Correlation between ion hopping conductivity and near constant loss in ionic conductors

C. León,[1] K. L. Ngai,[2] and A. Rivera[1]

[1]*GFMC, Departamento de Fisica Aplicada III, Universidad Complutense Madrid, 28040 Madrid, Spain*
[2]*Naval Research Laboratory, Washington, DC 20375-5320, USA*

For ionic conductivity relaxation in ionically conducting materials we predict in the framework of the coupling model that the magnitude of the ubiquitous near constant loss correlates with the activation energy E_a for independent ion hopping. Using experimental data of a variety of ionic conductors, this correlation has been borne out. The model also explains the observed correlation between the magnitude of the near constant loss and the value of the dc conductivity at room temperature, as well as the temperature dependence for the near constant loss.

Due to their technological importance in state-of-the-art batteries, sensors, and other devices, there is an increasing research activity on ion-conducting materials during last decades.[1,2] The challenge is to clarify the mechanism that limits the mobility of ions and consequently break new grounds for practical applications. Therefore, efforts have been focused on the dynamics of ionic hopping transport at low frequencies and near room temperature.[3,4] Only recently, the ac conductivity of ionic conductors at high frequencies and low temperatures has attracted the attention of workers in the field.[5–8] A ubiquitous nearly linear frequency dependent term $\sigma'(\omega) \approx A\varepsilon_o \omega^{1-\alpha}$ with α almost zero and ε_o the permittivity of a vacuum, becomes the dominant contribution in the ac conductivity at sufficiently high frequencies or low enough temperatures. This term is equivalent to a nearly frequency independent dielectric loss,

$$\varepsilon''(\omega) = \sigma'(\omega)/\varepsilon_o \omega \approx A\omega^{-\alpha}, \tag{1}$$

and naturally this contribution is known as the near constant loss (NCL).[9] The properties of the NCL are lesser known compared with the dc conductivity at room temperature in ionic conductors, and, at present there is an ongoing debate on the origin of the NCL.[8,10,11] On the other hand, it was pointed out that superionic conductors, characterized by their exceptional high dc conductivity at room temperature, show also the highest values of the near constant loss at low temperatures.[9] We show in this work that there exists a strong correlation, for a variety of ionic conductors, between the magnitude of the NCL observed at low temperatures and the dc conductivity and its activation energy at room-temperature. Therefore, understanding the origin of the NCL also may help to improve the understanding of the dynamics of ionic conductivity and the factors limiting the room-temperature dc conductivity in ionic conductors.[12]

The NCL appears at higher frequencies than the ion hopping ac conductivity, $\sigma'_{hop}(\omega)$. The latter is assumed by some workers to be represented by the Jonscher expression[13]

$$\sigma^*_{hop}(\omega) = \sigma_o[1 + (j\omega/\omega_p)^{n_J}], \tag{2}$$

where n_J is a fractional exponent, σ_0 is the dc conductivity, and ω_p a characteristic relaxation frequency. Both σ_0 and ω_p are found to be thermally activated with about the same ac-

tivation energy E_σ. Alternatively, in terms of the electric modulus,[14] the ion hopping ac conductivity is also well described by the one-sided Fourier transform,

$$M^*(\omega) = \frac{j\omega\varepsilon_o}{\sigma^*_{hop}(\omega)} = M' + jM''$$

$$= M_\infty \left[1 - \int_0^\infty dt \exp(-j\omega t)(-d\Phi/dt) \right], \tag{3}$$

of the time derivative of a stretched exponential function $\Phi(t) = \exp[-(t/\tau)^{1-n}]$ with $\tau \approx \omega_p^{-1}$. Experimental evidences indicate that the stretched exponential time dependence is caused by ion-ion correlation,[15] and therefore $\sigma'_{hop}(\omega)$ is a cooperative ion hopping contribution.

