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Relationship between charge carrier relaxation and peculiarities of electric response in some solid oxygen ion conductors

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ABSTRACT

The electrical properties (impedance, dielectric permittivity, and electric modulus) of various zirconia and ceria based oxygen ion conductors have been investigated in a broad frequency (from 1 Hz to 10 GHz) and temperature (from ambient to about 1100 K) ranges by impedance spectroscopy. A plateau of dielectric permittivity in frequencies lower than the frequency of impedance's imaginary part's peak was observed in the case of yttrium and calcium stabilized zirconia single crystals. The temperature dependence of the dielectric permittivity's plateau's value has been determined, which was found to decrease with increasing temperature. The temperature behaviour of characteristic frequencies, corresponding to peak values of the imaginary parts of electric modulus f_m and impedance f_z, was also investigated in single crystals and ceramics. The ratio $r = f_m/f_z$ was found to decrease with increasing temperature and decreasing dopant concentration in all compounds. A sharp peak of r was detected in the vicinity of the phase transition region in scandium stabilized zirconia. A simple interpretation, based on the behaviour of a conductive system with a variable distribution of relaxation times, was proposed to explain the observed phenomena.

1. Introduction

Frequency dispersion of electrical properties, related to the relaxation of charge carriers in solid oxide ion conductors, yields a lot of information about dynamics of charge carriers in the bulk or interfacial regions. Solid oxide ion conductor can be treated as a conductive system having a certain distribution of relaxation times (DRT) of charge carriers, which can be represented as a continuous probability density function. The main concepts and principal equations suitable to describe such systems can be found in the works [1,2]. Considerable efforts have been made to develop methods for extracting the DRT function of a conductive system directly from the experimental data, among which some successful examples for different types of conductive systems should be mentioned [3–6].

However, most of the experimental studies, related to the frequency response of mobile charge relaxation in the crystal lattice of solid oxide ion conductors, have been carried out at comparatively low temperatures. The main cause of this was the shifting of the dispersion, related to the relaxation of charge carriers, to the microwave region at elevated temperatures, as microwave measurements are not widely used in the field. In our previous works [7–9] we have presented data of broadband impedance measurements at temperatures up to 1150 K with DRT function extraction results of certain zirconia and ceria based electrolytes. The use of wide frequency and temperature intervals allowed us to observe the peculiarities of the DRT function's behaviour with changes in temperature. The DRT function was found to become narrower with increasing temperature and decreasing dopant concentration. A particular behaviour of the DRT function was observed in the vicinity of a structural phase transition in scandium stabilized zirconia, which abruptly changes the material's conductivity.

In this work we continue the study of electrical properties and DRT function behaviour of solid oxygen ion conductors by presenting measurement data and its analysis results, which were not published in works [7–9]. It will be shown, that the measurement of electrical properties, performed in the broad frequency and temperature intervals, allows us to observe important peculiarities of the behaviour of dielectric permittivity ($\tilde{\varepsilon} = \varepsilon' - i\varepsilon''$) and the ratio of characteristic frequencies (frequencies of imaginary part's peaks) of electrical modulus (f_m) and impedance (f_z) in the investigated oxygen ion conductors. It will also be shown how these two parameters are related to the DRT function of a conductive system and how they can be employed for the determination of the behaviour of DRT function.

2. Experiment

A wide range of materials was used in order to summarize the phenomenon of the DRT function behaviour with varying temperature in oxygen ion conductors. All of the samples studied are listed in Table 1. For the investigation of the frequency dispersion of permittivity YSZ10 and CaSZ15 single crystals, grown by the skull melting method, were

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Table 1
The studied oxygen ion conductors.

Compound	Chemical formula	Form
YSZ3	$Zr_{0.97}Y_{0.03}O_{1.97}$	Ceramic
YSZ8	$Zr_{0.92}Y_{0.08}O_{1.96}$	Ceramic
YSZ10	$Zr_{0.9}Y_{0.1}O_{1.95}$	Single crystal
ScSZ10	$Zr_{0.9}Sc_{0.1}O_{1.95}$	Ceramic
CaSZ15	$Zr_{0.85}Ca_{0.15}O_{1.85}$	Single crystal
GDC10	$Ce_{0.9}Gd_{0.1}O_{1.95}$	Ceramic
GDC20	$Ce_{0.8}Gd_{0.2}O_{1.9}$	Ceramic

used [10–12]. For the studies of temperature dependences of the characteristic frequencies f_z and f_m the above mentioned single crystals, as well as polycrystalline ceramics, sintered using powders available from Fuel Cell Materials, were used. The powders were formed in a steel die of 8 mm diameter by uniaxial cold pressing at 300 MPa. Sintering of the powder compacts was performed in an air atmosphere for 1 h at 1673–1773 K temperature. The resulting ceramics were processed to form cylindrical samples, 1.5 mm high and up to 3 mm in diameter, with Pt paste electrodes. Ag paste electrodes were also used in some cases in order to shift the interfacial dispersion region to lower frequencies.

