

Ionic Conductivity of Solid Polymer Electrolytes for Dye-Sensitized Solar Cells

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ABSTRACT: We developed an ionic conductivity model of solid polymer electrolytes for dye-sensitized solar cells (DSSCs) based on the Nernst–Einstein equation in which the diffusion coefficient is derived from the molecular thermodynamic model. We introduced concentration-dependence of the diffusion coefficient into the model, and the diffusion coefficient was expressed by differentiating the chemical potential by concentration. The ionic conductivities of polymer electrolytes (PEO/LiI/I₂ system) were investigated at various temperatures and compositions. We prepared a set of PEO in which an EO : LiI mole ratio of 10 : 1 was

kept constant for PEO·LiI·(I₂)_n compositions with $n = 0.02, 0.05, 0.1, 0.15, 0.2,$ and 0.3 (mole ratio of LiI : I₂). The ionic conductivities of the electrolytes were measured using a stainless steel/polymer-electrolyte/stainless steel sandwich-type electrode structure using alternating current impedance analysis. The values calculated using the proposed model agree well with experimental data. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3582–3587, 2010

Key words: DSSCs; polymer electrolytes; ionic conductivity model; PEO/LiI/I₂ system

INTRODUCTION

Photo-electrochemical solar cells based on dye-sensitized TiO₂ are promising alternatives to conventional silicon solar cells because of their low cost. Liquid state DSSCs and quasi-solid state DSSCs have been studied by many research groups. However, liquid-electrolyte-based DSSCs have some drawbacks, such as the leakage and evaporation of the electrolyte during long-term operation. To avoid leakage and evaporation of organic solvent, many efforts have been made to replace the liquid electrolyte with solid state media.¹ Despite the advantage of long-term stability, solid-state DSSCs are relatively inefficient. (~ 1%).² Research on the electrochemical applications of solid polymer electrolytes (PEO) has therefore focused on ionic conductivity and improvement of the ionic conductivity of each complex.

Adam and Gibbs³ developed a configurational entropy model for the quantitative study of ionic conduction, and many research groups^{4,5} have used this model and the Vogel–Tamman–Fulchur (VTF) equa-

tion to analyze the temperature dependence of conductivity. Models explaining the dependence of conductivity on composition have been introduced by other authors.^{6–8} Angell and Bressel⁶ explain the composition-dependence of transport properties on the basis of the VTF equation. Sørensen and Jacobsen⁷ developed a simple model that quantitatively accounts for the concentration-dependence of the conductivity of low purity electrolytes. Adam and Gibbs,³ MacFarlane et al.⁸ and Flory⁹ investigated the effect of a plasticizer on conductivity using the Adam–Gibbs model combined with Flory's configurational entropy at fixed temperature. Systematic studies of conductivity versus composition and temperature were made by Chabagno¹⁰ and Fauteux and Robitaille.¹¹ In light of recent research, we may conclude that ionic conductivity is a function of different experimental parameters and any given material's thermal history, both of which strongly influence the properties of the amorphous phase, ion association, ion-polymer interactions, and the local relaxations of the polymer. Recently, Pai et al.,¹² developed an ionic conductivity model for lithium secondary batteries based on the Nernst–Einstein equation which simultaneously takes into account the mobility of salt and the motion of the polymer host by expressing the effective chemical potential as the sum of the chemical potentials of the salt and polymer.

In this study, we developed an ionic conductivity model of PEO for DSSCs based on the Nernst–

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Einstein equation and in which the diffusion coefficient is derived from the molecular thermodynamic model. We introduced the concentration-dependence of the diffusion coefficient into the ionic conductivity model, and the diffusion coefficient was expressed by differentiating the chemical potential with the concentration. Comparisons of the proposed model with experimental data were made for the PEO/LiI/ I_2 , PEO/KI/ I_2 systems for DSSCs.

