

Testing the Applicability of an Expression for the Non-Arrhenius Ionic Conductivity in Solid Electrolytes

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Abstract. In a previous study, we have proposed a model that describes the non-Arrhenius ionic conduction behavior in superionic glasses. In the present report, the model is applied to analyze the conductivity behavior of a wide variety of solid electrolytes that include crystals, glasses, polymers, composites and mixed ionic-electronic conductors. From the analysis of the model, the physical factor responsible for the non-Arrhenius behavior has been extracted and discussed.

Introduction

Superionic conductors or solid electrolytes are widely applied in fuel cells, electrolytic condensers, gas sensors, batteries, etc. Understanding the fundamental properties of these materials is of primordial importance to expand their applicability. Usually, the temperature dependence of the ionic conductivity of many solid electrolytes follows the Arrhenius type behavior. However, it has been discovered that some optimized superionic conductors exhibit a non-Arrhenius behavior at high temperature, whereas at low temperature, they follow the usual Arrhenius behavior [1]. In order to explain this behavior, some works have been done [6]. However, the behavior is not fully understood yet. Recently, by employing the Zwanzig model for the velocity autocorrelation function [2] and the Nernst-Einstein relation, we have derived a simple expression for the ionic conductivity [3]. The application of the model to glassy $z\text{AgI}+(1-z)[0.525\text{Ag}_2\text{S}+0.475(\text{B}_2\text{S}_3:\text{SiS}_2)]$ has shown that it reproduces quite well the observed temperature dependence of the ionic conductivity. As shown in Fig. 1, the temperature dependence of the ionic conductivity depends strongly on the material. In order to verify the applicability of the model, in the present report, the ionic conductivity observed in various kinds of ionic conductors is analyzed by using the expression obtained.

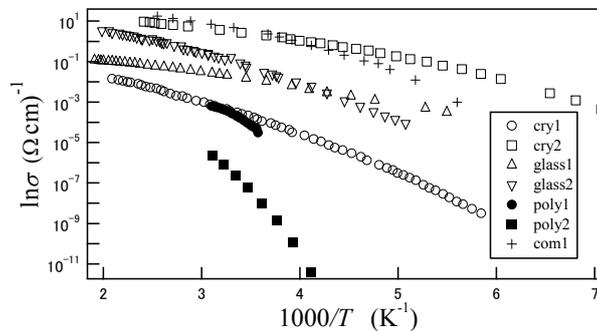


Fig. 1. The temperature dependence of ionic conductivity of several materials. The symbols represent the following materials, cry1: $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$, cry2: $\text{Ag}_7\text{GeS}_5\text{I}$ [4,5], glass1: $\text{Ag}_2\text{S}+(1-x)(0.67\text{B}_2\text{O}_3+0.33\text{GeS}_2)(x=0.3)$, glass2: $0.5\text{Ag}_2\text{S}-0.5\text{GeS}$ [4,6], poly1: polyorganophosphazene, poly2: $\text{PEO-LiCF}_3\text{SO}_3$ [7,8], com1: $\alpha\text{-AgI}$ (in glass matrix) [9], respectively.

Theory and Results

The model is based on the following assumptions.

- The particles that form the system are executing harmonic vibrations around the positions where the potential is minima.
- When the particle diffuses, it jumps in a very short time, to a new position which is almost equivalent to the old position. After the jump, the particle loses its memory.
- The particle jump rate is defined as $1/\tau = A \exp(-E_\tau/kT)$, where, τ is the relaxation time, A is the jumping rate at the high temperature limit, E_τ is the activation energy for diffusion and k is the Boltzmann constant.
- The harmonic oscillation in the potential well is described adequately by a fixed frequency ω as in the Einstein approximation.

From these assumptions, the following equation for the non-Arrhenius ionic conductivity has been derived [3],

$$\sigma = X_0 \exp\left(-\frac{E_n - E_\tau}{k_B T}\right) \times \left[1 + X_1 \exp\left(\frac{2E_\tau}{k_B T}\right)\right]^{-1}, \quad (1)$$

$$X_0 = \frac{(Ze)^2 n_0}{fMA}, \quad X_1 = \omega^2 A^{-2}. \quad (2)$$

Here, E_n is the activation energy for carrier creation, Z is the valence, e is the elementary charge, f is the Haven ratio, M is the mass of the diffusing particle and n_0 is the carrier number density at the high temperature limit. This equation gives a simple Arrhenius type temperature dependence of the ionic conductivity at low temperature or $X_1 \gg 1$. According to the model, the change from an Arrhenius to non-Arrhenius type temperature dependence is related with the change from jump diffusion to continuous diffusion. In the low-temperature domain, the particle's energy needs to overcome the potential barrier E_τ formed by the surrounding other particles. On the other hand, in the high temperature domain, the continuous diffusion originated by the cooperative dynamical motion of surrounding particles takes place.

