

## Separation of electronic and ionic conductivity in mixed conductors from the ac response: Application to $\text{Pr}_{0.56}\text{Bi}_{0.04}\text{Li}_{0.2}\text{TiO}_3$

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A method has been developed for separation of ionic and electronic conductivity in mixed conductors. The procedure is accomplished by using blocking electrodes and the Kramers–Kronig relations for separating the dc conductivity from total response. This method was applied to lithium inserted and deinserted sample of  $\text{Pr}_{0.56}\text{Bi}_{0.04}\text{Li}_{0.2}\text{TiO}_3$ . This material is an ionic conductor, and after insertion, electronic conduction appears in the sample. The deinserted sample has a similar electric behavior to the original material. This method does not need any previous model when processing the data. Hence, it avoids those modeling related mistakes and increases the possibilities of dielectric spectroscopy. © 2008 American Institute of Physics. [DOI: 10.1063/1.2959189]

ac relaxation methods have been the most important tools in the analysis of electrical properties of ionic conducting solids.<sup>1–7</sup> However, their application for determining the extent of the contribution to the total conductivity from ionic and electronic components in mixed conductors remains less explored. In principle, by using an appropriate equivalent circuit one might deal with it.<sup>8–13</sup> However, in practice this is usually hardly feasible in a meaningful manner due to strong overlaps, and thus, it is necessary to validate the interpretation by additional consistency checks.<sup>13–15</sup> On the other hand, still today, the usual way to extract the dc component from the ac data is by taking it from the real part of the AC conductivity at low frequencies,<sup>16–20</sup> or by fitting experimental data to an empirical function, like for instance the Barton–Nakajima–Namikawa relation.<sup>5,21,22</sup>

In the 80s a method for determining the dc component present in an ac data was developed based on the comparison of the experimental dielectric data with those obtained after the application of the Kramer–Kronig (K-K) Transforms.<sup>3,4</sup> Recently, some of us have modified the method for its use in ionic conductors, which has been applied to stabilized zirconia.<sup>23</sup> It was shown that the direct separation of the dc component without the use of equivalent circuits largely contribute to a better qualitative understanding of the overall electrical behavior of the materials, and emerged as an useful step in the electrical characterization prior to the use of equivalent circuits for the quantitative characterization. In this line, in present letter, a modification is introduced for the application to mixed conductors. Following the classical Wagner's procedure,<sup>24</sup> in order to separate the electronic conduction from total response, we use gold electrodes to block the lithium ionic dc conductivity.

The convenient use of K-K [Eqs. (2) and (3)] provides a unique tool for splitting conductivity and dielectric losses time/frequency dependency.<sup>3</sup> In general the dependence of conductivity with the frequency has the form,

$$\sigma(\omega) = \sigma_{\text{dc}} + \varepsilon_0 \omega \varepsilon''(\omega) + i \omega \varepsilon_0 \varepsilon'(\omega), \quad (1)$$

where  $\sigma_{\text{dc}}$  is the frequency independent conductivity, i.e., the dc conductivity,  $\varepsilon'$  and  $\varepsilon''$  are the real and imaginary parts of the dielectric permittivity, respectively. The measured data ( $\varepsilon^*$  versus  $\omega$  or  $C^*$  versus  $\omega$ ) can be used to calculate the real component from the imaginary one [Eq. (2)] and vice versa [Eq. (3)].

$$\varepsilon'(\omega) = \varepsilon_{\infty} + \frac{2}{\pi} \int_0^{\infty} \frac{x \varepsilon''(x)}{x^2 - \omega^2} dx, \quad (2)$$

$$\varepsilon''(\omega) = -\frac{2\omega}{\pi} \int_0^{\infty} \frac{\varepsilon'(x)}{x^2 - \omega^2} dx. \quad (3)$$

As it is shown in Eq. (1), the dc conductivity does not contribute to the real part of the permittivity and hence it is not included in  $\varepsilon''$  obtained from  $\varepsilon'$  through the K-K transformations. However, it is well established that finite boundary effects can introduce artifacts during the application of the K-K transforms.<sup>3,13–15</sup> We have used the approach introduced by Jonscher to circumvent this problem,<sup>3</sup> as applied before to other materials.<sup>23,25,26</sup>

