

Ionic conductivity and ambient temperature Li electrode reaction in composite polymer electrolytes containing nanosize alumina

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Abstract

A composite solid polymer electrolyte (CSPE) consisting of polyethyleneoxide (PEO), LiClO_4 and Al_2O_3 of particle size 24 nm was prepared by a melt-cast method. The differential scanning calorimetry (DSC) data suggested that the CSPE is in an amorphous state due to the presence of nanophase alumina. The specific conductivity versus temperature follows Vogel–Tamman–Fulcher (VTF) behavior and the activation energy has been calculated. By analogy with the Marcus theory of solvent reorganization during electron-transfer reactions, the reorganization energy of the polymer chain has been calculated from the energy of activation of ionic conduction. The ac impedance data was analyzed using a non-linear least square (NLLS) fitting program, and the resistance of the passivating film on Li and the charge-transfer resistance of the Li reaction have been evaluated. The charge-transfer resistance has been shown to follow Arrhenius behavior through the standard rate constant for the reaction. Cyclic voltammograms provided evidence of electrochemical activity at the Li/CSPE interface near ambient temperature.

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1. Introduction

There have been extensive research and development studies on solid polymer electrolytes during the past two decades. Polyethyleneoxide (PEO)-based Li^+ ion conducting polymer films are anticipated to be useful for solid-state rechargeable lithium batteries [1]. Due to poor conductivity of these electrolyte films at ambient temperature, however, several modification procedures have been investigated [2]. Among these methods, the addition of ceramic powders producing composite solid polymer electrolytes (CSPEs) is noteworthy. Following the studies of Weston and Steele [3], where the ceramic fillers mainly improved mechanical strength and ionic conductivity insignificantly, several studies have been reported and reviewed [2,4,5]. An increase in ionic conductivity has been reported in a majority of these studies and several explanations on the effect of ceramic fillers have been provided. In many of these studies, the particle size of the ceramic material is in micrometer range. In recent years, a few studies have been reported on

additions of nanophase ceramic materials for preparation and characterization of PEO-based CSPE films [6–9]. The effect of nanoscale alumina on the ionic conductivity and the stability of Li/CSPE interface has been reported by Krawiec et al. [6]. There has been an increase in ionic conductivity at ambient temperature. Also, the passivation of the interface is slow due to the presence of nanosize ceramic particles as revealed from the ac impedance measurements. Temperature dependent conductivity of CSPE containing nanosize titania has been analyzed by Kumar et al. [7]. The conductivity enhancement at ambient temperature has been concluded as due to the interaction of the dipoles within the CSPE. Persi et al. [8] have used a CSPE containing nanosize alumina as the electrolyte film for fabrication of a galvanic cell consisting of Li negative and LiMn_3O_6 positive electrodes. It has been shown that the cell functions satisfactorily at 70 °C. Although, the aims of these studies have been to obtain a high ionic conductivity of the solid polymer electrolytes, the suitability of these films for electrochemical reactions at ambient temperatures is not reported.

In the present study, alumina of 24 nm particle size is used to prepare CSPE films, and differential scanning calorimetry (DSC), ac impedance and cyclic voltammetry studies are carried out. Results showing total amorphicity of the CSPE,

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the Vogel–Tamman–Fulcher (VTF) behavior of the ionic conductivity, reorganization of the polymer chain during conduction, a high voltage stability window, temperature dependence in the charge-transfer resistance and electrochemical activity of the Li/CSPE interface at near ambient temperature are reported in this paper.

2. Experimental

PEO of molecular weight 2×10^6 (Aldrich), LiClO_4 (Aldrich), and Al_2O_3 (Nanophase Technologies Corp.) of 24 nm average particle size were used for making CSPE films by a melt casting method. Stoichiometric amounts of dry powders of PEO and LiClO_4 , required for O:Li ratio of 8:1 ($\text{PEO}_8\text{LiClO}_4$), were mixed thoroughly at ambient temperature. The mixture was heated in a stainless steel crucible to $160 \pm 10^\circ\text{C}$ and Al_2O_3 was gradually added to a concentration of 20 wt.%. The contents were thoroughly mixed while holding the crucible at 160°C for about 2 h. The melt was allowed to cool down to the room temperature. A small part of the material was placed between two Teflon sheets with a spacer of 300 μm thick and compacted at 100°C . On cooling, a mechanically stable CSPE film formed. Symmetrical cells, Li/CSPE/Li, were assembled in Teflon holders using stainless steel discs as current collectors and mounted inside sealed glass containers that had provisions for electrical connections. Preparation of the CSPE film and assembly of the cells were carried out in a dry room.

The ac impedance and cyclic voltammetry measurements were carried out by using Solartron electrochemical equipment Models 1260 and 1287. For impedance studies, the ac excitation signal was 5 mV in the frequency range of 100 kHz to 0.1 Hz. The data were analyzed by the non-linear least square (NLLS) curve-fitting program of Scribner Associates. A suitable electrical equivalent circuit was chosen from the ‘equivalent circuit’ sub-program and the starting values of the impedance parameters for NLLS fitting procedure were obtained from the ‘instant fit’ sub-program. Cyclic voltammetry of the symmetrical cells was performed at a sweep rate of 2 mV s^{-1} in the voltage range -2.5 to 2.5 V . Electrochemical stability of the CSPE films was estimated by subjecting a SS/CSPE/SS cell, where SS stands for stainless steel, to a linear sweep voltammetry at 2 mV s^{-1} between -5 and 5 V . DSC was carried out in N_2 atmosphere by using a Calorimeter TA Instruments model 2820. For the purpose of experiments at different temperatures, the cells were placed in a Tenney environmental chamber. The cells were thermally equilibrated for about 2 h at a selected temperature before obtaining experimental data.

