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Article in *EPL (Europhysics Letters)* · January 2007

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Effects of reduced dimensionality in the relaxation dynamics of ionic conductors

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received 2 November 2004; accepted in final form 3 January 2005

published online 4 February 2005

PACS. 66.30.Hs – Self-diffusion and ionic conduction in nonmetals.

PACS. 66.10.Ed – Ionic conduction.

Abstract. – We report on the dispersive ionic conductivity in $\text{Li}_{0.5-x}\text{Na}_x\text{La}_{0.5}\text{TiO}_3$ ($0 \leq x \leq 0.5$), where the number of available positions for the mobile Li ions is reduced by introducing immobile Na ions. At high frequency the conductivity is power law dependent with an exponent which increases as the number of accessible neighboring sites decreases. This result is quantitatively accounted for in terms of a one-parameter statistical microscopic model. We provide experimental and theoretical evidence for the importance of reduced dimensionality resulting from the blocked pathways in slowing down the dynamics of diffusing ions.

Understanding the dynamics of mobile ions in ionic conducting materials has been the focus of increasing research effort in recent years, mostly driven by the applications of these materials in fuel cells, batteries, and other solid-state devices [1]. Aside from its fundamental interest, this knowledge could be a key factor in the design of new materials with improved properties for specific applications. Ion dynamics can be accessed experimentally by measuring the system response to a particular excitation (electric field, mechanical stress, or nuclear magnetization, to name a few). In particular, electrical conductivity measurements are widely used to obtain the electric-field relaxation function in the time domain. It is well known that the asymptotic behavior of the response function at short times follows power laws of the form t^{-n} and then results in a dispersive conductivity depending on frequency as ω^n [2]. However, a microscopic theory of ion diffusion is lacking and there is not general agreement on the origin of this behavior. There is also no conclusive experimental evidence on how the structure itself, structural disorder and immobile counterions, or the dimensionality of the underlying network for ion diffusion may affect the value of n . We examine here the latter

issue by an experiment in which we consistently limit the number of available positions for the mobile ions in an ionic conductor while keeping the structure unaltered. We find the exponent n to increase systematically as the number of accessible sites decreases. This result is quantitatively accounted for in terms of a statistical microscopic model which considers the dimensionality of the effective diffusion pathways. We provide a consistent evidence for the importance of reduced dimensionality resulting of the blocked pathways at microscopic level in the slowing-down of relaxation dynamics in the case of ionic conductors [3].

The frequency dependence of the ionic conductivity can be usually well fitted by Jonscher's expression [4]

$$\sigma^*(\omega) = \sigma_0 [1 + (j\omega/\omega_p)^n], \quad (1)$$

σ_0 being the dc conductivity, ω_p a characteristic relaxation frequency, and n a fractional exponent. Both σ_0 and ω_p are thermally activated with about the same activation energy, indicating that the dispersive conductivity, $\sigma^*(\omega)$, originates from migration of hopping ions. Alternatively [5], electrical relaxation data can be described in terms of the electric modulus, $M^*(\omega)$, which is directly related to the conductivity through

$$M^*(\omega) = \frac{j\omega\varepsilon_0}{\sigma^*(\omega)}, \quad (2)$$

with ε_0 the permittivity of a vacuum. The electric modulus is related to the electric-field relaxation function in the time domain, $\Phi(t)$, by

$$M^*(\omega) = M_\infty \left[1 - \int_0^\infty dt e^{-i\omega t} \left(-\frac{d\Phi}{dt} \right) \right], \quad (3)$$

where M_∞ stands for the inverse of the dielectric permittivity at high frequency, and it is found [6] that ion dynamics is well described by the Kohlrausch-Williams-Watts (KWW) relaxation function [7]

