



Ion Conductivity and Thermal Properties of Nano-composite Polymer Gel Electrolytes containing NH₄SCN for Electrochemical Devices

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Abstract: Nano-composite polymer gel electrolytes consisting of polyethylene oxide (PEO) as polymer, ammonium thiocyanate (NH₄SCN) as salt, propylene carbonate (PC) as solvent, nano-sized titanium dioxide (TiO₂) as nano-filler has been prepared and characterized. The addition of polymer increases the viscosity of electrolytes alongwith a small increase in conductivity. An increase in conductivity with the addition of polymer has been explained to be due to the dissociation of ion aggregates and undissociated salt present in the electrolytes by increasing the dielectric constant of the electrolytes. The effect of addition of nano-sized titanium dioxide on the conductivity and viscosity behaviour of polymer gel electrolytes has been studied. The mechanical stability alongwith ionic conductivity of the gels has been improved. The thermal stability of nano-composite polymer gel electrolytes has been checked by DSC/TGA studies. The conductivity of nano dispersed gels does not show much change over 30-100°C temperature range and also remains constant with time, which is desirable for device applications like batteries, fuel cells, supercapacitors and other electrochromic devices.

Keywords : nano-composites; nano-filler; ion aggregates, conductivity, viscosity.

Introduction

Polymer electrolytes are attracting more attention in the recent past due to their use in various electrochemical devices viz. batteries, fuel cells, supercapacitors, sensors and other electrochromic devices¹⁻⁶. Polymer electrolytes in gel form obtained by the immobilization of salt solution in a suitable polymer matrix have high ionic conductivity than polymer electrolytes in film form. Polymer gel electrolytes belong to a hybrid system of salt, solvent and polymer in which solvent is retained in the electrolyte and provides medium for conduction. The addition of polymer to liquid electrolytes increases the mechanical stability by increasing the viscosity accompanied by a decrease in conductivity. Feuillade and Perche have reported first gel electrolytes containing lithium salts in 1975⁷. After then different polymer gel electrolytes have been widely studied due to their suitability as electrolytes in various devices⁸⁻¹⁰. Proton conducting polymer gel electrolytes are also important as they can find applications in different devices¹¹⁻¹⁹. In polymer electrolytes, the addition of inorganic fillers such as zeolite, SiO₂, Al₂O₃, TiO₂ etc. has been reported to result in an improvement in the electrode-electrolyte interfacial stability, conductivity alongwith an improvement in mechanical properties of electrolytes²⁰⁻³⁰. The aim of the present work is to develop nano-composite polymer gel electrolytes with high ionic conductivity and good mechanical and thermal stability.

In the present paper, nano-composite polymer gel electrolytes obtained by dispersing titanium dioxide with particle size in the nanometer range to polymer gel electrolytes containing NH₄SCN in propylene

carbonate have been studied. The effect of addition of nano-sized titanium dioxide on conductivity, viscosity and thermal properties of gel electrolytes has been studied. DSC/TGA studies have been carried out to check thermal stability of nano-composite polymer gel electrolytes.

Experimental methods

Polyethylene oxide (PEO) (Aldrich, av. mol. wt.= 5×10^6), ammonium thiocyanate (NH_4SCN), (AR grade sd. fine chem.), propylene carbonate (PC) (Merck) and titanium dioxide (TiO_2) nanopowder (Aldrich) with average particle size 21nm were used as the starting materials for the preparation of nano-composite polymer gel electrolytes. Nano-sized titanium dioxide was added as in different concentrations (expressed as wt% of polymer gel electrolytes) to polymer gel electrolytes alongwith continuous stirring till a homogeneous mixture is obtained. The conductivity of these electrolytes was measured by complex impedance spectroscopy with HP4284A precision LCR meter using a cell with platinum electrodes^{27-29, 31}. Viscosity was measured by Fungilab rotating viscometer (Visco Basic L) and temperature was maintained by Julabo water circulator (F-12EC)²¹⁻²². Thermal properties of gel electrolytes were studied by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) (SDT Q600 V8.0 Build 95) in the 25-300°C temperature range at the heating rate of 10°C/minute under nitrogen atmosphere.

