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EFFECT OF Mn^{2+} IONS ADDITION ON THE IONIC CONDUCTIVITY OF METHACRYLIC ACID – ETHYL ACRYLATE (MAA: EA) COPOLYMER ELECTROLYTE FILMS

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ABSTRACT

New polymer electrolyte films of Methacrylic Acid – Ethylacrylate (MAA:EA) copolymer embedded with different concentrations of Mn^{2+} ions were prepared by solution casting. Impedance measurements indicated that the room-temperature ionic conductivity of the films increased with increasing Mn^{2+} concentration until 4 mol%, being up to 0.202×10^{-4} S cm^{-1}, and then decreased with further increasing Mn^{2+} concentration. In addition, the temperature-dependent ionic conductivity of the polymer electrolyte films followed an Arrhenius relation and the 4 mol% of Mn^{2+} incorporated copolymer electrolyte film exhibited a low activation energy for ionic conduction, being about 0.28 eV. Which is a promising value for ion battery applications.

INTRODUCTION

Polymer electrolytes have been found to have a great deal of advantages in replacing conventional liquid electrolytes. These advantages includes high specific energy, high energy density, leak proof, high ionic conductivity, wide chemical stability windows, light, solvent free condition and easy processability [1]. The interest in the study of polymer electrolytes system is due to the potential application of these materials in a great variety of electrochemical devices such as higher density application of these materials [2 – 12]

Methacrylic Acid- Ethyl Acrylate (MAA:EA) copolymer has drawn special attention amongst the copolymers because of its good environmental stability, easy process and transparency. MAA:EA copolymer is a potential material having good charge capacity and dopant dependent electrical and optical properties. Bajaj *et al*. [13] studied the thermal behavior of MAA:EA copolymers. Wang *et al*. [14] studied the interaction between MAA:EA copolymer and bromide dopant. The method of choice for producing conducting organometallic polymers involves complexing transition metals with conjugated bridging ligands. The ability to alter the oxidation state of the metal ion, and thus the charge density along the polymer backbone, provides an alternative route to charge carrier creation as opposed to redox doping. Its electrical conductivity depends on the thermally generated carriers and the addition of suitable dopants [15, 16]. Manganese is well known as magneto-active multivalent element; thus its halides can be used as fillers to modify the electric conduction and optical absorption of polymer matrix. On the other hand, $MnSO_4$ is considered as a good candidate for one or two dimensional phenomena and for optical memory devices [17, 18] based on the importance and relevance of the MAA: EA copolymer as a suitable matrix a transition metal ion such as Mn^{2+} ions, the electrical conductivity investigations of MAA:EA films doped with different concentrations of Mn^{2+} ions represent an important task of this work. Moreover, so far no work was reported on Mn^{2+} ions doped MAA:EA films. Hence, the authors have aim at the present investigation.

MATERIALS AND METHODS

Methacrylic acid - ethyl acrylate (1:1) dispersion 30 percent copolymer with molecular weight 250,000 was purchased from Merck Millipore India Ltd. MAA:EA copolymer films (14µm thickness) doped with Mn^{2+}, in various concentrations were prepared at room temperature by solution casting method. The desired concentrations of $MnSo_4$ solution (1, 2, 3, 4 and 5 mol%) were prepared by using distilled water. 5ml of MAA:EA copolymer was dissolved in distilled water separately. Different amounts of (1, 2, 3, 4 and 5 mol%) Mn^{2+} ions were added into the copolymer solution. The solution was magnetically stirred for 10-12 hours to get homogeneous mixture and then cast onto plastic dishes. The film was slowly evaporated at room temperature to obtain free standing copolymer film at the bottom of the dishes.

The electrical properties of the polymer electrolyte films were measured by a computer controlled impedance analyzer (PSM

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1735, Newton 4th Ltd, UK) over the frequency range 1 Hz - 1 MHz with a signal level of 10 mV. The measurements were carried out by sandwiching the polymer electrolyte film between two stainless steel electrodes in the temperature range of 30 - 90 ^{o}C. The prepared samples were cut into circular pieces and dried at 50 ^{o}C under vacuum for 1 h to reduce the environmental moisture effect before the electrical measurements.

RESULT & DISCUSSIONS

Analysis of ionic conductivity

In solid state ionic batteries, the polymer electrolytes work as a separator as well as medium to transport ions from anode to cathode. Hence ionic conductivity of polymer electrolyte is a very important parameter for battery applications. It is discussed through impedance measurement. Figure 1 shows the room temperature Nyquist impedance plot of pure and various concentrations of Mn^{2+} ions doped MAA:EA copolymer electrolytes. All the plots have a semicircle in the high frequency followed by the spike in the low frequency region [19]. The high frequency is attributed to the combine behavior of the mobile ions and immobile polymer chins, which is equivalent to the parallel combination of bulk resistance and capacitance. The low frequency spike represents the formation of blocking double layer capacitor at electrode – electrolyte interface, which is produced by migration of ions.

