

On the Power Law Behavior of the A.C. Conductivity in Li Ion Conducting Perovskites

Jean L. NDEUGUEU* and Masaru ANIYA

Department of Physics, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan

(Received November 8, 2009; accepted December 11, 2009)

For a wide range of crystalline and amorphous materials, in the low frequency regime, the a.c. conductivity spectra is described by the well known Jonscher's power law equation. Recently, it has been shown that although the pre-exponential factor of the power law equation A and the power law exponent n are sensitive to the composition of materials, the ratio $(\log A)/n$ does not depend either on the composition or on the temperature. In the present work, in order to verify the universality of such behaviors, the variations of the ratio $(\log A)/n$ with respect to the lithium content, and to the temperature have been studied for $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$. The results indicate that for both variables, the constancy of the ratio is not universal. By analyzing the composition dependence of the power law exponent based on the dimensionality of lithium ion transport pathways in the material, we have satisfactorily explained the behavior of the ratio $(\log A)/n$.

KEYWORDS: A.C. conductivity, power law behavior, Li ion conducting perovskites

1. Introduction

So far, research on materials as potential electrolytes in new generation of energy sources has been a subject of considerable interest since the pioneer work of Latie et al.¹⁾ who firstly paid attention to lithium ion conducting perovskites. All-solid-state lithium batteries with high ionic conductivity and good cycling life, ion-selective membranes, sensors, etc., constitute some potential technological applications²⁻⁷⁾. In the structure of perovskites (ABO_3), there are a substantial number of vacant A-sites through which lithium ions can move easily. The formation of structural vacancies in the crystalline sublattices and the equivalency of conduction sites are essential for reaching fast ionic conduction⁴⁻⁶⁾.

To date, the best lithium ion conducting electrolyte is the lanthanum lithium titanate perovskite (LLTO) of general formula $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$. This material has been found to exhibit lithium ion conductivity as high as $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at room temperature, and is stable at high temperatures. Furthermore, pure phases of LLTO have been found for a range of composition corresponding to $0.03 < x < 0.167$ by sintering the samples at high temperature ($\sim 1350^\circ\text{C}$)^{4,8-10)}.

Recently, we have investigated the role of the medium range structure in ion dynamics in some ion conducting glasses^{11,12)}. There, the relationship between the first sharp diffraction peak (FSDP) wave number Q and the fitting parameters of the a.c. conductivity, precisely the ratio $(\log A)/n$ has been studied. Here, A and n represent respectively, the pre-exponential factor and the power law exponent of Jonscher's law. By using the concept of bond fluctuation in superionic conductors proposed by one of the authors¹³⁾, we have concluded that the universal aspect of the power law reflects the universal pattern of the potential barrier at intermediate length scales¹⁴⁾. This work was conducted after that of Papathanassiou who studied the composition dependence of the ratio $(\log A)/n$ for the glassy system $[(\text{Li}_2\text{O})_x(\text{Na}_2\text{O})_{1-x}]_{0.3}(\text{B}_2\text{O}_3)_{0.7}$, with $n > 1$ ¹⁵⁾.

There the constancy of the ratio $(\log A)/n$ has been found whose origin was attributed to the mixed alkali effect in the a.c. conductivity. Meanwhile, based on previous work¹⁴⁾, we have shown that the constancy is not satisfied¹²⁾. On the other hand¹⁶⁾, Papathanassiou studied also a set of materials with different structure and suggested an empirical law that states that the temperature evolution of $\log A$ is proportional to the temperature evolution of n .

The aim of the present work is multiple: firstly, to reinforce, after previous work¹²⁾, the idea that the constancy of the ratio $(\log A)/n$ with respect to the composition is not universal; secondly, to verify if the empirical law proposed by Papathanassiou is applicable to all Jonscher-like materials. The choice of $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ perovskite is not hazardous insofar as, on the one hand, over the imperious need to understand the transport mechanism in fast lithium conducting perovskites, this class of materials has not been considered in the previous analyses^{15,16)}. On the other hand, the experimental data needed are available^{17,18)}.

