고체전해질과 염의 혼합물에서의 이온전도도에 대한 압력의 영향

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The Pressure Effect on Conductivities of Solid Polymer Electrolyte/Salt Systems

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Introduction

Investigating the manufacturing process of lithium polymer battery, there is a pressure imposed on the SPE to improve the degree of contact between electrolyte and electrode. Physical properties of the compressed SPE systems would be totally different from those of the incompressed SPE systems. Therefore, it is desirable to develop a molecular thermodynamic framework in the prediction of ion conductivity for the compressed SPE systems . However, in previous thermodynamic approaches of the conductivity of SPE, it is hard to find a theoretical consideration that can predict the pressure effect in the conductivity.

In this study, we tried a new approach to understand the pressure dependence of the conductivity by combining the Adam-Gibbs configurational entropy model with the modified double lattice model.

Theory

1. Helmholtz energy of mixing

Oh *et al*. proposed a new Helmholtz energy of mixing as the form of Flory-Huggins theory.　The expression is given by

$$\frac{\Delta A}{N_r kT} = \left(\frac{\phi_1}{r_1}\right)\ln \phi_1 + \left(\frac{\phi_2}{r_2}\right)\ln \phi_2 + \chi_{OB}\phi_1\phi_2 \tag{1}$$

where N_r is the total number of lattice sites and k is the Boltzmann's constant. r_i is the number of segments per molecule *i*. χ_{OB} is a new interaction parameter defined by

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

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

$$\widetilde{\varepsilon} = \varepsilon/kT = (\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})/kT \tag{3}$$

where ε_{11}, ε_{22} and ε_{12} are for the corresponding nearest-neighbor segment-segment interactions

In Freed's theory, the solution of the Helmholtz energy of mixing for the Ising model is given by

$$\frac{\Delta A}{N_r kT} = x_1\ln x_1 + x_2\ln x_2 + \frac{z\widetilde{\varepsilon}x_1 x_2}{2} - \frac{z\widetilde{\varepsilon}^2 x_1^2 x_2^2}{4} + \cdots \tag{4}$$

where z is the coordination number and x_i is the mole fraction of the component *i*.

To obtain an analytical expression for the secondary lattice, we defined a new Helmholtz energy of mixing as the fractional form to improve the mathematical approximation defect by revising eqn. (4).　The expression is given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij}kT} = \frac{2}{z}\left[\eta\ln\eta + (1-\eta)\ln(1-\eta) + \frac{zC_\alpha\delta\widetilde{\varepsilon}_{ij}(1-\eta)\eta}{1 + C_\alpha\delta\widetilde{\varepsilon}_{ij}(1-\eta)\eta}\right] \tag{5}$$

where $\Delta A_{\text{sec},ij}$ is the Helmholtz energy of mixing of the secondary lattice for *i-j* segment-segment pair and N_{ij} is the number of *i-j* pairs, $\delta\widetilde{\varepsilon}$ is the reduced energy parameter contributed by the oriented interactions and η is the surface fraction permitting oriented interactions.

2.Equation of State

   We obtain an equation of state from the Helmholtz energy of mixing for the expanded polymer solution.   We defined a reduced temperature $\widetilde{T}$, a reduced pressure $\widetilde{P}$ and a reduced density $\widetilde{\rho}$;

$$\widetilde{T} = \widetilde{\varepsilon}_{II}^{-1} = kT \Big/ \varepsilon_{aa} \tag{6}$$

$$\widetilde{P} = P v^0 \Big/ \varepsilon_{aa} \tag{7}$$

$$\widetilde{\rho} = N_r v^0 \Big/ V \tag{8}$$

where v^0 is the hard-core volume of one site or one segment calculated by

$$v^0 = \sum_i \phi_i v_i^0 = \phi_1 v_1^0 + \phi_2 v_2^0 \tag{9}$$

The reduced density $\widetilde{\rho}$ is related to the volume fraction by

$$\widetilde{\rho} = N_r \Big/ N_l = \varphi_a \ , \ 1 - \widetilde{\rho} = \varphi_0 \tag{10}$$