On the other hand, experimental facts point to a different origin for the NCL.[9] It has been proposed that a distribution of asymmetric double-well potentials attributed to the motion of groups of ions[7] can give rise to a NCL. There are also different theoretical models[16,17] that propose no formal separation between the Jonscher term and the NCL. Recently, we have given a description of the evolution of ion dynamics with time[18] based on the coupling model (CM) for ionic conductors.[19] The NCL is identified with the dynamics of ions in the short-time regime when the probability of independent hop of the ions out of their potential wells is small,[18] and all ions essentially are still caged. This work presents experimental evidence in support of this origin of the NCL. First we derive from our model of NCL an expression for the temperature dependence of its magnitude. From this expression, a reciprocal correlation is expected between the magnitude of the NCL and the activation energy of independent ion hop given by the CM, which is confirmed by experimental data of a variety of ionic conductors. A correlation is also shown to hold between the magnitude of the NCL and the dc conductivity activation energy. Finally, the explicit temperature dependence of the NCL derived from the model is also found to describe well the experimental data.

In previous applications of the coupling model[19] for ionic conductors, we considered that all the mobile ions are ready to independently hop to neighboring sites with a relaxation rate τ_0^{-1} except that interactions and correlations make all

the attempting ions' success impossible. On the average the result is a slowed-down cooperative motion of all the ions with heterogeneous dynamics. The correlation function at short times is the linear exponential $\Phi(t)=\exp(-t/\tau_o)$ for independent hops, and changed after $t=t_c$ to the stretched exponential function $\Phi(t)=\exp[-(t/\tau)^{1-n}]$ which accounts for the average of the heterogeneous slowed down motions of the ions. The relation between τ and τ_0 is given by

$$\tau=[t_c^{-n}\tau_o]^{1/(1-n)}, \tag{4}$$

where $t_c \approx 2$ ps has been determined previously from experiments.[8,20,21] For vibrating ions to come out by thermal activation over an energy barrier E_a, the independent relaxation time is given by $\tau_o(T)=\tau_\infty\exp(E_a/kT)$. The reciprocal of τ_∞ is the vibration angular frequency of the ion.[20] It follows from Eq. (4) that

$$E_a=(1-n)E_\sigma. \tag{5}$$

As an extension of the CM, it has been recently shown[18,22] that the NCL originates during the time regime where most ions remain caged and independent hops are rare events. Molecular dynamics simulations in this time regime show that the mean-square displacement of ions, $\langle r^2(t)\rangle$, increases very slowly with time and in fact there are negligible independent hops from the van Hove function.[22] At sufficiently short times/low temperatures, few ions have succeeded to move away from their original sites, although the number increases with time albeit very slowly. A NCL then originates from very slow decay of the correlation function of the cage with time, which ultimately is due to those few ions that have succeeded to hop out of their cages to neighboring sites over decades of time in this short-time regime. In general, the cage or the potential well that confines a mobile ion is determined by the matrix atoms and the other mobile ions. This fact is evident from the form of typical potentials used in molecular-dynamics simulations.[22] The cage is not permanent and it changes or decays because of at least two reasons. First, the spatial relation with the immobile matrix atoms can change with time as suggested by the broadening of the first peak of the van Hove function with time.[22] Second, other ions may be leaving their cages and the probability of them doing so increases with time as can be seen from the development of intensity at neighboring initially vacant sites of the van Hove function with time. If the cage decay is a sufficiently slow function of time, the corresponding increase of $\langle r^2(t)\rangle$ is also very slow. Such a slow increase of $\langle r^2(t)\rangle$ with time is equivalent to a NCL if the particle is charged like ions in ionic conductors, and the quantity measured is dielectric loss due to conductivity relaxation. This result can be seen from the following approximate (neglecting cross correlations and that the Haven ratio is not unity) relation between mean-square displacement and complex conductivity:

$$\sigma^*(\omega)=-\omega^2\frac{Nq^2}{6kT}\int_0^\infty\langle r^2(t)\rangle e^{-j\omega t}dt, \tag{6}$$

