Electrolytes (CPE) has been prepared by using solution casting technique. In this technique, Poly (ethylene oxide) (PEO) and KNO₃ salt were dissolved separately in methanol and they were mixed together. Nano alumina (Al₂O₃) (particle size ~10nm) was doped to mixed solution and stirred for 24hrs. X-ray diffraction (XRD) technique has been obtained to determine complexation of salt and polymer in composite polymer electrolytes. Ionic and electronic transference numbers of these composite polymer electrolytes has been calculated by using Wagner's polarization technique. The DC Conductivity of these composite polymer electrolytes has been evaluated in the temperature range of 303-373 K.



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Introduction

In recent times Composite Polymer Electrolytes (CPE) has been drastically explored due to its various prospective applications such as batteries, fuel cells, smart windows, solar cells, display devices, etc¹⁻⁴. These composite polymer electrolytes were used widely due to easy fabrication technique of desirable size and facilitate proper contacts with electrode and electrolyte. When nano fillers doped to polymer electrolytes then, there was an increase in

the conductivity of the polymer electrolytes and also improves the mechanical strength⁵. Various types of nano fillers were reported to study the performance of composite polymer electrolytes⁶⁻²¹.

As per the literature, it was observed that majority of the authors were reported on Li based composite polymer electrolytes and scanty reports on potassium based composite polymer electrolytes. But potassium has several advantages compared to lithium such

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as easy contact ability, less moisture resistant, lower price, etc²². Therefore, in this present paper the authors reported (PEO+KNO₃+NanoAl₂O₃) based composite polymer electrolytes. The complexation of KNO₃ salt and Poly (ethylene oxide) (PEO) were confirmed by using X-ray diffraction (XRD) technique. Wagner's polarization technique has been obtained to determine transference number of these composite polymer electrolytes. The DC conductivity of these composite polymer electrolytes has been determined in the temperature range of 303-373K.

Experimental

Solution casting technique was used for preparation composite polymer electrolytes films. In this technique Poly (ethylene oxide) (PEO) [Aldrich: Molecular Weight (4X105)] and KNO₃ salt were dissolved separately in methanol and were mixed together. Nano alumina (Al₂O₃) (particle size ~10nm) was doped to mixed solution and stirred for 24hrs. Then after, it was casted on to polypropylene dishes, evaporated slowly at room temperature and vacuum dried carefully at 10⁻³ mbar to eliminate all traces of water. (PEO+KNO₃+Nano Al₂O₃) composite polymer electrolytes films (thickness $\approx$ 100 – 150 μ m) were prepared for the weight ratios (90:10), (80:20) and (70:30)²³. The complexation of KNO₃ and PEO have been confirmed by using X-ray diffraction setup of SIEMENS/D. 5000 X-ray diffractometer (Cu K α radiation λ = 1.5406Å)²³. The ionic and electronic transference numbers of these composite polymer electrolytes were evaluated by using Wagner's polarization technique²⁴. In this technique, a composite polymer electrolyte was placed between blocking electrode and non-blocking electrode and polarized by a constant DC voltage. Polarization current versus time have been obtained by using Keithley Electrometer [Model 604]. DC conductivity of these composite polymer electrolytes was determined by using lab made DC conductivity setup in the temperature range 303-373K²⁵.

Results and Discussion

(i) The X-ray diffraction (XRD):

The X-ray diffraction (XRD) pattern of pure Poly (ethylene oxide) (PEO), complexed PEO and pure KNO₃ salts were compared together and it was shown in Fig.1. From Fig.1 following results were observed:

- In the range of 20° to 30° of XRD pattern, intensity of the peaks was less in complexed PEO than pure PEO. Due to decrease in the degree of crystallinity of the polymer PEO by the addition of KNO₃ salts and Al₂O₃ to PEO.
- The peaks of pure PEO exist in complexed PEO. It was happen due to coincident existence of both crystalline uncomplexed and complexed PEO. Similar reports were observed for PEO based polymer electrolytes^{23,26}.
- Among all complexed PEO composite polymer electrolytes systems, (PEO+KNO₃+Nano Al₂O₃) (70:30) pattern less intensity peaks were observed due to dominant incidence of an amorphous phase.

From all the above observations, it was confirmed that KNO₃ and Nano Al₂O₃ were complexed with PEO.

