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Polymer electrolyte-graphene composites: Conductivity peaks and reasons thereof

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ABSTRACT

Composites of polymer electrolyte (PEO:NH_4I) with graphene have been prepared and characterized. Dispersal of graphene is found to introduce partial electronic conductivity in the ion conducting polymer electrolyte. The conductivity vs. composition of graphene plots exhibit two peaks. Conformational and structural changes have been investigated by Raman spectroscopy, differential scanning calorimetry (DSC) and positron annihilation lifetime spectroscopy (PALS). The peaks in the conductivity have been explained on the basis of changes in crystallinity of the host polymer and establishment of percolation paths.

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1. Introduction

Polymer electrolytes are ion conducting polymers which can be prepared by complexing appropriate salts to polar polymers [1–4]. They have good thermal, mechanical and electrical stabilities besides the ease in film formation in desired shape and size. Many approaches like copolymerization, plasticization and dispersion of fillers have been adopted to modify the conductivity of polymer electrolytes [5–10]. Several studies on PEO (polyethylene oxide) based polymer electrolytes using alkali salts have been done because of the high solvating power of PEO. Other salts include ammonium salts and examples of such electrolytes are PEO:NH_4SCN, PEO:$NH_4SO_3CF_3$ [11], PEO:NH_4I [12] and PEO:NH_4ClO_4 [13,14]. All these are reported proton conductors. The segmental motion of the polymer chain facilitates ion transport, thus, chain mobility and the free volume are of key interest and have been investigated by positron lifetime spectroscopy [15]. However, no clear correlation between free volume and change in conductivity was found. Also, other investigations [16] showed that the change of crystallinity can also be the reason of increase in ionic conductivity. A comparison of conductivity measurements and positron annihilation measurements showed a clear correlation between conductivity and free volume for Li doped polyethylene-glycol dimethacrylate [17]. Thus, it is clear that a combination of experimental techniques is necessary to clarify the contributions of the number of charge carriers, their respective charge and mobility to the overall conductivity.

In order to the improve conductivity and mechanical properties of polymer electrolytes, particles have been added, mostly in the form of metallic or ceramic nanoparticles [18,4]. Shape and size of the filler particles play an important role in modifying the mechanical, electrical and magnetic properties of the composites [19–22]. However, in contrast to ceramic–polycrystalline ionic composites, where since the pioneering work of C.C. Liang [23], much work has been done and the interpretation is quite clear, in polymer electrolyte (nano)-composites the situation is less clear, as seen by selected examples from literature [18]. Furtado et al. [24] showed that the changes in microstructure of the polymer and different phases strongly affect the conductivity. Investigations by Pandey et al. [25] showed a strong dependence of conductivity on the preparation method (hot pressed vs. solution casting). Additional dissociation by the addition of even small amounts of clay has been used as explanation for changes in conductivity by Sharma et al. [26].

Due to the variety of experiments, a variety of models have also been proposed to explain the changes in conductivity with the experimental parameters. Some are centered around changes in microstructure due to particle and salt addition, i.e., crystal size or crystalline volume fraction, as transport is mainly in the amorphous phase or near the crystals [27]. Other approaches are related to the increase or decrease in polymer chain mobility due to the binding between salt, nanoparticles and the polymer chain, which should affect – besides others – the caloric glass transition temperature [28,29]. Finally, some experiments have been interpreted by the addition of fast transport paths, either along interfaces between different areas of the polymer microstructure or along the nanoparticles (percolation theories) [30,31]. In particular, this has to be seen in the context of several possible charge carriers, i.e., cations, anions and

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sometimes even electrons. Thus, further experiments are needed to separate the individual contribution of these charge carriers to the total conductivity in polymer-electrolyte composites.

The present paper consists of a study on PEO:NH_4I (a well characterized proton conductor) polymer electrolyte dispersed with multilayered graphene. The effect on the structural, thermal and electrical properties of the polymer electrolyte on dispersion of graphene is being reported. Graphene is the two dimensional form of carbon, one of the methods of obtaining which is, micromechanical cleavage of graphite [32]. It is a zero gap semiconductor with good electronic properties [33] and a nearly perfect crystal free of structural defects [34,35]. Graphene has great importance in fundamental studies and technological applications due to its unique structure and a wide range of unusual properties [36], some of which are enumerated above. Graphene/polymer composites are technologically relevant with a variety of interesting properties [37]. Graphene is primarily an electronic conductor and so we, in the present study, dispersed it in an ion conducting polymer electrolyte to obtain novel mixed (ion + electron) conducting polymeric membrane.

A variety of techniques, namely, (i) impedance spectroscopy for determining the total conductivity and the relative contribution of electronic and ionic parts, (ii) differential scanning calorimetry (DSC) for melting temperature and melting enthalpies, (iii) transmission electron microscopy (TEM) together with energy dispersive analysis of X-rays (EDAX) for microstructural investigation and (iv) Raman spectroscopy have been employed in the present study to characterize the polymer electrolyte composite (PEO:NH_4I) + graphene. Positron annihilation lifetime spectroscopy (PALS) has been employed to determine the free volume in the composites.

In the discussion part of the paper, the composition dependence of electronic and ionic transport are correlated with the structural changes and discussed with respect to various models of conductivity in polymer-electrolyte composites.

