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Conductivity and Thermal Properties of PAN Based Polymer Electrolytes for Possible Application in Photo Electrochemical Solar Cells

Warakawe Jayasundara Mudiyanselage Jayabahugedara Saumya Rajinie Jayasundara[1, 2], Tennakoon Mudiyanselage Wijendra Jayalath Bandara[3], Pierisge Sadeesha Leonard Fernando[3], Hewage Dhanushka Naleen Sampath Fernado[3], Malavi Achchi Kankanamge Lakshman Dissanayake[1], Lekam Ralalage Anura Kalinga Bandara[4] and Bengt-Erik Mellander[5]

1. Institute of Fundamental Studies, Kandy 20000, Sri Lanka

2. Postgraduate Institute of Science, University of Peradeniya, Peradeniya 20404, Sri Lanka

3. Department of Physical Sciences, Rajarata University of Sri Lanka, Mihinthale 50300, Sri Lanka

4. Department of Physics, University of Peradeniya, Peradeniya 20404, Sri Lanka

5. Department of Applied Physics, Chalmers University of Technology, Goteborg 41296, Sweden

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Abstract: Two gel or quasi-solid-state electrolyte complexes based on PAN (polyacrylonitrile) host polymer and salts Hex_4NI (tetrahexylammonium iodide), MgI_2, LiI were prepared by incorporating plasticizers EC (ethylene carbonate) and PC (propylene carbonate). These are: $PAN/EC/PC/I_2/Hex_4NI:MgI_2$ and $PAN/EC/PC/I_2/Hex_4NI:LiI$. A clear glass transition was observed around -100 ℃ for all the electrolyte complexes. In the $PAN/EC/PC/I_2/Hex_4NI:MgI_2$ system, a decrease in conductivity was observed with the addition of MgI_2 and the electrolyte with Hex_4NI alone as the iodide salt gave the maximum ionic conductivity of 2.51×10^{-3} $S \cdot cm^{-1}$ at 25 ℃. In the $PAN/EC/PC/I_2/Hex_4NI:LiI$ system, an increase in conductivity was observed with the addition of LiI. Consequently the electrolyte with LiI as the only iodide salt gave the maximum ionic conductivity of 3.14×10^{-3} $S \cdot cm^{-1}$ at 25 ℃. The diffusion coefficient (D), the mobility (μ) and the density of charge carriers (n) in the electrolytes were calculated using complex impedance data and equations obtained for dielectric loss tangent. The measured data for dielectric loss tangent were fitted to the model equation. Calculated, n, μ and D values are around $\sim 10^{24}$ m^{-3}, $\sim 10^{-7}$ $m^2 \cdot V^{-1} \cdot s^{-1}$ and $\sim 10^{-9}$ $m^2 \cdot s^{-1}$ respectively for the two electrolyte systems. This type of iodide ion conducting electrolytes could be suitable materials for PEC (photo electrochemical) solar cells.

Key words: Quasi-solid-state, polyacrylonitrile, photoelectrochemical, dielectric.

1. Introduction

Fast ion conductors or electrolytes have many applications in the field of electrochemistry. Polymer electrolytes [1] have attracted much attention because of their use in practical application such as batteries, fuel cells, PEC solar cells, sensors and displays. Anion conducting PAN based polymer electrolytes are good candidate materials for the fabrication of photo-electrochemical solar cells [2]. Even though the PEC cell efficiencies are better with liquid type electrolytes, the usage of liquid type electrolytes in the cells meets durability issues. Use of polymer electrolytes in solar cell applications shows many advantages such as compatibility, no leakage, easy to prepare in different forms, chemical and physical

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Corresponding author: Warakawe Jayasundara Mudiyanselage Jayabahugedara Saumya Rajinie Jayasundara, Ph.D. student, research fields: polymer electrolytes and dye sensitized solar cells. E-mail: sjayasundara@yahoo.com.

stability and easy to process [2, 3]. A large number of studies were so far carried out by several groups using variety of single salt systems as electrolyte with the aim of enhancing cell efficiency [3-5]. The present study compares the novel polymer electrolyte different systems with double salts intended for PEC solar cells by analyzing electrical and thermal properties. Especially, the density of charge carriers and mobility in electrolytes were calculated by analyzing complex dielectric measurements.

2. Experiments

2.1 Materials

PAN, LiI, MgI_2, $\text{Hex}_4\text{N}^+\text{I}^-$, iodine ($\text{I}_2$), PC and EC all with purity greater than 98%, all from Aldrich were used as starting materials. Prior to use $\text{Hex}_4\text{N}^+\text{I}^-$ and PAN were vacuum dried for 24 h at 50 ℃ and LiI was vacuum dried for 4 h at 150 ℃ in a vacuum oven.

