A General Formula for Ion Concentration-Dependent Electrical Conductivities in Polymer Electrolytes

1Mahardika Prasetya Aji, 1Masturi, 2Satria Bijaksana, 1Khairurrijal and 1Mikrajuddin Abdullah
1Department of Physics, Faculty of Mathematics and Natural Science, 2Department of Global Geophysics, Faculty of Mining and Petroleum Engineering, Bandung Institute of Technology Jalan Ganeca 10, Bandung 40132, Indonesia

Abstract: Problem statement: The aim of this study is to develop a model for describing the effect of ion concentration on the electrical conductivity of polymer electrolytes by considering two mechanisms simultaneously: Enhancements of ion concentration and amorphous phase. Approach: The problems based on new observations in polymer electrolyte when ion concentration in the polymer electrolytes was increased, both the fraction of amorphous phase and the charge carriers increase simultaneously. The model was based on the assumption when ions were inserted into the polymer host, there was an optimum distance between ions at which the ions move easily throughout the polymer. The average distance between ions in the polymer depends on the ion concentration. And we also considered the effect of ion concentration on the amorphous phase in the polymer. Results: We inspected the validity of the model by comparing the model predictions with various experimental data. The new analytical expressions for the electrical conductivity dependent of ion concentration was developed by considering two mechanisms simultaneously in polymer electrolytes, i.e., enhancement of the carries concentration and amorphous phase fraction. Interestingly, most of fitting parameters were not arbitrarily selected, but were derived from the appropriate experimental data. Conclusion: The model can be used to explain the conductivity behavior of other polymer electrolyte systems by selecting appropriately less number of parameters. This model result is fully supported by available experimental data.

Key words: Electrical conductivity, polymer electrolyte, ion concentration effect, experimental data, amorphous phase, increase simultaneously

INTRODUCTION

The dependence of electrical conductivity of polymer electrolytes on ion concentration has been well known. The conductivity initially increases with ion concentration, reaches the maximum at a certain concentration after which it turns down at high ion concentrations (Khiar and Arof, 2011; Gong et al., 2008; Kang and Fang, 2004; Rajendran et al., 2003; Kang et al., 2003; Xu et al., 2001).

Many explanations have been exposed to explain these observations. At low concentrations the conductivity increases due to increasing in the charge carriers, while at high concentrations, repulsion between ions at short distances inhibits the transport of ions to weaken the conductivity.

New observations on this topic are interesting to be discussed (Aji et al., 2012; Bhargav et al., 2010; 2007a; 2007b; Mohamad et al., 2003). When ion concentration in the polymer electrolytes is increased, both the fraction of amorphous phase and the charge carriers increase simultaneously.

Fig. 1: Increasing the ion concentration will increase the carrier concentration and the fraction of amorphous phase

Corresponding Author: Mikrajuddin Abdullah, Department of Physics, Faculty of Mathematics and Natural Science, Bandung Institute of Technology Jalan Ganeca 10, Bandung 40132 Indonesia

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The ion concentration does not affect only the charge carriers, but also the structure of the polymer host from crystalline to amorphous. Therefore, a theory for explaining the electrical conductivity development due to insertion of ions must consider the occurrence of these two mechanisms.

The aim of this study is to develop a model for describing the effect of ion concentration on the electrical conductivity of polymer electrolytes by considering two mechanisms simultaneously: Enhancements of ion conductivity of polymer electrolytes by considering two carriers, but also the structure of the polymer host from crystalline to amorphous. Therefore, a theory for explaining the electrical conductivity development due to insertion of ions must consider the occurrence of these two mechanisms.