2. Universality of the a.c. conduction

There is abundant experimental evidence showing almost identical characteristics in the a.c. conductivity for a wide range of materials such as ion conducting glasses and perovskites, amorphous and polycrystalline semiconductors, electron and ion conducting polymers, transition metal oxides, metal cluster compounds, organic-inorganic composites, etc.¹⁹⁻²⁴⁾. The a.c. conductivity has been modeled in the low-frequency regime (i.e. below 100 MHz) by Jonscher¹⁹⁾ as

$$\sigma(\omega) = \sigma(0) + A\omega^n. \quad (1)$$

$\sigma(0)$ is the d.c. conductivity corresponding to the frequency-independent part of $\sigma(\omega)$, n is the power law exponent ($0 \leq n \leq 1$), and A is the pre-exponential factor,

* Corresponding author, e-mail: ndeugueu@yahoo.fr

$$A = \omega_c^{-n} \sigma(0), \quad (2)$$

where ω_c represents the onset frequency of the dispersive behavior,

$$\omega_c = \omega_{ph} \exp(-E_a / k_B T), \quad (3)$$

where the typical value of atomic vibration in solids ω_{ph} is usually taken as $10^{12} \text{ rad}\cdot\text{s}^{-1}$. E_a is the activation energy for the crossover frequency which is almost equal to that of the ionic conductivity⁵⁾, k_B is the Boltzmann constant and T is the temperature. Almond et al.²⁵⁾ have suggested that the crossover frequency and the power law exponent provide information on the mobility and the Coulomb interaction between mobile ions, respectively. In the Jonscher regime, from eq. (2) we can deduce the expression of the ratio $(\log A)/n$,

$$(\log A)/n = (\log \sigma(0))/n - \log \omega_c. \quad (4)$$

3. Relationship between the power law exponent and the dimensionality of lithium ion transport pathways

The carrier species in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ is lithium, with Li^+ transport number almost unity¹⁷⁾. In Fig. 1, we can observe that at room temperature, the power law exponent decreases monotonically by increasing the lithium content. Numerical data are given in Table I together with other quantities which will be used in our analysis.

Table I. D.C. conductivity $\sigma(0)$, activation energy for the crossover frequency, E_a , and the power law exponent, n , for different compositions of $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ ^{17,18)} at room temperature.

x	$\sigma(0) (\text{S}\cdot\text{cm}^{-1})$	$E_a (\text{eV})$	n
0.025	4.14×10^{-6}	0.45	0.85
0.05	5.62×10^{-5}	0.41	0.75
0.06	7.58×10^{-5}	0.39	0.68
0.075	6.87×10^{-5}	0.39	0.63
1/12	4.58×10^{-5}	0.39	0.61
0.09	3.33×10^{-5}	0.39	0.57
0.1	1.00×10^{-5}	0.45	0.56
0.12	8.33×10^{-7}	0.51	0.51
0.15	2.08×10^{-8}	0.65	0.49
1/6	8.75×10^{-9}	0.73	0.46

It has been discussed that the behavior shown in Fig. 1 cannot be explained by considering only the Coulomb interaction between $\text{Li}^{+17)}$. For instance, according to the well-known jump relaxation model²⁶⁾ which takes into account the interaction between mobile ions (Li^+), the power law exponent is expressed by

$$n = \frac{\text{backhop rate}}{\text{site relaxation rate}}, \quad (5)$$

where the term backhop is the backward motion of a hopping ion to its initial site. This movement is due to the Coulomb repulsive interaction between mobile ions. The site relaxation is the shift of a site potential minimum to the position of the hopping ion, due to the rearrangement of neighboring ions. The diminution of the Coulomb interaction between mobile ions with the decrease of their concentration, would reduce the backhop rate leading to a decrease in n . This situation is contrary to the experimental results shown in Fig. 1. Many approaches have been developed to explain such behavior. Among these, the average valence of the A-site cation^{17,27)}, and the dimensionality of ion transport pathways^{3,28)}.