Since Li-conducting perovskites are relevant materials for electrodes in Li-batteries, we use here  $\text{Pr}_{0.56}\text{Bi}_{0.04}\text{Li}_{0.2}\text{TiO}_3$ , which was prepared by conventional solid state reactions.<sup>27–29</sup> The insertion of Li is compensated by partial reduction from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ , which can enhance the electronic conductivity.<sup>30,31</sup> Chemical insertion and deinsertion of the Li were achieved using buthyl-Li, as described elsewhere.<sup>32,33</sup> The compositions obtained for the prepared, inserted and deinserted samples are

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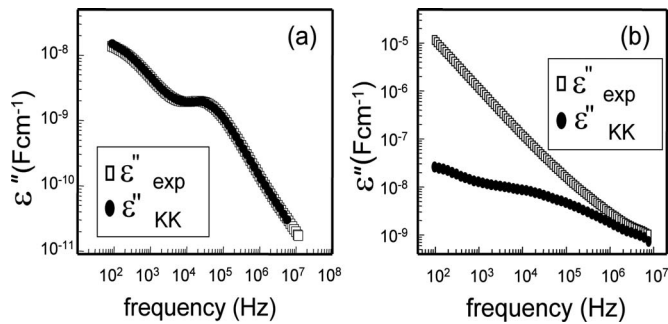
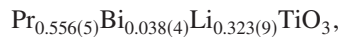
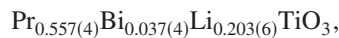
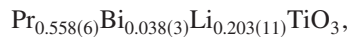


FIG. 1. Experimental and K-K relations calculated values of imaginary part of the permittivity of (a) starting and (b) inserted samples.



and



respectively, where the Inductively Coupled Plasma chemical analysis uncertainties are indicated in parentheses.

Ac measurements were carried out using an HP 4192A Impedance Analyzer over the range  $100 \text{ Hz} < f < 13 \text{ MHz}$ . Both sides of the pellets were painted with gold paste (Engelhard-Clal T-10112) and fired at  $900 \text{ }^\circ\text{C}$  in air. For the inserted samples the gold paste was fixed at  $500 \text{ }^\circ\text{C}$  in  $\text{N}_2$  atmosphere. Measurements were carried out, with  $\text{N}_2$  atmosphere, at fixed temperatures from  $25$  to  $450 \text{ }^\circ\text{C}$  and maintaining isothermal conditions within  $0.2 \text{ }^\circ\text{C}$ .

The electrical behavior of the sample is qualitatively modified upon Li insertion, as can be seen in Fig. 1, where the experimental imaginary part of the permittivity is plotted along with its counterpart curve obtained by the K-K Transform (ec. 3) from the experimental real part of the permittivity. The excellent match between the experimental and K-K calculated values before insertion [Fig. 1(a)] reveals the absence of dc component in the starting sample. In contrast, a large deviation is observed in the inserted sample [Fig. 1(b)]. A dc conductivity value can be determined for each frequency point, as the difference between the experimental and calculated imaginary parts of the permittivity multiplied by the frequency ( $\sigma_{\text{dc}} = \Delta\epsilon''\omega$ ). Since this is expected to be a constant magnitude in the whole frequency range, the dc conductivity can be calculated as the average over a large amount of data, while clear departure from a constant value is indicative of the absence of dc conductivity. In the present case, our results show that indeed in the inserted sample a true dc component is present; a conclusion has been arrived without the use of any modeling circuit.<sup>3,14,23</sup> This is therefore of particular importance for the study of mixed and

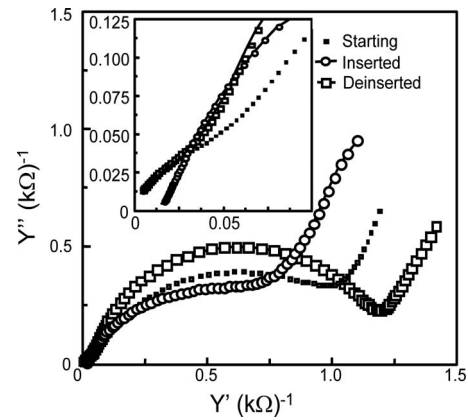


FIG. 2. Plots of  $Y''$  vs  $Y'$  of the starting, inserted, and deinserted samples at  $180 \text{ }^\circ\text{C}$ . An enlarged graph of the high-frequency values is also given.

ionic conductors. The dc conductivity calculated values for the temperature set, even for the initial and the deinserted samples too, follow Arrhenius behavior, whose values at  $25 \text{ }^\circ\text{C}$  and also the calculated activation energies are presented in Table I. Since  $\text{Li}^+$ -ion blocking electrodes are used, the dc conductivity is electronic in nature.

