A Model for the AC Ionic Conductivity in Solid Polymer Electrolytes

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A hydrodynamic model for solid polymer electrolyte which consists of negatively charged solid polymer chains immersed in a cation liquid is presented. From the model, an analytical expression for the AC ionic conductivity is obtained. The model permits us to understand how the relaxation time and the mass of the polymer chain affect the behavior of the ionic conductivity in the infrared region.

§1.   Introduction

Ion conducting polymers are receiving much interest due to their technological applications in a wide variety of devices such as batteries, fuel cells, supercapacitors, sensors, etc.[1,2] Many works have been done to enhance the ionic conductivity and the mechanical stability of solid polymer electrolytes.[3-5] Polymer electrolytes have been also the subject of many fundamental studies.[6-17] However, our understanding on the fundamental physical properties of polymer electrolytes is not sufficient.

Basically, a polymer electrolyte consists of a polymer matrix doped with a salt. Numerous experimental studies indicate that the physical properties of polymer electrolytes are controlled by both, the host polymer and the dopant salts. This material characteristic leads us to consider the solid polymer electrolytes as a system consisting of a solid polymer chain charged negatively which is immersed in a cation liquid. Such kind of model has been proposed previously and used to describe typical superionic conductors such as silver halides and silver chalcogenides.[18-21] However, no application to polymers has been done. The purpose of the present study is to show that such model could be a good model to study the physical properties of polymer electrolytes. In the present report, as a first step, the ac conductivity is considered.

§2.   The viscoelastic model for solid polymer electrolytes

As mentioned above, solid polymer electrolytes can be viewed as a system formed by a polymer matrix and doped salts. In our model, the matrix is considered to consist of solid polymer chains. The salt doped in the polymer is dissociated, and in our model, the negative ions are trapped to the polymeric chains. On the other hand, the positive ions are able to move through the interstices of the polymer. Thus, solid polymer electrolytes could be considered as a system that consists of solid polymeric chains charged negatively which is immersed in a cation liquid. A schematic representation of the model for polymer electrolytes used in our study is shown in Fig. 1.
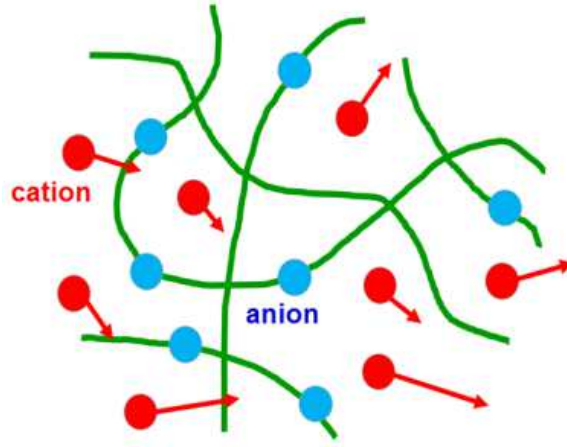
Fig. 1.   A schematic representation of the model for solid polymer electrolytes. The anions are trapped to
the solid polymeric chains, whereas the cations can move through the interstices of the chain.

In order to describe the model of polymer electrolytes mentioned above, we use the equation of motion for deformable solid bodies for the polymeric matrix, and the Navier-Stokes equation for the cation liquid. The equation of motion of the polymeric matrix which is charged negatively is written as

$$\frac{\partial^2}{\partial t^2}\xi(\boldsymbol{r},t)-\left(V_1^2+\Gamma_1\frac{\partial}{\partial t}\right)\nabla\nabla\cdot\xi(\boldsymbol{r},t)-\left(V_t^2+\Gamma_t\frac{\partial}{\partial t}\right)\left\{\nabla^2\xi(\boldsymbol{r},t)-\nabla\nabla\cdot\xi(\boldsymbol{r},t)\right\}$$

$$+\frac{1}{m_1}\int_{-\infty}^{t}dt'M(t-t')\left\{\frac{\partial}{\partial t'}\xi(\boldsymbol{r},t')-\boldsymbol{v}(\boldsymbol{r},t')\right\}+\frac{e}{m_1}\boldsymbol{E}(\boldsymbol{r},t)=0\,,\qquad(2.1)$$