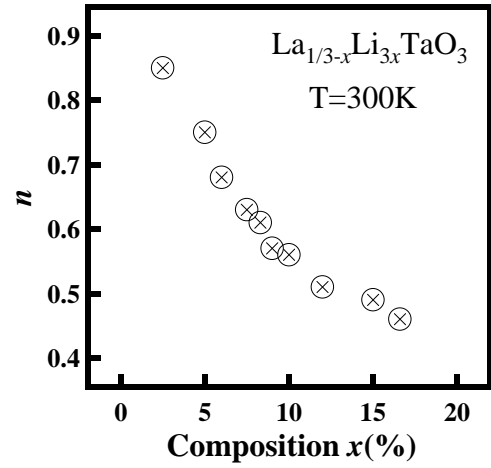


Fig. 1. Composition dependence of the power law exponent in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, at room temperature.

In our previous work¹⁴⁾, we have studied the effect of adding AgI salt on the glassy network AgPO_3 . There, it has been found that by increasing the amount of salt, the number of Ag^+ ions bonded to I^- and O^{2-} ions increase. This behavior leads to the increase of unstable ion sites which, due to the opening of many channels, results to an efficient ion transport over long distances. We have attributed the increase in the value of n with the increase of the salt concentration to the number of channels available for ion transport, i.e. to the dimensionality of ion transport pathways. This idea can be connected to that of Mazza et al.³⁾ and Inaguma et al.²⁸⁾ who have investigated the lithium ion conductivity in $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ based on the concept of bond valence sum (BVS) for Li^+ . They found that a value less than unity in BVS implies under-bond of Li and O, and lithium ions are much free to migrate through the bottleneck. On the other hand, a value higher than unity leads to a difficult migration through the bottleneck, due to electronic repulsion. Inaguma et al.²⁸⁾ found that by increasing the lithium content, from 0.16 to 0.35 (i.e. by decreasing the number of vacant A-sites through which lithium ions can move easily), the migration pathways for Li^+ change from two-dimensions to quasi-three-dimensions. In other words, the vacant sites available for the ion transport decrease with the increase in the lithium ion concentration. Therefore, the decrease in the value of n with the increase of lithium content deals with our predictions¹⁴⁾.

4. Variation of the ratio $(\log A)/n$

4.1 Composition dependence

The d.c. conductivity of ion conducting materials obeys the well-known Arrhenius relation

$$\sigma(0) = \sigma_0 \exp(-E_a / k_B T), \quad (6)$$

where the symbols have the usual meanings. The composition dependence of the ratio $(\log A)/n$ for $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ at room temperature is shown in Fig. 2. We can observe that by increasing the lithium content, the ratio decreases monotonically. This result contrasts with that behavior reported for the glassy system $[(\text{Li}_2\text{O})_x(\text{Na}_2\text{O})_{1-x}]_{0.3}(\text{B}_2\text{O}_3)_{0.7}$, with $n > 1$ ¹⁵⁾ which does not show a composition dependence.

As we can observe in Table I, the lithium ion conductivity reaches a maximum at $x = 0.06$ and decreases for further lithium concentrations. A similar behavior has been observed for lithium ion mobility. The increase of the mobility at lower concentrations has been attributed to the tetragonal distortion in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ ²⁸⁾. On the other hand, it has been found that the lithium ion conductivity is related to the lattice parameters of the perovskites^{28,29)}. For $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, a marked decrease in lattice parameters with the increase in lithium content has been observed. This behavior is due to the significant contraction of the bottleneck size for lithium ion transport with the decrease of the lithium ion mobility²⁸⁾.

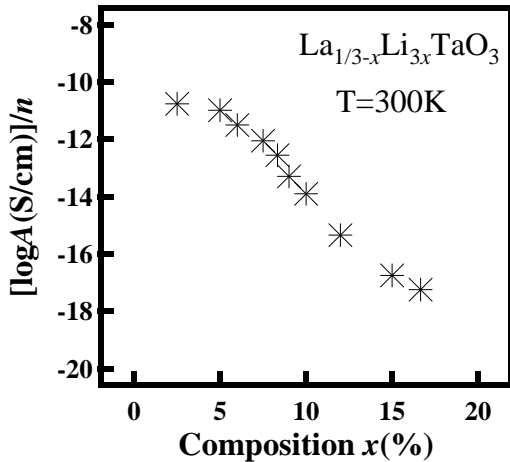


Fig. 2. Composition dependence of the ratio $(\log A)/n$ in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, at room temperature.