3. Results and discussion

In the present method of melt-casting, a thorough mixture of PEO, LiClO_4 and Al_2O_3 powder is heated to a high

temperature. The formation of a complex between PEO and Li^+ ion takes place in the molten state and in the absence of a solvent medium. This method ensures that the nanosize Al_2O_3 particles are not agglomerated which could otherwise happen in a liquid. Additionally, the absence of even trace amounts of the solvent in the CSPE film is also ensured. The CSPE is truly solvent less, dry electrolyte.

3.1. DSC studies

The glass transition temperature (T_g) was -33.8°C for a fresh CSPE film. It is generally believed that a high ionic conductivity is favored if the T_g is lower. Although the T_g of PEO is close to -65°C , it increases when complexed with a Li salt [10]. Results reported in the literature on the effect of ceramics on T_g appear to be inconsistent as there has been an increase in T_g of $\text{PEO}_8\text{LiBF}_4$ with an increase of zeolite [10], decrease in T_g of $\text{PEO}_{16}\text{LiClO}_4$ with an increase of SiC and Si_3N_4 [11] and constancy in T_g of $\text{PEO}_8\text{LiClO}_4$ with an increase of Al_2O_3 [12]. Thus, the effect of ceramic additives on T_g of PEO complexes appears to depend on the salt as well as the ceramic material and its particle size. In the present study, the value of T_g of $\text{PEO}_8\text{LiClO}_4$ with 20 wt.% of 24 nm Al_2O_3 is nearly the same as that reported without any additive [10–12]. It is thus inferred that the nanophase alumina has negligible influence on T_g , similarly to the studies reported [12].

A specimen of the CSPE was subjected to DSC between 20 and 100°C (Fig. 1). It is seen that the endothermic melting peak that is generally observed in the temperature range 65 – 70°C for PEO complexes [10–12], is absent. A PEO–Li salt complex is known to exist in a mixed phase consisting of both crystalline and amorphous forms at ambient temperature [10]. As the segmental motion of PEO chains in the amorphous phase favors ionic transport, more of the solid polymer electrolyte is preferred in the amorphous phase. The DSC results of CSPE films made with micron size ceramic particles show decreased crystallinity [10]. However, some crystalline phase remains at all concentrations of the ceramic additive. The crystallinity has not been completely eliminated by the addition of micron size alumina to $\text{PEO}_8\text{LiClO}_4$ [12]. In the present study, the absence of crystallinity is attributed to the nanoscale particles of Al_2O_3 and their uniform distribution in the CSPE in contrast to larger particle size used in the previously reported studies [10,12]. Thus, the use of nanoscale alumina is advantageous. The CSPE specimen was repeatedly cycled between 20 and 100°C in DSC measurements, and it was found that the data of Fig. 1 are reproducible suggesting that the thermal cycling does not affect the amorphousness of the CSPE. After three thermal cycles, the T_g value of the specimen was found to be -30.8°C , which is marginally higher than the initially measured value of -33.8°C .

3.2. Ac impedance studies

The ac impedance data of a fresh Li/CSPE/Li cell at ambient temperature were found to be variable. However,

