Solid State Ionics 281 (2015) 43–48

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Non-Arrhenius ionic conductivity in solid electrolytes: A theoretical model and its relation with the bonding nature

Yohei Okada [a,*], Masahiro Ikeda [b], Masaru Aniya [a]

[a] Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan
[b] Course of General Education, Natural Science, Applied Physics, Fukui National College of Technology, Geshi-cho, Sabae, Fukui 916-8507, Japan

ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form 31 August 2015
Accepted 31 August 2015
Available online 23 September 2015

Keywords:
Solid electrolytes
Non-Arrhenius ionic conductivity
Bond strength–coordination number fluctuation model
Bonding characterization of materials

ABSTRACT

Some solid electrolytes exhibit the non-Arrhenius type ionic conductivity whose origin is still not well understood. In the present study, a model for the non-Arrhenius ionic conductivity is proposed by exploiting the formulation of the bond strength–coordination number fluctuation (BSCNF) model developed originally to describe the transport properties of supercooled liquids. According to the present model, the origin of the non-Arrhenius ionic conductivity as described by the VFT equation traces back to the bonding energy fluctuations of the diffusing ions within the solid. The model suggests that good ionic conductors exhibit a non-Arrhenius behavior in the ionic conductivity. The present study reveals also that the degree of the non-Arrhenius behavior of different materials is separated roughly into two groups depending on the nature of the chemical bonds. One of these groups consists mainly of compounds such as Ag ion conductors, and the other group contains materials such as Li ion conductors.

1. Introduction

Most ionically-conducting solid materials that have promising field of applications in batteries, fuel cells, and other electrochemical devices [1,2], show Arrhenius temperature dependence in the dc ionic conductivity [1–4]. It is well established that the Arrhenius-type temperature dependence is explained based on the theory of point defects in crystalline materials [4]. In recent decades, however, the non-Arrhenius temperature dependence of ionic conductivity has been found in different types of solid ionic conductors [5–9]. For example, the pioneering work by Kincs and Martin [5] demonstrated that ion-conducting glasses optimized by doping metal halide exhibit an Arrhenius behavior at low temperature, while a deviation from the Arrhenius behavior is clearly observed at high temperature. In this regard, the result reported by Kincs and Martin [5] has attracted much interest, because their measurement of the ionic conduction shows both, the Arrhenius and the Vogel–Fulcher–Tammann (VFT)-like behaviors in a continuous pattern [5–7]. In addition, it was also suggested by the same authors [5] that the non-Arrhenius temperature dependence of the ionic conductivity is a ubiquitous feature in optimized fast ionic conducting glasses. Motivated by their work, a large number of studies have been done to understand the behavior of the non-Arrhenius ionic conductivity [9–15]. For instance, the ion trapping model [9,10] and the coupling model [11] have been applied to account for the peculiar behavior of the ionic conductivity. The problem of non-Arrhenius ionic conductivity has been also tackled in our research group [14,15]. According to a model developed based on the Zwanzig model of diffusion, the non-Arrhenius behavior becomes apparent when the lifetime of the oscillating particle in a potential well becomes comparable with the inverse of oscillation frequency [14]. The proposed model applied to different materials indicated that the non-Arrhenius behavior can be described as a result of the interplay between carrier generation and relaxation processes [15]. These studies provided a background to understand the phenomenon of non-Arrhenius ionic conductivity. However, these works have little relation with the model presented here. The model presented in the present study is completely independent from the previous one.

Regarding the temperature dependence of the ionic conductivity, different types of non-Arrhenius behavior are observed, such as the positive curvature upwards when the temperature is increased [16,17], and the behavior described by a single VFT equation in a wide temperature range [18,19]. From a fundamental point of view, it is of primordial importance to understand why a bending behavior of the ionic conductivity emerges in the solid state, and how such behavior is related to other physical quantities known as key parameters in the study of structural relaxation, such as the fragility [20] and the decoupling index [21].

In the analysis of the temperature dependence of dc ionic conductivity that exhibits a convex shape upwards when the conductivity is plotted versus the inverse of temperature, the VFT equation or its modified version have been often used to describe the measured data [18,19,22]. The interpretation of the result by the VFT-type expression, however, is still being debated heatedly even today. Regarding this point, in one of

---

* Corresponding author.
E-mail address: okada855@yahoo.co.jp (Y. Okada).

http://dx.doi.org/10.1016/j.ssi.2015.08.020
0167-2738/

our recent studies, an interpretation of the VFT-like pattern for the viscosity of supercooled liquids was given in terms of the bond strength–coordination number fluctuation (BSCNF) model [23] originally proposed by one of the authors [24]. According to the BSCNF model, the effective activation energy and the Vogel temperature, B_{VFT} and T_0 of the VFT expression, correspond to the mean value of the bond energy and its fluctuations, respectively. The BSCNF model combined with the fractional Stokes–Einstein law has been applied to study the ionic conductivity in ionic liquids [25]. The successful application of the BSCNF model in the study of transport properties in the liquid phase prompted us to apply the concept of the model to treat the properties in the solid phase. In the present study, with the objective to understand the origin of the non-Arrhenius ionic conductivity in solid materials, we propose a model for the ionic conductivity by exploiting the formulation of the BSCNF model. In addition, by relating the model with the bonding trends of the materials, we show that from the chemical bond point of view, one can deduce a condition for the occurrence of high ionic conductivity in solid ionic conductors. In what follows, we discuss the properties of solid ionic conductions in terms of the proposed model. A preliminary result of the research was presented in a minor conference proceeding [26]. There, the analysis was focused mainly in Ag ion conductors. The present paper reports an extended version of the study. We have included the whole derivation of the model supplementing with the detailed explanation on the background and extended discussions. New results not addressed in the previous report are also included. In particular, we have extended the analysis to compounds other than Ag ion conductors.

