Ionic Transport Study Of Plasticized Salicylic Acid Doped Polymethylmethacrylate Based Electrolytes

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Abstract

In this work, the ionic transport of DBP/DMF plasticized salicylic acid doped PMMA based gel electrolyte has been studied. The samples were prepared using solution cast technique. The number density of mobile ions and mobility of mobile ions were obtained from calculations based on the Rice and Roth Model. The mobility of the ions is between 10^{-9} to 10^{-6} $cm^2V^{-1}s^{-1}$ and the number density of mobile ions is between 10^{20} to 10^{23} cm^{-3}

Keywords: ionic transport, PMMA, gel electrolytes, number of mobile ions

1. INTRODUCTION

Much attention has been directed to proton conducting polymeric electrolytes because of their possible applications in advanced electrochemical devices such as batteries, capacitors, sensors, electrochromic displays, photoelectrochemical solar cells and fuel cells [1]. A lot of efforts have been done to enhance the transport properties of polymer electrolytes (PEs) in order to make them feasible for power applications.

Polymer electrolytes can be grouped into several classes, namely solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs) and composite polymer electrolytes (CPEs). These polymer electrolytes have the advantages of space and mass, structural stability and low volatility.

In this work, the ionic transport of DBP/DMF plasticized salicylic acid doped PMMA gel electrolyte has been studied. The number density of mobile ions and mobility of mobile ions were obtained from calculations based on the Rice and Roth Model [2]. The conductivity of the GPE was influenced by the number density and mobility of the mobile ion.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation

The solvents (EC-PC) were mixed at room temperature. Salicylic acid (SA) was then added and/or dissolved. The plasticizers, DMF and DBP were then added. After adding poly (methyl methacrylate) (PMMA), the whole mixture was heated to 70 °C to promote gel formation. Finally the mixture was cast into petri dishes for the gel to form in a silica gel containing dessicator.

The sample composition was 25 wt. % PMMA, 35 wt. % EC, 30 wt. % PC, 5 wt. % SA, 5 wt. % DMF for DMF plasticized gel; 25 wt. % PMMA, 35 wt. % EC, 30 wt. % PC, 5 wt. % SA, 5 wt. % DBP plasticized gel; 35 wt. % EC, 30 wt. % PC, 5 wt. % SA, 4 wt. % DBP, 1 wt. % DMF and 25 wt. % PMMA for DBP-rich dual plasticizer and 35 wt. % EC, 30 wt. % PC, 5 wt. % SA, 1 wt. % DBP, 4 wt. % DMF and 25 wt. % PMMA for DMF-rich dual plasticizer gel. Transparent, colorless and jelly-like samples were obtained.

2.2. Electrochemical Impedance Spectroscopy (EIS) Study

The gel was sandwiched between two stainless steel electrodes under spring pressure. Impedance spectroscopy was measured using a computer-interfaced HIOKI 3531-01 LCR bridge with frequency ranging from 42 Hz to 1 MHz. The impedance of the sample was measured at every frequency, at room and elevated temperatures. The electrical conductivity was obtained by inserting the bulk resistance value, thickness and area into the equation below.

$$\sigma = \frac{t}{R_b A} \tag{1}$$

Here t is thickness of the gel and A is the area of contact between the gel and the electrolyte. The bulk resistance, R_b was obtained from the complex impedance plot, $-Z_i$ versus Z_r.

3. RESULTS AND DISCUSSION

The conductivity increases as temperature increases. The regression value is almost unity and the plot can be considered Arrhenian. From Fig. 1, the slope of log σ versus $1000/T$, the conductivity activation energy, E_A was calculated as (0.12 ± 0.04) eV, (0.21 ± 0.04) eV, (0.30 ± 0.06) eV and (0.30 ± 0.08) eV for DMF, DBP, DMF rich dual plasticizer and DBP rich dual plasticizer gel respectively.