Results and Discussion

The ionic conductivity of liquid electrolytes was measured as a function of salt concentration and results are shown in Fig.1. The conductivity of propylene carbonate has been found to increase by four orders of magnitude (i.e. 10^{-6} to 10^{-2} S/cm) with the addition of NH_4SCN . At low salt concentrations, the conductivity increases sharply which is due to an increase in free ion concentration by dissociation of salt. But at high salt concentrations, the increase in conductivity is small, which is possibly due to the formation of ion aggregates that do not contribute to the conduction process of electrolytes. Similar results have already been reported by various authors^{21,22,30}.

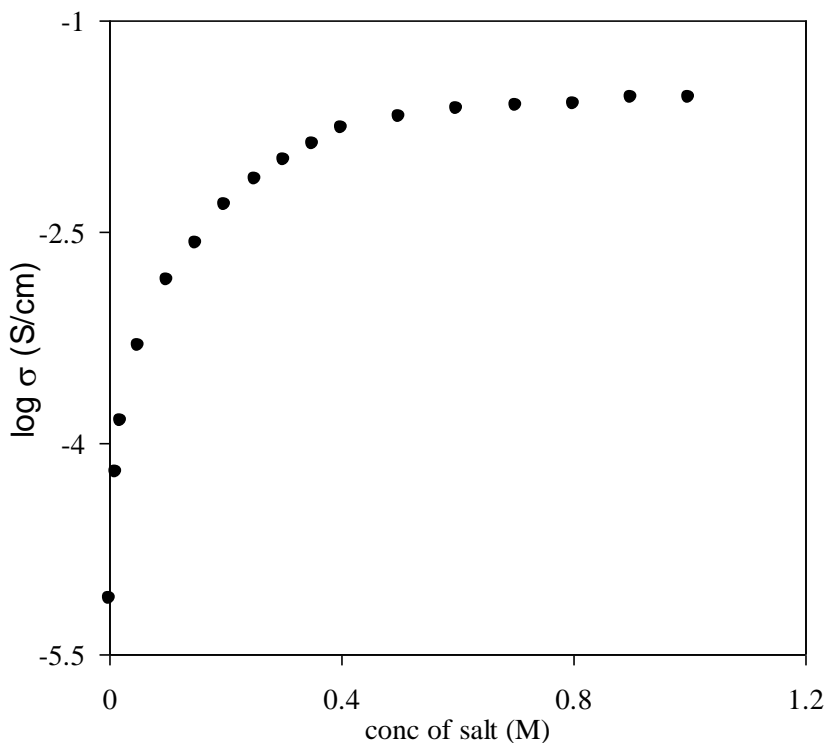


Figure 1: Variation of log conductivity of liquid electrolytes ($\text{PC}+x(\text{M})\text{NH}_4\text{SCN}$) with the concentration of salt.

Polymer gel electrolytes have been prepared by adding PEO (wt%) to liquid electrolytes containing 1M NH_4SCN in propylene carbonate and the variation of ionic conductivity of polymer gel electrolytes as a function of PEO concentration is given in Fig. 2. The conductivity shows a small increase at low concentrations of PEO (upto 2wt%) and then decreases at higher concentrations of PEO. The increase in conductivity at low PEO concentrations is possibly due to the increase in free ion concentration provided by dissociation of ion aggregates/undissociated salt present in the liquid electrolytes. Chandra *et. al* have explained the increase in conductivity with the addition of polymer by “Breathing Polymeric Chain Model” for proton conducting polymer gel electrolytes³². The maximum conductivity of 3.02×10^{-2} S/cm has been observed for gel electrolytes at 2wt% concentration of PEO. The decrease in conductivity at high PEO concentrations is due to increase in viscosity of gel electrolytes as given in Fig. 2. The conductivity decreases by a small factor and still polymer gel electrolytes have conductivity of the same order (10^{-2} S/cm) as observed for liquid electrolytes. The viscosity of liquid electrolytes has been increased from 5.4 mPas to 5,012 mPas.