2.2 Gel Electrolyte Preparation

Two gel electrolyte complexes were prepared by keeping the mass fractions of PAN (0.10 g), PC (0.40 g), EC (0.40 g) unchanged and varying the amount of salt according to Table 1. The amount of iodine added was fixed at 0.1 times of the total number of moles of salts in the electrolyte.

Initially the relevant weights of EC, PC and salts were mixed in a closed glass bottle by continuous stirring at 50 ℃ for about 3 h. Then PAN was added to the mixture which was stirred further keeping it at 40 ℃ for about 2 h. Finally, iodine was added to the mixture and heated to ~100 ℃ along with continuous stirring for a few more minutes until a homogeneous viscous solution was obtained. The resulted hot viscous gel was pressed between two glass plates (laboratory microscope glass slides) in order to obtain a quasi-solid-state polymer electrolyte film of a thickness of about 0.5 mm.

2.3 Measurements

The complex impedance measurements were performed using a HP 4292A RF impedance analyzer in the 10 Hz-10 MHz low frequency range to evaluate the samples. The temperature of the sample varied from 0 ℃ to 60 ℃ and the measurements were taken at 5 ℃ intervals.

DSC (differential scanning calorimetric) thermograms were obtained using a Mettler Toledo DSC 30 differential scanning calorimeter to understand the thermal behavior of the sample. The glass transition temperature (T_g) was extracted from DSC thermograms. Each sample was scanned between -130 ℃ and 100 ℃ with a rate of 10 ℃ min^{-1}. Thermal measurements were carried out with several consequent heating and cooling cycles with the same sample. A flow of nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture.

3. Theory

The conductivity (σ) of a single ion conducting electrolyte is given by the equation

$$\sigma = ne\mu \tag{1}$$

In order to characterize the electrolyte, it is important to calculate mobility (μ) and charge carrier density (n).

According to the Refs. [5, 6] the effective dielectric constant of an electrolyte sandwiched between two blocking electrodes can be represented by

$$\varepsilon^* = \varepsilon'_\infty \left\{ \left(1 + \frac{\delta}{1 + (\omega\tau)^2 \delta} \right) - i \left(\frac{\omega\tau\delta^{3/2}}{1 + (\omega\tau)^2 \delta} \right) \right\} \tag{2}$$

where, ε'_∞ is the high frequency permittivity, ε^* is the effective complex dielectric constant, ω is the angular frequency of the signal, δ is a constant and τ is the dielectric relaxation time corresponding to the maximum dielectric loss tangent. Therefore, tan(ϕ), the dielectric loss tangent can be obtained by equation

$$\tan(\phi) = \frac{\omega\tau\sqrt{\delta}}{1 + \omega^2\tau^2} \tag{3}$$

The δ is given by

$$\delta = \frac{d}{(D\tau)^{1/2}} = \frac{d}{\lambda} \tag{4}$$

Table 1 Electrolyte composition, where the amount of PAN, PC and EC were kept at 0.10 g, 0.40 g and 0.40 g respectively.

System (1)	$PAN/EC/PC/I_2/Hex_4NI:MgI_2$						
Electrolyte	*A*1	*B*1	*C*1	*D*1	*E*1	*F*1	*G*1
MgI_2 / g	0.00	0.02	0.04	0.06	0.08	0.10	0.12
$Hex_4N^+I^-$ / g	0.12	0.10	0.08	0.06	0.04	0.02	0.00
I_2 / g	0.0063	0.0071	0.0078	0.0086	0.0094	0.0102	0.0109
System (2)	$PAN/EC/PC/I_2/Hex_4NI:LiI$						
Electrolyte	*A*2	*B*2	*C*2	*D*2	*E*2	*F*2	*G*2
LiI / g	0.00	0.02	0.04	0.06	0.08	0.10	0.12
$Hex_4N^+I^-$ / g	0.12	0.10	0.08	0.06	0.04	0.02	0.00
I_2 / g	0.0063	0.0090	0.0118	0.0145	0.0173	0.0200	0.0227

$$D = \frac{d^2}{\delta^2 \tau} \qquad (5)$$

where, 2*d* and λ are sample length and the Debye length. The Nernst-Einstein relation gives the relationship between the mobility (μ) and the diffusion coefficient (*D*).

$$\mu = \frac{eD}{k_B T} \qquad (6)$$

Charge carrier density (*n*) is given by Eq. (5), where, k_B is the Boltzmann constant, σ is the conductivity and *T* is the absolute temperature.

$$n = \frac{\sigma k_B T}{e^2 D} \qquad (7)$$

The conductivity (σ) can be calculated using

$$\sigma = \frac{l}{RA} \qquad (8)$$

where, *l* is the sample length (2*d*), *R* is the resistance and *A* is the area of the sample.