where N is the density of mobile ions, q the ion charge, and k the Boltzmann constant. For a slowly varying mean-square displacement of the form $\langle r^2(t)\rangle\propto t^\alpha$ with α small, Eq. (6) gives $\sigma'(\omega)\propto\omega^{1-\alpha}$ and $\varepsilon''(\omega)\propto\omega^{-\alpha}$ or the NCL. In the limiting case of a logarithmic time dependence, $\langle r^2(t)\rangle\propto\ln t$, the dielectric loss $\varepsilon''(\omega)$ would be frequency independent.

Since there are very few ionic jumps, no cooperative dynamics are involved. At sufficiently short times, when most of the ions are still being caged, the successful jumps out of the cages are independent of each other because there are very few such events and therefore no cooperative dynamics are involved. The independent ion jump has rate τ_o^{-1}. At times much shorter than τ_o, successful hops of ions out of their cages are rare and few in between. Hence the decay of the cages or the increase of $\langle r^2(t)\rangle$ with time has to be very slow, resulting in the NCL. Naturally the NCL defined as such is a very slow relaxation process and can exist in the time regime $t\ll\tau_0$ where the increase of the number of successful hops of ions out of their cages over decades of time is insignificant. The NCL terminates at some time t_{x1}, when afterwards the successive independent ion hops have become more significant and lead to a more rapid increase of $\langle r^2(t)\rangle$ with time beyond t_{x1}, which can no longer justify the NCL to continue. Still t_{x1} has to be much smaller than τ_o because τ_o is the characteristic time for the ions to leave their cages. Therefore, only at times much shorter than τ_0 will ionic jumps be rare events, the increase of $\langle r^2(t)\rangle$ with time very slow, and resulting in the NCL. This in fact has been recently shown to be the case in several ionic conductors[18] by experimental data obtained over broad frequency ranges that allow t_{x1} and τ_0 to be determined. Thus, NCL exists in the short-time regime, $t_{on}<t<t_{x1}\ll\tau_0$, where t_{on} is the onset time of the NCL. Experimental data extending to very high frequencies show that the NCL continues to exist up to about 10^{11} Hz, from which we deduce that t_{on} is of the order in between 10^{-11} and 10^{-12} s. The probability of an ion to have jumped out of its cage at time t_{x1}, given by $[1-\exp(-t_{x1}/\tau_0)]$, is small. It has the same value for all temperatures as required by the same convention used to determine that the NCL terminates at t_{x1}. Hence t_{x1} has the same temperature dependence as τ_0, i.e., $t_{x1}(T)=t_\infty\exp(E_a/kT)$, a result supported by experimental data.[8]

