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Simulation of Ionic Conductivity of Lithium Borate Thin Films Using a Network of Electrical Resistors

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Abstract

Previous experiments show that the ionic conductivity of lithium borate thin films is strongly dependent on the thickness of the layers. A network of electrical resistors has been used as a model to describe the ionic conductivity of lithium borate films. This network consists of a large number of electrical resistors that have two different values. According to the percolation theory, the resistant network model describes the ion-conducting pathways inside the network of lithium borate glass. A MATLAB code has been written to calculate the equivalent network resistance, according to Kirchhoff's laws. The number of resistors in each direction of the network is proportional to the dimensions of the sample. The distribution of resistors in the network is random, but the relative probability of distribution for each of the two types of resistors is one of the parameters of this model. Experimental results show that the specific conductivity in thin films depends on the thickness of the layers, while it is constant in thicker layers. By examining various effective parameters in this model and according to the percolation theory, the non-trivial conductivity increase, observed in very thin layers, is simulated. The simulation performed by this model is satisfactory for both thin and thicker layers.

1. Introduction

Ionic glass conductors have attracted lots of attention in recent decades due to their potential industrial applications as solid electrolytes in electrochemical devices [1-3].

Studies on the ionic conductivity of lithium borate layers with amorphous structure in terms of thickness show significant changes in the conductivity of the layer at small thicknesses of a few nanometers [4, 5]. Schmitz et al. studied the ion conductivity of lithium borate thin films [4]. They observed that the conductivity of thin films of lithium borate increases as the layer thickness decreases, while for thick layers, the conductivity is almost constant.

There are several research on ionic glasses that confirm the existence of ion-conducting pathways inside the network of oxide glasses [6-10]. Varsamis et al. investigated ion dynamics by molecular dynamics simulations in lithium borate glasses [6]. They found that the ratio of 〖BO〗_4^- units and non-bridging oxygen (NBO) increases with both the lithium oxide content and the temperature. The calculation of diffusion coefficients of Lithium ions indicated that diffusion is carried out predominately through NBO sites. In addition, the NBOs tend to form clusters and percolate eventually into micro-channels suitable for ion migration.

The existence of such pathways or channels of the finite length of a few nanometers can also explain the conductivity enhancement which is observed for thin glass films [4, 5].

In this research, a model consisting of a network of electrical resistors is used to describe the ionic conductivity of lithium borate layers. The network of resistors consists of two types of resistors, namely R_1 and R_2, in which $R_2 >> R_1$. These resistors are randomly distributed in a square network between two metal electrodes. As R_1 and R2 have different probability distributions, the probability distribution is used as one of the model parameters. The change in layer thickness is achieved by changing the number of network resistors in one dimension. By calculating the equivalent resistance of this network and assigning a certain length to each of the resistors, the conductivity of the layer can be obtained.

2. Materials and Methods

In this model, the lithium-ion electrolyte layer is simulated by a network of resistors located between two metal electrodes. The cross-section of this layer is shown in Figure 1. This network consists of two types of resistors, namely R_1 and R_2, in which $R_2 >> R_1$. Resistor R_1 indicates paths within the electrolyte in which ions move more quickly, and R_2 shows paths that are more resistant to ion motion. This can be explained by ion-conducting pathways inside the network of oxide glasses [6-10]. These resistors are randomly distributed in the network, but the probability of R_1 and R_2 presence is different. As one of the parameters of this model, $P(R_1)$ shows the probability of distribution of R_1. The number of resistors in the x-direction, denoted by n_x, specifies the layer thickness and is a variable parameter. For each resistor, a length of dR of a few nanometers is considered. This length is the same for both types of resistors, so the layer thickness between the two metal electrodes is ($t = n_x \times dR$). The number of resistors in the direction parallel to the electrode is considered a constant value and denoted by n_y.