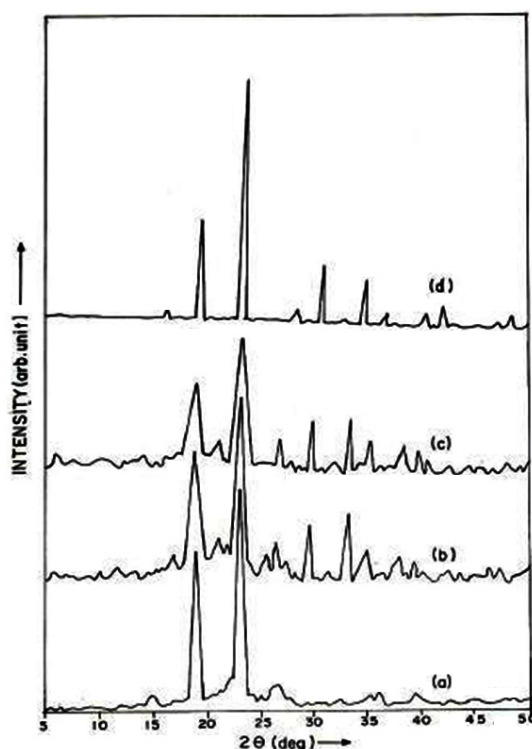


Fig.1: X-ray diffraction pattern
(a) Pure PEO, (b) [PEO+KNO₃+Nano Al₂O₃] (80:20) (c) [PEO+KNO₃+ Nano Al₂O₃] (70:30) and (d) KNO₃.

(ii) Transference Numbers:

Wagner's polarization technique was employed to determine transference numbers of t_{ion} and t_{ele} of (PEO+ KNO₃+Nano Al₂O₃) composite polymer electrolytes systems^{24,27}. In this context, polarization current versus time plots were obtained for (PEO+KNO₃+Nano Al₂O₃) (90:10), (80:20) & (70:30) composite polymer electrolytes. Current versus time plots of (PEO+KNO₃+Nano Al₂O₃) (70:30) was shown in Fig. 2. Transference numbers of t_{ion} and t_{ele} were calculated and tabulated in Table -1. From the obtained t_{ion} and t_{ele} values, it is clear that the conductivity occurring in these composite polymer electrolytes due to majority charge carriers i.e. ions and negligible contribution from the electronic²⁸.

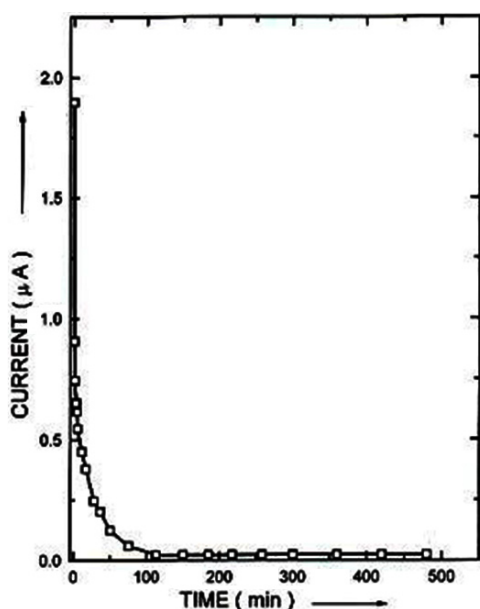


Fig. 2: Polarization current versus time plot for the complexed (PEO+KNO₃+Nano Al₂O₃) (70:30).

(iii) DC Conductivity:

The conductivity versus temperature plots were obtained in the temperature range of 303-373K for (PEO+KNO₃) & (PEO+KNO₃+nano Al₂O₃) composite polymer electrolytes systems and following facts were observed:

- The conductivity versus temperature plots were obeying Arrhenius nature throughout, but showing two regions. The region-I was

emerged below melting temperature (T_m) of (PEO+KNO₃+nano Al₂O₃) composite polymer electrolytes. The region-II was emerged above melting temperature (T_m) of (PEO+KNO₃+nano Al₂O₃) composite polymer electrolytes. However, in the both regions the conductivity increases with an increase of temperature, while a sudden sharp increment in the current was observed at T_m . It was occurred due to phase change from semi-crystalline phase to amorphous at T_m ²⁹.