4. Results and Discussion

Two different quasi-solid-state electrolyte systems were compared in this study. System 1 is $PAN/EC/PC/I_2/Hex_4NI:MgI_2$ electrolyte and system 2 is $PAN/EC/PC/I_2/Hex_4NI:LiI$ electrolyte. The conductivity variation as a function of 1,000/*T* is shown in Fig. 1 for system 1. Eq. (8) was used to calculate the conductivity. Hex_4NI alone as the iodide salt (sample *A*1) gave the maximum ionic conductivity, 2.51×10^{-3} S cm^{-1} at 25 ℃ out of samples in system 1. In this $PAN/EC/PC/I_2/Hex_4NI:MgI_2$ system, a reduction in conductivity is observed with added amount

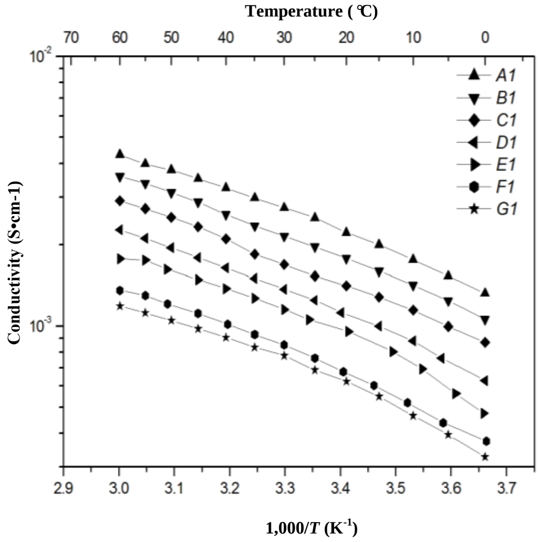

Fig. 1 Conductivity vs. 1,000/*T* for $PAN/EC/PC/Hex_4NI:MgI_2$ electrolytes containing different Hex_4NI and MgI_2 compositions as given in Table 1.

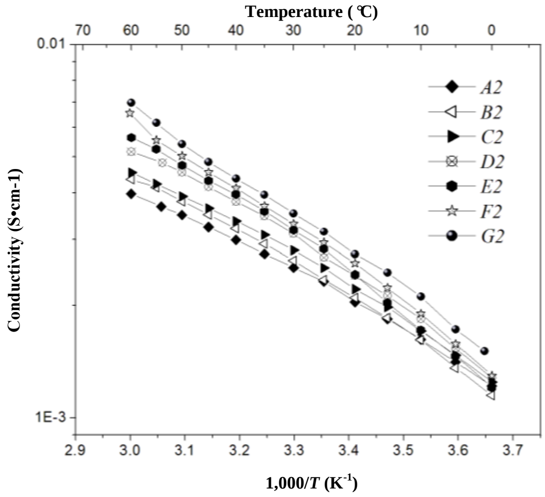

Fig. 2 Conductivity vs. 1,000/*T* for $PAN/EC/PC/Hex_4NI:LiI$ electrolytes containing different Hex_4NI and LiI compositions as given in Table 1.

of MgI_2 (Fig. 1) which may be a result of cross link formation of Mg^{+2} ions with CN groups in PAN chains [4]. Hence, the lowest conductivity is given by sample *G*1. Higher flexibility in polymer chains is necessary to obtain higher conductivity. The higher the cross links the lower the polymer flexibility, leading to lower the conductivity.

In system 2 ($PAN/EC/PC/I_2/Hex_4NI:LiI$), an increase in conductivity is observed with added amount of LiI (Fig. 3). The maximum ionic conductivity of 3.14×10^{-3} $S \cdot cm^{-1}$ at 25 ℃ is shown by the sample which contained only the LiI salt (sample *G*2). In system 1, neither Hex_4N^+ nor Mg^{2+} is moving since Hex_4N^+ is a bulky cation and Mg^{2+} can form cross links [2-4]. In the present system, Li^+ ion can be considered as a moving ion and contributes to the conductivity [7, 8]. The mobility of Li^+ ion is higher than that of Hex_4N^+ and Mg^{2+}. The increasing trend in T_g observed with added amount of LiI reveals the reduction of flexibility of polymer chains with LiI amount. This may be a result of ionic complexes and undissolved solutes at higher LiI concentrations.