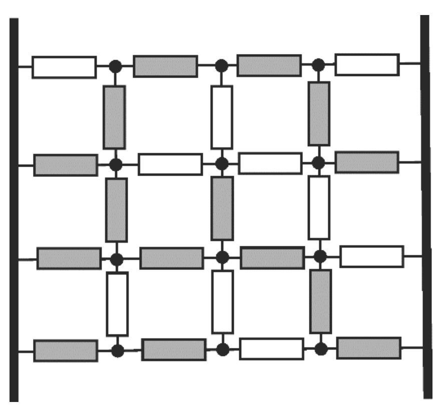

Figure 1. A square network of electrical resistors consisting of two types of resistors, namely R_1 and R_2. The resistors are randomly placed inside this network between two metal electrodes.

This model can be explained using percolation theory [11, 12]. The random distribution of resistors R_1 and R_2 between two electrodes creates clusters of resistors R_1 or R_2, the size of which depends on the distribution probability of the resistors. If the layer thickness is small enough, it is possible that at least one of the connection paths between the two electrodes consists only of clusters of R_1. As a result, the conductivity of the layer increases significantly for very small thicknesses. If the thickness of the layers exceeds a specific value (percolation threshold), the clusters consisting of R_1 remain separated. In this case, the resistance of the layer increases and results in a reduction in the layer conductivity. Further increase in layer thickness, due to the constant possibility of the resistors R_1 and R_2 presence, no longer affects the conductivity of the layer.

The two layers with different n_x values and $P(R_1)=0.4$ are compared as in Figures 2 and 3. In this network of resistors, the solid lines show the R_1 resistors, and the blank spaces correspond to resistors R_2. As illustrated in Figure 2 for $n_x = 10$, it is possible to find interconnected clusters of resistors R_1 between the two electrodes. This connection path is marked with a bold line on the figure. In Figure 3, for $n_x = 20$, no continuous path of resistors R_1 is seen between the two electrodes.

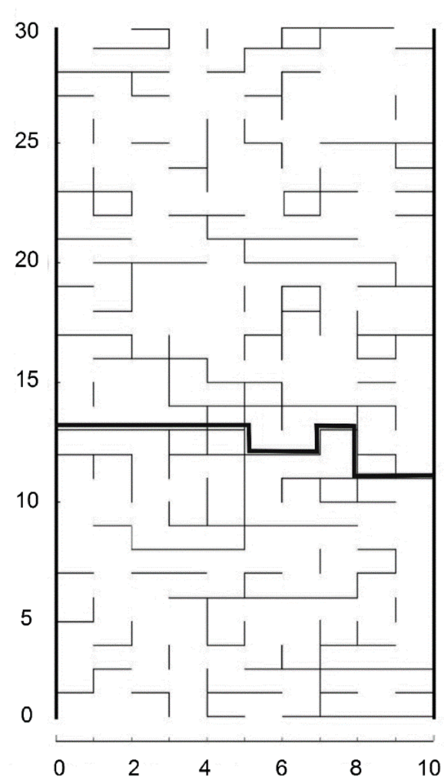

Figure 2. The network of resistors R_1 and R_2 for $n_x = 10$ and $n_y = 30$ and assuming $P(R_1) = 0.4$. Resistors R_1 are indicated by a solid line, and the empty spaces show resistors R_2. A path of resistors R_1 that connects the two electrodes is shown in bold.

According to the parameters defined above, the equivalent resistance of this network of resistors, R_{eq}, is calculated using Kirchhoff's laws, as well as solving a set of equations. The conductivity of the layer is obtained using (Equation 2.1), where A is the area of the electrodes.

$$\sigma = \frac{t}{A\, R_{eq}} \qquad (2.1)$$

In calculating area A, it is assumed that the other dimension of the electrode has a thickness dR equal to the length of a resistor. That is, $A= n_y (dR)^2$.

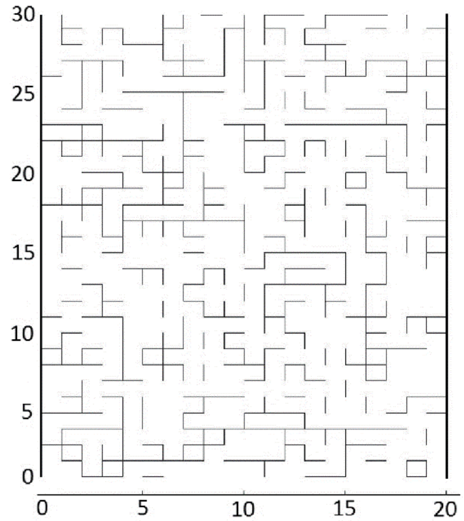

Figure 3. The network of resistors R_1 and R_2 for $n_x = 20$, and $n_y = 30$, and assuming $P(R_1) = 0.4$. Resistors R_1 are indicated by solid lines, and the empty spaces show resistors R_2. The figure shows no path of clusters of resistors R_1 connecting the two electrodes