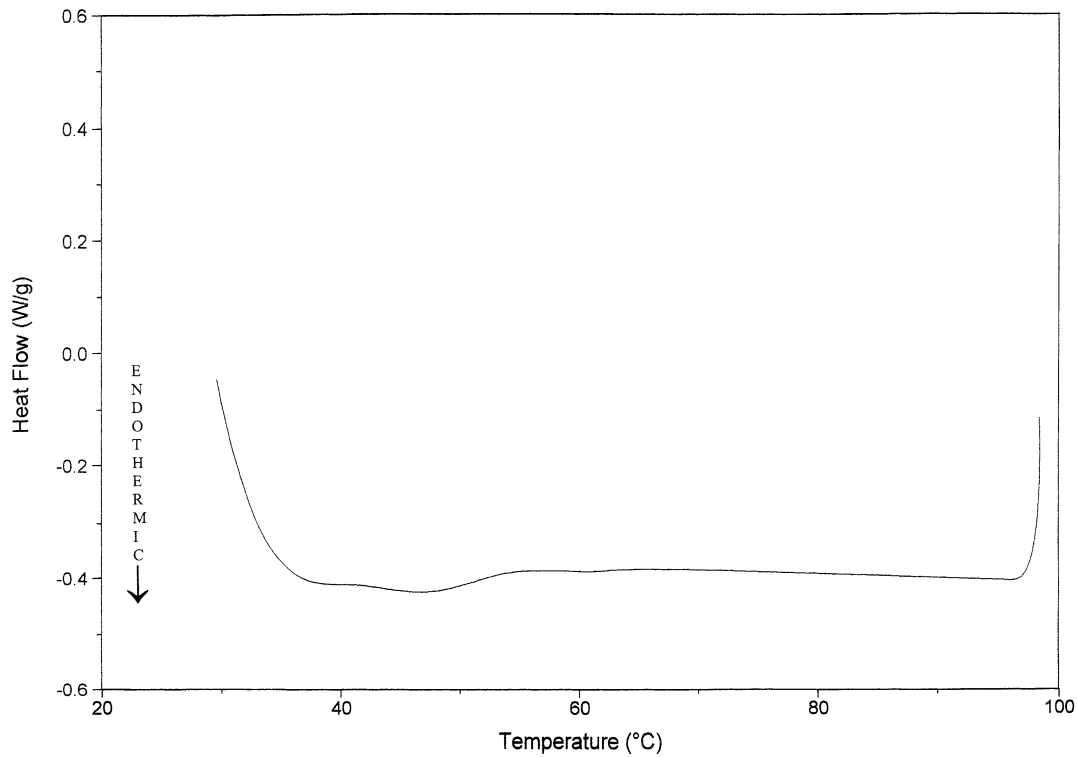


Fig. 1. DSC trace of a CSPE specimen.

the data turned out to be less variable after the cell was thermally cycled three times between -40 and 80 °C. The thermal cycling is expected to provide improved electrical contact between the Li surface and the CSPE film.

The Nyquist impedance spectrum at ambient temperature of a thermally cycled Li/CSPE/Li cell and the equivalent circuit are shown in Fig. 2. The high frequency semicircle (100–2.51 kHz) corresponds to the resistance (R_b) of the CSPE film and its capacitance (C_g) in parallel (Fig. 2). Since the semicircle is depressed, a constant phase element (CPE), Q_g , is considered in place of C_g in the equivalent circuit (Fig. 2). The necessity of using a CPE arises due to microscopic inhomogeneity of the system and distributed nature of the capacitor. In admittance form, a CPE is defined as [13]:

$$Q = Q_0(j\omega)^n \quad (1)$$

where Q_0 is an adjustable parameter and $\omega = 2\pi f$, f being the ac frequency. For $n = 0$, CPE represents a resistance R ($= Q_0^{-1}$); for $n = 1$, a capacitance, C ($= Q_0$); for $n = 0.5$, a Warburg impedance, and for $n = -1$, an inductance, L ($= Q_0^{-1}$).

The broad skewed semicircle (Fig. 2) in the frequency range 2.51 kHz to 0.1 Hz is due to the Li/CSPE interface. The interfacial resistance (R_i) and its capacitance (C_i) in parallel respond to the ac measurements producing a semicircle in the Nyquist impedance spectrum (not shown in the equivalent circuit, Fig. 2). A close observation of the data reveals that the semicircle is elongated suggesting the

merging of a pair of semicircles. Accordingly, the resistance, R_i , is considered to comprise of a surface film resistance (R_f) on Li and the charge-transfer resistance (R_{ct}) of the $\text{Li}^+ + e^- = \text{Li}$ reaction. It is known, [14,15] that the surface of Li is covered by a passive film consisting of primary and secondary layers. The primary layer present on the metallic surface is thin and coherent, whereas the secondary film

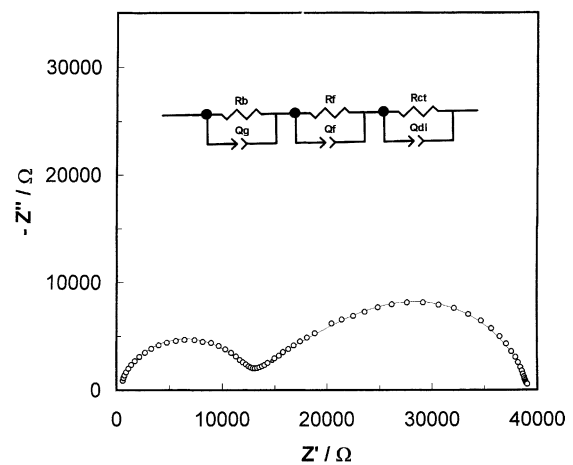


Fig. 2. ac Impedance plot of a Li/CSPE/Li cell at 20 °C and the equivalent circuit. See text for symbols. The values of the impedance parameters obtained from NLLS fitting are: $R_b = 12230 \Omega$; $Q_g = 2.25 \times 10^{-9}$; $n_g = 0.83$; $R_f = 13170 \Omega$; $Q_f = 2.33 \times 10^{-6}$; $n_f = 0.59$; $R_{ct} = 13990 \Omega$; $Q_{dl} = 1.95 \times 10^{-6}$ and $n_{dl} = 0.89$. The experimental data are shown as symbols and the theoretical data as solid curve. Thickness of CSPE = 250 μm , and area of cross-section = 1.23 cm^2 .

present on top of the primary layer is porous [15]. The composition and porosity of the passive film depends on several parameters such as the electrolyte medium, aging time, temperature, thermal history, electrochemical history, etc. Therefore, the nature of the surface film is complex. However, in a simple approach, the properties of the interface can be separated into components of the surface film and the electron-transfer reaction. Accordingly, R_f and Q_f in the equivalent circuit (Fig. 2), respectively, are the resistance and CPE of the surface film, and R_{ct} and Q_{dl} , respectively, are the charge-transfer resistance of the reaction and CPE of the double-layer. The surface film capacitance (C_f) and double-layer capacitance (C_{dl}) are replaced by the CPE Q_f and Q_{dl} , respectively (Fig. 2).