EXPERIMENTAL

Preparation of PEO

Poly(ethylene oxide) (PEO, $M_w = 1 \times 10^6$ g/mol), lithium iodide (LiI, 99.99%), and iodine (I_2 , 99.98%) were purchased from Aldrich Chemical. All chemicals were used without further purification. These were dissolved in acetonitrile (Aldrich) at room temperature and continuously stirred in a magnetic stirrer for about 24 h until a homogeneous viscous liquid was formed. We prepared a set of polymer electrolyte compositions. An EO : LiI mole ratio of 10 : 1 was maintained for PEO·LiI·(I_2) $_n$ compositions with $n = 0.02, 0.05, 0.1, 0.15, 0.2,$ and 0.3 (mole ratio of LiI : I_2). Polymer films were prepared by casting solutions on Teflon plates and allowing the solvent to evaporate slowly at room temperature in air for 24 h. The films were dried in a vacuum oven for 48 h at room temperature. Bubble free regions of the films were employed for conductivity measurements.

Ionic conductivity measurements

The ionic conductivities of the PEO were measured using a stainless steel/polymer-electrolyte/stainless steel sandwich-type electrode structure and an alternating current (AC) impedance technique on an impedance analyzer (Gamry reference 600) at frequencies from 1 MHz to 0.1 Hz (signal amplitude 10 mV). Measurements were carried out over the temperature range from 298 to 343 K. The samples were allowed to equilibrate at each temperature for 15 min before data collection. The ionic conductivity (σ) was calculated from the bulk electrolyte resistance value (R_b) found in the complex impedance diagram according to the following equation:

$$\sigma = \frac{l}{R_b A} \quad (1)$$

where l is the thickness of the polymer electrolyte which was measured using a micrometer, and A is the surface area of the polymer electrolyte. The resistance (R_b) was taken at the intercept of Nyquist plot with the real axis.¹³

MODEL DEVELOPMENT

Modified double lattice model

Oh and Bae¹⁴ proposed a new Helmholtz energy of mixing in the form of the Flory-Huggins theory. The expression is given by

$$\frac{\Delta A}{N_r k T} = \left(\frac{\phi_1}{r_1} \right) \ln \phi_1 + \left(\frac{\phi_2}{r_2} \right) \ln \phi_2 + \chi_{OB} \phi_1 \phi_2 \quad (2)$$

where N_r is the total number of lattice sites for the mixture, k is the Boltzmann constant, r_i is the number of segments per molecule, ϕ_i is the volume fraction of component i with $\phi_i = N_i r_i / N_r$, where $N_r = \sum_i^m N_i r_i$, and χ_{OB} is a new interaction parameter and is a function of r_i and $\tilde{\varepsilon}$:

$$\chi_{OB} = C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} \phi_2 + C_\gamma \tilde{\varepsilon}^2 \phi_2^2 \quad (3)$$

where $\tilde{\varepsilon}$ is a reduced interaction parameter given by

$$\tilde{\varepsilon} = \varepsilon / k T = (\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}) / k T \quad (4)$$

where ε_{11} , ε_{22} , and ε_{12} are the corresponding nearest-neighbor segment-segment interactions. The parameters C_β and C_γ are universal constants. These constants are not adjustable parameters and are determined by comparison with Madden et al.'s Monte-Carlo simulation data ($r_1 = 1$ and $r_2 = 100$). The best fitting values of C_β and C_γ are 0.1415 and 1.7985, respectively.¹⁴

Correlating equations

To correlate the MDL model to the ionic conductivity model, the chemical potentials of Components 1 and 2 are needed. The definition of chemical potential is

$$\frac{\Delta \mu_i}{k T} = \frac{\partial (\Delta A / k T)}{\partial N_i} \quad (5)$$

The final expressions for the chemical potential can be written as

$$\begin{aligned} \frac{\Delta \mu_1}{k T} = & \ln(1 - \phi_2) - r_1 \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \phi_2 + r_1 \left[C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 \right. \\ & + \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \left. \right] \phi_2^2 \\ & - 2r_1 \left[\left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + C_\gamma \tilde{\varepsilon}^2 \right] \phi_2^3 + 3r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^4 \end{aligned} \quad (6)$$

and

$$\begin{aligned}
\frac{\Delta\mu_2}{kT} = & \ln \phi_2 + r_2 \left[\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 \right. \\
& + \left. \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \right] - r_2 \left[\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + 2 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} \right. \\
& + \left. 2C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + 2 \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \right] \phi_2 \\
& + r_2 \left[4 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon}^2 \right. \\
& + \left. C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + 3C_\gamma \tilde{\varepsilon}^2 \right] \phi_2^2 - r_2 \left[6C_\gamma \tilde{\varepsilon}^2 \right. \\
& + \left. 2 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} \right] \phi_2^3 + 3r_2 C_\gamma \tilde{\varepsilon}^2 \phi_2^4 \quad (7)
\end{aligned}$$