The materials and methods

The model was based on the assumption when ions are inserted into the polymer host, there is an optimum distance between ions at which the ions move easily throughout the polymer. This distance corresponds to the lowest energy for ion hopping. If ion distances are shorter, repulsion between ions might cause a reduction in the electrical conductivity. On the other hand, when the ion distances are too far, a long distance hopping is required to generate the conductivity, which implies the reduction in the conductivity too. If the distance between ions at a specific concentration is \( \ell \), the interaction energy experiences by an ion can be expressed in the Taylor series as Eq. 1:

\[
\Delta E(l) = \Delta E(l_0) + \frac{d\Delta E}{dl} (l - l_0)_0 + \frac{1}{2} \frac{d^2\Delta E}{dl^2} (l - l_0)^2_0 + ...
\]

with \( l_0 \) is the optimum distance as mentioned above. Since at \( l_0 \), \( d\Delta E/dl|_{l_0} = 0 \), we obtain the deviation of energy from the energy when the ions are separated by \( l_0 \) as Eq. 2:

\[
\Delta E(l) = \Delta E(l_0)\left(1 - \left(1 - \frac{l}{l_0}\right)^3\right) + \frac{1}{6} \frac{d^2\Delta E}{d\ell^2} \left(1 - \frac{l}{l_0}\right)^3 + ... \tag{2}
\]

Actually, the distances between ions in the polymer host are not equal. The ion positions distribute randomly, ranging from the shortest to the longer ones. Therefore, it is more accurate if we introduce a probability function to explain the distance distribution. Since the distances are always positive, the proper distribution function for explaining this distance is the log normal distribution. This selection can be compared to selection of the log normal distribution for explaining size distribution of particles (Chen et al., 2009; Haefraoui et al., 2008; Berret et al., 2007; Feng and Bertelo, 2004; Teraoka, 2002). The particle sizes are never negative so that the log normal distribution is the best function to explain it.

Suppose the distribution density of ion distances separated by \( \ell \) is \( f(\ell) \). The fraction on ions that are separated by distances between \( \ell \) and \( \ell + d\ell \) are Eq. 3 (Mikrajuddin et al., 2001):

\[
f(\ell) d\ell = \frac{1}{\sqrt{2\pi\delta^2}} e^{-\frac{(\ln(\ell/l_0))_0^2}{2\delta^2}} d\ell \tag{3}
\]

With \( l_0 \) is the average distance between ions and \( \delta \) is the geometrical standard deviation. The average deviation of energy for ion hopping is Eq. 4:

\[
\Delta E(l_0) = \int_{0}^{\ell} \Delta E(\ell) f(\ell) d\ell = \frac{1}{2} \frac{d\Delta E}{d\ell}\bigg|_{l_0} \]

\[
\int_{0}^{\ell} (\ell - l_0)^2 f(\ell) d\ell + \frac{1}{6} \frac{d^2\Delta E}{d\ell^2}\bigg|_{l_0} \int_{0}^{\ell} (\ell - l_0)^3 f(\ell) d\ell + ...
\]

If \( \Delta S \) is the change in entropy relative to the entropy when all ions are separated by \( l_0 \), the expression for the free energy change is \( \Delta F(l_0) = \Delta E(l_0) - \Delta S \). The probability of ion hopping caused by ion concentration will be proportional to Eq. 5:

\[
P_{\text{hop}} = \exp\left(-\frac{\Delta F(l_0)}{kT}\right) \propto e^{-\Delta E(l_0) / kT} \tag{5}
\]

We also considered the effect of ion concentration on the amorphous phase in the polymer. We assumed the amorphous phase is composed of a large number of “islands” (Fig. 2) with an average size L. In the amorphous phase, the ions are very mobile. We assumed the ions diffuse in one-dimensional “cages” bounded by \(-L/2, +L/2\) and are absorbed when reaching the cage wall. The cage corresponds to the amorphous island and the wall corresponds to the boundary between amorphous and crystalline phases. We determined the survival probability of the ions in the amorphous phase and assumed this probability controls the ionic conductivity.
Fig. 2: The amorphous phase was assumed to be composed of amorphous islands of average size $L$.