The behavior shown in Fig. 2 can be explained as follows. By increasing the concentration of Li^+ , the activation energy increases¹⁷⁾. This leads to the decrease of the crossover frequency under eq. (3). At the same time, as shown in Fig. 1, the power law exponent decreases, and the pre-exponential factor increases according to eqs. (2) and (3). These observations together with the negative values of $\log A$ will result to the decrease of the ratio $(\log A)/n$.

To our knowledge, no study either theoretical or experimental on the relationship between the structure and the dimensionality of lithium ion transport, and its composition dependence for $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ has been

published yet. However, some structural investigations of migration pathways of lithium ion transport in $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ have been carried out²⁸⁾. From such a study, Inaguma et al. found that the dimensionality increases with lithium content. Strengthened by such finding, we can evoke the idea that the dimensionality of lithium ion transport pathways plays a key role in the understanding of Li^+ dynamics in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$.

4.2 Temperature dependence

The temperature dependence of the ratio $(\log A)/n$ for $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ is shown in Fig. 3. We can observe that the ratio is nearly constant for lower concentrations of lithium ($x = 0.025$, and $x = 0.06$), i.e. the temperature evolution of $\log A$ is proportional to the temperature evolution of n , as suggested by Papathanassiou¹⁶⁾. By increasing the lithium content, this constancy disappears progressively and the ratio starts to decrease with the decrease in temperature. This behavior is probably due to the slightly decrease of the crossover frequency with the decrease in temperature.

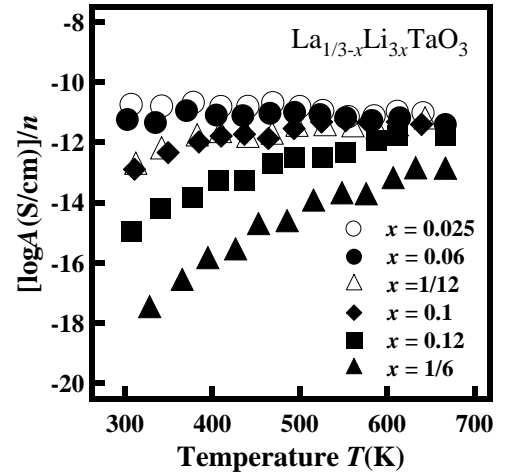


Fig. 3. Temperature dependence of the ratio $(\log A)/n$ in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$, for different compositions.

An interesting behavior is also observed in Fig. 3. Except for $x = 1/6$, the ratio $(\log A)/n$ approaches the same value of ~ -12 at higher temperatures, independently of the composition. A decade ago¹⁸⁾, it has been found that the lithium ion conductivity at room temperature in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ is mainly governed by the lithium ion mobility. Furthermore, the Arrhenius plot of the lithium ion conductivity has been found to exhibit a common value of $\sim 10 \text{ S}\cdot\text{cm}^{-1}\cdot\text{K}$ for all the compositions at higher temperatures ($\sim 666 \text{ K}$), except for $x = 1/6$ ¹⁸⁾. This result, which is roughly similar to that observed in Fig. 3 indicates that the correlation between lithium ions decreases as the temperature increases. In other words, the lithium ion transport phenomena in $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ become utterly temperature independent at higher temperatures. For $x = 1/6$, the deviation of the ratio $(\log A)/n$ to the common value of ~ -12 at higher temperatures is predominately due to the large value of the activation energy. It is valuable to note here that many works related to the a.c.

conductivity universality in a wide range of crystalline and amorphous materials have been carried out. However, to date works connecting the pre-exponential factor A and the power law exponent n with microscopic interpretation as shown here are not available in the literature.