$$\Phi(t) = \exp \left[-(t/\tau)^{1-n} \right]. \quad (4)$$

Such a time dependence gives an asymptotic power law dependence of the form t^{-n} at short times for the response function $\phi(t) = -d\Phi/dt$. Correspondingly, the imaginary part of the electric modulus, $M''(\omega)$, shows a relaxation peak at $\omega\tau \approx 1$ characteristic of the susceptibility function for the electric-field relaxation process, *i.e.* the Laplace transform of the response function $\phi(t)$. The fractional exponent n defines also the power law dependence of $M''(\omega)$ above the peak frequency as ω^{n-1} . The correlation between the value of n and the activation energy of the dc conductivity is well known [8]. This correlation results in ionic conductors characterized by higher values of n showing generally lower values of the dc conductivity at room temperature. Hence the importance of understanding the factors that determine the value of the exponent n which characterizes ion dynamics at short times.

In order to investigate the influence of immobile counterions on the conduction network in ion dynamics we have performed electrical relaxation measurements in the series $\text{Li}_{0.5-x}\text{Na}_x\text{La}_{0.5}\text{TiO}_3$ ($0 \leq x \leq 0.5$). It has been shown previously that Li ions are able to hop through the disordered distribution of vacant sites in the perovskite structure, while Na and La ions remain immobile in the A sites [9]. Consequently, while $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ is a superionic conductor with σ_0 as high as 10^{-3} S/cm at 300 K [10], $\text{Na}_{0.5}\text{La}_{0.5}\text{TiO}_3$ shows an insulating behavior with σ_0 lower than 10^{-10} S/cm at the same temperature [11]. Neutron diffraction studies have shown that changing the relative Na/Li concentration does not produce changes in the symmetry group ($R\bar{3}c$) not even in the lattice parameters, which remain unaltered

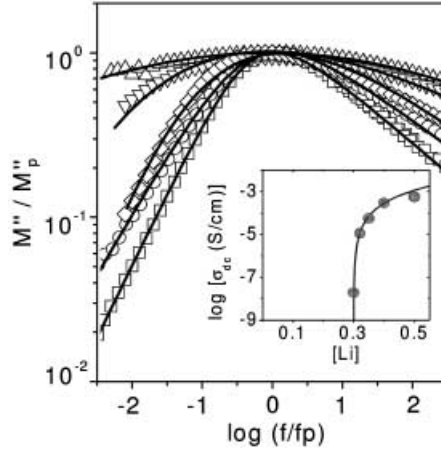


Fig. 1 – Frequency dependence of the imaginary part of the electric modulus for $\text{Li}_{0.5-x}\text{Na}_x\text{La}_{0.5}\text{TiO}_3$ samples with $x = 0$ (\square), $x = 0.1$ (\circ), $x = 0.15$ (\diamond), $x = 0.18$ (∇) and $x = 0.2$ (\triangle). Solid lines are fits using the proposed model from which values of the effective dimension d of the diffusion network are obtained (see table I). Note that data sets have been normalized for better comparison. The inset shows the dc conductivity at 300 K as a function of lithium content of the samples $[\text{Li}] = 0.5 - x$.

within 1 percent, showing that no cation or vacancy ordering is induced upon Na substitution. Thus, Na, Li and La remain randomly distributed in a cubic perovskite structure for the $\text{Li}_{0.5-x}\text{Na}_x\text{La}_{0.5}\text{TiO}_3$ ($0 \leq x \leq 0.5$) solid solution. The dc conductivity σ_0 shows a sharp decrease above $x \approx 0.2$ (see inset of fig. 1) as a result of the percolative blocking of the conduction network [9]. While Li ions move easily in a cubic three-dimensional network when $x = 0$, increasing the concentration of Na ions blocks conduction pathways and hence the dimensionality of the effective network for Li diffusion is reduced towards a one-dimensional ionic transport near the percolation threshold at $x = 0.2$. For $x > 0.2$, Li ions are limited to finite clusters and samples no longer exhibit long-range ionic conductivity. It is important to remark that this reduction of the conductivity is not a consequence of the mixed alkali effect observed in glassy materials when two different *mobile* species simultaneously contribute to the conductivity [12, 13].