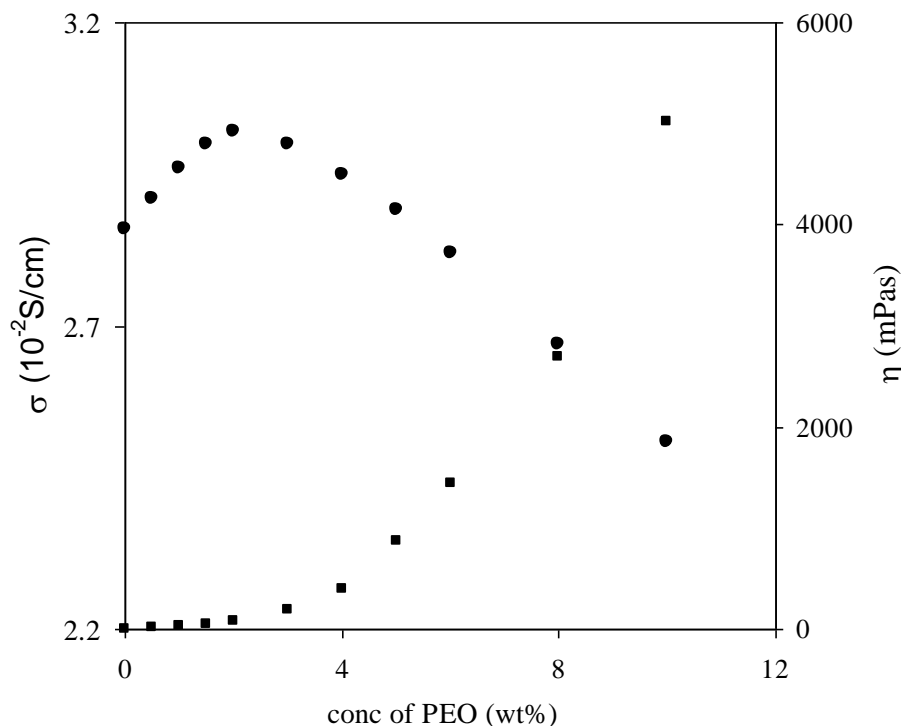


Figure 2: Dependence of conductivity (●) and viscosity (■) with the concentration of PEO for polymer gel electrolytes containing PC+1M NH_4SCN +xwt% PEO.

The variation of conductivity of polymer gel electrolytes containing PC + 1M NH_4SCN + 2wt% PEO with the concentration of titanium oxide is given in Fig.3. From Fig. 3, it has been observed that the conductivity of polymer gel electrolytes increases with the addition of TiO_2 , and maximum have been observed in the conductivity variation at 6wt% TiO_2 . The addition of TiO_2 nano-particles leads to the dissociation of ion aggregates/undissociated salt into free ions in nano-composite polymer gel electrolytes. So higher number of free ions is generated due to addition of TiO_2 particles and hence conductivity increases upto 6wt% concentration. The maximum ionic conductivity of 4.56×10^{-2} S/cm at room temperature has been obtained. After 6wt% TiO_2 , the conductivity shows a continuous decrease, which is due to higher viscosity of the electrolytes and blocking of conducting paths by the grains of TiO_2 , which restricts the motion of free mobile ions³³⁻³⁵. The viscosity of electrolytes was also measured and its variation with the concentration of titanium oxide is given in Fig.3. The maximum viscosity of 7621 mPas has been obtained at 10wt% TiO_2 .

