ORIENTING SENIOR SECONDARY PHYSICS STUDENTS, ABOUT MEASURING CONDUCTIVITY OF A NEW MATERIAL AND ITS APPLICATIONS

Rana Pratap

Regional Institute of Education, NCERT, Ajmer, Rajasthan-305004
E-mail: paratap2008@gmail.com

Plasticizer (Propylene Carbonate, PC) is enhancing the conductivity of a polymer electrolyte PEO: NH_4ClO_4 (85:15 wt %) prepared by solution cast method. Preliminary IR and XRD studies suggested that the above said polymer electrolyte is a result of complexation of polymer PEO and salt NH_4ClO_4. Two types of charge carriers are shown to be present in this polymer electrolyte by using transient ionic current measurements. The ionic conductivity of the polymer electrolyte with different amounts of plasticizer PC has been measured by Impedance Spectroscopy and it is shown that the maximum conductivity occurs for 5 wt% of PC which is 10-4 S.cm-1 (approximately 10 times higher than the conductivity of polymeric membrane without PC). The plasticised stable film has been used as an electrolyte in fabrication of a rechargeable polymeric solid state proton battery. The fabricated polymeric re-chargeable batteries uses PEO: NH_4ClO_4 (85:15 wt %) + PC 5wt % as the electrolytes with $Zn+ZnSO_4.7H_2O+MHx$ as anode and intercalating layered cathode material (PbO2+V2O5). The discharge characteristics have been studied at different loads. It is found that the addition of metal hydride (as hydrogen supplying anode) improves the time of stable performance, current drain and rechargeability as it ensures a continuous supply of H+ ions. It may be remarked that the use of H+ intercalating/de-intercalating layered material cathode (viz. $(PbO_2+V_2O_5)$ is essentially responsible for the rechargeability of the cells over many cycles.

Key word: *Polymeric proton battery; polymer electrolyte*

Introduction

The interest in the important ion conducting solid polymer electrolytes (or polymer-salt complexes) began after the pioneering studies of materials based on alkali salts complexed with polyethylene oxide (PEO) reported first by Fenton, et al., 1973; Wright, 1975 and Armand, et al., 1978; 1979. Polyethylene oxide (PEO) in particular is an exceptional polymer which dissolves high concentrations of a wide variety of salts to form polymer electrolytes (Armand, 1987). In such polymer complexes, the cations of the salts coordinate with the hetero-atom (polar group) of the polymer (such as oxygen, in the case of (PEO) as follows:

$$—(CH_2\text{-}CH_2\text{-}O)_{-n} + MX \quad \text{-}(CH_2\text{-}CH_2\text{-}O).\ MX\text{-} \qquad (1)$$

Polymer Salt Polymer Complex

Proton transport in polyethylene oxide complexed with NH_4ClO_4 has been earlier studied by Hashmi, et al., 1990. They found that polymer complex having configuration $PEO:NH_4ClO_4$::85:15 wt% possesses maximum conductivity ~ 10^{-5} $S.cm^{-1}$ which is nearly 4 decades higher than pure PEO. They also observed that apart from H+, the anions (i.e., ClO_4^-) are also mobile in the bulk material.

The present study is also related with $PEO:NH_4ClO_4$ (85:15 wt%) polymer complex with the aim of further enhancing its conductivity by adding suitable plasticiser which is expected to amorphicise the lattice. This polymer complex of appropriate composition has been prepared by us by solution cast method which has ~ 10^{-5} $S.cm^{-1}$ at room temperature. Complexation has been confirmed by IR and XRD studies. Two types of charge carriers are present in the bulk material. This has been confirmed by transient ionic current measurements. Dependence of it's conducting with temperature has also been studied. As pointed out earlier, in an effort to enhance its conductivity at room temperature for device purposes, we added plasticizer, propylene carbonate (PC) to it. The added wt% of plasticizer has been optimised to get maximum conductivity ~ 10^{-4} $S.cm^{-1}$ which is approximately 10 times higher than the conductivity of polymeric membrane without PC. The plasticised stable film has been used as an electrolyte in fabrication of a re-chargeable solid state proton battery.