3. Results and Discussion

3.1 *Parameters of the Resistor network model*

In this section, the effect of the parameters defined in the resistance network model is investigated. First, the ratio of the number of resistors R_1 to total network resistors is examined, which is indicated by $P(R_1)$. In Figure 4, the two modes are compared with $P(R_1) = 0.6$ and $P(R_1) = 0.7$. It is observed that in these cases, the conductivity difference between thin and thick layers is of the order of 10 ($\Omega^{-1}cm^{-1}$). In addition, the conductivity of the layers changes almost continuously in terms of thickness.

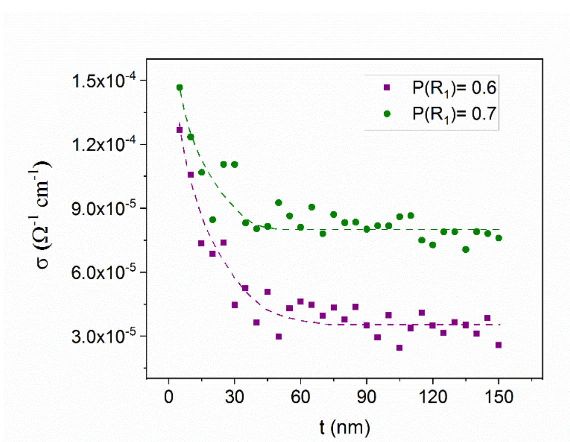

Figure 4. Conductivity of layers in terms of layer thickness. Two cases are compared with the probability of distribution $P(R_1) = 0.6$ and $P(R_1) = 0.7$. Other parameters used in this figure are $R_1=10^{10}\ \Omega$, $R_2=10^{15}\ \Omega$, and dR= 5nm. The dashed lines are a guide for the eyes.

The conductivity of the layers for the two modes $P(R_1) = 0.3$ and $P(R_1) = 0.4$ is shown in Figure 5. In this case, the probability of the presence of resistors R_1 in the network is almost halved compared to the conditions in Figure 4. In addition, the conductivity difference between thin and thick layers is of the order of 10^4 ($\Omega^{-1}cm^{-1}$). There is also a discontinuity in the conductivity diagram in terms of thickness related to the percolation threshold. From Figures 4 and 5, it is evident that the conductivity in thin films is thickness dependent and decreases with increasing thickness. In contrast, in thicker layers, the conductivity is constant and independent of the layer thickness.

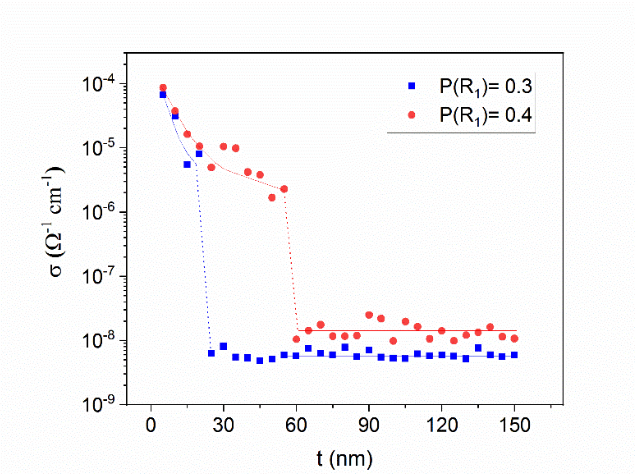

Figure 5. The conductivity of layers in terms of layer thickness. The two cases are compared with the probability of distribution $P(R_1) = 0.3$ and $P(R_1) = 0.4$. Other parameters used in this figure are $R_1=10^{10}\ \Omega$, $R_2=10^{15}\ \Omega$, and dR= 5nm. The lines are a guide for the eyes.