The survival probability of ions in the amorphous phase satisfies Eq. 6 (Krapivsky and Redner, 1996):

$$S(t) = \int_{-L/2}^{+L/2} C(x,t) \, dx$$

where, $C(x,t)$ is the ionic concentration at position $x$ and at time $t$. The ion concentration evolves according to the diffusion Eq. 7:

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2}$$

With $D$ is the diffusion coefficient. Since the ions are absorbed by the cage wall, the ion concentration satisfies the boundary condition of $C(\pm L/2, t) = 0$.

The survival probability of an ion may be obtained by integration of ion concentration over the region. For simplicity, we assumed the initial concentration was homogeneously distributed or $C(x, 0) = \gamma L$, with $\gamma$ is a constant. Using both the boundary and the initial condition we obtained the following solution for the ion concentration Eq. 8 (Krapivsky and Redner, 1996):

$$C(x,t) = \sum_{n=0}^{\infty} A_n \sin \left( \frac{n\pi x}{L} \right) e^{-\frac{Dn^2\pi^2t}{L^2}}$$

With $A_n = \frac{2}{L} \int_0^L \gamma \sin \left( \frac{n\pi x}{L} \right) dx$. Assuming that the first term in Eq. 8 is very dominant, we can approximate Eq. 9:

$$C(x,t) \approx \frac{4\gamma}{\pi L} \sin \left( \frac{\pi x}{L} \right) e^{-\frac{D\pi^2t}{L^2}}$$

Indeed, the ratio of the first to the second terms is proportional to $\exp(3D\pi^2t/L^2)$. The survival probability is then Eq. 10:

$$S(t) = \frac{4\gamma}{\pi L} e^{-\frac{D\pi^2t}{L^2}} \int_{-L/2}^{+L/2} \sin \left( \frac{\pi x}{L} \right) dx$$

And the time average of the survival probability can be written as Eq. 11:

$$\langle S(t) \rangle \approx e - D\pi^2 \tau_c / L^2$$

where, $\tau_c$ is referred to the characteristic time and might be related to the relaxation time of polymer segmental motion in the amorphous phase. The motion of ions in the amorphous phase is assisted by this segmental motion (Vogel, 1921; Li et al., 2008; Fonseca et al., 2007; Xu et al., 2001; Noda and Watanabe, 2000).

We assumed the second term in Eq. 4 is much smaller than the first term. Since we don’t have data of the distance distribution of ions, at present we assumed the ions are separated equally so that we can replace the distribution function as a Dirac delta function, $\delta(\ell - \ell_0)$ and finally found that Eq. 12:

$$P_{\text{hop}} \propto e^{-\frac{1}{2}dE/d\ell^2} \left[ \frac{\ell_0 - \ell}{\ell_0} \right]^{1/2}$$

The average distance between ions in the polymer depends on the ion concentration. If $C$ is the ion concentration (number per unit of volume) we may write $\ell_0 = 1/C^{1/3}$ and the probability of ion hopping becomes Eq. 13 and 14:

$$P_{\text{hop}} \propto e^{-\alpha} \exp \left[ -\alpha \left( \frac{1}{C^{1/3} - 1/C_0^{1/3}} \right) \right]$$

With:

$$\alpha = \frac{1}{2kT} \int_0^{dE/d\ell}$$

We speculated that the size of amorphous islands is proportional to the fraction of amorphous phase. This assumption is valid when the number of amorphous islands remains constant as the ion concentration is varied. Taking this assumption as a very rough approximation, we obtain a relation $L^2 = \xi ^2 v_a ^{2/3}$, where $v_a$ is the fraction of amorphous phase and $\xi$ is a constant. Since $v_a$ is in the order of unity, the value of $\xi$ approaches $L$. The average survival probability becomes Eq. 15 and 16:

$$\langle S(t) \rangle \approx \exp \left\{ -\beta v_a ^{2/3} \right\}$$

With:

$$\beta = \frac{D\pi^2 \tau_c}{\xi^3}$$
Since the electrical conductivity depends simultaneously on ion concentration and amorphous phase fraction, a general expression for the electrical conductivity satisfies Eq. 17:

$$\sigma = \sigma_0 e^{-2\beta_0^3 - \alpha \left[ \left( \frac{C}{C_0} \right)^{\frac{2}{3}} - \frac{1}{C_0} \right]^2}$$  \hspace{1cm} (17)$$

With $\sigma_0$ as a constant for a specific polymer electrolyte.