The impedance spectra (Fig. 2) were subjected to the NLLS fitting using the equivalent circuit to obtain the impedance parameters. The fitting proceeded through several iterations. The best fitting was judged by low values of χ^2 and also by a close agreement between the experimental curve with the theoretical curve as shown in Fig. 2. The impedance parameters are given in the caption of Fig. 2. Data similar to Fig. 2 were obtained in the temperature range 20–80 °C. However, with an increase of temperature, the high frequency semicircle gradually decreases in size and disappears at about 60 °C. For analysis of the data not containing this semicircle, the parameter Q_g in the equivalent circuit (Fig. 2) was dropped and the rest of impedance parameters obtained.

From the value of R_b , the specific conductivity (σ) of the CSPE film was calculated using,

$$\sigma = \frac{l}{R_b A} \quad (2)$$

where l and A are the thickness and area of the CSPE film, respectively. From the data of Fig. 2, a value of $1.66 \times 10^{-6} \text{ S cm}^{-1}$ is obtained for σ at 20 °C. This value is at least 2 orders of magnitude higher than the value for PEO-LiClO₄ film in the absence of Al₂O₃ powder [16]. The higher value of σ is therefore attributed to the presence of the nanoscale Al₂O₃ particles present in the CSPE film.

Quartarone et al. have reviewed the mechanism of influence of ceramic particles in PEO-based solid polymer electrolytes recently [2]. Plochanski and Wiczorek [17] have shown that the conductivity of PEO-NaI has improved by an order of magnitude at ambient temperatures due to the presence of NASICON. The conductivity enhancement has been attributed to the augmentation of the amorphous phase. Results showing enhancement in conductivity of PEO-NaSCN due to Al₂O₃ and increase in amorphous phase have also been reported by Liqian [18]. The degree of crystallinity has been calculated by Munichandraiah et al. [10], and it has been shown that the crystallinity of PEO-LiBF₄ decreases to about 32% due to the presence of zeolite. Interaction between the polymer chain and zeolite particles has also been shown to exist from IR spectroscopy [10]. Enhancement in polymer amorphicity, and hence

conductivity by preventing agglomeration of the polymer chains have been reported for PEO-LiClO₄ due to LiAlO₂ by Capuani et al. [19]. Kumar and Scanlon [4] have reported a review of their observations on polymer-ceramic composite electrolytes. Concerning the ionic conductivity, the incorporation of ceramic powders in a polymer matrix leads to two competing effects: (i) enhancement of amorphous phase and hence, of the ionic conductivity and (ii) increase in T_g , which reduces the segmental motion of the polymer chain and hence the conductivity. Boron-based glasses have been incorporated in PEO-LiClO₄ by Mustarelli et al. [20] and conductivity enhancement due to the existence of subtle interactions between the polymer and glass have been reported. Interaction between the ceramic additive and the polymer due to their dipolar nature has been reported by Kumar et al. [7]. As commented by Quartarone et al. [2], the present overall knowledge of composite polymer electrolytes is still quite unsatisfactory. It is not clear about the level of interaction between the ceramics, host polymers and doping salts. More systematic experimental studies are required to unravel the mechanism of the influence of the ceramics on PEO-based solid polymer electrolytes.

The temperature dependence of σ of the CSPE is shown in Fig. 3(a) as an Arrhenius plot. It is seen that the data are non-linear in the temperature range 20–80 °C. The temperature dependence of σ of solid polymer electrolytes has been analyzed by Ratner in detail [21]. Accordingly, $\sigma(T)$ curves for polymer electrolytes show one of the following five patterns of behavior: (i) VTF behavior throughout the temperature range, (ii) Arrhenius behavior at low temperatures and VTF behavior at higher temperatures, (iii) Arrhenius behavior throughout, but with two different activation energies, (iv) VTF behavior at temperatures slightly greater than T_g , but Arrhenius behavior at higher temperatures, and (v) behavior which is very unlike either Arrhenius or VTF at all temperatures.

It is known that PEO₈LiClO₄ exhibits Arrhenius behavior with two different activation energies (that is, type (iii) discussed earlier) [21]. In the temperature region below the melting point of PEO (≈ 70 °C), the activation energy is higher than in the region above the melting point. Thus, as a result of the nanophase alumina present in PEO-LiClO₄ complex, there is a change from double Arrhenius behavior to non-Arrhenius behavior. The data were, therefore, examined in view of the VTF equation:

$$\sigma = A_0 T^{-1/2} \exp\left(\frac{-E_a}{R(T - T_0)}\right) \quad (3)$$

where E_a the activation energy and T_0 the equilibrium glass transition temperature, which is close to the experimental T_g . The VTF equation was developed to deal with the viscosity of supercooled liquids. Although, it is an empirical equation, it can also be arrived at starting from a free-volume model [21]. The free-volume of a polymer is defined as:

