J Mater Sci (2006) 41:6171–6173
DOI 10.1007/s10853-006-0162-0

LETTER

Ion transport and battery studies of a new (PVP + KIO_3) polymer electrolyte system

J. Siva Kumar · M. Jaipal Reddy · U. V. Subba Rao

Received: 8 August 2003 / Accepted: 14 October 2005 / Published online: 8 July 2006

Polymer materials in combination with suitable metal salts give electrolytes for advanced high energy electrochemical devices, e.g. batteries/fuel cells, electrochemical display devices/smart windows and photoelectrochemical cells, etc. [1–5]. The main advantages of polymeric electrolytes are satisfactory mechanical properties, ease of fabrication as thin films and an ability to form good electrode/electrolyte contact. Most of the studies in this field are devoted to poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) based polymer electrolytes using alkali metal salts [6–11]. Some conducting polymer electrolytes have been reported based on PEO complexed with ammonium salts such as NH_4SCN and $NH_4CF_3SO_3$ [12], NH_4ClO_4 [13, 14] and NH_4I [15].

In an attempt to study the possibility of fabricating electrochemical cells based on polymers other than widely studied polymers such as PEO, PPO, etc., studies have been undertaken on electrochemical cells based on poly (acrylamide) (PA) and poly (vinyl pyrrolidone) (PVP) polymers [16–19]. This letter deals a new polymer electrolyte namely (PVP + KIO_3) and its application as electrochemical cell.

Thin films (thickness: 150–200 μm) of pure PVP (M.W. 4×10^4) and various compositions of complexed films of PVP with potassium iodate (KIO_3) were prepared in the weight ratios (90:10), (80:20) and (70:30) by a solution cast technique. Aqueous solution of PVP and KIO_3 mixtures were stirred for about 10–12 h. The stirred solution was cast onto polypropylene dishes and evaporated slowly at room temperature. The final product was vacuum dried thoroughly at 0.13 Pa. The Differential Scanning Calorimetry (DSC) measurements have been taken in the temperature range 30–180 °C with the help of Differential Scanning Calorimeter (DSC) [Model TA–2010] thermal analysis system at a heating rate of 4 °C per minute. The dc conductivity of this polymer electrolyte system was measured in the temperature range of 303–393 K. The ionic and electronic transport numbers (t_{ion} and t_{ele}) were evaluated by means of Wagner's polarization technique [20]. Using this polymer electrolyte an electrochemical cell was fabricated with the configuration K/PVP + KIO_3/(I_2 + C + electrolyte) and studied its characteristics.

The DSC measurements of pure PVP and PVP complexed with KIO_3 (70:30) composition are shown in Fig. 1. An endothermic peak is observed at about 95 °C, which corresponds to the melting temperature (T_m) of pure PVP. The melting temperature (T_m) is decreased and also the melting endotherm becomes broader with the addition of KIO_3 salt to PVP. Both the reduced melting temperature and the broadening of the melting endotherm are clear indication of complexation of the KIO_3 salt with the polymer PVP.

The variation of dc conductivity (σ) as a function of KIO_3 composition in PVP at various temperatures is shown in Fig. 2. From the figure, it is seen that the conductivity of pure PVP is about 10^{-13} S cm^{-1} at room temperature and its value increases sharply to about 10^{-9} S cm^{-1} on complexing with 10 wt.% of KIO_3. The increase in conductivity becomes slower on further addition of KIO_3 to the polymer. This behaviour has been explained by various researchers, who have studied PVP and PEO based polymer electrolytes in terms of ion association and the formation of charge multiples [19, 21–24]. The conductivity is increased with temperature in pure PVP and also in all the (PVP + KIO_3) polymer electrolyte films. The ionic conductivity in the

J. Siva Kumar (✉) · M. Jaipal Reddy · U. V. Subba Rao
Department of Physics, Osmania University, Hyderabad 500 007
AP, India
e-mail: julurusivakumar@yahoo.com.uk