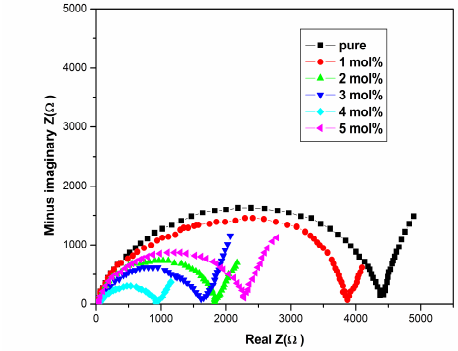

Figure 1 Room-temperature Nyquist impedance plots of MAA:EA+ Mn^{2+} ions copolymer electrolyte films.

Further more, the inclination of the spike at angle less than 90 ^{o}C to the real axis is due to the inhomogeneity at the electrode electrolyte interface. In the ideal case, the spike should be parallel to the imaginary axis. The intercept at high frequency end of semi circle to the real axis gives the bulk resistance of the polymer electrolytes (R_b). As can be seen, the bulk resistance decreases with increasing the concentration of Mn^{2+} ions.

The ionic conductivity of the polymer electrolyte films were calculated by

$$\sigma = \frac{l}{R_b A}$$

Where l is the thickness of the film, A is the area of electrode – electrolyte contact area and R_b represents the bulk resistance obtained from the Nyquist impedance. The room temperature ionic conductivity of 4 mol% of Mn^{2+} ions doped MAA:EA copolymer electrolyte is 0.20×10^{-4} Scm^{-1}. This means that addition of Mn^{2+} ions in the MAA:EA copolymer system has enhanced the ionic conductivity.

The ionic conductivity of polymer electrolyte depends on the number of mobile charge species and mobility along with polymer segmental mobility or polymer chain mobility. The room temperature ionic conductivity of MAA:EA copolymer electrolyte is plotted in Figure 2 as a function of Mn^{2+} concentration. Obviously the ionic conductivity increases with increasing Mn^{2+} ions content upto 4 mol% then decreases with further increasing Mn^{2+} content. Compared with 4 mol% of Mn^{2+} doped MAA:EA copolymer electrolyte, the conductivity of the 5 mol% of Mn^{2+} ions doped MAA:EA copolymer system has dropped dramatically. Consequently 4 mol% of Mn^{2+} incorporated MAA:EA copolymer electrolyte exhibit maximum ionic conductivity 0.20×10^{-4} Scm^{-1}. It is worth meaning that this ionic conductivity could be higher because electrode – electrolyte contact area could be smaller than the apparent electrode – electrolyte contact is usually not 100%. The improvement in the ionic conductivity of copolymer electrolytes by incorporating increasing Mn^{2+} concentration is due to the mobile charge carrier increase and the charge carrier mobility enhancement, as well as the improvement of amorphous nature/polymer segmental mobility. This can be explained by the general conductivity relation $\sigma = n_i q_i \mu_i$, where n_i is the number of charge carriers, q_i is the charge of mobile charge carrier and μ_i is the mobility of charge carriers. According to this relation, the enhancement in the ionic conductivity of polymer electrolytes can be achieved by increasing n_i and μ_i because q_i is the same for all charge carriers in the gel polymer electrolyte system.

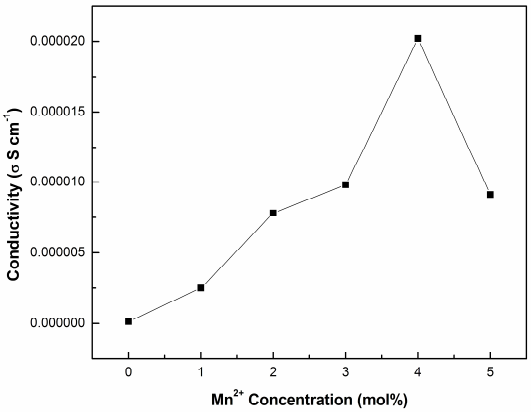

Figure 2 Room-temperature ionic conductivity as a function of Mn^{2+} concentration for the MAA:EA copolymer electrolyte system.