where

$$M(t)=m^*\omega_t^2\exp(-t/\tau_c)\,,$$

and

$$\frac{1}{m^*}=\frac{1}{m_1}+\frac{1}{m^2}\,.$$

Here $\xi(\boldsymbol{r},t)$ is the displacement field of the deformable body at point $\boldsymbol{r}$ and time t. V_1 and V_t are the longitudinal and transverse sound velocities, Γ_1 and Γ_t are the longitudinal and transverse damping coefficients, respectively, $\boldsymbol{v}$ is the velocity field of the cation liquid, e is the elementary charge and $\boldsymbol{E}(\boldsymbol{r},t)$ is the electric field. Here, $\boldsymbol{E}$ represents the total electric field acting at $(\boldsymbol{r},t)$, that is, $\boldsymbol{E}$ incorporates the applied external field and the field created by the ions present in the system. $M(t)$ is the memory function, where ω_t is the frequency of the oscillator formed by cation and anion pairs,

τ_c is the viscoelastic relaxation time. m^* is the reduced mass, where m_1 and m_2 are the masses of the polymer chain and the cation, respectively.

The cation liquid is regarded as a viscous fluid. Therefore, it is described by the Navier-Stokes equation.

$$\frac{\partial}{\partial t}\boldsymbol{v}(\boldsymbol{r},t) + c_0^2 \nabla n(\boldsymbol{r},t) - \eta \nabla^2 \boldsymbol{v}(\boldsymbol{r},t) - \left(\zeta + \frac{\eta}{3}\right)\nabla\nabla\cdot\boldsymbol{v}(\boldsymbol{r},t)$$

$$+ \frac{1}{m_2}\int_{-\infty}^{t} dt' M(t-t')\left\{\boldsymbol{v}(\boldsymbol{r},t') - \frac{\partial}{\partial t'}\boldsymbol{v}(\boldsymbol{r},t')\right\} - \frac{e}{m_2}\boldsymbol{E}(\boldsymbol{r},t) = 0, \tag{2.2}$$

where

$$n(\boldsymbol{r},t) = [N(\boldsymbol{r},t) - N_0]/N_0.$$

Here c_0 is the sound velocity in the liquid, η and ζ are the kinematic shear and bulk viscosities, and $n(\boldsymbol{r},t)$ is the number density fluctuation. The number density and the velocity field of the liquid are linked through the continuity equation

$$\frac{\partial}{\partial t}n(\boldsymbol{r},t) + \nabla\cdot\boldsymbol{v}(\boldsymbol{r},t) = 0. \tag{2.3}$$

The electric field $\boldsymbol{E}(\boldsymbol{r},t)$ appearing in Eqs. (2.1) and (2.2) obeys the Maxwell equation

$$\nabla^2\boldsymbol{E}(\boldsymbol{r},t) - \nabla\nabla\cdot\boldsymbol{E}(\boldsymbol{r},t) = \frac{\varepsilon_\infty}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{E}(\boldsymbol{r},t) + \frac{4\pi}{c^2}\frac{\partial}{\partial t}\boldsymbol{j}(\boldsymbol{r},t), \tag{2.4}$$

where ε_∞ is the high-frequency dielectric constant and c is the velocity of light. The current density in written in terms of the velocity fields of polymer matrix and cation liquid as

$$\boldsymbol{j}(\boldsymbol{r},t) = N_0 e\left[-\frac{\partial}{\partial t}\xi(\boldsymbol{r},t) + \boldsymbol{v}(\boldsymbol{r},t)\right]. \tag{2.5}$$

