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# A novel model for the ionic conducting polymers with non-Arrhenius temperature dependence

Gu Xu

Department of Materials Science, McMaster University, Hamilton, Ontario, Canada L8S 4L7

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**Abstract.** A novel model is proposed to describe the ionic conduction process of polymer electrolytes with non-Arrhenius temperature dependence expressed by the empirical Vogel–Tamman–Fulcher (VTF) equation,  $\exp[Q/(T - T_0)]$ . Following the previous numerical simulation work and the series hopping calculation scheme, a microscopic model was constructed assuming random hopping energy distribution. Using the Arrhenius form for thermal activation and order statistics, the overall resistivity was found to be related to the sum of  $\exp(E/kT + cE^{1/2} - E/D)$  where  $E$  is the hopping energy barrier,  $\exp(-cE^{1/2})$  the WKB term, and  $D$ , an energy-related constant. Calculated from the steepest descent method, the model is able to reproduce the VTF type of temperature dependence analytically.

## 1. Introduction

The study of the ionic conduction mechanism for ionic conducting polymers has long been a challenge due to the practical demand for polymer electrolytes for use in compact, *high-efficiency batteries and fuel cells*. Still, a *satisfactory microscopic model is lacking* [1] to describe the formation of, and transport properties within, polymer electrolytes. Traditional lattice hopping theory involving exponential temperature dependence (the Arrhenius equation) fails because of the fact that the conducting process in these polymer electrolytes is largely promoted by the host polymer chain movement, which has been confirmed by experiments to show that ions are much less diffusive below  $T_g$  of the host polymers [2]. The temperature dependence of their resistivity is usually non-Arrhenius, with a concave curvature on the logarithmic plot against the reciprocal temperature. On the other hand, excellent fitting can be obtained by employing the Vogel–Tamman–Fulcher (VTF) semi-empirical equation [3]  $\exp[-Q/(T - T_0)]$  (or the closely related WLF equation) [4], for typical experimental results such as those of polyethylene oxide (PEO)-based polymer electrolytes [1, 2]. However, the theoretical constructs of these equations based on the free-volume and/or configuration entropy models are not of the microscopic level for polymeric materials and lack mechanistic details [1].

The only microscopic model available to describe ionic transport assisted by the polymer host thus far has been the dynamic bond percolation theory (DBPT) [5], which simulates the continuous diffusion of ions by introducing ‘renewal of the random bond configuration’ on a statically disordered lattice where the charge carriers diffuse to simulate the chain segment motion of the host polymer. The DBPT does not, however, lead to the non-Arrhenius temperature dependence for the resulting conductivities, simply because it does not account for the temperature during the hopping of the charge carriers [5]. Although it appears to be possible to fit, within a small temperature range, a few data points from experiments

by DBPT using two Arrhenius hopping parameters, such a procedure cannot be repeated in general, since analytically the sum of two Arrhenius functions with two different activation energies would only give a double-Arrhenius curve.

Based on our previous numerical simulation work [6,7], where convex-curved logarithmic conductivities were generated by introducing an activation energy distribution for the ionic hopping process [7], in this paper a novel microscopic model is proposed to recover the non-Arrhenius temperature dependence of ionic transport for conventional solid-state polymer electrolytes (PEO, for example). Instead of dealing with a lattice picture, the model is outlined under the practical framework of a bulk containing hopping barriers with distribution barrier energies. Using a series hopping scheme proposed elsewhere [8], the overall resistivity, rather than the conductivity, will be formulated and the random distribution of the barrier heights be manipulated using the so called 'order statistics'. The result is expected not only to regenerate the convex-bent Arrhenius temperature dependence of the conductivities for these systems, but also to provide some clue to the general mechanisms involved in the amorphous materials exhibiting non-Arrhenius behaviour.