We can now derive an explicit expression for the magnitude of the NCL. Again from the definition of t_{x1}, the mean-square displacement $\langle r^2(t_{x1})\rangle_{NCL}$ corresponding to the NCL regime increases by the same small amount in the period $t_{on}<t<t_{x1}(T)$ at all temperatures, i.e., $\langle r^2(t_{x1})\rangle_{NCL}\approx K[\ln_e(t_{x1})-\ln_e(t_{on})]$ is temperature independent. However, because t_{x1} is thermally activated, this same increase of $\langle r^2(t_{x1})\rangle_{NCL}$ is spread over a number of decades of time given by $[\ln_e(t_{x1})-\ln_e(t_{on})]/2.303$. Therefore, the factor K in the expression for the mean-square displacement $\langle r^2(t_{x1})\rangle_{NCL}$ is inversely proportional to $\ln_e(t_{x1}/t_{on})$. From this and Eq. (6), we deduce that the intensity of the NCL measured by A in Eq. (1) is inversely proportional to $(1/T)\ln_e(t_{x1}/t_{on})$ and then given by the proportionality relation
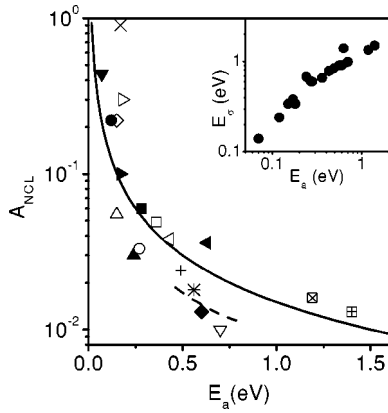
FIG. 1. A remarkable correlation is observed when plotting the magnitudes A of the NCL at $T = 100$ K vs the activation energy E_a for a variety of ionic conductors. The reference from which the experimental data are taken is given in Table I. Li_2O-$3B_2O_3$ ($+$), Na_2O-$3B_2O_3$ ($*$), K_2O-$3B_2O_3$ ($\blacklozenge$), Rb_2O-$3B_2O_3$ (∇), $LiPO_3$ ($\blacktriangle$), $35Li_2O$-$61SiO_2$-$3Al_2O_3$-P_2O_5 ($\bigcirc$), $Li_{0.18}La_{0.61}TiO_3$ ($\times$), $(ZrO_2)_{0.84}(Y_2O_3)_{0.16}$ ($\blacktriangleleft$), Na_2O-$3SiO_2$ ($\square$), $(AgI)_{0.3}$-$(AgPO_3)_{0.7}$ ($\triangleright$), $(AgI_2)_{0.48}$-$(Ag_2SeO_4)_{0.52}$ ($\diamondsuit$), Na-βAl_2O_3 ($\blacktriangledown$), $(Li_2S)_{0.56}$-$(SiS_2)_{0.44}$ ($\blacktriangleright$), $(Ag_2S)_{0.5}$-$(GeS_2)_{0.5}$ ($\triangle$), Ag_7GeSe_5I ($\bullet$), $(LiF)_{0.8}[Al(PO_3)_3]_{0.2}$ ($\blacksquare$), xK_2O-$(1-x)GeO_2$ ($x = 0.2$) at $T = 381$ K ($\triangleleft$), xK_2O-$(1-x)GeO_2$ ($x = 0.02$) at $T = 367$ K ($\boxtimes$), xK_2O-$(1-x)GeO_2$ ($x = 0.0023$) at $T = 374$ K ($\boxplus$). Solid line represents an inversely proportional relation as derived from the model for the NCL [see Eq. (7) in the text]. Dashed line represents a fit to Eq. (7) for the family of alkali triborate glasses. The inset shows that the smaller the value of E_a, the smaller the activation energy E_σ for the dc conductivity for the set of ionic conductors shown in the main panel.

$$A \propto \frac{1}{E_a}[1-(T/T_0)]^{-1} \qquad (7)$$

with $T_o = E_a/k \ln_e(t_{on}/t_\infty)$.

Equation (7) predicts then an approximate reciprocal correlation between the magnitude A of the NCL and the activation energy E_a for independent ion hopping. Figure 1 shows the remarkable agreement between experimental data for a variety of ionic conductors and the reciprocal correlation predicted by the model. The solid line in the figure represents an exact inversely proportional relation. It is indeed noteworthy that such a correlation holds considering there are other factors which affect the magnitude of the NCL [see Eq. (6)] and have not been taken into consideration in Fig. 1. In fact, the different ion jump distances and the different densities of mobile ions of the different ionically conducting materials might be responsible for the deviations observed from a perfect correlation. The question arises if the correlation still holds when considering the activation energy E_σ for the dc conductivity instead of E_a. It has been shown in the past,[3,23] for different families of ionic conductors, that smaller activation energy E_a corresponds to smaller E_σ. This correlation is shown in the inset of Fig. 1 for the ionic conductors considered in this work. From this empirical relation between E_a and E_σ, and the correlation that holds between A and E_a, we expect also a correlation between A and E_σ. The magnitude A of the NCL is plotted in Fig. 2
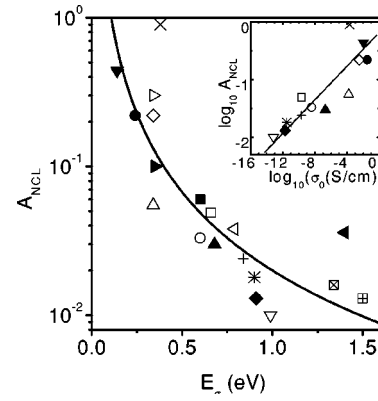