We inspected the validity of the above model by comparing the model predictions with various experimental data. At present we compared the model with the conductivity data of PVA, PEO and PEMA based polymer electrolytes containing different ions such as PVA.NaF (Bhargav et al., 2009), PVA.LiOH (Aji et al., 2012), PVA.AgNO$_3$ (Hirankumar et al., 2006) and PEO.LiCF$_3$SO$_3$ with plasticizer ENR50 (Noor et al., 2010) and PEMA.LiClO$_4$ (Amir et al., 2011). Initially we must estimate the values of $\alpha$ and $\beta$ parameters. Based on Eq. 14, the $\alpha$ parameter originated from the second derivative of the interaction energy of ion. We assumed the interaction energy satisfies the Lennard-Jones potential Eq. 18 and 19:

$$E(\ell) = -\epsilon \left[ 2 \left( \frac{\ell_0}{\ell} \right)^{\frac{12}{6}} - \left( \frac{\ell_0}{\ell} \right)^{\frac{6}{6}} \right]$$  \hspace{1cm} (18)$$

So that:

$$\alpha = 36 \frac{\epsilon'}{kT\ell_0^3}$$  \hspace{1cm} (19)$$

with $\epsilon'$ is energy when the ions are separated by $\ell_0$. This energy is not equal to the lowest energy in the pair of atoms making a direct bonding. We derived $\epsilon'$ based on data of the lowest energy in the atomic bonding. Since at large distances the dominant part in the Lennard-Jones potential is the power six of the distance, we speculated the lowest energy in case of ion potential in the polymer electrolytes satisfies Eq. 20:

$$\epsilon' = \frac{\epsilon}{k} \left( \frac{\sigma}{\ell_0} \right)^{\frac{6}{3}}$$  \hspace{1cm} (20)$$

with $\sigma$ is the distance of atoms making direct bonding and $\epsilon$ is the lowest energy of the corresponding direct bonding.

If N is the number of ions and V is the volume of composite we have $C = N/V$. Let us estimate the $\alpha$ parameter for PVA containing Na ions. In this case, $N = m_{Na} \times N_A/MR_{Na}$, with $MR_{Na}$ is the atomic mass of Na and $N_A$ is the Avogadro number. Furthermore, $V = m_{PVA}/\rho_{PVA}$ with $\rho_{PVA}$ is the mass density of PVA. Therefore Eq. 21 adn 22:

$$C = \left( \frac{m_{Na}}{m_{PVA}} \right) \frac{\rho_{PVA} - N_A}{MR_{Na}} \approx \frac{C(\text{wt\%})}{100} \frac{\rho_{PVA} - N_A}{MR_{Na}}$$  \hspace{1cm} (21)$$

And:

$$\ell = \frac{1}{C^{\frac{1}{3}}} \approx \frac{100MR_{Na}}{\rho_{PVA} N_A} \left( \frac{1}{C(\text{wt\%})^{\frac{1}{3}}} \right)$$  \hspace{1cm} (22)$$

The peak of conductivity occurs at a weight fraction of ions at around 20%. The atomic mass of Na is 23 and the density of PVA is around 1.26 g cm$^{-3}$. Therefore, the estimated value for $\ell_0 = 5.3 \times 10^{-8}$ cm. Assume the corresponding values for others ions are not so far from this value so that we can use $\ell_0 = 5.3 \times 10^{-8}$ cm to estimate the $\alpha$ parameter for other ions.