2. Model for the ionic conductivity

In a solid material, each ion oscillates in a potential well formed by the surrounding ions, and some of these can escape from the potential well with a certain probability that follows the Boltzmann distribution law [27]. Under the action of an external field, the net event of these processes results in the macroscopic transport property observed in solid materials. When the mobile ion overcomes the potential barrier by hopping to an adjacent site, the bonds connecting the oscillating ions to the surrounding components are broken. Thus, the mobile ion is excited to a site with higher energy. The series of such processes are mediated by the bond-breaking which is triggered by thermal fluctuation.

The above picture of ionic excitation is often represented by the Arrhenius equation. On the basis of this expression, the mean residence time of the ion placed in a potential well can be written as

$$\tau = \nu^{-1} \exp\left(\tilde{E}\tilde{Z}/RT\right), \tag{1}$$

where, ν represents the oscillation frequency of the ion trapped in the potential well, $\tilde{E}$ is the bond energy between the mobile and the surrounding ion, $\tilde{Z}$ is the coordination number of the mobile ion, and R is the gas constant. From the point of view of the mobile ion, the bond energy and the coordination number vary depending on the sites that the mobile ion occupies, and thus, $\tilde{E}$ and $\tilde{Z}$ are thought to have distributions.

Based on the above discussion, the mean residence time of the mobile ions can be determined statistically. Namely, denoting by i the different sites that the mobile ion can occupy, the mean residence time τ is written as

$$\tau = \sum_i P_i \tau_i, \tag{2}$$

and

$$\sum_i P_i = 1, \tag{3}$$

where P_i is the concentration of the i site. From the point of view of diffusing ion, the available sites along the diffusion path are distributed continuously. Hence, Eq. (2) is rewritten as

$$\tau = \nu^{-1} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} d\tilde{E}d\tilde{Z} f(\tilde{E}) g(\tilde{Z}) \exp\left(\frac{\tilde{E}\tilde{Z}}{RT}\right). \tag{4}$$

Here, $f(\tilde{E})$ and $g(\tilde{Z})$ are the distribution function of $\tilde{E}$ and $\tilde{Z}$, respectively. By adopting the Gaussian distribution function for $f(\tilde{E})$ and $g(\tilde{Z})$, Eq. (4) reduces to

$$\tau = \frac{\nu^{-1} T}{\sqrt{T^2 - \left(\Delta\tilde{E}\Delta\tilde{Z}/R\right)^2}} \exp\left(\frac{\tilde{E}_0\tilde{Z}_0/R}{T - \Delta\tilde{E}\Delta\tilde{Z}/R}\right), \tag{5}$$

where $\tilde{E}_0$ and $\tilde{Z}_0$ are the mean values of $\tilde{E}$ and $\tilde{Z}$ and $\Delta\tilde{E}$ and $\Delta\tilde{Z}$ are their fluctuations. In the derivation of Eq. (5), it was assumed that the fluctuations of $\tilde{E}$ and $\tilde{Z}$ normalized by their mean values are equal each other, that is, $\Delta\tilde{E}/\tilde{E}_0 = \Delta\tilde{Z}/\tilde{Z}_0$. As long as this condition is satisfied, Eq. (4) reduces to the VFT-like expression given in Eq. (5). The mathematical derivation of Eq. (5) is analogous to that of the BSCNF model of viscosity for supercooled liquids [23]. However, it is important to note that the physical meanings of the parameters are different. In the case of liquids, the quantities E_0, Z_0, ΔE and ΔZ are associated with the structural units or group of atoms, whereas in the present model which deals with atomic transport in the solid state, they correspond to atoms or ions.

Once having an expression for the residence time τ, we obtain the expression of the ionic conductivity by using the expression for the diffusion coefficient $D = gl^2/\tau$, and the Nernst–Einstein relation, $\sigma = (Ze)^2 nD/fk_BT$ [3], where g is the geometrical factor, l is the jump distance, Ze is the charge of the ion, f is the correlation factor, and n is the concentration of the mobile ions. Using the above relations together with Eq. (5), we finally obtain an expression for σ as

$$\sigma T = \frac{A_{\sigma T}\sqrt{T^2 - \left(\Delta\tilde{E}\Delta\tilde{Z}/R\right)^2}}{T} \exp\left(-\frac{\tilde{E}_0\tilde{Z}_0/R}{T - \Delta\tilde{E}\Delta\tilde{Z}/R}\right). \tag{6}$$

In this equation, $A_{\sigma T}$ is defined as $A_{\sigma T} = g\nu(Ze)^2 l^2 n/fk_B$. In the next section, we will discuss the ionic conductivity by applying Eq. (6) to solid electrolytes.

3. Application of the model

Fig. 1 shows the temperature dependence of the ionic conductivity of some solid ionic conductors. The symbol and the solid line denote the experimental data and the theoretical curves drawn by using Eq. (6), respectively. The values of the parameters for each material determined by fitting the experimental data are given in Table 1. From Fig. 1, we can see that Eq. (6) describes well the experimental data over a wide temperature range, excepting $Ag_6SnS_4Br_2$, which shows a sudden drop at around 234 K. Nonetheless, Eq. (6) describes reasonably well the experimental data that ranges from Arrhenius to VFT-like behaviors. In particular, it is noted that Eq. (6) describes well the behavior of $0.8Na_2S + 0.2B_2S_3$, $Li_{0.5}La_{0.5}TiO_3$ and $Li_{10}(SiO_4)_6O_3$ which show Arrhenius-type behavior. For these cases, the Arrhenius-like behavior is reproduced when the following condition is satisfied,

$$T \gg \Delta\tilde{E}\Delta\tilde{Z}/R. \tag{7}$$