$$V_f = \bar{V} - V_0 \quad (4)$$

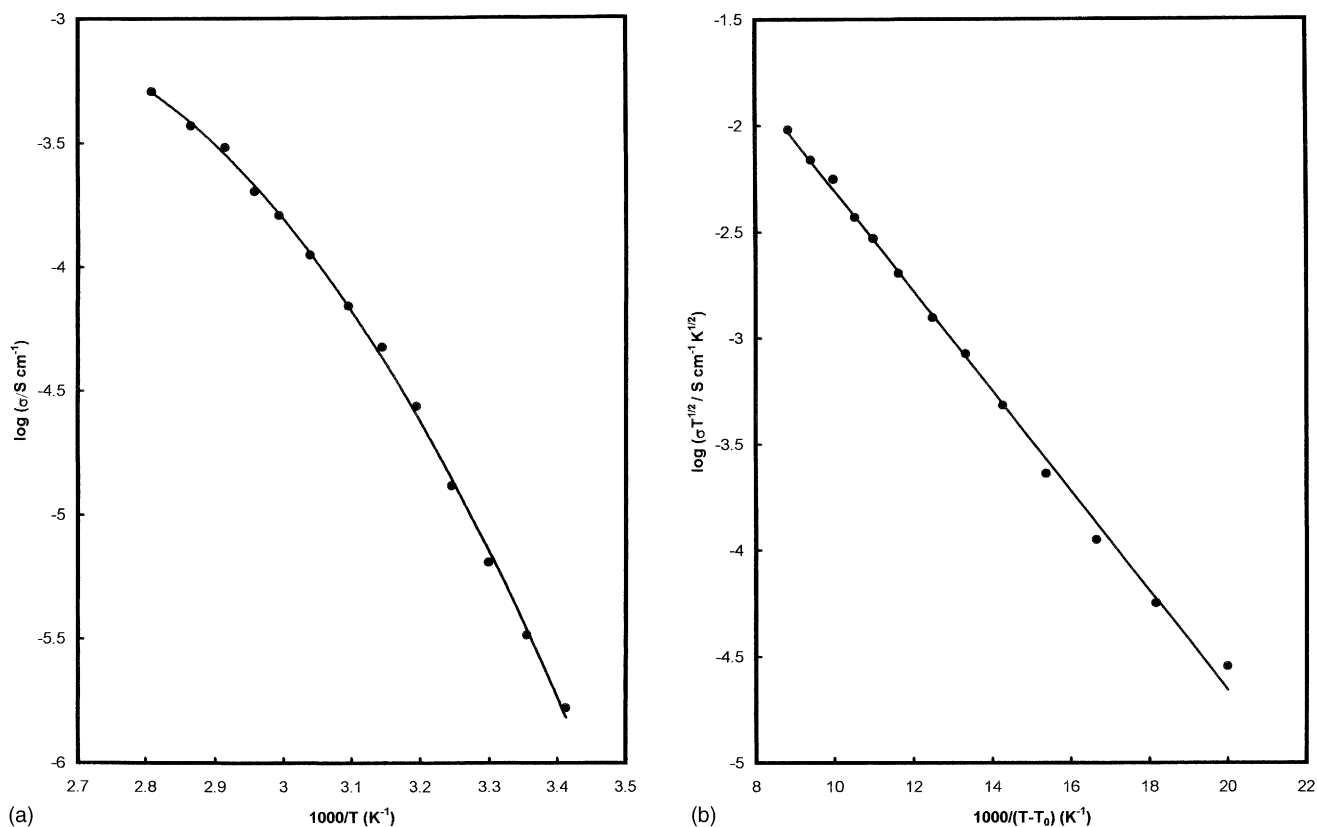


Fig. 3. Variation of specific conductivity (σ) of the CSPE with temperature (T) as (a) Arrhenius plot and (b) VTF plot.

where V_f is the average free volume per molecule, \bar{V} is the average volume per molecule in the sample, and V_0 is the van der Waals volume. By re-plotting the data shown in Fig. 3a as $\log(\sigma T^{1/2})$ versus $1/(T - T_0)$, assuming $T_g = T_0$, a linear plot is obtained as shown in Fig. 3b. From the slope of the line, a value of 0.046 eV is obtained for E_a .

The conduction of Li^+ ion in the CSPE is pictorially shown in Fig. 4. Under the influence of a potential gradient, the coordination spheres of the Li^+ ions keep changing to adjacent locations and this is assisted by the segmental motion of the polymer chain. The polymer chain undergoes reorganization during the course of continuous breaking and reforming of coordination sphere for Li^+ ions.

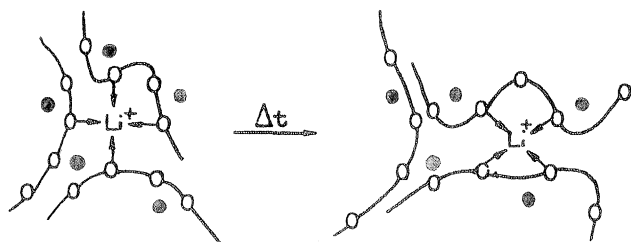


Fig. 4. Schematic view of chain mobility, change of coordination sphere, and chain reorganization during conduction in CSPE. Nanosize Al_2O_3 particles are shown as closed circles and oxygen of the PEO chain as open circles.