Samples of the $\text{Li}_{0.5-x}\text{Na}_x\text{La}_{0.5}\text{TiO}_3$ series were prepared by a ceramic method. Details about sample preparation and structure characterization by X-ray and neutron diffraction can be found elsewhere [9]. Samples for electrical measurements were cylindrical pellets with evaporated Ag contacts on both sides. Electrical conductivity measurements in the frequency range 20 Hz–30 MHz (HP 4284A and HP 4285A LCR meters) have been performed to investigate the electric-field relaxation.

Figure 1 shows the imaginary part of the electric modulus for five different samples with $x = 0$, $x = 0.1$, $x = 0.15$, $x = 0.18$ and $x = 0.2$. The real part of the conductivity is shown in fig. 2 for samples with $x = 0$ (a) and $x = 0.2$ (b). Note the different slopes in the log-log plot of the conductivity spectra and also at the high-frequency side of the modulus peaks, which define the exponent n characterizing Li dynamics. For the sample without Na ions, where Li ions move through a three-dimensional network, we find $n = 0.60 \pm 0.01$. Interestingly, for the sample with $x = 0.2$, in the limiting one-dimensional effective diffusion network at the percolation threshold, we obtain that $n = 0.81 \pm 0.01$. For Na concentrations in between ($0 < x < 0.2$) we find that the exponent n systematically increases upon increasing

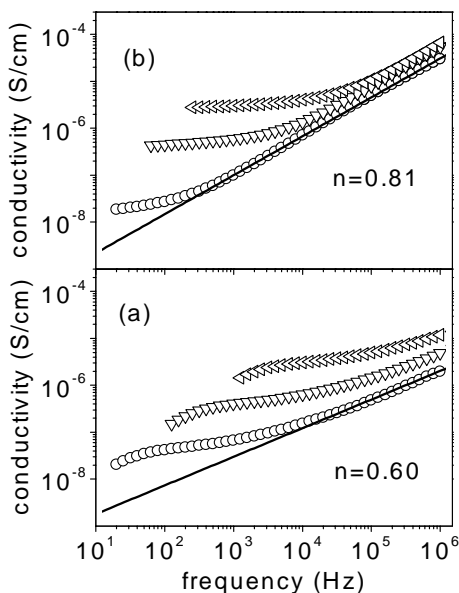


Fig. 2 – Frequency dependence of the real part of the conductivity for $\text{Li}_{0.5-x}\text{Na}_x\text{La}_{0.5}\text{TiO}_3$ with (a) $x = 0$ at 186 K (\circ), 202 K (∇) and 221 K (\triangleleft) and (b) $x = 0.2$ at 298 K (\circ), 390 K (∇) and 505 K (\triangleleft). Solid lines represent power laws with $n = 0.6$ and $n = 0.81$, respectively.

the concentration x of immobile Na ions towards the percolation threshold. We would like to emphasize that the observed increase in the exponent n is not due to the appearance of a nearly constant loss behavior [14], which is observed at higher frequencies or lower temperatures and characterized by an almost linear frequency-dependent conductivity with $n \approx 1.0$. Percolation theory does not either provide a direct explanation for the change of the exponent n when the percolation threshold is approached [15]. It is well known that slightly below the percolation threshold ($x < x_c$) there appear percolation clusters with a fractal dimensionality below the Euclidean dimension of the embedding medium. At x_c one cluster becomes infinite but coexists with finite-size clusters. It is often argued that cluster size limited diffusion causes the mean-square displacement to depend on time as a power law with a fractional exponent (anomalous diffusion). Anomalous diffusion at short times survives for $x > x_c$, and could provide an explanation for the frequency exponent n . However, according to critical scaling laws around the percolation threshold the exponent of anomalous diffusion is expected to remain constant when concentration is varied in the critical region [15]. Moreover, Monte Carlo studies on ion diffusion have not evidenced any changes in the exponent that characterizes anomalous diffusion in lattices with structural disorder when approaching the percolation threshold [16].