Ionic conductivity model

For binary diffusion in gases or liquids, the generalized Fick's equation for heat and mass is as follows¹⁵:

$$\begin{aligned}
J_A^* = & -cD_{AB} \left[x_A \nabla \ln a_A + \frac{1}{cRT} [(\phi_A - \omega_A) \nabla p \right. \\
& \left. - \rho \omega_A \omega_B (\mathbf{g}_A - \mathbf{g}_B)] + k_T \nabla \ln T \right] \quad (8)
\end{aligned}$$

This equation states that the thermodynamics of irreversible processes dictate using the activity gradient as the driving force for concentration diffusion. This requires a diffusion coefficient different from Fick's first law. When the pressure-, thermal-, and forced-diffusion terms are dropped, eq. (8) for a binary electrolyte is simplified to

$$J_s^* = -D^* C_s \nabla \ln a_s \quad (9)$$

where D^* , C_s , and a_s are the self-diffusion coefficient, concentration, and activity of salt, respectively. Making use of the fact that the activity is a function of concentration, this may be rewritten to obtain

$$J_s^* = -D^* C_s \left(\frac{d \ln a_s}{d C_s} \right) \nabla C_s \quad (10)$$

With the original Fick's equation, $J_s^* = -D_s \nabla C_s$, eq. (10) can be related to the measured diffusion coefficient D_s (based on the concentration driving force) using¹⁵

$$D_s = D^* \left(\frac{d \ln a_s}{d \ln C_s} \right) \quad (11)$$

where D^* characterizes the component mobility in the absence of any interactions in the system.¹⁶ This

may be rewritten using the fact that the activity is related to the chemical potential by $\ln a = \frac{\Delta\mu}{RT}$

$$D_s = D^* C_s \frac{d \left(\frac{\Delta\mu_s}{RT} \right)}{d C_s} \quad (12)$$

The transport of ions in solvent-free PEO differs from that in systems based on molecular liquids or low molar mass polymers. In the latter systems, ions can move together with their co-ordinated solvent, but in high molecular weight polymers, the centre of gravity of the chain cannot be moved a significant distance.

This in turn yields, using the Nernst-Einstein relationship for a multicomponent system, the conductivity equation for SPE having the form:

$$\sigma = \frac{F^2}{RT} \sum_i z_i^2 v_i D_i C_i \quad (13)$$

where F is the Faraday constant. Since we assume that the phase at the given condition is a binary system of polymer and salt, the moving object is the salt itself. If the charge effect of each ion remains for the ion interactions, this assumption allows us to put eq. (13) into a simple form:

$$\sigma = \frac{F^2 C_s}{RT} D_s \sum_i z_i^2 \quad (14)$$

Substituting eq. (12) into eq. (14) gives the final ionic conductivity equation for SPE systems:

$$\sigma = \frac{F^2 C_s}{RT} D^* C_s \frac{d \left(\frac{\Delta\mu_s}{RT} \right)}{d C_s} \sum_i z_i^2 \quad (15)$$

where the chemical potentials are given by

$$\begin{aligned}
\frac{\Delta\mu_s}{kT} = & \ln(1 - \phi_2) - r_1 \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \phi_2 + r_1 \left[C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 \right. \\
& + \left. \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left(2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \right] \phi_2^2 \\
& - 2r_1 \left[\left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + C_\gamma \tilde{\varepsilon}^2 \right] \phi_2^3 + 3r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^4 \quad (16)
\end{aligned}$$

RESULTS AND DISCUSSION

To apply our binary lattice model to this ternary case (PEO/LiI/I₂), PEO, and LiI were considered to be pseudo-pure components. Therefore, in the ionic conductivity model, I₂ was used as the salt. Because