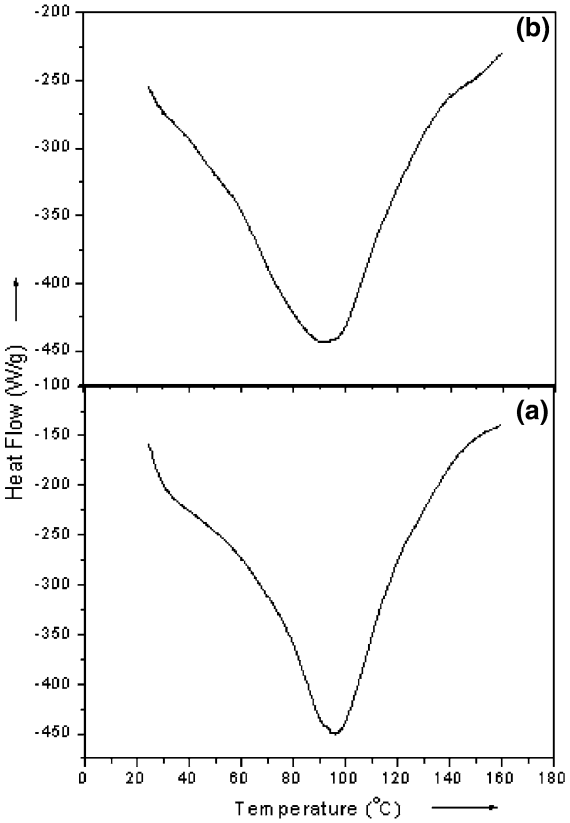

Fig. 1 DSC curves of (**a**) Pure PVP, (**b**) (PVP + KIO3) (70:30)

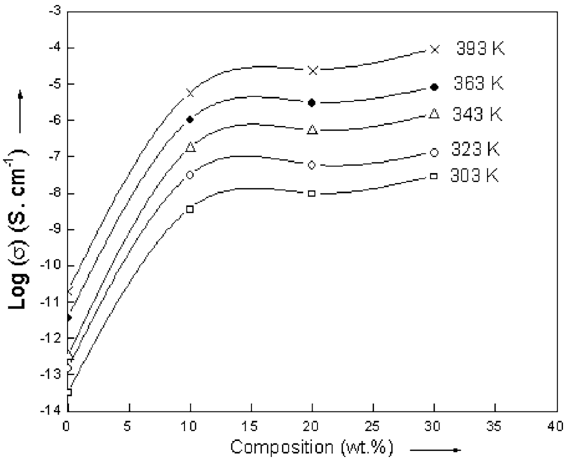

Fig. 2 Composition dependence conductivity plots of (PVP + KIO_3) electrolyte system

polymer complexes maybe considered as a hoping mechanism between coordinating sites, local structural relaxations and segmental motions of the polymer chains [19, 25–27].

In the Wagner's polarization method [20], the dc current was monitored as a function of time on application of a fixed dc voltage of 1.5 V across the cell K/(PVP + KIO_3)/C. The current vs. time plot of (PVP + KIO_3) (70:30) is shown in Fig. 3. From the figure, the transference numbers (t_{ion} and t_{ele}) have been evaluated using the formula:

$$t_{\mathrm{ion}} = (I_{\mathrm{i}} - I_{\mathrm{f}})/I_{\mathrm{i}} \quad \text{and} \quad t_{\mathrm{ele}} = I_{\mathrm{f}}/I_{\mathrm{i}}$$

where I_{i} and I_{f} are the initial and final currents, respectively. The resulting data are shown in Table 1. For all the compositions of the (PVP + KIO_3) electrolyte system, the values of the ionic transference number are in the range of 0.96–0.98. This suggests that the charge transport in these polymer electrolyte films is mainly due to ions and only a negligible contribution comes from the electrons.

The discharge characteristics of the cell K/(PVP + KIO_3)/(I_2 + C + electrolyte) at an ambient temperature for a constant load of 100 kΩ is shown in Fig. 4. The initial sharp decrease in the voltage and current in these cells may be due to polarization and/or to the formation of a thin layer of potassium at the electrode − electrolyte interface. The Open circuit voltage (OCV) and short circuit current (SCC) of the cell are 2.76 V and 1.79 mA, respectively. Other cell parameters calculated are:

Cell mass = 0.819 g,
Area of the cell = 134 mm^2,
Discharge time for plateau region = 69 h,
Specific power = 26.9 mW kg^{-1} and
Specific energy = 1795 mW h kg^{-1}.

On the basis of present study, a solid state battery with (PVP + KIO_3) polymer as electrolyte is found to be promising compared to that of (PVP + $NaNO_3$) polymer electrolyte [19]. Further work is in progress aimed to obtain higher capacities and specific energy.

In conclusion the charge transport in this (PVP + KIO_3) polymer electrolyte system is mainly due to ions. The Open circuit voltage (OCV) and short circuit current (SCC) of a cell with the configuration K/(PVP + KIO_3)/(I_2 + C + electrolyte) are 2.76 V and 1.79 mA, respectively.