Several data on the interaction of atoms via Lennard-Jones potential have been available. For example, parameters of potential for interaction of metal ions with oxygen atoms are $\epsilon/k = 1575.3$ K and $\sigma = 0.34276$ nm for Na$^+$ ion and $\epsilon/k = 2315.6$K and $\sigma = 0.28517$ nm for Li$^+$ ion (Zhen and Davies, 1983; Lee and Rasaiah, 1996). Using these data into Eq. (20) we obtained $\epsilon'/k = 115.5$ K for Na ions and $\epsilon'/k = 56.2$ K for Li ions.

The exponential factor controlling the ion concentration is:

$$\alpha \left( \frac{1}{C^{\frac{1}{3}}} - \frac{1}{C_0^{\frac{1}{3}}} \right) = 36 \frac{\epsilon'}{kT\ell_0^3} \left( \frac{1}{C^{\frac{1}{3}}} - \frac{1}{C_0^{\frac{1}{3}}} \right) = 36 \frac{\epsilon'}{kT} \left( \frac{C^{\frac{1}{3}}}{C_0^{\frac{1}{3}}} - 1 \right)$$

If we use the unit of wt\% for concentration, we obtain an approximated estimation for $\alpha$ parameter as Eq. 23:

$$\alpha = \frac{36 \epsilon' C_0^{\frac{2}{3}} (\text{wt\%})}{kT}$$  \hspace{1cm} (23)$$

Using $\epsilon'/k = 115.5$ K for Na and $\epsilon'/k = 56.2$ K for Li, T = 300 K and $C_0 = 20$ wt\% we obtain $\alpha = 102$ for Na and $\alpha = 50$ for Li. Throughout the simulations we selected the parameter $\alpha$ within this range.
The amorphous phase size can be estimated as following. From the SEM images, the darker tone color can be related to amorphous phase as suggested by Zygadło-Monikowska et al. (2007). SEM images of grafted natural rubber containing LiF as reported by Ahmad et al. (2011a) showed darker tones in order of submicrometer sizes (Ahmad et al., 2011b). Roiter and Minko (2005) reported the appearances of real linear polymer chains in liquid state on a surface as recorded using an atomic force microscope have contour length of about 204 nm (Roiter and Minko, 2005). This size might be related to the size of "bulk amorphous island" of the polymer. Using a high resolution solid state $^{13}$C NMR, Zhang et al. (1992) measured the amorphous phase size in polymer can ranged from 2-30nm (Zhang et al., 1992). From these reports, it is acceptable to assume $\xi$ values range from 0.01-0.1 $\mu$m. The diffusions coefficient of ions in polymer is around $10^{-7}$ cm$^2$s$^{-1}$ (Klimuk and Kuczajowska-Zadroza, 2002; Stolwijk and Obeidi, 2004; Obeidi et al., 2004; 2005; Bracht et al., 1991). Hirankumar et al. (2006) reported that the relaxation time in polymer is around $10^{-5}$ s (Hirankumar et al., 2006). From these data, we obtained the estimated values of $\beta$ range from 0.1-10. In the following simulation we used the values of $\beta$ parameter of around unity and the value of $\alpha$ parameter of around 100.

**RESULTS**

Figure 3 shows the comparison of experimental data of conductivities of polymer electrolytes (Bhargav et al., 2009; Aji et al., 2012; Hirankumar et al., 2006; Mohamad et al., 2003; Noor et al., 2010; Amir et al., 2011) and the fitting results. The fitting parameters for each data are listed in the figure. In the fitting results, the values of the volume fractions of amorphous phase were selected so that the model prediction fit the data properly. The selected volume fractions are also displayed in the figure. It is clear from Fig. 3a-d the fitting curves accurately fit the experimental data for all polymer electrolytes.
Fig. 3: Comparison of the experimental data (symbols) and the model predictions for polymer electrolytes of (a) PVA.NaF, (b) PVA.LiOH, (c) PVA.AgNO₃, (d) PEO.LiCF₃SO₃ with ENR50 plasticizer and (e) PEMA.LiClO₄.

The corresponding curves of dependence of amorphous phase on the ion concentration are also displayed.