TABLE I
Physical Properties of Materials

	M_w (g mol ⁻¹)	Density (g cm ⁻³)	V_u (cm ³ mol ⁻¹)
PEO	1,000,000	1.28	36.6
LiI	133.85	3.494	38.30
KI	166.00	3.123	53.15
I_2	253.18	4.933	51.32

the mole ratio of PEO and LiI was constant, the system composition varied between only I_2 and the pseudo-pure component. This assumption was thought to be reasonably applicable to our experimental data. Therefore, Component 1 is I_2 and Component 2 is the pseudo-pure component. We let the number of I_2 segments, r_1 , be unity and calculated the number of the units, r_2 , using the specific volumes V_1 and V_2 for I_2 and PEO. Because the molecular weight of PEO (1×10^6 g/mol) is much higher than that of LiI, and the value $M \cdot V$ of LiI is relatively small, we can neglect the properties of LiI in calculating r_2 . Therefore, the values of M_2 , and V_2 are used for only the pure properties of PEO,

$$r_2 = \frac{M_2 V_2}{M_1 V_1} \quad (17)$$

where M_1 and M_2 are the molecular weights for I_2 and PEO, respectively.

To differentiate chemical potential with concentration, the salt concentration was calculated from the salt mass fraction as follows:

$$C_1 = \frac{\rho_1 w_1}{M_1} \quad (18)$$

where w_1 is the weight fraction of I_2 . The density of I_2 , ρ_1 , is given by

$$\frac{1}{\rho_1} = \frac{1}{\rho_2} + w_1 \left(\frac{V_1}{M_1} - \frac{1}{\rho_2} \right) \quad (19)$$

where ρ_2 is the density of PEO.

Table I gives the physical properties of PEO, LiI, KI, and I_2 . Figure 1 shows a typical Nyquist plot of the impedance data for the PEO/LiI/ I_2 system at 295 K. The bulk electrolyte resistance (R_b) was estimated from the corresponding component of an equivalent circuit to account for the impedance diagrams. The ionic conductivity (σ) of the PEO/LiI/ I_2 system was calculated according to eq. (1) from the impedance diagram of the SS/SPE/SS symmetrical cell. The conductivity of the system (mole ratio $I_2 = 0.02$) was 4.158×10^{-6} S/cm.

Figure 2 shows the ionic conductivity of the PEO/LiI/ I_2 system. The points represent experimental data at different temperatures, and the lines were

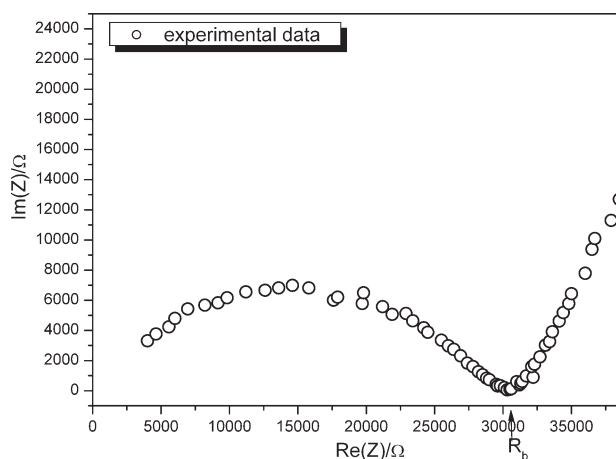


Figure 1 Plot of the imaginary vs. the real impedance, Z , using a blocking electrode (stainless steel) at 295 K with film thickness 633 μm and cross-sectional area 0.16 πcm^2 . R_b is the bulk resistance of the PEO/LiI/ I_2 system.

calculated using the proposed model. The calculated model parameters are listed in Table II. The ionic conductivity of the system was calculated as a function of the I_2 mole ratio. In general, in a binary polymer electrolyte system, the ionic conductivity is a product of the concentration and mobility of the charged carriers. Thus, the ionic conductivity increases with the salt concentration at low salt concentrations. This is primarily due to the increased concentration of the charge carrier. However, the ionic conductivity reaches a maximum, followed by a decrease with increasing salt concentration. The metal cations are generally coordinated by more than two oxygen atoms, resulting in physical cross-linking points, causing the polymeric chain to be stiff and have a low ionic conductivity.¹⁷ However, in the experimental conductivity values of the PEO/