The conductivity changes in thickness for different values of resistor R_1 are shown in Figure 6. The conductivity of the layers is compared for three values: $R_1 = 10^9\ \Omega$, $R_1 = 10^{10}\ \Omega$, and $R_1 = 10^{11}\ \Omega$. As expected, as the resistance R_1 increases, the conductivity of the thin films decreases. It is also observed that the conductivity of thick layers is independent of the resistance R_1.

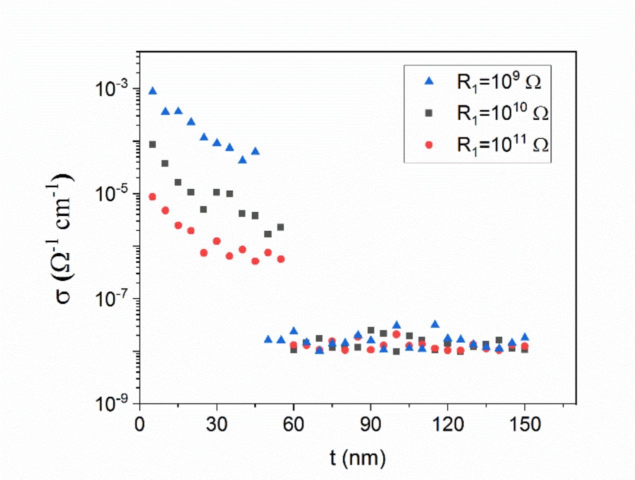

Figure 6. The effect of resistance R_1 on the layer conductivity of layers. Increasing the resistance R_1 reduces the conductivity in thin layers but does not affect the conductivity of thick layers. Other parameters used in this figure are $R_2=10^{15}\ \Omega$, dR= 5nm, and $P(R_1) = 0.4$

The effect of resistance R_2 on layer conductivity is shown in Figure 7. The change of R_2 does not affect the conductivity of thin layers whereas, with increasing resistance of R_2, the conductivity of thick layers decreases.

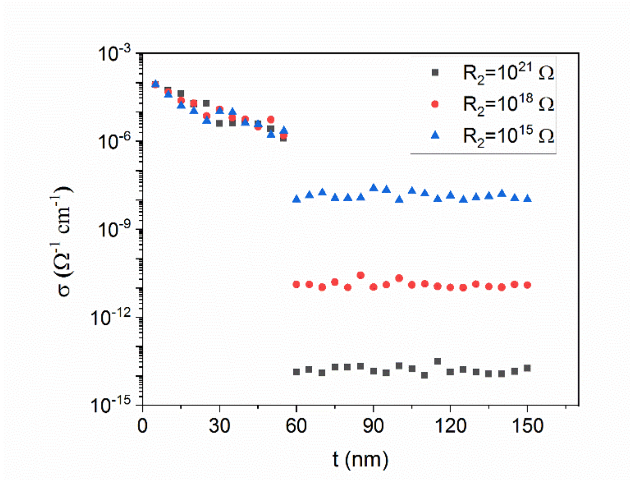

Figure 7. The effect of resistance R_2 on the conductivity of layers. Increasing the resistance R_2 reduces the conductivity in thick layers, but does not affect the conductivity of thin layers. Other parameters used in this figure are: $R_1=10^{10}\ \Omega$, dR=5nm, and $P(R_1) = 0.4$

The number of resistors in a direction parallel to the metal electrode is indicated by n_y. Three different values of n_y are compared in Figure 8. For $n_y = 20$, it is observed that the conductivity drop occurs in a layer with a thickness of 35 nm. In contrast, for $n_y = 30$ and $n_y = 40$, this happens later in a layer with a thickness of d = 60 nm. As expected, by reducing n_y, which is equivalent to shrinking the dimensions of the electrodes, at a given n_x, the probability that a continuous path of resistors R_1 will be found between the two electrodes decreases. As a result, the percolation threshold and consequently the conductivity drop occur in smaller n_x values. The larger n_y, the more suitable it is in terms of similarity to experimental conditions, in which the dimensions of the electrodes are large. Indeed this makes it necessary to solve larger matrices to obtain the equivalent resistance, which is a time-consuming task. A comparison of $n_y = 30$ and $n_y = 40$ conductivity charts shows that the conductivity drop occurs in layers of the same thickness. Therefore, according to these results, $n_y = 30$ seems to be a suitable choice for this model.