Table 1: Transference Number Data and Dc Conductivity data Of (Peo+Kno₃+Nano Al₂O₃) Composite Polymer Electrolytes Systems.

Polymer Electrolyte	Transference Number		Dc Conductivity (σ) (S.Cm ⁻¹)
	tion	tele	at Rt
Pure Poly (Ethylene Oxide) (Peo)	-	-	8.35×10^{-10}
(Peo+Kno ₃ + Nano Al ₂ O ₃) (90:10)	0.98	0.02	5.59×10^{-8}
(Peo+Kno ₃ + Nano Al ₂ O ₃) (80:20)	0.98	0.02	4.88×10^{-8}
(Peo+Kno ₃ + Nano Al ₂ O ₃) (70:30)	0.99	0.01	2.05×10^{-7}

- The conductivity of the composite polymer electrolytes increases with an increase of temperature due to hopping mechanism between coordinating sites, local structural relaxations and segmental motions of polymer.
- When amorphous region gradually increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This was in turn favours the hopping inter-chain and intra-chain ion movements and the conductivity of the polymer electrolytes become high³⁰⁻³¹.

Similar results were observed for all the systems of (PEO+KNO₃) & (PEO+KNO₃+nano Al₂O₃) (90:10), (80:20) & (70:30). The conductivity versus temperature plots of PEO, (PEO+KNO₃) (70:30) and (PEO+KNO₃+nano Al₂O₃) (70:30) shown in Fig.3.

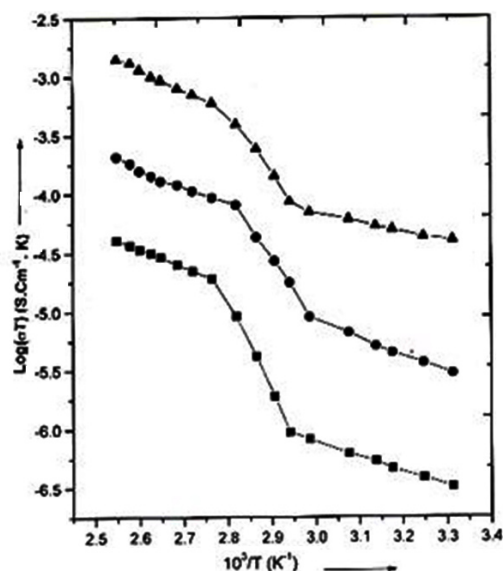


Fig. 3: The temperature dependence of D.C conductivity (a) Pure PEO, (b) [PEO+KNO₃] (70:30) and (c) [PEO+KNO₃+nano Al₂O₃] (70:30).

The Role of the Nano Al₂O₃:

From DC Conductivity studies (Fig.3) following observations were found:

- Nano filler Al₂O₃ doped with complexed PEO conductivity was very high compare to complexed PEO and pure Poly (ethylene oxide) (PEO). Once nano Al₂O₃ doped to polymer then, it reduce the crystallinity of polymer, hold back them from re-crystallization and boost the degree of amorphicity, which lead to better ionic conductivity of the polymer³². The conductivity values of (PEO+KNO₃+nano Al₂O₃) composite

polymer electrolytes systems were obtained and tabulated in Table-1.

Conclusions

Solid state (PEO+KNO₃+nano Al₂O₃) composite polymer electrolytes have been prepared by using solution casting technique. The complexation of salt and polymer were confirmed by using X-ray diffraction (XRD) technique. XRD was obtained in the range of 20° to 30°, intensity of the peaks was less in complexed PEO than pure Poly (ethylene oxide) (PEO). The degree of crystallinity of the polymer decreases by the addition of KNO₃ salt and Al₂O₃ to Poly (ethylene oxide) (PEO). From Wagner's polarization technique it was clear that, conductivity occurring in these composite polymer electrolytes due to ions and negligible contribution from the electronic. The DC conductivity increase with increase of temperature due to hopping mechanism between coordinating sites, local structural relaxations and segmental motions of polymer. Nano filler Al₂O₃ doped with complexed PEO shown high conductivity compared to complexed PEO composite polymer electrolytes systems.

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Conflict of Interest

The author(s) declare(s) that there is no conflict of interests regarding the publication of this article.

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