In devices based on solid state ionic materials, while the ion transport takes place within the device, electron transport takes place in the external circuit. Therefore, such materials are desired for the interface which can conduct via both, ions and electrons. Mixed (ion + electron conductors) conducting polymeric membranes play an important role having various applications, such as, air-separating membranes, electrodes, gas sensors, electrochemical devices and fuel cells [38].

2. Experimental and results

2.1. Sample preparation

For obtaining polymer electrolyte films, PEO (molecular weight ~6×10^5, Aldrich) was dissolved in distilled methanol into which varying amounts of NH_4I (Aldrich) were added. The solution was stirred at 40 °C for ~5 h using a magnetic stirrer till the solution became highly viscous. Subsequently, it was poured into polypropylene petri-dishes. After drying in room temperature, the films were further dried in vacuum (~10^{-3}Torr) for 2–3 h to eliminate traces of the solvent. A preliminary study of the composition dependent conductivity showed that the 90:10 weight ratio ($NH_4^+/EO = 0.034$) of PEO:NH_4I gave stable as well as high conducting polymer electrolyte films. This polymer electrolyte was selected as the host for dispersion of graphene. Multilayered graphene was obtained by micromechanical cleavage of graphite.

For obtaining graphene dispersed polymer electrolyte composite films, desired amount of graphene in THF (tetrahydrofuran) was dispersed in the PEO:NH_4I (90:10) solution and ultrasonicated for ~15 min. When the solution became highly viscous, it was poured into petri-dishes. The drying of the films was done as described above. To check traces of residual solvents, in particular THF, FTIR of the films was done and no peak of the C−H stretching vibration between 2800 and 3000 cm^{-1} was obtained, confirming non-complexation of the solvents. Different films of polymer electrolyte composites were prepared having composition (90PEO:10NH_4I) + x graphene, where, x = 0.00–0.09 wt.%. Note that the solubility limit of graphene in the polymer electrolyte was 0.09 wt.% after which mechanically stable films could not be obtained as they were brittle.

2.2. Conductivity measurements

The total electrical conductivity (σ_T) of the polymer composite films has been evaluated by complex impedance spectroscopy in the frequency range of 1 mHz to 100 kHz by using HIOKI 3522-50 LCR Hi Tester. It must be noted that each conductivity data point is an average of 64 readings (inbuilt in software). Their reproducibility has been checked.

In Fig. 1(a), the total, the electronic and the ionic conductivities at room temperature (300 K) are shown as a function of graphene concentration. The electronic and ionic transference numbers (t_e and t_i), have been measured using Wagner's polarization method [39], Fig. 1(b), from which the contributions from the electronic (σ_e) and

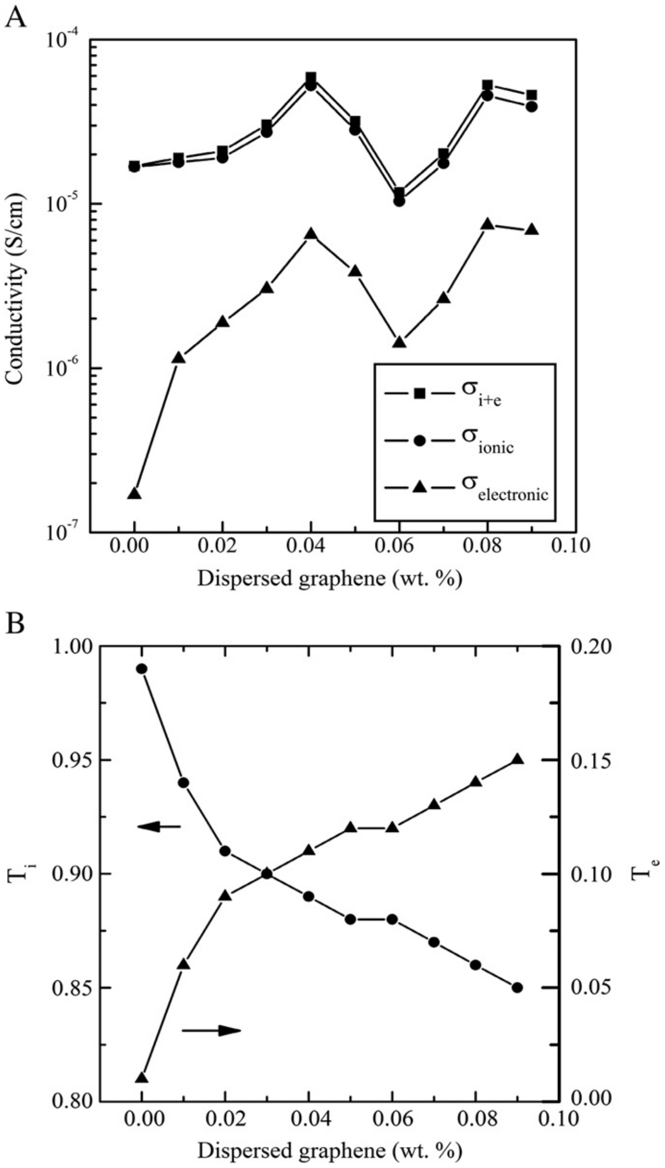

Fig. 1. Variation of (a) electronic, ionic and total conductivities and (b) electronic and ionic transference numbers for the (90PEO:10NH_4I) + x wt.% graphene where, x = 0.00–0.09 wt.%.

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