Thus, to obtain an expression for the current density, we need the expressions for $\xi(\boldsymbol{r},t)$ and $\boldsymbol{v}(\boldsymbol{r},t)$. These are obtained by solving simultaneously the Eqs. (2.1) to (2.5). Following the previous works,[18] - [20] this has been done by Fourier transforming the above equations. After lengthy calculation, we obtain the following expressions for the current density and conductivity

$$\boldsymbol{j}(\boldsymbol{k},\omega) = \sigma(\boldsymbol{k},\omega)\boldsymbol{E}(\boldsymbol{k},\omega), \tag{2.6}$$

$$\sigma(\mathbf{k},\omega) = \frac{\varepsilon_\infty \omega}{4\pi} \mathrm{Im}\left[\frac{G(\mathbf{k},\omega)}{F(\mathbf{k},\omega)}\right], \tag{2.7}$$

where $\mathbf{k}$ and ω are the wave number and the frequency introduced in the Fourier transformation. $G(\mathbf{k},\omega)$ and $F(\mathbf{k},\omega)$ are lengthy polynomial functions of $\mathbf{k}$ and ω. The explicit expressions for $G(\mathbf{k},\omega)$ and $F(\mathbf{k},\omega)$ are given in[20] and are not repeated here.

§3.   AC conductivity

The formulation presented above provides a mean to describe different physical quantities. In the past, it has been applied to study ionic conductivity,[18,21,22] diffusion,[20,22,23] sound velocity,[20,22,24] relaxations[20] and collective excitations[18-20,25] in typical inorganic superionic conductors such as Ag halides and chalcogenides[18,19,21,22] and systems having layered structures.[20] Modified version of the model has been applied to study liquid systems.[22-25] The present study is the first application to polymers. As a first step, we studied the behavior of AC conductivity.

Fig. 2 and Fig. 3 show the characteristics of the AC ionic conductivity which is described by our model. For the numerical evaluation, the following typical vales of the parameters were used.[18,20] $\varepsilon_\infty = 5$, $N_0 = 1.6 \times 10^{22}$ cm^{-3}, $m_2 = 1.79 \times 10^{-22}$ g, $\omega_t = 105$ cm^{-1}, $V_l k = 0.8$ cm^{-1}, $V_t k = 0.27$ cm^{-1}, $c_0 k = 0.2$ cm^{-1}, $\Gamma_{l,t} k^2 = 0.1 V_{l,t} k$, $\eta k^2 = 0.01$ cm^{-1}, $(\zeta + 4\pi/3)k^2 = 0.05$ cm^{-1}, where $k = 10^5$ cm^{-1}. The results obtained show how the relaxation time τ_c and the mass of the polymer chain m_1 affect the ionic conductivity. These two quantities are expected to play important roles in the dynamic processes of polymers.
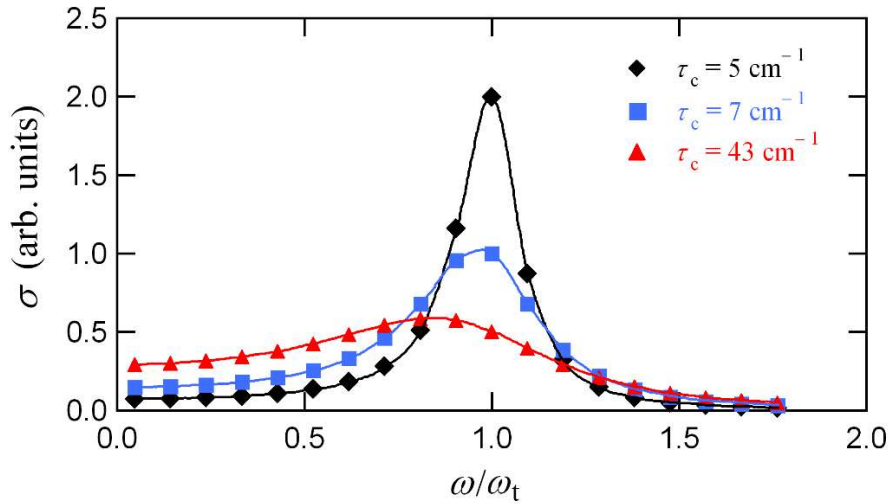