And, we obtain the reduced Helmholtz energy of mixing for the compressible part.

$$\widetilde{A}_{r.II} = \frac{\Delta A_{II}}{N_r kT} = \widetilde{T}\left[\widetilde{\rho}^{-1}(1-\widetilde{\rho})\ln(1-\widetilde{\rho}) + \left(\frac{1}{r_a}\right)\ln\widetilde{\rho} + \chi_{OB}{}^0(1-\widetilde{\rho}) \right] \tag{11}$$

   Then, the reduced pressure becomes

$$\widetilde{P} = \widetilde{\rho}^2 \left(\frac{\partial A_{r.II}}{\partial\widetilde{\rho}}\right)_{\widetilde{T}.\phi} \tag{12}$$

$\widetilde{A}_{r.I}$ (eqn. (1)) for the first step is independent of density due to the closed-packing, therefore it makes no contribution to the pressure. Substitution of eqn. (11) into eqn. (12) gives an equation of state for polymer solutions.

$$\widetilde{P} = \widetilde{T}\left[-\ln(1-\widetilde{\rho}) - (1-\frac{1}{r_a})\widetilde{\rho} + \left\{ C_\beta\left(\frac{1}{r_a}-1\right)^2 + \left(2+\frac{1}{r_a}\right)\widetilde{\varepsilon}_{II} - \left(\frac{1}{r_a}-1+C_r\widetilde{\varepsilon}_{II}\right)\widetilde{\varepsilon}_{II}(1-2\widetilde{\rho})\right\}\widetilde{\rho}^2 \right.$$

$$\left. + C_r\widetilde{\varepsilon}_{II}{}^2(2-3\widetilde{\rho})\widetilde{\rho}^3 \right] \tag{13}$$

3. Ionic Conductivity

   Adam and Gibbs construct the partition function for fractions of the overall system that can or cannot undergo a configurational transition, and then evaluate the overall entropy in terms of the configurational entropy of oligomer subunit. For the probability of a mass-transporting cooperative rearrangement this yields:

$$\widetilde{W} = A\exp\left[\frac{-\Delta E_P s_c^*}{kTS_c^{Total}}\right] \tag{14}$$

where A is a constant, ΔE_P is the potential energy hindering the cooperative rearrangement per monomer unit, s_c^* is a critical configurational entropy, and S_c^{Total} is the total molar configurational entropy at temperature T.

   In this study, we introduce a confugurational entropy model as a function of isothermal composition. The primary exposition of theory is concerned with amorphous polymer/salt systems. To do so, we appeal to the modified double lattice model treatment of polymer solutions.

$$S = S_{comb} + S_{vac} \tag{15}$$

S_{comb} is a well-known combinatorial entropy of mixing and S_{vac} is an entropy of mixing holes in lattice with molecules given. There are

$$S_{comb} = -k\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right] \tag{16}$$

$$S_{vac} = -k\left[\frac{1-\widetilde{\rho}}{\widetilde{\rho}}\ln(1-\widetilde{\rho}) + \frac{\ln\widetilde{\rho}}{r}\right] \tag{17}$$

The mixing entropy does not take into account the difference between the salt cation and anion. In a solid polymer electrolyte system, we consider a drop of chain flexibility with an increase of salt concentrations (i.e., the configurational entropy loss). Hence, the entropy introduced to correct a drop of chain flexibility is

$$S_{flex} = kf(\phi_1)\ln\frac{z-1}{e} \tag{18}$$

$$f(\phi_1) = \lambda_s\phi_1 \tag{19}$$

where λ_s is a degree of specific interaction between the salt ion and the base group of polymer, which is inversely proportional to temperature. $\lambda_s\phi_1$ is associated with the length of coordinated chain. The entropy, $k\ln[(z-1)/e]$, arises from the fact that the segment location relative to that of the immediate predecessor is not predetermined in the lattice. The total configurational entropy S_c^{Tatal} of the amorphous polymer/salt system is obtained by combining eqns. (16), (17), and (18).