In a different but analogous problem, relaxation dynamics of mobile Lennard-Jones particles interacting with immobile particles by the same potential, Scheidler *et al.* have recently found by molecular-dynamics simulations a similar increase of the exponent n and a slowing-down of relaxation rates [17]. This result has been interpreted in terms of the enhanced constraints on particle motion for particles interacting with immobile ones [18]. In the case of ion diffusion we can alternatively describe these more stringent constraints on ion motion by making use of a statistical microscopic model which takes into account the effective dimensionality of the conduction path. Note that the effect of increasing the number of Na ions is reducing the effective dimensionality of the conduction path. We do not know *a priori* the

TABLE I – Exponent $1-n$, obtained experimentally in the series $\text{Li}_{0.5-x}\text{Na}_x\text{La}_{0.5}\text{TiO}_3$, and the effective dimension d of the diffusion path, obtained by fitting the experiments according to the theory.

x	$1-n$	d
0	0.40 ± 0.01	> 2
0.1	0.36 ± 0.02	1.8 ± 0.1
0.15	0.33 ± 0.01	1.65 ± 0.1
0.18	0.24 ± 0.02	1.2 ± 0.1
0.2	0.19 ± 0.01	0.95 ± 0.1

effective dimension d of the diffusion path formed by vacant A sites accessible to mobile Li ions, when x is changed between the limiting cases $x = 0$ ($d = 3$) and $x = 0.2$ ($d = 1$). However, by comparison with theory below, we will claim that d is progressively decreasing when more Na ions are introduced in the structure and the percolation threshold is approached.

As we stated above, the crystalline structure provides a disordered distribution of vacancies through which ionic jumps take place and, more interestingly, the local potential each ion sees is random. We define $\Psi(\mathbf{r}, t)$ as the local waiting time distribution at position \mathbf{r} at time t , and assume that the spatial ion jumps cannot be infinitely large, but remain finite. Thus, the mean-square displacement of ions is bounded. This distribution depends on time due to local relocation of the surrounding ions. It is well established from experimental data, and accounted for in different phenomenological models, that the mean waiting time diverges, which gives rise to the observed power law frequency dependence of the conductivity [19,20]. Hence, the waiting time distribution $\Psi(\mathbf{r}, t)$ has infinite mean value. This distribution can be analyzed through its Laplace transform $\hat{\psi}(u) \equiv \int_0^\infty \Psi(\mathbf{r}, t) \exp[-ut] dt$ with the following asymptotic behavior:

$$\hat{\psi}(u) \simeq 1 - Au^\gamma, \quad u \longrightarrow 0, \quad (5)$$

where $0 < \gamma < 1$ and A is a real, positive constant.

The electrical relaxation of mobile ions can be related to their dynamics in the framework of the Continuous Time Random Walk Theory [21]. Being more specific, when we apply an electric field to the system, small dipoles form everywhere. Let us assume that those dipoles are frozen and cannot relax until an ion migrates to their vicinity [22], and that those ions remain there a random time given by the distribution $\Psi(\mathbf{r}, t)$. Moreover, we will assume that the system contains N noninteracting ions, initially distributed with concentration $c = N/V$, V being the volume of the system. Thus, the probability of dipole surviving for at least a time t before an ion reaches its position is given by (in the thermodynamic limit with $N/V = c$)

$$\Phi(t) = \exp[-ch(t)], \quad (6)$$

where $h(t)$ is related to the probability for an ion to reach its initial position [23]. Consequently, we only need to calculate $h(t)$ to relate both micro and macroscopic descriptions of the system. It can be shown that [23]

$$\hat{h}(u) = \frac{1}{u(1 - \hat{\psi}(u))F(\hat{\psi}(u))} - \frac{1}{u}, \quad (7)$$