Since the plots are Arrhenian, they can be described by

$$\sigma = \sigma_0 \exp\left(-E_A/kT\right) \tag{2}$$

where σ_0 is the pre-exponential factor, E_A is the activation energy, k is Boltzmann constant and T_0 is absolute temperature. To evaluate transport parameters such as the number density and mobility of mobile carriers, the Rice and Roth model has been adopted.

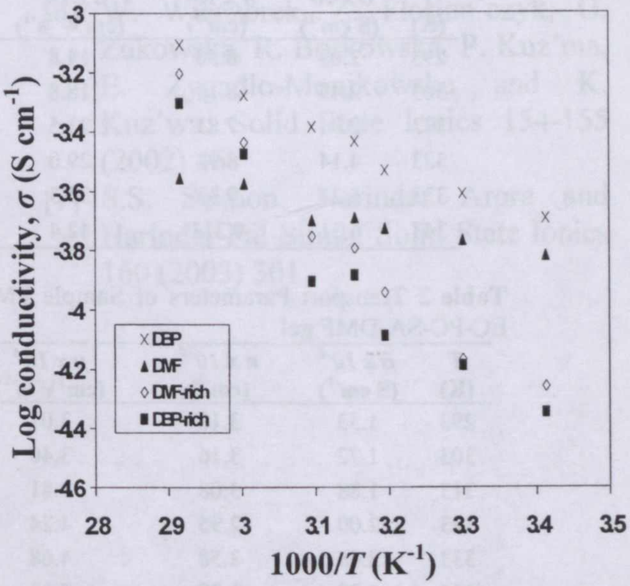

Fig. 1 Conductivity as a function of temperature

The model states that

$$\sigma = \frac{3e^2}{2kTM} n E_A \tau [\exp(-E_A/kT)] \tag{3}$$

Here M is the mass of the conducting ion (H^+), e is electron charge and τ is the time taken to travel between two transit sites. In this work, τ is taken to be of the order 10^{-13} s. Comparing Equation (2) and (3), it can be deduced that

$$\sigma_0 = \frac{3e^2}{2kTM} n E_A \tau \tag{4}$$

and that the Rice and Roth model has the same form as the Arrhenius equation. Using the value of τ and the activation energy from the log σ versus $1000/T$ plot, the number density of mobile ions, n and mobility, μ of mobile ions were calculated. was calculated from the equation

$$\mu = \frac{\sigma}{ne} \tag{5}$$

Table 1, Table 2, Table 3 and Table 4 list the estimated values of n and μ for the plasticized gel electrolyte of the present work. The conductivity value for the sample plasticized with 5 wt. % DMF is almost similar to that reported in [3] but the value of n obtained in this work is one order of magnitude higher.

Table 1 Transport Parameters of Sample PMMA-EC-PC-SA-DBP gel

T (K)	$\sigma \times 10^{-4}$ (S cm^{-1})	$n \times 10^{21}$ (cm^{-3})	$\mu \times 10^{-10}$ (cm^{2}V^{-1}s^{-1})
293	2.03	8.58	14.8
303	2.45	8.14	18.8
313	2.94	7.81	23.5
323	4.14	8.92	29.0
333	5.27	9.33	35.3
343	6.31	9.311	42.4

Table 2 Transport Parameters of Sample PMMA-EC-PC-SA-DMF gel

T (K)	$\sigma \times 10^{-4}$ (S cm^{-1})	$n \times 10^{20}$ (cm^{-3})	$\mu \times 10^{-6}$ (cm^{2}V^{-1}s^{-1})
293	1.53	3.18	3.01
303	1.72	3.16	3.40
313	1.88	3.08	3.81
323	2.00	2.95	4.24
333	2.68	3.58	4.68
343	2.78	3.38	5.13

Table 3 Transport Parameters of Sample PMMA-EC-PC-SA-4 wt. % DMF-1 wt. % DBP gel

T (K)	$\sigma \times 10^{-4}$ (S cm^{-1})	$n \times 10^{22}$ (cm^{-3})	$\mu \times 10^{-9}$ (cm^{2}V^{-1}s^{-1})
293	0.55	5.73	6.00
303	0.68	4.95	8.58
313	1.14	5.94	11.99
323	1.77	6.75	16.39
333	2.09	5.95	21.96
343	2.88	6.23	28.91