The problem of solvent reorganization during electron-transfer reactions in liquid electrolytes has been studied by Marcus [22]. In a simple electron-transfer reaction, where a reactant species crosses the energy barrier to form the products, the solvation sheath around the species undergoes a change with respect to the number and orientation of the solvent dipoles. Accordingly, the energy (λ) of reorganization of the solvent molecule is related to the activation energy (E_a) of the electron-transfer reaction and it is approximately given as [22]:

$$E_a \approx \frac{1}{4} \lambda \quad (5)$$

Thus, the activation energy required for the reactant to cross the barrier is only a fraction of the solvent reorganization energy.

Although, there is no net electron-transfer, the physical situation during the conduction process in a solid polymer electrolyte is comparable to the Marcus theory outlined above. The cations that are solvated by the O atoms of the PEO chain keep changing the solvation sphere with a simultaneous reorganization of the PEO chain (Fig. 4). A rigorous theoretical treatment of the problem pertaining to solid polymer electrolytes is not available in the literature. As an approximation, using Eq. (5), the value of λ obtained for PEO is 0.18 eV.

The variations of R_f with temperature are shown in Fig. 5. There is a decrease in R_f with temperature suggesting that

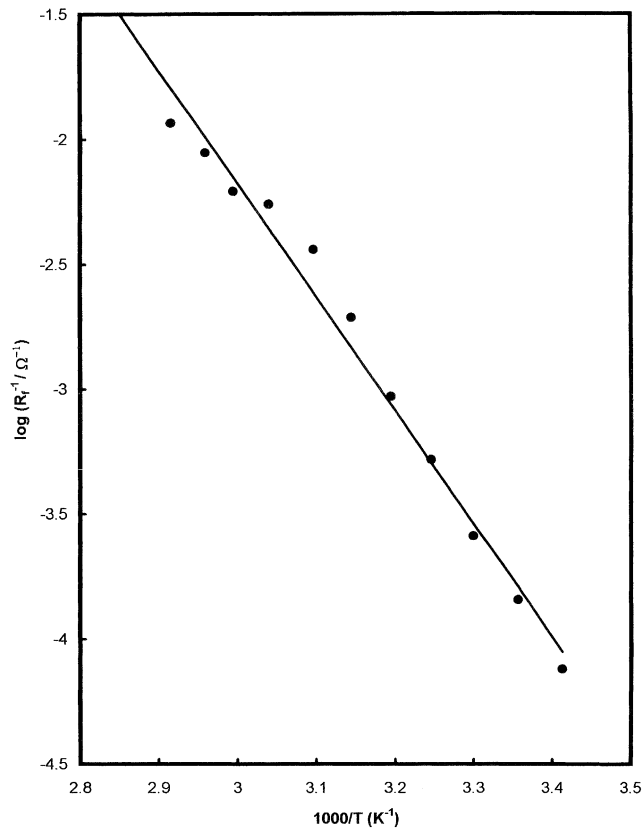


Fig. 5. Variation of inverse of film resistance (R_f) with temperature (T) as Arrhenius plot.

the surface film on Li is ionically conducting. Inverse of R_f follows an Arrhenius-type behavior (Fig. 5) with activation energy of 0.9 eV.

The parameter, R_{ct} , is related to the exchange current density (i_0) of the $\text{Li}^+ + e^- = \text{Li}$ reaction as:

$$R_{ct} = \frac{RT}{i_0 F} \quad (6)$$

where R is the gas constant, T the absolute temperature and F the Faraday constant. The i_0 is related to the standard rate constant (k_s) of the reaction, which in turn depends on temperature in Arrhenius fashion. Thus,

$$i_0 = F A k_s C^\alpha \quad (7)$$

where C is the concentration of Li^+ ions in the CSPE and α the transfer coefficient.

$$k_s = A_0 \exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

where A_0 is the pre-exponential factor. By substitution of Eqs. (7) and (8) in (6), we get

$$\log\left(\frac{R_{ct}}{T}\right) = \log k + \frac{E_a}{2.3 RT} \quad (9)$$

where k is a constant. Thus, a plot of $\log(R_{ct}/T)$ versus $1/T$ is expected to be linear and E_a can be calculated from its slope.