where $\hat{h}(u)$ is the Laplace transform of $h(t)$ and $F(z) = \sum_{k=1}^\infty z^k f_k$ is the generating function of the probability for an ion to return to its initial position after k jumps, f_k . This function depends on the system dimension and, as we will show below, the same waiting time distribution provides different relaxation functions depending on the dimensionality of the underlying

network where ions diffuse. The assumption of the same distribution of waiting times for different Na concentrations can be justified as follows. Li diffusion along the percolation path is limited by immobile La and Na ions but also by mobile Li ions. Thus when Li (mobile) is substituted by Na (immobile), the local landscape *seen* by a mobile ion has not changed substantially and thus the waiting time is expected to remain essentially unchanged, although the dimension of the conduction path for long-range diffusion has been reduced.

Equations (6) and (7) allow us to compare the predictions of the model with the experiments reported above. In the general case, when the system dimension is d , we can estimate the behavior of $h(t)$. The probability of return in k jumps in a d -dimensional system scales as $f_k \sim k^{d/2}$, hence $F(z) \sim [\log(1/z)]^{d/2-1}$ if $d < 2$ and tends to a constant for $d > 2$. We thus obtain

$$F(\widehat{\psi}(u)) \sim u^{\gamma d/2-\gamma} \implies h(t) \sim t^{\gamma d/2}, \quad \text{if } d < 2, \quad (8a)$$

$$F(\widehat{\psi}(u)) \sim \text{const} \implies h(t) \sim t^\gamma, \quad \text{if } d > 2. \quad (8b)$$

In particular, $h(t)$ can be computed analytically when $d = 1$ or 3 , $h(t)$ being proportional to $t^{\gamma/2}$ and t^γ , respectively, in agreement with eqs. (8). Comparing this theory to the experiments, we find that $1 - n = 0.4$ for the sample with $x = 0$ for which a three-dimensional diffusion process is well established ($d = 3$), so we set $\gamma = 0.4$. Assuming that the value of γ is constant and related to the waiting time distribution but has nothing to do with the dimensionality of the system, we can determine the effective dimension d of the diffusion path along which Li ions move for the remaining samples. This is done by fitting experimental moduli of fig. 1 to susceptibility functions built using eqs. (3), (6) and (8a) (see lines in fig. 1). Table I shows the values of d obtained using this procedure. Interestingly, eq. (8a) predicts $1 - n = \gamma/2 = 0.2$ for $d = 1$, which is, within error bars, the same as the experimental result for the sample with $x = 0.2$, *i.e.* near the percolation threshold for Li diffusion.

In summary, we have conducted conductivity relaxation measurements, systematically, in the series $\text{Li}_{0.5-x}\text{Na}_x\text{La}_{0.5}\text{TiO}_3$ ($x \leq 0.5$), where mobile Li ions can be randomly substituted by immobile Na ions. We have found a significant slowing-down of relaxation dynamics when increasing Na content from $x = 0$ towards the percolation threshold for ionic conductivity observed at $x \approx 0.2$. This result has been interpreted in terms of the reduced dimensionality resulting of blocked pathways for Li diffusion. Li ions diffuse in a three-dimensional cubic network for $x = 0$, while the effective dimension of the diffusion path decreases with Na content towards the percolation threshold. We made use of a simple theoretical approach to examine dimensionality effects on relaxation dynamics, and found the theoretical predictions to be in excellent quantitative agreement with the experimental findings. Thus we have provided complementary theoretical/experimental evidence for the slowing-down of the relaxation dynamics of ionic conductors when the effective dimensionality of the conduction pathways is reduced.

* * *

Work supported by Spanish MCyT through projects MAT2003-01533 and MAT2001-3713-C4. MC thanks the financial support by DGES (Spain), grant Nos. BFM2000-0006 and BFM2003-07749-C05-05.

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