With the addition of Mn^{2+} ions in the MAA:EA copolymer system, new charge carriers/ions are introduced and then the overall charge carrier concentration is increased, which will be partially responsible for the increase of ionic conductivity. Furthermore, the new charge carriers interact with the polymer structure, reducing the intermolecular interaction between the polymer chains, and thus increasing the polymer chain segment mobility. Higher segmental mobility of the polymer chains means a greater disorder in their arrangement/structure, which

may result in an increased amorphicity in the gel polymer electrolyte system. When the Mn^{2+} concentration increases from 0 to 4 mol%, within the amorphous matrix, the mobile ions may travel a long distance (i.e., the mobility increases) before being deviated from their paths, thus leading to an increased ionic conductivity [20]. As the Mn^{2+} concentration increases up to 5 mol%, the number of mobile charge carriers and the polymer chain segment mobility are both increased but the mobility of charge carriers is reduced due to the interaction of ions. The improvement in the polymer chain segment mobility and charge carrier population will dominate as compared with the reduction of charge carrier mobility. Then, the overall ionic conductivity is apparently increased (see Fig. 4). As the Mn^{2+} concentration is further increased (more than 5 mol%), the ions will be very close to each other and form ion pairs and ion triplets. These ion pairs and ion triplets hinder the ion transport and block the segmental motion of polymer chains, i.e, the mobile charge carrier population, charge carrier mobility, and polymer chain segment mobility are all reduced, so that the overall conductivity is decreased.

Figure 3 shows typical Nyquist impedance plots of the 4 mol% of Mn^{2+} doped MAA:EA copolymer electrolyte film at different temperatures in the frequency and temperature ranges 1 Hz - 1 MHz and 30 - 90 ^{o}C, respectively. The plots exhibit the general behavior of ionic solids with blocking electrode i.e., a semi-circle with an inclined spike [19]. The diameter of the semi-circle shrinks with raising temperature, indicating a negative temperature coefficient for resistance or a positive temperature coefficient for conductivity. Moreover, with increasing temperature, the spikes/lines slightly get parallel to the imaginary axis, which is an indication of better contact of the copolymer electrolyte film with the electrode.

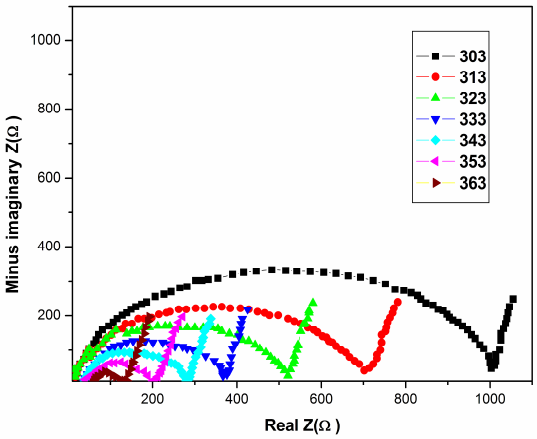

Figure 3 Nyquist impedance plots of the copolymer electrolyte film with 4 mol% Mn^{2+} at different temperatures.

The temperature dependence of ionic conductivity is represented in the inset of Figure 4. Clearly, lnσ has a linear relationship with reciprocal temperature (1/T), following Arrhenius relation $\sigma = \sigma_0 \exp(-E_a / kT)$, where σ_0 is the pre-exponential factor, E_a is the activation energy for ionic conduction, k is the Boltzmann constant, and T is the absolute temperature.

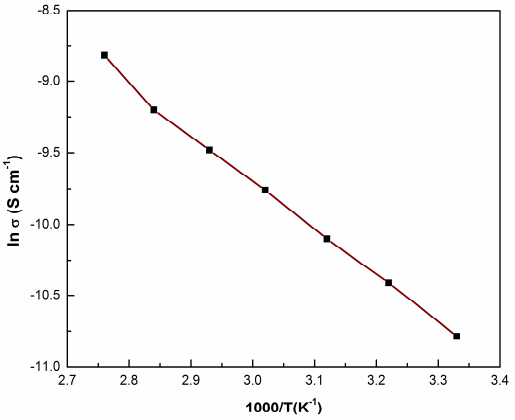

Figure 4 ln (conductivity) of the film (lnσ) as a function of reciprocal temperature (1/T).

The conductivity increase with rising temperature may be due to the reduced viscosity and enhanced mobility of polymer chains. This can be explained on the basis of the free volume and the hopping of charge carriers between localized sites [21]. At low temperatures, the crystallinity of the polymer (regular arrangement of polymer chains) is high, which hinders the motion of ions, so that the overall ionic conductivity is low. As the temperature increases, the amorphicity of the polymer increases progressively, i.e., the segmental mobility of the polymer chains increases. This increased segmental mobility of polymer chains can promote inter and intra-chain ion hopping movements, leading to an increase in ionic conductivity. The 4 mol% of Mn^{2+} incorporated in MAA:EA copolymer electrolyte possesses ionic conductivities of 0.202x10^{-4} S cm^{-1} and 0.127 x10^{-4} S cm^{-1} at room temperature and 90 ^{o}C, respectively, suggesting that it is a promising electrolyte material for battery applications in a wide temperature range. In addition, linear fitting obtains 0.28 eV as the activation energy for ionic conduction of the polymer electrolyte is. It is well known that a polymer electrolyte with a low activation energy for ionic conduction is desirable for practical applications [22].