Methods and Procedure

Material Preparation

Polymer Complex: Polymer complex film of composition PEO:NH_4ClO_4 (85:15 wt%) was prepared by using high molecular weight polyethylene oxide (PEO) (Aldrich, MW = 5x106) and NH_4ClO_4 (VEB Laborchemie Apolda, Germany) by solution casting technique using methanol as solvent. Solutions of weighed amounts of PEO and NH_4ClO_4 were prepared in methanol. These solutions were mixed and stirred for 5 hours. The resulting viscous solution was poured into petri-dishes. After ambient drying for 2-3 days a thin polymer film or membrane was obtained. This was further vacuum (10-4 Torr) dried to eliminate remaining methanol.

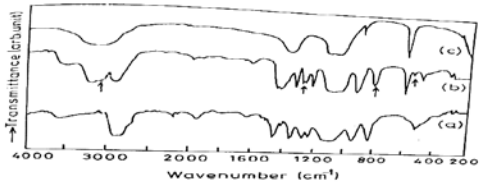
Plasticised polymer complex: The required amounts of plasticiser propylene carbonate and above prepared polymer complex electrolyte were put together and dissolved in methanol to get a clear solution. It was well stirred to get a viscous solution. This solution was poured into petri dishes and dried as above for few days in ambient and in vacuum to get thin plasticized polymer electrolyte films having composition [PEO:NH_4ClO_4 85:15 wt%] + 5 wt% PC and 10 wt% PC. For higher PC content, stable films could not be obtained as the material was becoming soggy.

Results and Discussion

Structural Studies

Infrared spectroscopy: The infrared spectra of (a) pure PEO, (b) polymer complex: PEO:NH_4ClO_4 (85:15 wt%) and (c) pure NH_4ClO_4 .

A comparison shows that the IR spectrum of the complex material is different than the spectra of constituent materials PEO and NH_4ClO_4. Some new peaks (marked by) appear in the new complex spectrum. Appearance of these peaks proves with complexation occurs between PEO and NH_4ClO_4 to yield the polymer electrolyte.

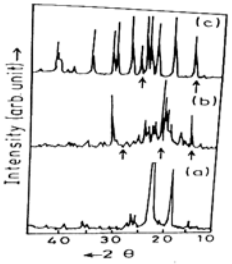


Infrared spectra of (a) Pure PEO (b) Polymer complex: PEO:NH_4ClO_4 (85:15 wt%) and (c) pure NH_4ClO_4

Fig. 1. Infrared spectroscopy

X-ray diffraction: XRD patterns of (a) pure PEO (b) polymer complex PEO:NH4ClO4 (85:15 wt%) and (c) pure NH_4ClO_4.

On careful examination of the XRD patterns, it is clear that some new peaks have appeared in the complex. The intensity of the X-ray peaks are also modified in the complex. Hence this confirms that the complexation of the system has taken place. It may be noted that the distinct peaks are over-riding a 'broad hallow' between two values of 15-30°. The broad hallow is indicative of amorphous phase. Therefore, it can be concluded that complexation has increased the amorphicity of the PEO-lattice.



X-ray diffraction patterns of (a) pure PEO. (b) polymer complex: PEO:NH_4ClO_4 (85:15 wt%) and (c) Pure NH_4ClO_4

Fig. 2. X-Ray diffraction pattern

Ion Transport Studies: Hashmi, et al. (1990) in their studies have shown that in polymer complex PEO:NH_4ClO_4 (85:15 wt%) the charge transport in the material mainly occurs due to motion of H^+ ions (tH^+ 0.85) but to some extent, it is also due to motion of ClO_4^- ions ($tClO_4^-$ 0.08). In order to provide an experimental evidence to the motion of these ions in the complex system, we have carried out transient ionic current (TIC) measurements by the methods proposed by Chandra, et al. (1988). The plot of TIC Vs time.