The determination of the ionic conductivity in a direct way, as shown above for the electronic conductivity, is not possible. Instead, we need to determine the total conductivity and then by difference the ionic component can be calculated. In order to do so, we analyze the electrical behavior in complex planes formalism to qualitatively identify the measured data corresponding to the grain behavior, and later to fit the total conductivity by an equivalent circuit.

The complex admittance spectra of starting and deinserted samples are featured by three semicircles (Fig. 2). One semicircle starts from zero, which is indicative of the presence of spike, associated to polarization effects in the material,<sup>5,6</sup> here developed at the material-electrode surfaces.<sup>27-31</sup> In the inserted samples this semicircle was not found, which suggests the presence of dc conductivity upon insertion, as was expected from the result obtained by the direct method using K-K.

The equivalent circuit used for modeling the impedance spectra of inserted samples is composed by two series blocks formed each one by parallel R-C-CPE (constant phase element) elements. Another CPE in series was added for fitting the response of the spike in starting and deinserted compositions, as in Refs. 28 and 29. All fits were made by using the ZVIEW software package.<sup>34</sup> The dependences of the conductivities with temperature also follow Arrhenius behavior. The conductivities and the activation energies are reported in Table I.

The electronic transport number ( $t = \sigma_{\text{electronic}} / \sigma_{\text{total}}$ ) of starting and deinserted samples are lower than  $10^{-5}$ , in the

TABLE I. Conductivity and activation energy for starting, inserted, and deinserted samples, obtained from total response (equivalent circuit) of material, dc processing and its difference (more details in text). Calculated uncertainties are indicated in parentheses.

	Starting sample		Inserted sample		Deinserted sample	
	$\sigma(\Omega \text{ cm})^{-1}$	Ea(eV)	$\sigma(\Omega \text{ cm})^{-1}$	Ea(eV)	$\sigma(\Omega \text{ cm})^{-1}$	Ea(eV)
Total conductivity	$4.41(9) \times 10^{-6}$	0.441(7)	$9.07(13) \times 10^{-6}$	0.379(6)	$2.90(6) \times 10^{-6}$	0.416(8)
dc (electr.) conductivity	$1.7(2) \times 10^{-12}$	0.73(11)	$3.28(2) \times 10^{-10}$	0.84(3)	$9.8(1.2) \times 10^{-13}$	0.83(14)
Ionic conductivity	$4.41(9) \times 10^{-6}$	0.441(7)	$3.38(14) \times 10^{-6}$	0.38(4)	$2.90(6) \times 10^{-6}$	0.416(8)

same order as values reported for LLTO system.<sup>30</sup> In the inserted sample, conversely, an important increase can be observed in dc conductivity. More details about the conduction mechanism in these materials will be published elsewhere.<sup>33</sup>

The goodness of the fitting of the Arrhenius plots for the conductivities (supplementary information), and the big difference between  $E_a$  values for both, electronic and total conduction, strongly suggest that the mechanisms are independent, as was previously suggested by Emery *et al.* using NMR relaxation in similar materials.<sup>31</sup> Then, the ionic conductivity was calculated from the complex plane constructed using the imaginary part of the permittivity obtained from K-K transform (Table I). As in the starting and deinserted compositions, a spike appears in the admittance plots (supplementary information). Such result provides confidence on the processing analysis we have implemented here, and reveals the importance of considering the dc conductivity in dielectric spectroscopy data processing.

In conclusion, the proposed method goes further than an unambiguous and confident dc conductivity determination with high precision and without the use of any predefined model. The achieved separation allows calculating the ionic and the electronic conductivities and the corresponding activation energies from the same measured data by an easy experimental procedure. The knowledge about the conductivity is essential for the applications of these materials, while the activation energy allows insight into the physical and chemical nature of the conduction mechanisms. This can become a useful tool for the analysis of these materials, providing a solid background that can conduce to a better choice of the equivalent circuits to be used and the physical and chemical interpretations of their elements. The proposed methodology therefore increases the possibilities of dielectric spectroscopy for the study of electrical properties of a large variety of materials and devices.

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