$$S_c^{Total}/k = -\frac{\phi_1}{r_1}\ln\phi_1 - \frac{\phi_2}{r_2}\ln\phi_2 - \frac{1-\widetilde{\rho}}{\widetilde{\rho}}\ln(1-\widetilde{\rho}) - \frac{\ln\widetilde{\rho}}{r} + \lambda_s\phi_1\ln\frac{z-1}{e} \tag{20}$$

By substituting eqn. (20) and $s_c^* = k\ln 2$ into eqn. (14), we obtain a configurational entropy model as a function of isothermal composition.

$$\widetilde{W} = \sigma(\phi) = A\exp\left[\frac{-B'}{S_c^{Total}/k}\right] \tag{21}$$

where B' is defined

$$B' = \frac{\Delta E_P\ln 2}{kT} \tag{22}$$

From eqns. (20)-(22), we can describe the dependence of conductivity on salt composition and the chain length and calculate qualitatively the change of ionic conductivity with various pressure for the given systems.

Result and Conclusion

Figs. 1 and 2 represent conductivity data with various pressure at *T*= 333 and 373K for the PEO/ZnI$_2$ system, respectively. Open circles are experimental data from Yang and Farrington. Solid, dashed and dotted lines are calculated by the proposed model with *P*= 0, 10,20 atm, respectively. As shown in *Figs. 1 and 2*, for *P*= 0 atm, the theoretical prediction (solid lines) gives a good agreement with experimental data. Dashed(P=10atm) and dotted(P=20atm) lines in *Figs. 1 and 2* definitely show that ionic conductivity decreases with pressure. Adjustable model parameters are listed in Table I. When the temperature was raised from 333 to 373K, values of *A, B'* and -λ_s decrease without losing physical meaning of each parameter.

In this study, we develop a thermodynamic model taking into account the pressure effect on the ionic conductivities of the compressed SPE systems. The proposed model based on the Adam-Gibbs configurational entropy model and modified double lattice model with free volume effect could describe the compression dependence of the conductivity for the polymer/salt systems and agree fairly well with experimental data.

Our results show that the ionic conductivity decreases with increasing pressure.

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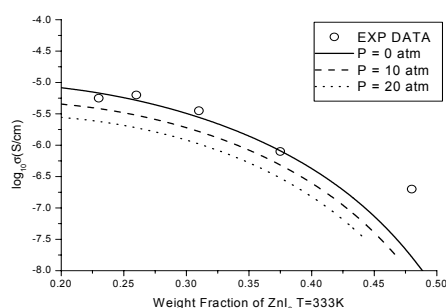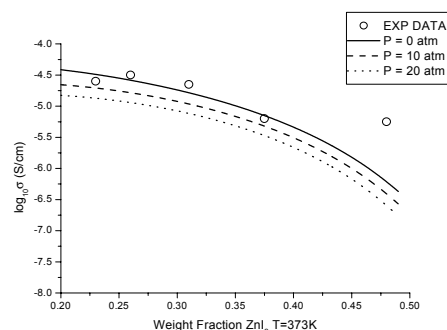
Figure and Table

Fig.1

Fig.2

Fig.1. The composition dependence of the conductivity at various pressures for the PEO/ZnI$_2$ system. The conductivity was obtained using an a.c. impedance analysis (○) at T = 333K. The solid, dashed and dotted lines are calculated by the proposed model with P = 0, 10, 20 atm, respectively

Fig.2. The composition dependence of the conductivity at various pressures for the PEO/ZnI$_2$ system. The conductivity was obtained using an a.c. impedance analysis (○) at T = 373K. The solid, dashed and dotted lines are calculated by the proposed model with P = 0, 10, 20 atm, respectively.

Table I. Adjustable model parameters of given systems for the configurational entropy model

Polymer (MW_2)	Salt	T(K)	A	$B^{'}$	λ_s	ε_{11}/k (K)	ε_{12}/k (K)	$\delta\varepsilon_{12}/k$ (K)
PEO (5000)	ZnI$_2$	333	0.00091	3.005	-0.695	445.66	186.81	301.18
PEO (5000)	ZnI$_2$	373	0.00082	2.319	-0.651	445.66	186.81	301.18