FIG. 2. Main figure shows the correlation between the magnitude A of the NCL at $T = 100$ K and the activation energy E_σ of the dc conductivity. Symbols are the same used in Fig. 1. References from which the experimental data are taken are given in Table I. The inset shows same NCL data vs the dc conductivity at room temperature. Lines are guides for the eye.

versus the activation energy E_σ of the dc conductivity, showing that a strong correlation indeed exists between both magnitudes. This correlation is noteworthy because completely different time and spatial scales are involved in dc conductivity and the NCL. While the dc conductivity is related to charge transport over long range at long times, the NCL observed at high frequencies in the ac conductivity originates from motion while the ions are still caged. The inset shows a correlation is also observed between A and the logarithm of the dc conductivities σ_o at room temperature. Since $\sigma_o(T) = \sigma_\infty \exp(-E_\sigma/kT)$, and the prefactor σ_∞ takes not too different values in all ionic conductors, the rule that higher the E_σ smaller the dc conductivity at room temperature is usually obeyed. Therefore, the correlation observed between A and the dc conductivities at room temperature can be considered simply to follow from the correlation between A and E_a deduced from Eq. (7).
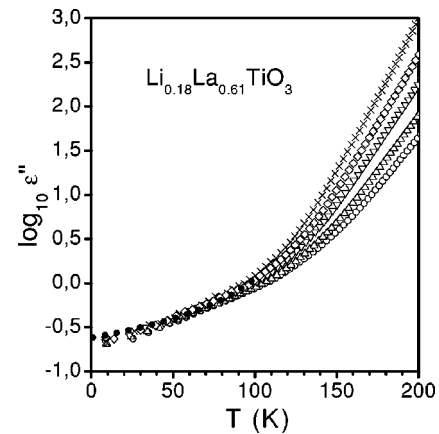

FIG. 3. Temperature dependence of the dielectric loss $\varepsilon''(\omega)$ at fixed frequencies for $Li_{0.18}La_{0.61}TiO_3$. Experimental data are shown for different frequencies [300 Hz ($\times$), 1 kHz ($\diamondsuit$), 3 kHz (∇), 10 kHz ($\triangle$) and 30 kHz ($\bigcirc$)]. At low temperatures, data are almost frequency independent, $\varepsilon''(\omega) \approx A$, showing a NCL behavior. Solid circles are a fit to Eq. (7) (see text).

TABLE I. Activation energies $E_a = (1-n)E_\sigma$ for the ionic conductors shown in Fig. 1 E_σ and $(1-n)$ were obtained from electrical conductivity measurements at temperatures where ionic hopping is the dominant contribution to the ac conductivity [see Eqs. (2) and (3)].