5. Conclusion

The composition and temperature dependences of the conductivity dispersion in Li ion conducting perovskites $\text{La}_{1/3-x}\text{Li}_{3x}\text{TaO}_3$ have been studied. Concerning the composition dependence, it has been found that by increasing the lithium content, the ratio $(\log A)/n$ decreases. For the temperature dependence, it has been observed that the ratio is constant for lower concentrations of lithium. By increasing the lithium content, this constancy disappears progressively and the ratio starts to decrease with the decrease in temperature. The composition dependence of the power law exponent has been analyzed based on the dimensionality of lithium ion transport pathways in the material. By using information extracted from such analysis, we have satisfactorily explained the behavior of the ratio $(\log A)/n$.

Acknowledgment

This work was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 19560014). J.L.N. acknowledges for the MONBUKAGAKUSHO-Scholarship.

- 1) L. Latie, G. Villeneuve, D. Conte and G. L. Flem: *J. Solid State Chem.* **51** (1984) 293.
- 2) P. Birke and W. Weppner: *Electrochim. Acta* **42** (1997) 3375.
- 3) D. Mazza, S. Ronchetti, O. Bohnke, H. Duroy and J.L. Fourquet: *Solid State Ionics* **149** (2002) 81.
- 4) C. H. Chen and K. Amine: *Solid State Ionics* **144** (2001) 51.
- 5) K. Mizumoto and S. Hayashi: *Solid State Ionics* **127** (2000) 241.
- 6) A. G. Belous: *J. Eur. Ceram. Soc.* **21** (2001) 1797.
- 7) Y. Inaguma and M. Itoh: *Solid State Ionics* **86-88** (1996) 257.
- 8) A. G. Belous, G. N. Novitskaya, S. V. Polyanetskaya and Yu. I. Gornikov: *Inorg. Mater.* **23** (1987) 412.
- 9) Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta and M. Wakihara: *Solid State Commun.* **86** (1993) 689.
- 10) H. Kawai and J. Kuwano: *J. Electrochem. Soc.* **141** (1994) L78.
- 11) J. L. Ndeugueu and M. Aniya: In B.V.R. Chowdari et al. (eds.), *Solid State Ionics*, Macmillan, India, 2008, p. 401.
- 12) J. L. Ndeugueu and M. Aniya: *J. Mater. Sci.* **44** (2009) 2483.
- 13) M. Aniya: *J. Phys. Soc. Jpn.* **61** (1992) 4474.
- 14) M. Aniya: *J. Non-Cryst. Solids* **354** (2008) 365.
- 15) A. N. Papathanassiou: *Mater. Lett.* **59** (2005) 1634.
- 16) A. N. Papathanassiou: *J. Non-Cryst. Solids* **352** (2006) 5444.
- 17) K. Mizumoto and S. Hayashi: *Solid State Ionics* **127** (2000) 241.
- 18) K. Mizumoto and S. Hayashi: *J. Ceram. Soc. Jpn.* **106** (1998) 369.
- 19) A. K. Jonscher: *Nature* **267** (1977) 673.
- 20) A. R. Long: *Adv. Phys.* **31** (1982) 553.
- 21) S. R. Elliott: *Adv. Phys.* **36** (1987) 135.
- 22) H. Namikawa: *J. Non-Cryst. Solids* **18** (1975) 173.
- 23) B. K. Kuanr and G. P. Srivastava: *J. Appl. Phys.* **75** (1994) 6115.
- 24) J. C. Dyre and T. B. Schrøder: *Rev. Mod. Phys.* **72** (2000) 873.
- 25) D. P. Almond, C. C. Hunter and A.R. West: *J. Mater. Sci.* **19** (1984) 3236.
- 26) K. Funke: *Solid State Ionics* **94** (1997) 27.
- 27) C. León, M. L. Lucia, J. Santamaria, M. A. Paris, J. Sanz and A. Varez: *Phys. Rev. B* **54** (1996) 184.
- 28) Y. Inaguma, T. Katsumata, M. Itoh, Y. Morii and T. Tsurui: *Solid State Ionics* **177** (2006) 3037.
- 29) M. Itoh, Y. Inaguma, W. H. Jung, L. Chen and T. Nakamura: *Solid State Ionics* **70-71** (1994) 203.