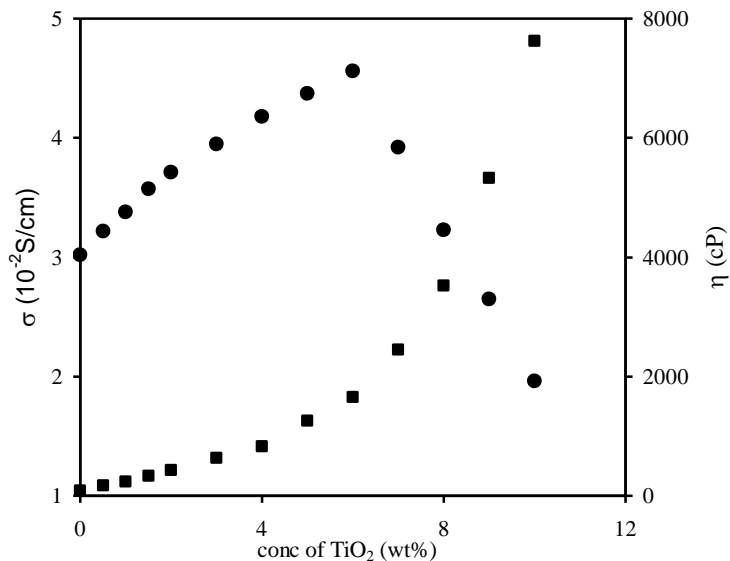


Figure 3: Variation of conductivity (●) and viscosity (■) with the concentration of TiO₂ for nano-composite polymer gel electrolytes containing PC+1M NH₄SCN +2wt% PEO+xwt% TiO₂.

Thermal stability of nano-composite polymer gel electrolytes with composition PC + 1M NH₄SCN + 2wt% PEO+ 10wt% TiO₂ has been studied by simultaneous DSC/TGA measurements and the results are given in Fig. 4. A small exothermic peak at 88°C corresponding to weight loss of 5% has been observed in nano-composite polymer gel electrolytes, which may be due to the evaporation of residual moisture absorbed when the sample was loaded. Decomposition temperature corresponding to the weight loss of 10% has been observed at 125°C in nano-composite polymer gel electrolytes. An endothermic peak at 198°C with a weight loss of 82% has been attributed to be due to the thermal decomposition of polymer in electrolytes. Rapid weight losses of 94% has been observed corresponding to an endothermic peak at about 226°C due to the evaporation of PC (boiling point=242 °C) in nano-composite polymer gel electrolytes. DSC/TGA studies show that these electrolytes are thermally stable up to 125°C only.

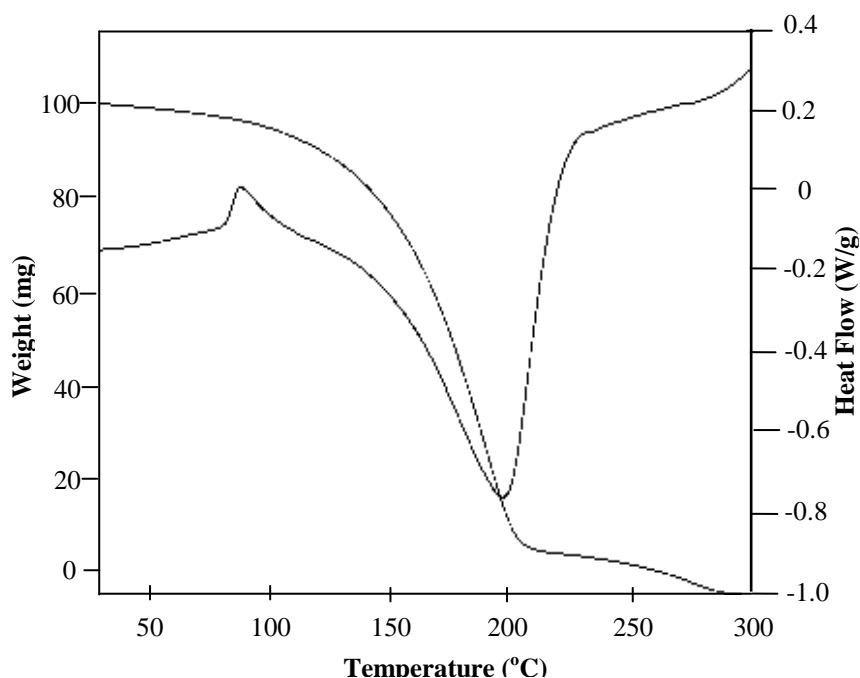


Figure 4: DSC and TGA plots for nano-composite polymer gel electrolytes having composition PC+1M NH₄SCN+2 wt% PEO+10 wt% TiO₂.

The dependence of ionic conductivity and viscosity of nano-composite polymer gel electrolytes on temperature was also studied. The variation of log conductivity and log viscosity of nano-composite polymer gel electrolytes having composition PC+1M NH₄SCN+2wt% PEO+10wt% TiO₂ with reciprocal temperature is given in Fig. 5. The conductivity of nano composite polymer gels shows only a small increase over the 30-100°C temperature range. The conductivity of nano-composite polymer gels does not show any appreciable change with time over a limited period of 30 days as given in Fig. 6, which is desirable from application point of view.