**DISCUSSION**

The selected prefactors conductivity $\sigma_0$ for all polymer electrolytes were very close to the values measured by many authors (Khiar and Arof, 2011; Gong et al., 2008; Kang and Fang, 2004; Rajendran et al., 2003; Kang et al., 2003; Xu et al., 2001). We also see that the fraction of amorphous state increases with the ion concentration and mostly saturates at high ion concentration. These results are also consistent with the observation of the XRD patterns of samples containing different ion concentrations. Figure 4 shows the XRD patterns of PVA.LiOH at different LiOH concentrations. The XRD patterns confirmed the dependence of the amorphous content on the ion concentration (Aji et al., 2012). Reduced XRD intensity is indicative of reduced crystallinity in the samples. Similar observation has also been reported by other authors in other polymer electrolyte systems (Ahmad et al., 2011a; Fonseca et al., 2007). Ahmad et al. (2011b) reported that in grafted natural rubber and poly (methyl methacrylate), containing lithium tetrafluoroborate. The degrees of crystallinity in systems of PCL-biodegradable gel polymer electrolyte with LiClO₄, LiF₃CSO₃ and LiBF₄ salts decreased nearly linear with increasing the salt concentration (Ahmad et al., 2011a).

The increase in the amorphous content resulted from inhibition of recrystallization of the host polymer after the ions were dispersed. Ions located near the polymer chains possess weak net electric charges that could disturb the tendency of the chain to recrystallize after heat treatment. Heat treatments are commonly performed after addition of salts to polymer electrolytes and consist of heating the polymer to near the melting or glass transition temperature and slow cooling to room temperature. This step increases the amorphous phase content at room temperature, which is the working temperature of most devices.

From the above results we selected a set of conductivity parameters capable of predicting many observed data reported by authors. The proposed model was successful in describing the electrical conductivity with two mechanisms in polymer electrolyte systems.

Assume, the apparent activation energy for ion to transport satisfies $\sigma = \sigma_0 \exp \left[-\frac{E_a}{k T}\right]$, by considering Eq. 17 we can approximate the activation energy as Eq. 24:

$$E_a = kT \left[ \beta \frac{v}{C_1^{1/3}} + \alpha \frac{1}{C_1^{1/3}} - 1 \right]$$

(24)

Using data in Fig. 4, we can calculate the effect of salt or base weight fraction on the activation energy for ion transport. Figure 5 shows the activation energy of ions in several polymer electrolytes as function of salt/base concentration.

The activation energy decreases with ion concentration. At high ionic concentration, the activation energies located at around 0.05 eV. This activation energy corresponds to the activation energy in amorphous phase. This value is comparable to what we have reported previously when simulating the activation energies of amorphous phase in various polymer electrolytes of around 0.04 eV (Mikrajuddin et al., 2000).
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Fig. 4: XRD patterns for (a) PVA powder, (b) PVA membrane, (c) PVA.1wt%LiOH, (d) PVA.3wt%LiOH, (e) PVA 5wt%LiOH, (f) PVA.7wt%LiOH, (g) PVA.9wt%LiOH, (h) PVA.10wt%LiOH and (i) LiOH powder.

Fig. 5: Effect of salt or base weight fractions on the activation energies for ion transport in the polymer electrolytes.

Furthermore, Mertens et al. (1999) reported, the Vogel-Tamman-Fulcher activation energy of most amorphous poly (ether-ester) s containing 1, 4, 7-trioxanonyl main chain units at various LiClO$_4$ concentrations were mostly at around 8 kJ mol$^{-1}$ or 0.08 eV (Mertens et al., 1999).

**CONCLUSION**

The new model introduced here succeeded to explain the dependence of electrical conductivities of various polymer electrolytes as function of ion concentration. We only used a minimum number of freely adjustable parameters to fit the data since some parameters can be derived from experimental or previously reported data. The model also predicted the dependence of activation energies for ion transport that were very close to those previously reported.

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