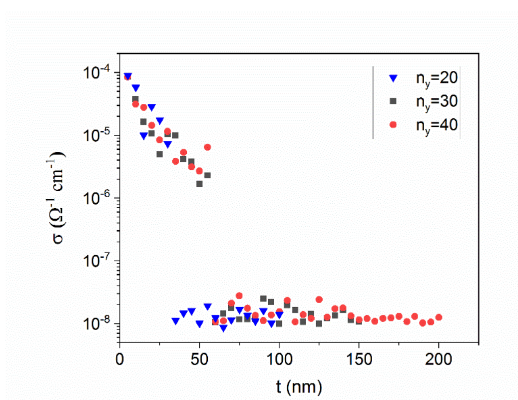

Figure 8. Investigation of the effect of n_y on the conductivity diagram. As n_y decreases, the conductivity drop for the thick layers occurs at a smaller thickness. Other parameters used in this figure are $R_1= 10^{10}\ \Omega$, $R_2= 10^{15}\ \Omega$, dR= 5nm, and $P(R_1) = 0.4$

Another parameter used in this model is dR, the length of each resistor. Changing this parameter only shifts the conductivity curve to the left or right. Therefore, the size of dR is selected according to the experimental results and fits the model. In this model, dR = 5nm is preferred.

3.2 *Comparison of experimental results with resistance network model*

The experimental results obtained from the measurement of ionic conductivity in thin films of lithium borate are reported by Schmitz et al. [4]. The simulation of these experimental results by the model discussed in this research is shown in Figure 9. The experimental data in this diagram correspond to $(Li_2O)_{0.2}(B_2O_3)_{0.8}$ thin films at 120 °C. The selected parameters for this model are $R_1 = 10^{11}\ \Omega$, $R_2 = 2\times10^{15}\ \Omega$, $P(R_1) = 0.4$, and dR= 5nm. The used the resistor size (dR) in this simulation is comparable to $\sqrt{\langle R^2\ (t_p)\rangle}$, which is a measure of the average length of the conduction pathways [10]. It can be seen that, by selecting these parameters, the conductivity of lithium borate thin films in very thin as well as thicker layers can be described with adequate accuracy by the resistor network model.

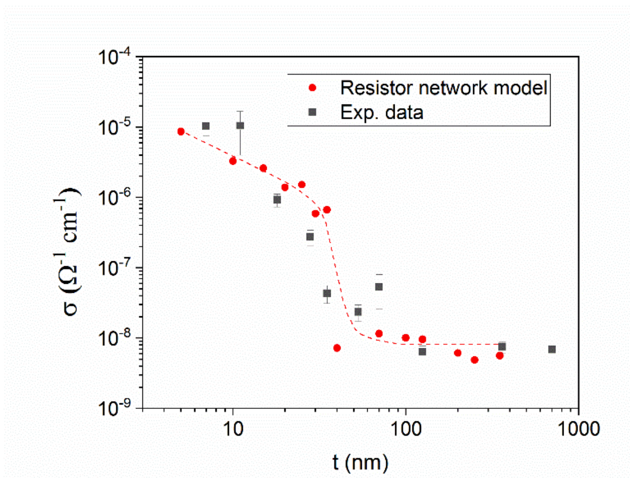

Figure 9. Description of ionic conductivity of lithium borate thin films, using the network model of electrical resistors. To fit the model with the experimental data, the parameters described in the text are used. The dashed line is a guide for the eyes.

4. Conclusions

Using a network of electrical resistors, changes in the conductivity of lithium borate thin films can be described. One of the important features of this model is the use of two different types of resistors in the network, which describe different ion pathways in lithium borate layers. In addition to the value of each resistor, the relative probability of their presence in the network is also one of the effective parameters in changing the conductivity of layers. By changing these parameters, the conductivity pathways and the percolation threshold change. Using the appropriate parameters, conductivity can be simulated in thin layers as well as in thicker layers of lithium borate.

Conflicts of Interest

The author declares that there are no conflicts of interest regarding this article.

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