## 2. The model

Following current understanding, the dominant class of polymer electrolytes are formed using a neutral polar polymer complexed with a uni-univalent metal salt, and involving the solvation of the cations by the Lewis basic components of the polymer (oxygen, in the case of PEO). For practical purposes, the ion pairing in these systems is reduced to a minimum. In fact in certain cases such as  $\text{LiCF}_3\text{SO}_3$  the cations and anions are totally dissociated [1]. Both cationic and anionic motions contribute to the overall ionic conduction and are further characterized by their transport numbers. The translational motions of cations, which involve breaking one bond and forming a new one to a different Lewis base, and the anions, which move freely into available seats in the structure, are both facilitated by the segmental motions of the host polymer within amorphous regions (as the crystallinity of these polymers can be as high as 70%). Following the convention, the ionic conduction of these systems is modelled as the hoppers jumping on a set of sites randomly distributed in space. The spatial distribution of the barriers between the sites is also constantly changing with time due to the chain movement. Obviously, the non-Arrhenius behaviour of the ionic conductivity must originate from the fact that the hopping barriers within these amorphous regions are not associated with a unique energy value, but related to the random distribution of the activation energy  $E$ .

Moreover, due to the construction of the ionic complex, only one ion can usually be accommodated by each site. Some jumps may be forbidden due to the possible involvement of occupied ionic sites. Since ions are much larger than electrons, the mobility of the charge carriers is much lower than those of electronic conductors. As a result, very high carrier density is expected (in fact, in some cases nearly all cation sites are occupied since each cation must be coordinated by four oxygens) [2]. This implies a high likelihood of encountering forbidden jumps. To find a connected hopping route, the concept of 'holes', namely, empty sites, must be introduced. The motion of these 'holes' in the opposite direction to the ions will not be interrupted by the occupied sites, but only occasionally terminated by a group of empty sites. As a major consequence, the overall travel time of each 'hole' through the bulk is computed by summing the hopping time,  $\tau$ , of each step along the route. Following the homogeneity of the material, the overall resistance is, therefore, proportional to the sum of  $\tau$ s along an averaged or a typical path. Assuming

an Arrhenius form for thermal activation, the probability of finding a 'hole' is related to the temperature via  $\exp(-E/kT)$ , where the activation energy is chosen to be roughly the hopping barrier height. Since  $E$  ( $> 0.1$  eV) is usually much higher than the thermal energy,  $kT$  ( $< 0.05$  eV for  $T < 600$  K), the corresponding ion 'mobility' may be approximated by the WKB result [9],  $\exp(-c[E - K]^{1/2})$ , where  $c$  is a constant related to the ion mass, the  $K$  the kinetic energy of the jumpers, which is omitted in the following calculation. For amorphous PEO, the separation distance between the sites can be regarded as a constant since ion sites are almost uniformly distributed by the oxygen atoms on the backbone ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) between every two carbon atoms. Therefore, the overall hopping rate between any pair of sites,  $\tau^{-1}$ , becomes the product of the mobility and the probability of finding a 'hole', namely,  $\exp(-cE^{1/2} - E/kT)$ .