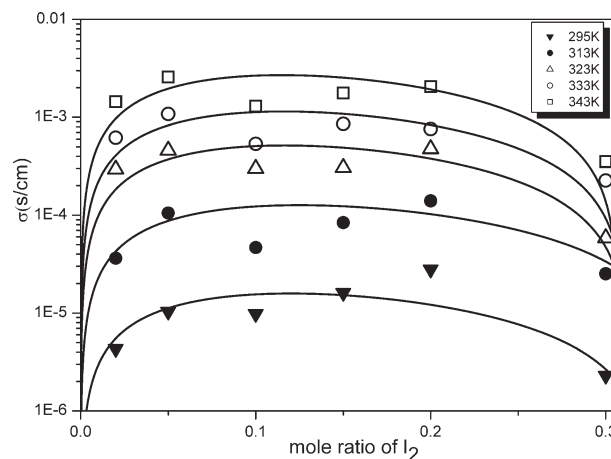


Figure 2 Ionic conductivity of PEO/LiI/ I_2 system. Mole ratio of PEO : LiI was fixed [EO : LiI = 10 : 1]. Points are experimental data at different temperatures. Lines were calculated using the proposed model.

TABLE II
Calculated Model Parameters

	D^* ($\text{cm}^2 \text{s}^{-1}$)	ϵ/k (K)
PEO/LiI/I ₂		
295 K	4.226×10^{-9}	150.241
313 K	3.458×10^{-8}	154.313
323 K	1.544×10^{-7}	168.443
333 K	3.547×10^{-7}	174.206
343 K	8.692×10^{-7}	180.986
PEO/KI/I ₂		
303 K	7.342×10^{-9}	-1397.55
318 K	9.143×10^{-9}	-1390.95
333 K	1.415×10^{-8}	-1487.70

LiI/I₂ system, the maximum values were observed at both a 0.05 and 0.2 mole ratio of I₂, which shows that the charge transfer mechanism of the PEO/salt binary electrolyte system cannot be applied to a real PEO/LiI/I₂ electrolyte system in DSSCs. As a result, discrepancies between the experimental and calculated values might have originated from the simple ionic conductivity model of PEO for DSSCs which correlates the thermodynamic model with the Nernst-Einstein relationship. Actually, the concentration-dependence of conductivity is a complex function in PEO for DSSCs, and it is still unclear what actual species are involved in carrying the electric charge. It has even proved difficult to reliably establish the fraction of current carried by the cationic and anionic constituents. The proposed model does not perfectly explain the concentration-dependence of ionic conductivity in PEO for DSSCs. However, it predicts the tendency of this dependence in general polymer electrolyte systems using a simple but reasonable equation. In a wide range of I₂ mole ratios (~0.3), the calculated conductivity values generally showed maximums in the 0.1–0.2 range, and decreases with increasing I₂ mole ratios. The increase in the mole ratio of I₂ initially enhances the conductivity up to a maximum point. This may be due to the presence of a higher concentration of polyiodide (I₃⁻, I₅⁻) ions. Many research groups have demonstrated the formation of polyiodide ions caused by the addition of iodine using Raman spectroscopy.^{18,19} With increasing number of charge carriers (polyiodide ions), the ionic conductivity increases with the concentration of I₂. However, after reaching a maximum value, further increase of I₂ concentration reduce the conductivity. As mentioned above, I₂ exists in the form of polyiodide ions (I₃⁻, I₅⁻) by reaction with I⁻ in the polymer electrolyte. At high polyiodide ion concentrations, larger ionic aggregates are also formed. Most of these ionic aggregates are charged and these reduce ionic conductivity due to the stiffening of the matrix by the ionic aggregates acting as cross-linking node like the formation of physical cross linking between cation and oxygen

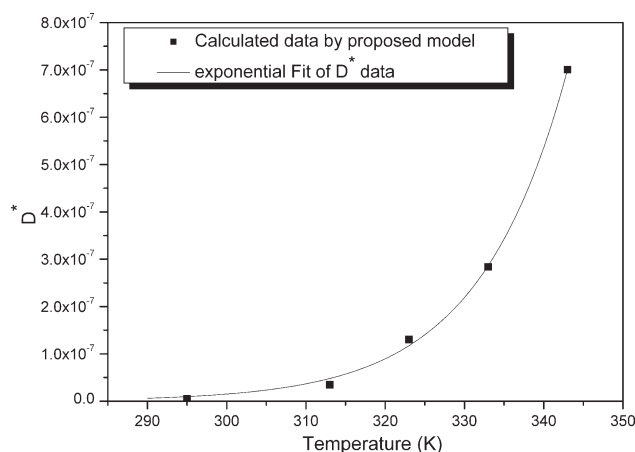


Figure 3 The calculated value of the self-diffusion coefficient (D^*) plotted against T . (PEO/LiI/I₂ system) $\ln D^* = 0.1089T - 49.893$.