CONCLUSIONS

Polymer electrolytes based on MAA:EA copolymer with Mn^{2+} as the dopant at different concentrations were prepared using solution casting technique. The room-temperature ionic conductivity increases with increasing Mn^{2+} ions up to 4 mol% and then decreases with further increasing Mn^{2+} ions. The 4mol% of Mn^{2+} MAA:EA copolymer electrolyte film exhibits the highest ionic conductivity (0.202x10^{-}4 S cm^{-1}) at room temperature. The temperature dependence of ionic conductivity of the electrolyte film shows an Arrhenius relation and the activation energy for ionic conduction is quite low, being 0.28 eV. These data suggest that the present electrolyte system is a worthy candidate for electrochemical device applications.

References

1. J.Y. Kim, S.H. Kim, *Solid State Ionics*, 124 (1999) 91.
2. J. Gao, J. Liu, W. Liu, B. Li, Y. Xin, Y. Yin, Z. Zou, *Int. J. Electrochem. Sci.,* 6 (2011) 6115.
3. L.C. Xuan, Y.X. An, W. Fang, L.X. Liao, Y.L. Ma, Z.Y. Ren, G.P. Yin, *Int. J. Electrochem. Sci.,* 6 (2011) 6590.

4. M.S.M. Eldin, M.A. Abu-Saied, A.A. Elzatahry, K.M. El-Khatib, E.A. Hassan, K.M. El-Sabbah, *Int. J. Electrochem. Sci.,* 6 (2011) 5417.
5. J.H. Kim, S.K. Kim, Y.Z. You, D.I. Kim, S.T. Hong, H.C. Suh, K.S. Weil, *Int. J. Electrochem. Sci.,* 6 (2011) 4365.
6. A. Anis, S.M. Al-Zahrani, A.K. Banthia, S. Bandyopadhyay, *Int. J. Electrochem. Sci.,* 6 (2011) 2461.
7. A. Anis, S.M. Al-Zahrani, A.K. Banthia, S. Bandyopadhyay, *Int. J. Electrochem. Sci.,* 6 (2011) 2652.
8. W.H. Chen, T.H. Ko, J.H. Lin, C.H. Liu, C.W. Shen, C.H. Wang, *Int. J. Electrochem. Sci.,* 6 (2011) 2192.
9. C.H. Wan, J.M. Wei, M.T. Lin, C.H. Lin, *Int. J. Electrochem. Sci.,* 6 (2011) 889.
10. B.C. Ng, H.Y. Wong, K.W. Chew, Z. Osman, *Int. J. Electrochem. Sci.,* 6 (2011) 4355.
11. P.C. Barbosa, M. Fernandes, S.M.F. Vilela, A. Goncalves, M.C. Oliveira, E. Fortunato, M.M. Silva, M.J. Smith, R. Rego, V.D. Bermudez, *Int. J. Electrochem. Sci.,* 6 (2011) 3355.
12. T.Y. Wu, H.C. Wang, S.G. Su, S.T. Gung, M.W. Lin, C.B. Lin, *J. Chin. Chem. Soc.*, 57 (2010) 44.
13. P. Bajaj, G. Meenakshi, R.B. Chavan, *J. Appl. Poly. Science* Vol: 51 (1994) 423.
14. C. Wang , K.C. Tam, R.D. Jenkins, C.B. Tan*, J. Phys. Chem. B*, 107 (2003) 4667
15. P.C. Mehendru, K. Pathak, K. Jain, P. Mehendru, *Phys. Stat. Sol.* 42, (1997) 403.
16. H.C. Shinka, I.M. Talwar, A.P. Srivastava, *Thin Solid Films* 82, (1989) 229.
17. M Abdelaziz, E M Abdelrazek, *Phy B*., 349 (2004) 84.
18. Q Zhang, RW Whatmore, *J Phy D*., 34 (2001) 2296.
19. K. Kiran Kumar, M. Ravi, Y. Pavani, S. Bhavani, A.K. Sharma, V.V.R. Narasimha Rao, *J. Membr. Sci.* 454 (2014) 200.
20. S.K. Chaurasia Shalu, R.K. Singh, S. Chandra, J. Phys. Chem. B 117 (2013) 897.
21. Reddeppa Nadimicherla, Ramamohan Kalla, Ravi Muchakayala, Xin Guo, *Solid State Ion.*278 (2015) 260.
22. G. Hirankuram, S. Selvasekarapandian, M.S. Bhuvaneswari, R. Baskaran, M. Vijayakumar, *J. Solid State Electrochem*. 10 (2006) 193.

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