Eqs. (5)-(7) were used to calculate D, μ and n. The parameters δ and τ were obtained by fitting measured data to Eq. (3).

Calculated values D, μ, n for system 1 (in Table 2) also show minimum at the sample *G*1 (sample which contained only the salt MgI_2) providing evidence for the observed lower conductivity. Highest mobility value of 6×10^{-7} $m^2 \cdot V^{-1} \cdot S^{-1}$ observed for the system 1 containing only the Hex_4NI salt (sample *A*1) may be an effect of presence of large Hex_4N^+ ion where large cations can place within the polymer network making polymer chains more separated and flexible. Diffusion coefficient values also shows maximum at sample *A*1 by giving 2×10^{-8} $m^2 \cdot s^{-1}$. In general electrolyte containing LiI has shown higher mobilities than that of containing MgI_2. This can be due to the ability of Mg^{+2} ions to make stronger interactions with ionic species in the electrolyte than Li^+ ions.

Fig. 3 shows the DSC thermograms of electrolyte systems 1 and 2. All the samples have shown clear glass transition at around 100 ℃. The T_g (glass transition temperature) also can be related to the flexibility of the polymer chains [9, 10] and the highest T_g is observed for the electrolyte containing only the MgI_2 salt (sample *G*1). Low T_g values were observed for the samples which contained salt mixtures and this may be a result of increased flexibility in polymer chains due to structural disorders imposed by small and large cations. Lower T_g values are shown for the electrolytes containing MgI_2 and then that of sample containing LiI. For electrolyte sample preparation the weights ratio of the salts were kept fixed. Since LiI has lower molar weight than other iodides in these electrolytes, the

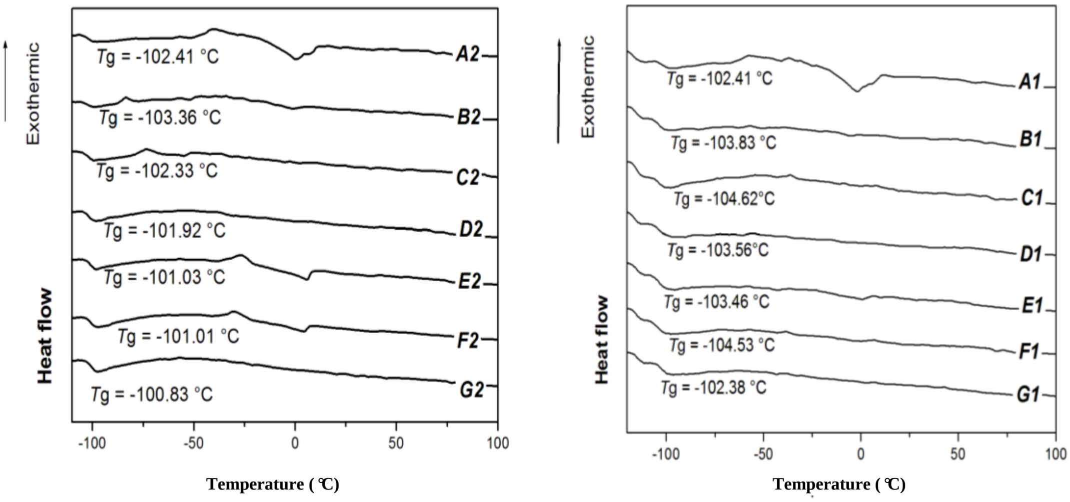

Fig. 3 DSC thermograms of electrolyte samples given in Table 1 under heating rate of 10 ℃ min^{-1}.

Table 2 The diffusion coefficient (*D*), the mobility (*μ*) and the density of charge carriers (*n*) of some electrolyte samples at 25 ℃.

Sample	D ($m^2 \cdot S^{-1}$)	μ(m^2 $V^{-1} \cdot S^{-1}$)	n (m^{-3})
System 1	PAN/EC/PC/I_2/Hex_4NI :MgI_2		
A1	2×10^{-8}	6×10^{-7}	2×10^{24}
B1	6×10^{-9}	5×10^{-7}	5×10^{24}
E1	5×10^{-9}	2×10^{-7}	3×10^{24}
F1	6×10^{-9}	2×10^{-7}	2×10^{24}
G1	8×10^{-10}	3×10^{-8}	9×10^{23}
System 2	PAN/EC/PC/I_2/Hex_4NI :LiI		
A2	2×10^{-8}	6×10^{-7}	2×10^{24}
B2	1×10^{-8}	4×10^{-7}	3×10^{24}
E2	4×10^{-8}	2×10^{-6}	2×10^{24}
F2	3×10^{-8}	2×10^{-6}	2×10^{24}
G2	7×10^{-9}	3×10^{-7}	7×10^{24}

number of ions in LiI containing electrolytes are higher. Hence, number of intermolecular interactions is higher for the electrolytes in system 2 leading higher T_g.