in PEO repeating unit, which was observed in polymer-salt system. As a result, the availability of vacant coordinating groups to form transition states will be greatly restricted.¹⁸ This tendency is found in all temperature ranges, and the calculated values show that an increase in temperature favors conductivity at all mole ratios. It is widely accepted that the change in conductivity with temperature is due to the polymer segmental motion.²⁰

In Figures 3 and 4 representing the PEO/LiI/I₂ system, the model parameters increase with increasing temperature. It is believed that the self-diffusion coefficient follows an Arrhenius-like relation with temperature.^{21,22} This behavior is observed in Figure 3. The calculated values of the self-diffusion coefficient (D^*) increased exponentially with increasing temperature, but the interaction parameter (ϵ/k) used in the lattice model represents a segment-segment interaction independent of temperature. The calculated interaction parameters increased

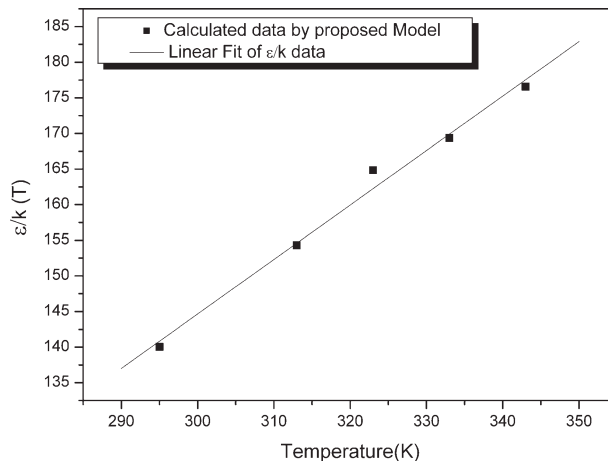


Figure 4 The calculated value of energy parameter (ϵ) plotted against T . (PEO/LiI/I₂ system) $\epsilon/k = 0.68335T - 53.989$.

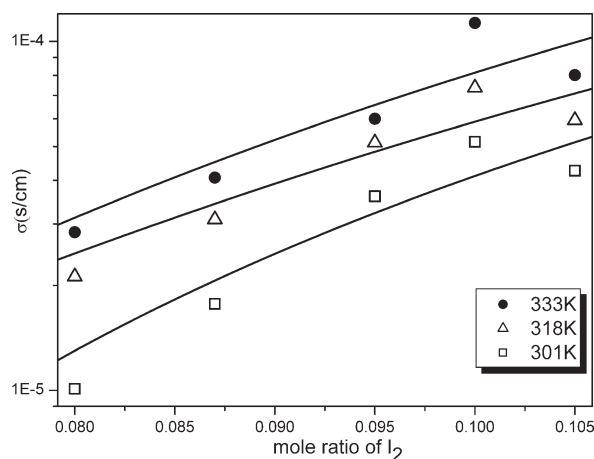


Figure 5 Ionic conductivity of PEO/KI/I₂ system. Mole ratio of PEO : KI was fixed [EO : KI = 10 : 1]. Experimental data are reported by Kalignan et al.¹⁸ Lines were calculated using the proposed model.

linearly with increasing temperature. However, in the experimental temperature range, no large difference was found. As can be seen in Figure 2, the proposed model agreed well with the ionic conductivity data.

Figure 5 shows the ionic conductivity of the PEO/KI/I₂ system for which experimental data are reported by Kalignan et al.¹⁸ Some deviation is also seen in Figure 5 between the proposed model and the experimental data because the data were gathered in a narrow range, and the amount of data at one temperature point was not sufficient for the model. Table II shows that the calculated model parameters also increased with increasing temperature.

CONCLUSION

We developed an ionic conductivity model for DSSCs based on the Nernst–Einstein equation, in which the diffusion coefficient was derived from the molecular thermodynamic model. We introduced the concentration-dependence of the diffusion coefficient

into the ionic conductivity model, and the diffusion coefficient was expressed by differentiating the chemical potential with concentration. The values calculated using the proposed model agreed with the experimental data.

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