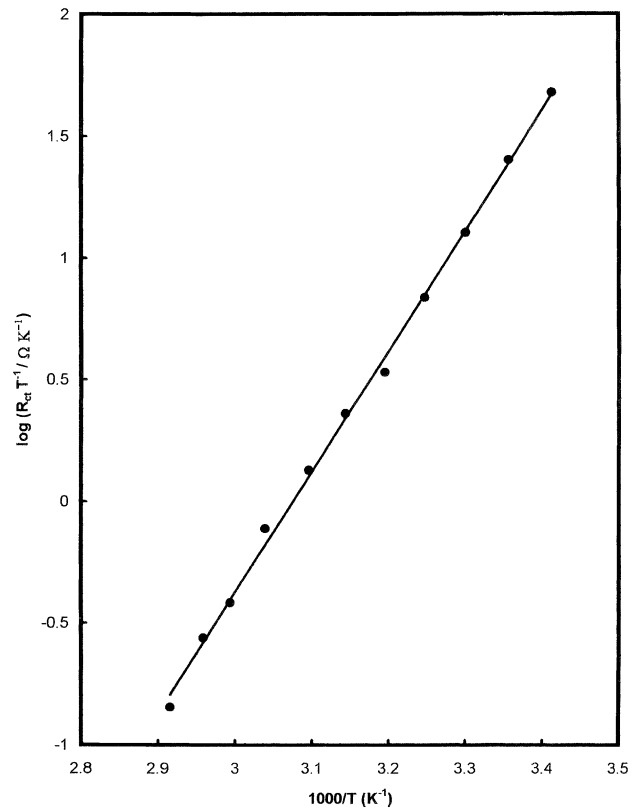


Fig. 6. Variation of $\log(R_{ct} T^{-1})$ with temperature (T) as Arrhenius plot.

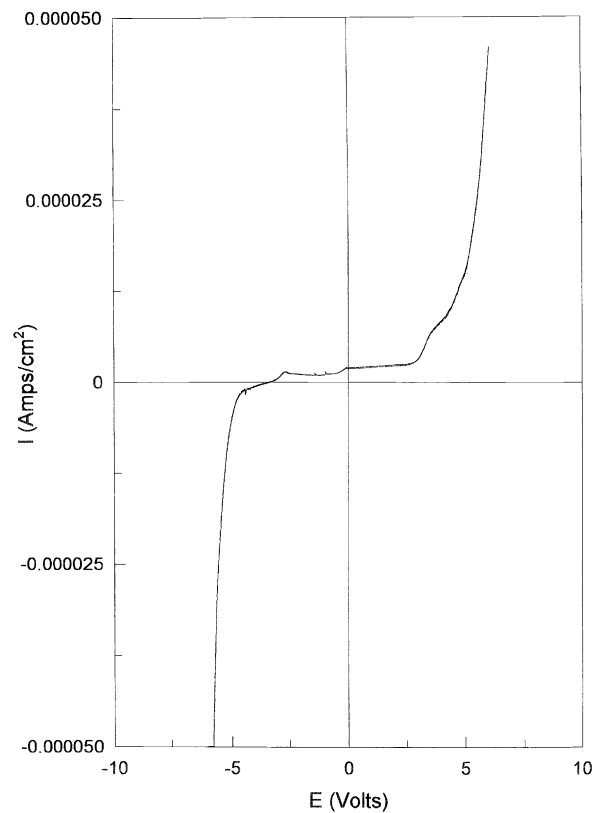


Fig. 7. Linear sweep voltammetry of SS/CSPE/SS cell at a sweep rate of 2 mV s^{-1} showing a high voltage window of CSPE film.

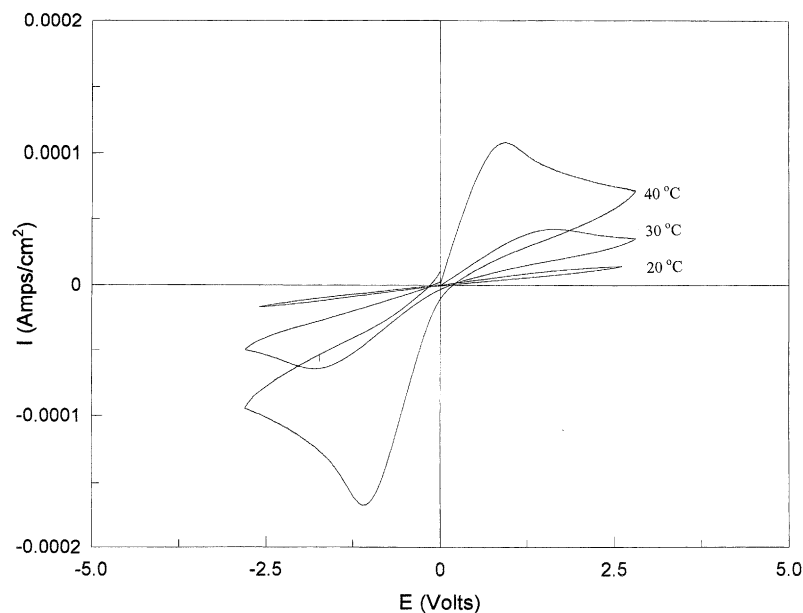


Fig. 8. Cyclic voltammogram of Li/CSPE/Li cell at 2 mV s^{-1} sweep rate at temperatures near ambient.

A plot of $\log(R_{ct}/T)$ versus $1/T$ is shown in Fig. 6. The value of E_a obtained for the reaction is 0.98 eV.

3.3. Voltage stability window of the CSPE

PEO-based solid polymer electrolytes are known to possess a wide voltage stability window. For the purpose of measuring safe voltage limits of the CSPE, the film between two blocking electrodes is usually subjected to a slow voltage sweep. These studies have been generally carried out at high temperatures [8]. Since the ambient temperature behavior is considered important in the present study, a SS/CSPE/SS cell was subjected to potentiodynamic experiment at a slow sweep rate between -5 and 5 V at several temperatures. The data at 40°C are shown in Fig. 7. The magnitude of current is fairly low between -4.5 and 4.5 V, and current starts increasing at potentials beyond this limit due to decomposition of the electrolyte. This study suggests a voltage window of ± 4.5 V of the CSPE at near ambient temperatures. The voltage window remained unchanged in the temperature range from 40 to 60°C .