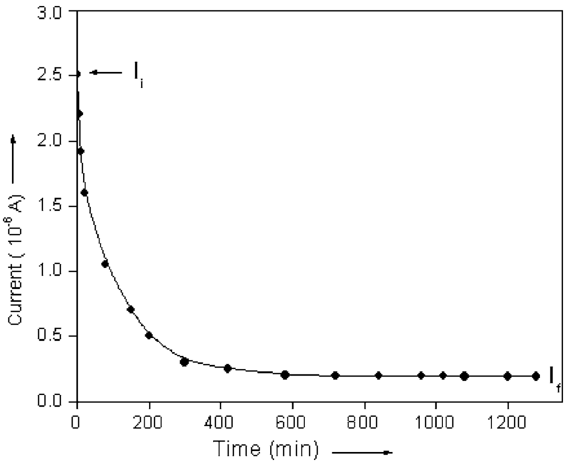

Fig. 3 Current vs. Time plot of (PVP + KIO_3) (70:30) electrolyte

Table 1 Transference number data for (PVP + KIO_3) electrolyte system

Polymer electrolyte	Transference number	
	t_{ion}	t_{ele}
(PVP + KIO_3) (90:10)	0.96	0.04
(PVP + KIO_3) (80:20)	0.98	0.02
(PVP + KIO_3) (70:30)	0.97	0.03

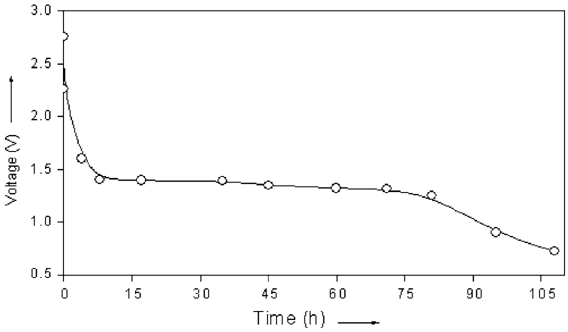

Fig. 4 Discharge characteristics of the cell of configuration K/(PVP + KIO_3) (70:30)/(I_2 + C + electrolyte) at ambient temperature for a constant load of 100 kΩ

Acknowledgements The author M. Jaipal Reddy thanks CSIR, New Delhi, India for the financial support under Scientist's Pool scheme.

References

1. Mac Callum JR, Vincent CA (eds) (1987) Polymer electrolyte Rev. Elsevier, Amsterdam
2. Armand MB (1986) Ann Rev Mater Sci 16:245
3. Ratner MA, Shriver DF (1988) Chem Rev 88:109
4. Owen JR (1989) In: Lasker AL, Chandra S (eds) Superionic solid electrolytes—recent trends, Academic Press, New York, p 111
5. Shriver DF, Papke BL, Ratner MA, Doppon R, Wong T, Brodwin M (1981) Solid State Ionics 5:83
6. Reitman EA, Kaplan ML, Cava RJ (1985) Solid State Ionics 17:67
7. Sorenson PR, Jacobson T (1985) Electrochem Acta 27:67
8. Fautex D, Robitaille C (1986) J Electrchem Soc 133:307
9. Lee YL, Crist B (1986) J Appl Phys 60:2683
10. Rao SS, Jaipal Reddy M, Laxmi Narsaiah E, Subba Rao UV (1995) Mater Sci Engg B 33:173
11. Watanabe M, Sanui K, Ogata N, Inoue F, Kabayashi T, Ohtaki Z (1985) Polymer J 17:549
12. Stainer M, Hardy LC, Whitmore DH, Shriver DF (1984) J Electrochem Soc 23:784
13. Hashmi SA, Kummar A, Maurya KK, Chandra S (1990) J Phys D Appl Phys 23:1307
14. Chandra S, Hashmi SA, Prasad G (1990) Solid State Ionics 40/41:651
15. Maurya KK, Srivastava N, Hashmi SA, Chandra S (1992) J Mater Sci 27:6357
16. Rao SS, Subba Rao UV (1994) J Mater Sci Lett 13:1771
17. Jaipal Reddy M, Rao SS, Laxmi Narsaiah E, Subba Rao UV (1995) Solid State Ionics 80:93
18. Laxmi Narsaiah E, Jaipal Reddy M, Subba Rao UV (1995) J Power Sour 55:255
19. Jaipal Reddy M, Sreekanth T, Chandrasekhar M, Subba Rao UV (2000) J Mater Sci 35:2841
20. Wagner JB, Wagner CJ (1957) Chem Phys 26:1597
21. Jaipal Reddy M, Srinivas Reddy D, Rao SS, Subba Rao UV (1995) Mater Lett 23:129
22. Ratner MA, Nitzman A (1989) Faraday Discuss Chem Soc 88:19
23. Maurya KK, Battacharya B, Chandra S (1995) Phys Stat Sol (a) 148:347
24. Jaipal Reddy M, Subba Rao UV (1998) J Mater Sci Lett 17:1613
25. Scrosati B (1988) In: Chowdari BVR, Radha Krishna S (eds) Solid state ionic devices, World Scientific Publ. Company, Singapore, p 113
26. Vincent CA (1987) Prog Solid State Chem 17:145
27. Steele BCH, Weston SE (1981) Solid State Ionics 2:347