At the high ($i = H$) and low ($i = L$) temperature limits, Eq. 1 could be written as

$$\sigma_i = s_i \exp\left(-\frac{E_i}{kT}\right), \quad (3)$$

where, s_i is a constant and E_i , ($i = H, L$) is the activation energy that is observed experimentally. Eq. 1 can be rewritten by using Eq. 3. In this course, the following relations are obtained.

$$X_0 = s_H, \quad X_1 = \frac{s_H}{s_L}, \quad E_n = \frac{E_H + E_L}{2}, \quad E_\tau = \frac{E_L - E_H}{2}. \quad (4)$$

According to Eq. 4, we can discriminate the activation energies for carrier creation and migration from the measured data.

Application to Crystalline Ionic Conductors. The non-Arrhenius temperature dependence of ionic conductivity have been observed in Na- β'' -alumina, $\text{Ag}_7\text{GeS}_5\text{I}$, $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ and related compounds [4,5]. In this study, the data of $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ and $\text{Ag}_7\text{GeS}_5\text{I}$ have been analyzed. Fig. 2(a) and 2(b) show the temperature dependence of the ionic conductivity of $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ and $\text{Ag}_7\text{GeS}_5\text{I}$,

respectively. The best fitted parameters obtained from the model are shown in Table 1. From Fig. 2, we can see that the theory can reproduce quite well the experimental data. It is gratifying to note that the values of E_H and E_L of $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ are the same to those reported in reference [5].

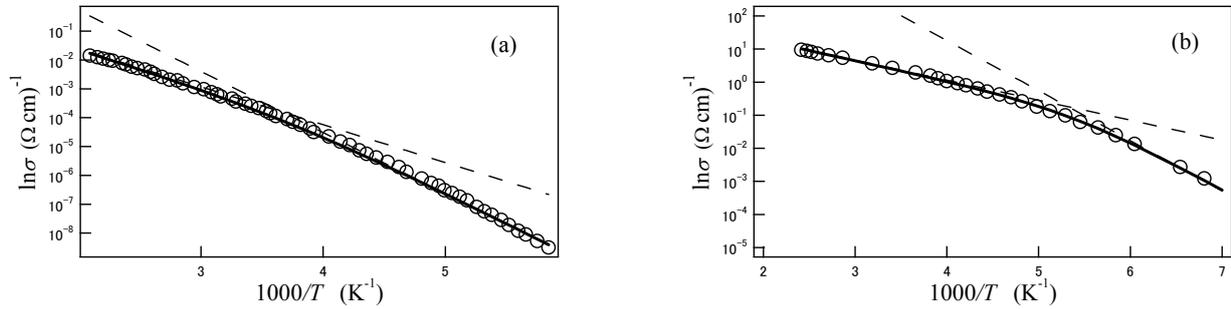


Fig. 2: The temperature dependence of ionic conductivity of $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (a) and $\text{Ag}_7\text{GeS}_5\text{I}$ (b). The circles represent measured data. The dashed lines show the fitting lines at high and low temperature domains. The solid line denotes the theoretical line described by Eq. 1.

Table.1: Best fitted parameters for several materials.

Material	E_n [eV]	E_τ [eV]	E_H [eV]	E_L [eV]
$\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$	0.34	0.095	0.26	0.44
$\text{Ag}_7\text{GeS}_5\text{I}$	0.21	0.089	0.12	0.3
$\alpha\text{-AgI}$ (in glass matrix)	0.3	0.14	0.16	0.44
$\text{Ag}_2\text{S}+(1-x)(0.67\text{B}_2\text{O}_3+0.33\text{GeS}_2)$ ($x=0.3$)	0.15	0.049	0.1	0.2
$0.5\text{Ag}_2\text{S}-0.5\text{GeS}$	0.28	0.093	0.19	0.38
polyorganophosphazene	0.57	0.33	0.24	0.9
$\text{PEO-LiCF}_3\text{SO}_3$	1.17	0.28	0.89	1.4

Application to Glassy Ionic Conductors, Mixed Conductors and Polymers. As examples, the model has been applied to $\alpha\text{-AgI}$ (in glass matrix), $\text{Ag}_2\text{S}+(1-x)(0.67\text{B}_2\text{O}_3+0.33\text{GeS}_2)$ ($x=0.3$) and $0.5\text{Ag}_2\text{S}-0.5\text{GeS}$ [4,6,9]. It has been found that these glasses and mixed conductors show clearly a non-Arrhenius ionic conduction behavior. In particular, $\text{Ag}_2\text{S}+(1-x)(0.67\text{B}_2\text{O}_3+0.33\text{GeS}_2)$ ($x=0.3$) is one of the optimized glass to obtain the highest conductivity. About the polymers, we focused on polyorganophosphazene and $\text{PEO-LiCF}_3\text{SO}_3$ [7,8]. Fig. 3(a) and 3(b) show the temperature dependence of ionic conductivity in several materials. Best fit parameters are given in Table. 1. Concerning the value of E_n , measured data is available only for $\text{Ag}_2\text{S}+(1-x)(0.67\text{B}_2\text{O}_3+0.33\text{GeS}_2)$ ($x=0.3$), $E_n = 0.196\text{eV}$ [6]. We can see that this value is nearly equal to the value obtained in our analysis.