	E_a (eV)	$(1-n)$	E_σ (eV)	References
$Li_2O\text{-}3B_2O_3$	0.49	0.58	0.84	24,25
$Na_2O\text{-}3B_2O_3$	0.56	0.62	0.90	24,25
$K_2O\text{-}3B_2O_3$	0.60	0.66	0.91	24,25
$Rb_2O\text{-}3B_2O_3$	0.70	0.71	0.99	24,25
$LiPO_3$	0.24	0.35	0.68	26
$35Li_2O\text{-}61SiO_2 - 3Al_2O_3\text{-}P_2O_5$	0.27	0.45	0.60	8,27
$Li_{0.18}La_{0.61}TiO_3$	0.17	0.45	0.38	8
$(ZrO_2)_{0.84}(Y_2O_3)_{0.16}$	0.63	0.54	1.40	9,20
$Na_2O\text{-}3SiO_2$	0.36	0.55	0.66	9,28
$(AgI)_{0.3}\text{-}(AgPO_3)_{0.7}$	0.18	0.54	0.34	9
$(AgI_2)_{0.48}\text{-}(Ag_2SeO_4)_{0.52}$	0.15	0.45	0.34	9
$Na\text{-}\beta Al_2O_3$	0.07	0.5	0.14	9
$(Li_2S)_{0.56}\text{-}(SiS_2)_{0.44}$	0.17	0.48	0.35	9
$(Ag_2S)_{0.5}\text{-}(GeS_2)_{0.5}$	0.15	0.45	0.34	18
Ag_7GeSe_5I	0.12	0.48	0.24	18,29
$(LiF)_{0.8}\text{-}[Al(PO_3)_3]_{0.2}$	0.26	0.44	0.60	18
$xK_2O\text{-}(1-x)GeO_2$ $(x=0.2)$	0.43	0.54	0.79	7
$xK_2O\text{-}(1-x)GeO_2$ $(x=0.02)$	1.19	0.89	1.34	7
$xK_2O\text{-}(1-x)GeO_2$ $(x=0.0023)$	1.40	0.93	1.50	7

The systematic decrease of the NCL observed in the family of alkali triborate glasses when changing the alkali ion from lithium to rubidium had been reported as a mass dependence of the NCL.[24] From the present perspective, such a decrease in the NCL when increasing the mass of the alkali ion follows as a consequence of the more basic correlation between A and E_a, and arises from the increase of E_a when increasing the mass of the alkali ion in the alkali triborate glasses. This predicted correlation between A and E_a is approximately verified in the family of the alkali triborate glasses as shown by the dashed line in Fig. 1.

Finally, by inspection of Eq. (7), it is easy to see that the commonly observed weak temperature dependence of the NCL is also captured by our interpretation of the origin of the NCL. As an example, the temperature dependence of the NCL of the crystalline ionic conductor $Li_{0.18}La_{0.61}TiO_3$ is shown in Fig. 3 in the temperature range from 200 K down to 8 K. It can be observed that, at low temperatures, experimental data show a genuine NCL behavior, $\varepsilon''(\omega) \approx A$. The NCL in $Li_{0.18}La_{0.61}TiO_3$, like in most ionic conductors,[9] shows a weak temperature dependence which can be approximately described by $A \propto \exp(bT)$. It is worthwhile to emphasize that no previous consideration of the NCL by others has explained such temperature dependence. Solid circles in Fig. 3 are a fit to Eq. (7). The activation energy E_a was fixed at the value calculated by $E_a = (1-n)E_\sigma = 0.17$ eV (see Table I) from conductivity measurements at higher temperatures, where ionic hopping is the dominant contribution to the ac conductivity. The fit to Eq. (7), deduced from the coupling model, describes accurately the temperature dependence of the NCL observed in experimental data.

In summary, we have theoretically predicted a correlation between the magnitude A of the NCL and the activation energy E_a of independent hops from the coupling model. This correlation is confirmed by experimental data of a variety of ionic conductors. We have also shown from experimental data that A also correlates with the activation energy E_σ of the dc conductivity, which can be explained readily as a consequence of the predicted correlation of A with E_a. In addition, the model predicts explicit temperature dependence for the NCL, which is shown to be in good agreement with the weak temperature dependence of experimental data. Our results give thus additional support to the idea that the NCL originates from the slow decay of the cages during the time regime while most of the ions remain caged and independent jumps are rare events. Nonetheless, we point out that there are also other different contributions that can give rise to NCL[7] and may be relevant in data obtained under different conditions (especially at lower temperatures) than that for the data considered in this work.

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