The above summation of  $\tau$  would produce an Arrhenius temperature dependence for crystalline hosts where only a single value of  $E$  is encountered. For amorphous polymers, however, a weight function should be included to take into account the probability distribution of having a jump with energy  $E$ . This distribution function is in general related to the structural information of the host material, such as the geometry and separation between the ion sites. In order to accommodate a wide range of amorphous systems, only completely random distribution of the barrier energy is assumed here, i.e., the probability density function  $f(E)$  is a constant for  $E$  between  $E_0$  ( $E$ -minimum) and  $E_m$  ( $E$ -maximum) beyond which  $f$  becomes negligible. Since there is usually more than one choice of site for the hopper to jump into, following the minimum energy principle the jumping probability is maximized at the sites having the lowest value of  $E$ . As a consequence, the probability distribution of having a jump with the chosen energy  $E$  has to obey the so-called 'order statistics' and the resulting distribution function,  $P(E)$ , is given by  $n(1 - F(E))^{n-1}f(E)$ , where  $F(E)$  is the cumulative probability distribution of  $f(E)$  and  $n$  is the number of choices at each jump. For constant  $f(E)$ ,  $F(E)$  is simply  $(E - E_0)/(E_m - E_0)$ , a linear function of  $E$ . Ideally, both  $n$  and  $E$  should be very large, because in the vicinity of an ion site within the amorphous host, the average number of choices  $n$  can be much larger than 12, the close-packing number, due to the fact that the microscopic configuration of the host is changing with time and there is no clear distinction between the nearest, second-nearest and third-nearest neighbours. To obtain the temperature dependence, however, only the ratio of the maximum barrier  $E_m$  and  $n$  is needed. Representing  $(E_m - E_0)/n$  by  $D$  and  $(E - E_0)/D$  by  $x$  (ranging from 0 to  $n$ ),  $P(E)$  can be written as  $(1 - x/n)^{n-1}/D$ . Note  $(1 - x/n)^{n-1}$  can be approximated by  $\exp(-x)$  for  $n \gg 1$ . Even  $n = 12$  was found to be large enough to support this approximation for small  $x$ , and either expression becomes negligible when  $x$  is large. Therefore, for the amorphous system possessing a constant activation energy distribution with minimum energy selection for hopping,  $P(E)$  is approximated by  $\exp[-(E - E_0)/D]/D$ .

Since the total travel time for each ion can be computed by summing the  $\tau(E)$  along its path, and the distribution of hopping with  $E$ ,  $P(E)$ , is expected to be the same throughout the volume of a homogeneous bulk, the overall resistivity is, therefore, proportional to the sum of  $P(E)\tau(E)$  over  $E$ ;

$$R(\beta) = \text{constant} \times \sum_E \exp[\beta E + cE^{1/2} - E/D] \quad (1)$$

where  $\beta = 1/kT$ . Due to the presence of the non-linear exponent (to be called  $f(\beta, E)$  hereafter) the sum cannot be calculated analytically. However, a more intuitive approach can be taken to approximate the sum of exponential functions by the envelope profile of the exponent family on a logarithmic plot, as shown in figure 1. The two results differ by

a slow temperature-dependent factor, which is overwhelmed by the exponential part. The envelope  $f(\beta, E(\beta))$  is obtained by finding  $E(\beta)$ , the particular  $E$  values when  $f(\beta, E)$  is maximized, through  $\partial f/\partial E = 0$ . Since  $f(\beta, E) = \beta E + cE^{1/2} - E/D$ ,  $\partial f/\partial E = 0$  gives

$$E(\beta) = 0.25c^2(D^{-1} - \beta)^{-2} \quad (2)$$

which leads to the envelope curve  $f(\beta) = 0.75c^2(D^{-1} - \beta)^{-1}$ . Representing  $0.75c^2D^2/k$  as  $Q$  and  $D/k$  as  $T_0$ , we recover the VTF expression (plus a temperature-independent term):  $(Q/T_0)T/(T - T_0)$ , or  $Q/(T - T_0) - Q/T_0$ .