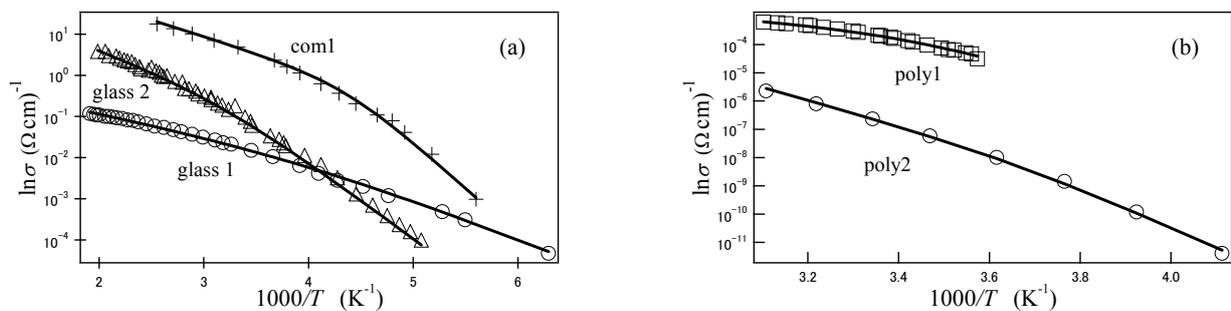


Fig. 3: The temperature dependence of ionic conductivity of several materials. The symbols represent measured data. The solid lines denote the theory described by Eq. 1. The labels indicate the same compounds designated in Fig.1.

Discussion

Concerning the description of non-Arrhenius type ion conduction behavior, the most famous expression is the VFT formula. In the present study, we have shown that the non-Arrhenius type behavior could be reproduced without using the VFT formula. The most important parameters for such a description are the values of the activation energies at the high and low temperature domains. Concerning the values of X_0 , X_1 , s_H and s_L , there are large difference between the different materials. According to Eqs. 1, 2 and 4, the degree of deviation from the Arrhenius behavior which is described by the ratio E_H/E_L increases with E_τ . On the other hand, according to Fig. 4(a), E_n/E_τ is almost constant against the variation of E_τ . Thus, E_n increases with the increase of E_τ . From Fig. 4(b), we note clearly that E_H/E_L is proportional to E_n/E_τ . Therefore, our model suggests that the non-Arrhenius behavior arises from the different activation processes determining E_n and E_τ .

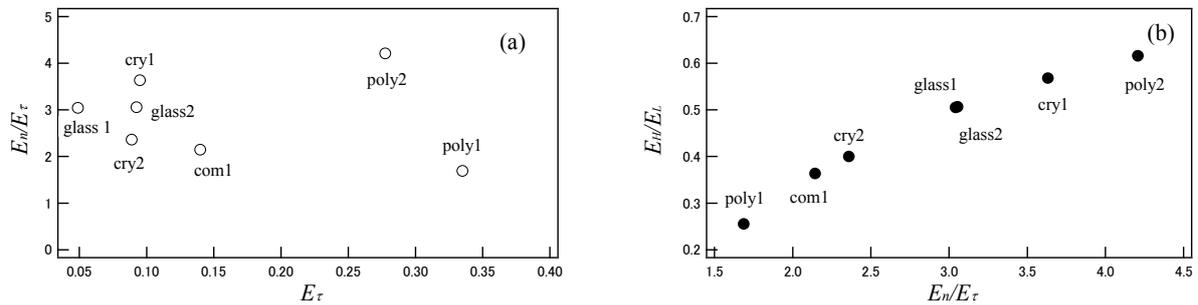


Fig. 4: E_n/E_τ vs E_τ (a) and E_H/E_L vs E_n/E_τ (b) of several materials.

Summary

The non-Arrhenius type temperature dependence of ionic conductivity observed in various materials has been analyzed by our model proposed recently. According to the model, the activation energies for carrier creation and carrier migration can be discriminated from measured data. The model suggests that the non-Arrhenius behavior arises from the different activation processes involved in the determination of these activation energies.

References

- [1] J. Kincs and S.W. Martin: Phys. Rev. Lett. Vol. 76 (1996), p. 70
- [2] R. Zwanzig: J. Chem. Phys. Vol. 79 (1983), p. 4507
- [3] T. Indoh and M. Aniya: J. Phys. Soc. Jpn. Vol. 79 (2010) Suppl. A, p. 113
- [4] M. Ribes, G. Taillades and A. Pradel: Solid State Ionics Vol. 105 (1998), p. 159
- [5] C. León, J. Santamaría, M.A. París, J. Sanz, J. Ibarra and A. Várez : J. Non-Cryst. Solids Vol. 235-237 (1998), p. 753
- [6] Q. Mei, B. Meyer, D. Martin and S.W. Martin: Solid State Ionics Vol. 168 (2004), p. 75
- [7] S. Zhou and S. Fang: Eur. Polym. J. Vol. 43 (2007), p. 3695
- [8] N.K. Karan, D.K. Pradhan, R. Thomas, B. Natesan and R.S. Katiyar: Solid State Ionics Vol. 179 (2008), p. 689
- [9] M. Tatsumisago, T. Saito and T. Minami: Solid State Ionics Vol. 70/71 (1994), p. 394