5. Conclusions

Two gel type or quasi solid state electrolyte systems namely PAN/EC/PC/I_2/Hex_4NI:MgI_2 and PAN/EC/PC/I_2/Hex_4NI:LiI were prepared and complex impedance measurements and differential scanning calorimetric measurements were carried out. The diffusion coefficient, the mobility and the density of charge carriers in the electrolytes were calculated using complex impedance data and equations obtained for dielectric loss tangent. In the PAN/EC/PC/I_2/Hex_4NI:MgI_2 system a decrease in conductivity was observed with the increasing of MgI_2 amount while an increase in conductivity was observed with the increasing of LiI amount in the system PAN/EC/PC/I_2/Hex_4NI:LiI. All the samples show clear glass transition temperature around -100 ℃. The resulted values for the density of charge carriers, the mobility and the diffusion coefficient are around 10^{24} m^{-3}, 10^{-7} $m^2 \cdot V^{-1} \cdot s^{-1}$ and 10^{-9} $m^2 \cdot s^{-1}$. These types of iodide ion conducting electrolytes are suitable to use in photoelectrochemical solar cells.

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References

[1] M.B. Armand, M.J. Chabagno, M.J. Duclot, Fast ion transport in solids, Elsevier North Holland, New York, 1979, pp. 131-136.

[2] T.M.W.J. Bandara, M.A.K.L. Dissanayake, W.J.M.J.S.R. Jayasundara, I. Albinsson, B.E. Mellander, Efficiency enhancement in dye sensitized solar cells using gel polymer electrolytes based on a tetrahexylammonium iodide and MgI_2 binary iodide system, J. Physical Chemistry Chemical Physics 14 (2012) 8620-8627.

[3] T. Svensson, T.M.W.J. Bandara, E. Lundell, I. Svensson, M. Furlani, I. Albinsson, B.E. Mellander, Estimation of ion transport parameters by modeling space charge relaxation in PEO based solid polymer electrolyte intended for photoelectrochemical solar cells, in: Proceedings of Solar Asia 2011 Int. Conf., Institute of Fundamental Studies, Kandy, Sri Lanka, 2011, pp. 221-227.

[4] T.M.W.J. Bandara, M.A.K.L. Dissanayake, I. Albinsson, B.E. Mellander, Dye-sensitized nono-porus TiO_2 solar cell with Polyacrylonitrile: MgI_2 plasticized electrolyte, J. Power Sources 195 (2010) 3730-3734.

[5] T.M.W.J. Bandara, M.A.K.L. Dissanayake, I. Albinsson, B.E.Mellander, Mobile charge carrier concentration and mobility of a polymer electrolyte containing PEO and $Pr_4N^+I^-$ using electrical and dielectric measurements, Solid State Ionics 189 (2011) 63-68.

[6] T.M.W.J Bandara, B.E. Mellander, Evaluation of mobility, diffusion coefficient and density of charge carriers in ionic liquids and novel electrolytes, In: Alexander Kokorin (Ed.), Ionic Liquids: Theory,

Properties, New Approaches, In Tech, Rijeka, Croatia, 2011, pp. 383-406.

[7] A.M. Stephan, Review on gel polymer electrolytes for lithium-ion batteries, Eur. Polym. J. 42 (2006) 21-42.

[8] J.Y. Song, Y.Y. Wang, C.C. Wan, Review of gel-type polymer electrolytes for Lithium-Ion batteries, J. Power Sources 77 (1999) 183-197.

[9] Y. Tominaga, S. Asai, M. Sumita, S. Panero, B. Scrosati, A novel composite polymer electrolyte: Effect of mesoporous SiO_2 on ionic conduction in poly (ethylene oxide)-$LiCF_3SO_3$ complex, J. Power Sources 146 (2005) 402-406.

[10] Y.J. Wang, Y. Pan, L. Wang, M.J. Pang, L. Chen, Conductivity studies of plasticized PEO-Lithium chlorate-FIC filler composite polymer electrolytes, Mater. Lett. 59 (2005) 3021-3026.