Fig. 2.   Relaxation time dependence of the ionic conductivity in polymer electrolytes. The magnitude of the vertical axis has been normalized by an arbitrary reference value, the peak value for the case of $\tau_c = 7$ cm^{-1}.
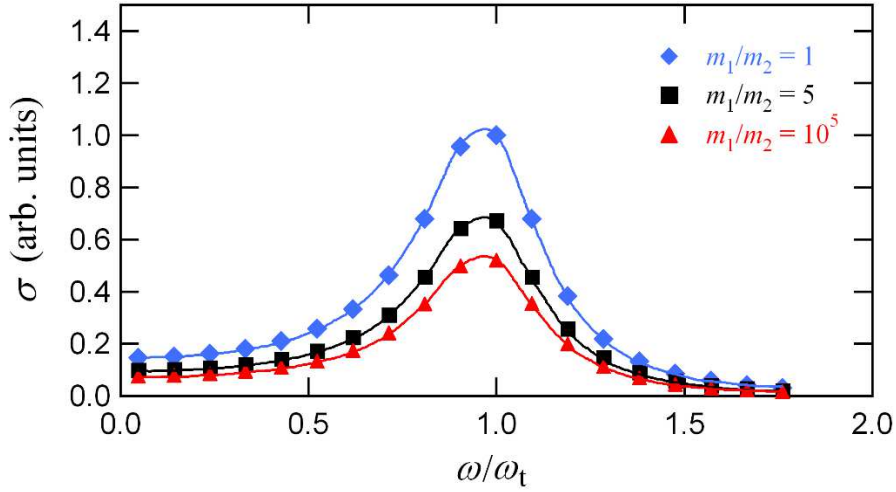
Fig. 3. Mass ratio dependence of the ionic conductivity in polymer electrolytes. Here, m_1 is the mass of polymer chain and m_2 is the mass of mobile ion. The normalization factor for the vertical axis is the same to that of Fig. 1.

Fig. 2 shows how the conductivity varies with the viscoelastic relation time τ_c. We see that the conductivity exhibit a peaked behavior around the oscillation frequency ω_t. Furthermore, the peak position of the conductivity shifts to lower values and its intensity diminishes with the decrease of the viscoelastic relaxation time. Such kind of behavior is expected to occur in the relaxation of displacive-type polarization. There are many studies regarding the DC conductivity in polymer electrolytes. Regarding AC conductivity, data up to 10MHz range are abundant.[13), 15), 16)] However, for frequencies above 10 KHz, the number of studies is quite limited.[11)] Therefore, we were not able to find an experimental data to verify our model. The behavior of the conductivity shown in Fig. 2 is expected to resemble the temperature dependence of the conductivity in the infrared region in polymer electrolytes. Triangle and diamond symbols correspond to high and low temperatures, respectively.

Fig. 3 shows the effect of polymer chain mass on the ionic conductivity around the oscillation frequency ω_t. We observe that the conductivity decreases with the increase of the mass ratio between polymer chain and mobile ion. Many researchers have discussed the role of segmental motion in the ion transport mechanism.[15) - 17)] The result shown in Fig. 3 is probably related with such motion. However, it should be noted that the frequency region we are focusing here is different from the frequency region where the segmental motion is expected to occur. A molecular dynamics study in polymer electrolytes has shown that the ionic conductivity decreases with the number of monomers in the chain[26)]. Although detailed analysis is required, the result shown in Fig. 3 seems consistent with that result.

The values of the parameters used in the evaluation of Fig. 2 and 3 are those for typical inorganic ionic conductors such as AgI. We used such values, because some numerical values were not available for polymers. Thus, refinements of numerical

values appropriate for polymer electrolytes are necessary for a detailed study. However, we believe that the qualitative results will remain the same. The next step is to extend our analysis to lower frequency regions, where experimental data are available. A further study is in progress.

§4. Conclusion

A model for solid polymer electrolytes has been presented by assuming that the system consists of polymeric chains charged negatively and cation liquid. An analytical expression for the ionic conductivity was derived by using hydrodynamic equations coupled with Maxwell equation. Based on the obtained expression, the expected behavior of the ionic conductivity in the infrared region was discussed. In particular, the role of the relaxation time which resembles the temperature dependence and the mass dependence of the polymer chain in the ionic conductivity were shown. Our first step analysis indicates that the model could be a good model to understand the behavior of solid polymer electrolytes.

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