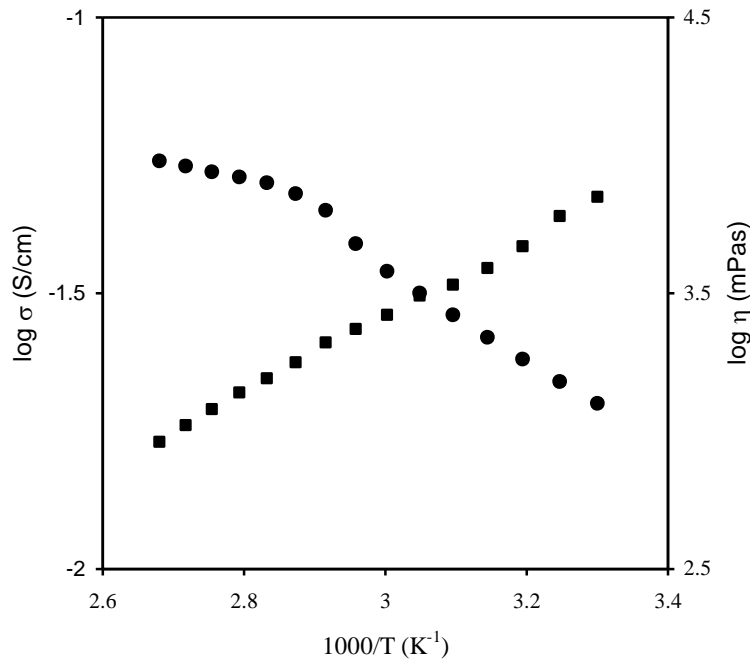


Figure 5: Variation of log conductivity (●) and log viscosity (■) with reciprocal temperature for nano-composite polymer gel electrolytes containing PC+1M NH₄SCN+2 wt% PEO+10 wt% TiO₂.

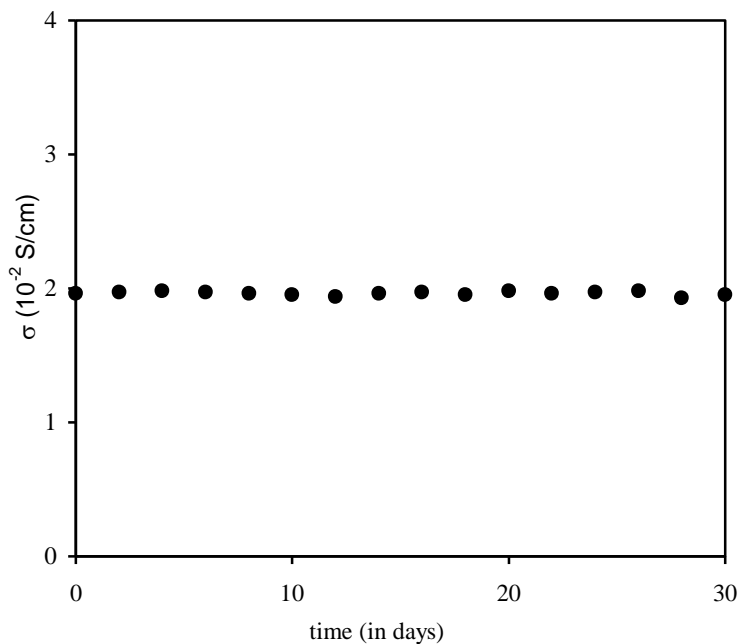


Figure 6: Variation of conductivity with time for nano-composite polymer gel electrolytes containing PC+1M NH₄SCN+2 wt% PEO+10 wt% TiO₂.

Conclusions

The addition of PEO and nano-sized titanium oxide results in an increase in ionic conductivity, which has been found to be due to an increase in free ion concentration by dissociating ion aggregates/undissociated salt present in the electrolytes. The addition of nano-sized titanium oxide to polymer gel electrolytes results in nano-composite polymer gel electrolytes with ionic conductivity of the order of 10^{-2} S/cm at room temperature. A small change in conductivity and viscosity observed over the 30-100°C temperature range alongwith constant value of conductivity with time is desirable for their potential use in different applications.

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