Two peaks are observed in the i Vs time curve. The first peak at t = 0.35 sec corresponds to the motion of H^+ ions whereas second peak at t = 0.68 sec. corresponds to the motion of ClO_{4-} ions. This identification is 'tentative' and guided by the fact that we have presumed that the lighter species (i.e., H^+) is likely to move faster than ClO_{4-}.

Conclusion

Polyethylene oxide (PEO) complexed with ammonium perchlorate (NH_4ClO_4) having composition PEO: NH_4ClO_4 (85:15 wt%) is found to be predominantly an ionic conductor. Transient ionic current measurements indicate that both cations and anions are mobile. The electrical conductivity at room temperature is of the order of 10^{-5} S.cm^{-1}. The plasticised polymer electrolyte having composition [PEO: NH_4ClO_4 (85:15 wt%) + 5 wt% of PC] shows maximum conductivity ~ 10^{-4} S.cm^{-1} at room temperature in ambient. Hence, it can be a good material for the fabrication of a re-chargeable solid state proton battery.

References

Abe, Y., H. Hosano., Y. Ohta and L.L. Hench. 1988. *Phys. Rev.* B 38 (1988) 10167.

Abraham, K.M., M. Alamgir and R.D. Moulton. 1991. *J. Electrochem. Soc.* 138. 921.

Agrawal, R.C., R.K. Gupta and J. Mater. 1995. *Sci. 30.* 3612.

Alberti, G. and M. Casciola. 1997. *Solid State Ionics.* 97. 177.

Anantha, P.S. and K. Hariharan. 2005. *Solid State Ionics.* 176. 155.

Angell, C.A. 1986. *Solid State Ionics,* 18/19 72.

Armand, M.B., J.M. Chabagno, and M.I. Duclot. 1978. Extended Abstract, Second International Meeting on Solid Electrolytes, St. Andrews, Scotland, Sept. 20-22.

———. 1979. *Fast Ion Transport in Solids* (Eds. Vashishta, P., Mundy, J.N. and Shenopy, G.K.) Elsevier North Holland, New York. p. 131.

———. MacCallum, J.R. and Vincent, C.A. Elsevier. 1987. *Polymer Electrolyte Review-1,* Applied Science. London.

Arof, A.K. 1994. J. Phys. III: *Appl. Phys. Mater. Sci. 4* 849.

Bandarnayake, P.W.S.K. and B.-E. Mellander. 1990. *Solid State Ionics* 40-41 31

Bhoga, S.S. and K. Singh. 1998. *Solid State Ionics* 111 85

Blender, R. and W. Dieterich. 1987. *J. Phyus.* C. 20 6113

Cava, R.J., F. Reidinger and B.J. Wuench. 1997. *Solid State Commun.* 24. 411

Chandra, A. and S. Chandra. 1993. *Phys. Rev.* B 68 633

Chandra, S., in Handbook of Solid State Batteries and Capacitors (Ed.) M.Z.A. Munshi (World Scientificc, Singapore, 1995) 579. Introduction

———. S.K. Tolpadi, and S.A. Hashmi. 1988. *Solid State Ionics.* 28–30. 651.

———. and S.A. Hashmi. 1990. 25 2459

Chandra, S. 1981. *Superionic Solids – Principles and Applications.* North Holland, Amsterdam.

Fenton, B.E.I., J.M. Parker and P.V. Wright. 1973. *Polymer 14.* 589.

Hashmi, S.A., A. Kumar, K.K. Maurya and S.J. Chandra. 1990. Phys. D: *Applied Physics.* 23:1307.

Pratap, Rana. 2013. *Polymer Bull.* Springer-Verlag, Berlin, Heidelberg.

Wright, P.V. 1975. *Polymer,* 27:319.