Table 4 Transport Parameters of Sample PMMA-EC-PC-SA-1 wt. % DMF-4 wt. % DBP gel

T(K)	$\sigma \times 10^{-4}$ (S cm^{-1})	$n \times 10^{22}$ (cm^{-3})	$\mu \times 10^{-9}$ (cm^{2}V^{-1}s^{-1})
293	0.45	4.69	6.00
303	0.65	4.73	8.58
313	0.82	4.28	11.99
323	1.24	4.73	16.39
333	1.91	5.44	21.96
343	2.51	5.43	28.91

From Tables 1, 2, 3 and 4, the increase in conductivity with temperature is observed to be influenced by the number density of mobile ions and the mobility. The number density of mobile ions seem to be quite constant although there are some undulations in the value with temperature i.e., μ increases with temperature. From these results, it may be inferred that mobility has a greater influence on the σ of the samples [1, 3-7].

To obtain the ionic transference number of the material, transference number measurement was carried out. The samples were sandwiched between two stainless steel blocking electrodes and the current through the circuit was monitored with time until it saturates. The value of the transference number for all samples is ~0.9. Table 5 lists the value for the samples studied in the present work. Fig. 2 shows the plot of normalized polarization current with time.

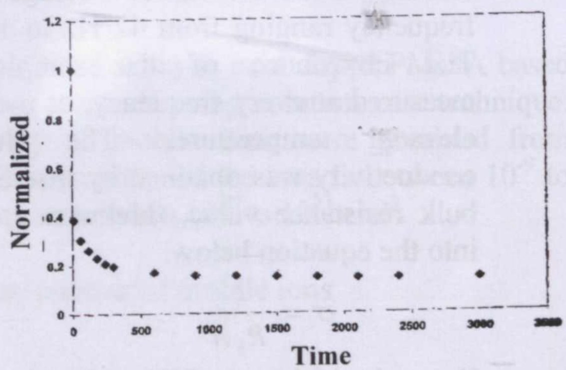

Fig. 2 Normalized polarization current versus t (s) plot for PMMA-EC-PC-SA-DBP gel

Table 5 Transference number for samples studied. Taken at 293 K. Only the DMF and DBP contents are stated

Sample	t_{ion}
1 wt. % DMF	0.84
4 wt. % DMF + 1 wt. % DBP	0.94
1 wt. % DMF + 4 wt. % DBP	0.89
5 wt. % DBP	0.86

4. CONCLUSIONS

The conductivity may be inferred to be controlled by the number density of mobile ions, n and their mobility, μ. The ionic transference number for all samples is ~0.9.

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REFERENCES

[1] W. Wieczorek, Z. Florjan´czyk and J.R. Stevens. Electrochimica Acta 40 (1995) 2327

[2] M.J. Rice and W.L. Roth. J. of Solid State Chemistry 4 (1972) 294

[3] H. Ericson, C. Svanberg, A. Brodin, A.M. Grillone, S. Panero, B. Scrosati. and P. Jacobsson. Electrochimica Acta 45 (2000) 1409

[4] G. Zukowska, Rogowska, A. Wodja, M.Zygadlo-onikowska,Z.Florjan´czyk and W. Wieczorek. Solid State Ionics 136-137 (2000) 1205

[5] W. Wieczorek, G. Zukowska, R. Borkowska, S.H. Chung and S. Greenbaum. Electrochimica Acta 46 (2001) 1427

[6] W. Wieczorek, Z. Florjan´czyk, G. Zukowska, R. Borkowska, P. Kuz´ma, E. Zygadlo-Monikowska and K. Kuz´wa. Solid State Ionics 154-155 (2002) 45

[7] S.S. Sekhon, Narinder Arora and Harinder Pal Singh. Solid State Ionics 160 (2003) 301