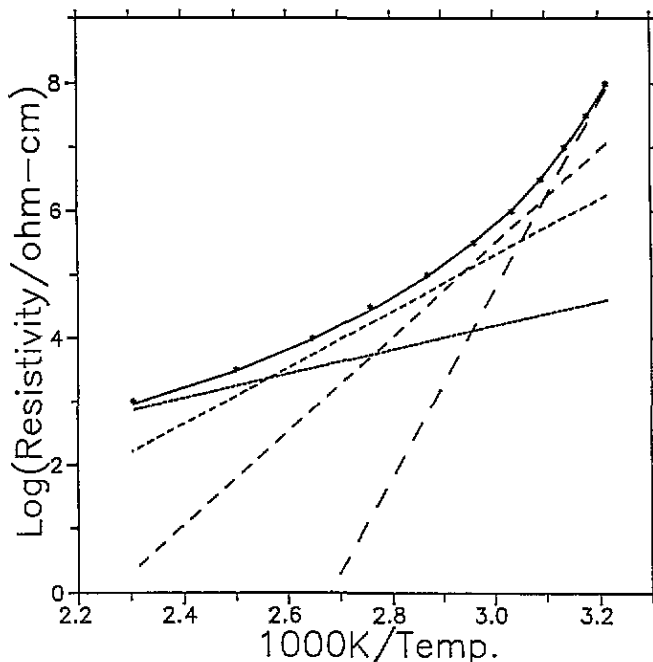


Figure 1. The non-Arrhenius resistivity of PEO-SCN fitted by the proposed model; the Arrhenius line family of four values of  $E$  are given by the lines in the ascending order of dash spacing with  $E = 0.268, 0.415, 0.637$  and  $1.07$  eV; the sum of the four Arrhenius lines is shown by the solid curve with concave curvature; the experimental data are represented by \*.

### 3. Discussion

To illustrate the model proposed, the numerical example of PEO-SCN [2] has been provided in figure 1, where only four  $E$  values for equation (1) (0.268, 0.415, 0.637 and 1.07 eV) were used to simplify the calculation. Physically, it shows that at high temperatures the overall resistance is mainly contributed by the hops with small  $E$ , while the ionic transport is gradually blocked by larger energy barriers when the system is cooled down. The slopes ( $E$  values) and the intercepts ( $Y(E)$ ) of these Arrhenius lines were obtained by the fitting on the experimental data plotted against  $\beta$ .  $Y(E)$  is given by  $cE^{1/2} - E/D$ , and the constants  $c$  and  $D$  (hence  $Q$  and  $T_0$ ) are obtained by data fitting. The resulting  $kQ$  and  $T_0$  were 0.071 eV and

260 K, respectively. In the meantime,  $c$  can be found from  $(kQ/0.75)^{1/2}/D = 14 \text{ (eV)}^{-1/2}$ . This value is compared to the WKB result, which is given by  $(2M)^{1/2}d/(h/2\pi)$ , where  $M$  is the mass of the particle,  $d$  the jumping distance and  $h$  the Planck constant. Note that  $M \simeq$  several proton masses and  $d \simeq 0.1 \text{ nm}$ , with the resulting  $c$  (WKB) around  $17\text{--}30 \text{ (eV)}^{-1/2}$ , in the same order of magnitude. The discrepancy between this  $c$  (WKB) and  $c$  found from the fitting can be further traced back to our expression of mobility,  $\exp(-cE^{1/2})$ , which is approximated from the WKB result:  $\exp(-c(\text{WKB})[E - K]^{1/2})$ . Since  $K$ , the kinetic energy, is always positive,  $c$  has to be smaller than  $c$  (WKB) to make the balance. Since  $D$  is given by  $(E_m - E_0)/n$ , the cut-off temperature,  $T_0$ , is thus controlled by ratio of the highest energy barrier and the number of neighbouring sites approachable, whereas  $E_m$  and  $n$  cannot be identified individually. Obviously our model is not limited to the polymer electrolytes under consideration, since the derivation does not involve any detailed information on the host chain configuration, etc. Therefore, the analysis can be applied to a wide variety of hopping systems with fully random energy distribution.

Moreover, our scheme is not limited to describing the VTF-type conductors. In fact the functional form of the probability for finding a barrier having  $E$ ,  $P(E)$ , can be modified to apply to other systems. Conversely, the deviation of the experimental data from the VTF equation can be employed to study the changes in functional forms of  $P(E)$  leading to the structural information. However, no matter what modifications are made, the resulting envelope will always show a concave curvature on the logarithmic resistivity plot as long as each site accommodates only one ion at a time, so the overall resistivity is characterized by the sum of jumps in series. When a different microscopic mechanism is involved, the convex curvature may appear, as was shown in the case of granular metals [10].

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