3.4. Cyclic voltammetry

The conductivity studies revealed that there is considerable increase in ionic conductivity at ambient temperature due to the presence of nanosize Al_2O_3 particles in CSPE. Since the polymer electrolytes are intended to be useful at ambient temperature, studies on electrochemical activity of the Li/CSPE interface at ambient temperature are considered to be important. Such studies are not reported in the literature hitherto. The cyclic voltammogram of a Li/CSPE/Li cell are shown in Fig. 8. At 20°C , the voltammogram does

not consist of sharp peaks although broad humps are noticeable in both the cathodic and anodic regions. At 30°C , however, the current peaks are noticeable although they are broad. On the other hand, the current peaks are sharp at 40°C . There is an increase in current with temperature. The cathodic and anodic peaks are separated by about 2 – 2.5 V. This is due to the presence of ohmic drop across the CSPE film and the absence of a reference electrode in the cell. The difficulties associated with the assembly of a cell with a reference electrode in a thin film of solid polymer electrolyte are reported elsewhere [23]. Nevertheless, the cyclic voltammetric data qualitatively suggest that the Li/CSPE interface is electrochemically active around ambient temperatures.

4. Conclusions

The CSPE consisting of PEO, LiClO_4 and Al_2O_3 of particle size 24 nm is found to be in a complete amorphous state. The σ versus temperature follows VTF behavior and the activation energy was calculated. By an analogy to the Marcus theory of electron-transfer reactions, the reorganization energy of the polymer chain was calculated from the activation energy of ionic conduction. The resistance of the passivating film on Li and the charge-transfer resistance of the Li reaction were evaluated. The charge-transfer resistance is shown to follow the Arrhenius behavior through the standard rate constant of the reaction. A stable voltage window of ± 4.5 V was found. The cyclic voltammograms provided an evidence for electrochemical activity at the Li/CSPE interface at ambient temperature.

References

- [1] M. Gauthier, A. Belanger, B. Kapper, G. Vasort, M. Armand, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews*, Vol. 2, Elsevier, London, 1989, pp. 285.
- [2] E. Quartarone, P. Mustarelli, A. Magistris, *Solid State Ionics* 110 (1998) 1.
- [3] J.E. Weston, B.C.H. Steele, *Solid State Ionics* 7 (1982) 75.
- [4] B. Kumar, L.G. Scanlon, *J. Power Sources* 52 (1994) 261.
- [5] B. Kumar, L.G. Scanlon, *J. Electroceram.* 5 (2000) 127.
- [6] W. Krawiec, L.G. Scanlon, J.P. Fellner, R.A. Vaia, S. Vasudevan, E.O. Giannelis, *J. Power Sources* 54 (1995) 310.
- [7] B. Kumar, L.G. Scanlon, R.J. Spry, *J. Power Sources* 96 (2001) 337.
- [8] L. Persi, F. Croce, B. Scrosati, E. Plichta, M.A. Hendrickson, *J. Electrochem. Soc.* 149 (2002) A212.
- [9] F. Croce, G.B. Appetechi, L. Persi, B. Scrosati, *Nature* 394 (1998) 456.
- [10] N. Munichandraiah, L.G. Scanlon, R.A. Marsh, B. Kumar, A.K. Sircar, *J. Appl. Electrochem.* 25 (1995) 857.
- [11] B.K. Choi, K.H. Shin, *J. Appl. Electrochem.* 27 (1997) 365.
- [12] C.C. Tambelli, A.C. Bloie, A.V. Rosario, E.C. Pereira, C.J. Magon, J.P. Donoso, *Electrochim. Acta* 47 (2002) 1677.
- [13] J.R. Macdonald, *Impedance Spectroscopy*, Wiley, New York, 1987, pp. 77.
- [14] A.N. Dey, *The Electrochemical Society Extended Abstracts, Fall Meeting, Atlantic City, NJ, 1970*, pp. 154.
- [15] E. Peled, *J. Electrochem. Soc.* 126 (1979) 2047.
- [16] H.B. Armand, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews*, Vol. 1, Elsevier, London, 1989, p. 1.
- [17] J. Plochanski, W. Wiczorek, *Solid State Ionics* 28–30 (1988) 973.
- [18] C. Liqun, in: B.V. Chowdari, S. Radhakrishnan (Eds.), *Materials for Solid State Batteries*, World Scientific, Singapore, 1988, p. 69.
- [19] F. Capuani, F. Croce, B. Scrosati, *J. Electrochem. Soc.* 138 (1991) 1918.
- [20] P. Mustarelli, E. Quartarone, C. Tomasi, A. Magistris, *Solid State Ionics* 86 (1996) 347.
- [21] M.A. Ratner, in: J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews*, Vol. 1, Elsevier, London, 1989, p. 173.
- [22] R.A. Marcus, *Pure and Appl. Chem.* 69 (1997) 13.
- [23] N. Munichandraiah, L.G. Scanlon, R.A. Marsh, B. Kumar, A.K. Sircar, *J. Electroanal. Chem.* 379 (1994) 495.