Most of the electrical property measurements were performed by taking advantage of our newly developed impedance spectroscopy technique [13,14], which allowed us to perform more accurate measurements in wider frequency range than in previous experiments described in [7,8]. This new technique involves two different methods in one: a conventional 2-electrode method, described in more detail in our work [15], and a modified and enhanced coaxial line method [16]. This new equipment enables measurements in an ultra-broadband frequency range (0.1 Hz–10 GHz) at temperatures up to 1300 K and avoids the problems associated with combining of the data obtained by different equipment during distinct thermal cycles. Part of the investigation was carried out by our former equipment [15,16]. In addition, a 4-electrode method [15] was used in the low frequency range (10 Hz–2 MHz) as needed for elucidating the causes of frequency dispersions in the 2-electrode data. A sample voltage of 25–100 mV at low frequencies and incident wave power of −10–0 dBm in the case of the coaxial method were used. All measurements provided up to 26 frequency points per decade and were carried out in atmospheric air.

The obtained impedance data was checked utilizing integral Kramers–Kronig relations as described in [9]:

$$z'_{KK}(\omega) = \left(\frac{2}{\pi}\right)\int_0^{\infty} \frac{x \cdot z''_m(x) - \omega \cdot z''_m(\omega)}{x^2 - \omega^2}\,dx, \tag{1}$$

$$z''_{KK}(\omega) = -\left(\frac{2\omega}{\pi}\right)\int_0^{\infty} \frac{z'_m(x) - z'_m(\omega)}{x^2 - \omega^2}\,dx, \tag{2}$$

where ω and x are angular frequencies, and z' and z''—real and imaginary parts of complex impedance, respectively. Straightforward integration in the experimental (instead of infinite) frequency range, without any extrapolation or other procedures, was employed due to the broadband nature of the obtained data. Close similarity was observed when comparing initial and transformed data (an example of such comparison is presented in Fig. 1), except a significant deviation in the regions of the lowest and highest frequencies. However, this disagreement is related to the limited boundaries of integration rather than a poor quality of the experiment in these frequency ranges. It should be noted, that only relevant data were selected for detailed analysis in this study. Experimental data in the lowest frequency region (Fig. 2, region I) was disregarded due to it being related to the properties of the electrode–electrolyte interface.

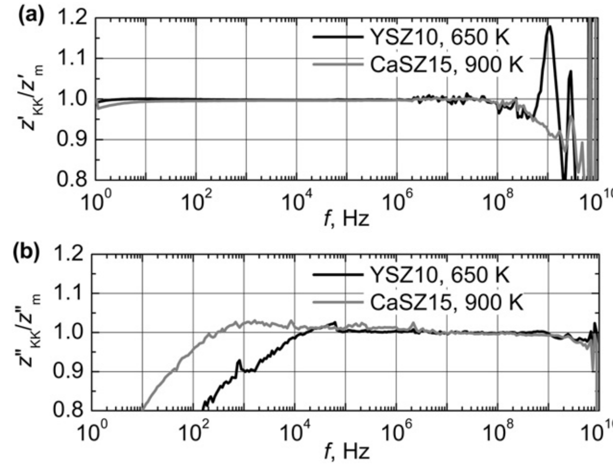

Fig. 1. A typical picture of the real and imaginary impedance parts ratio as calculated using Kramers–Kronig relation (z_{KK}', z''_{KK}) and measured (z_m', z''_m).

High frequency region with very low impedance values (Fig. 2, region III) was also excluded from the obtained impedance spectra, which were further analysed in order to find the DRT function. The method of analysis is predicated on the assumption that the impedance spectrum $\tilde{z}(\omega) = z'(\omega) - iz''(\omega)$ can be represented as a sum of elements with individual relaxation times [7]:

$$\frac{\tilde{z}(\omega)}{z_b} = \frac{z_\infty}{z_b} + \int_{-\infty}^{+\infty} f(\tau) \cdot \frac{1 - i\omega\tau}{1 + \omega^2\tau^2}\,d\lg(\tau), \tag{3}$$

where $f(\tau)$ is the DRT function to be found, z_∞—the impedance at the high frequency limit (in our case $z_\infty \to 0$), z_b—bulk resistance, τ—relaxation time, and i—imaginary unit. The distribution functions $f(\tau)$ have been found by numerically solving integral Eq. (3) with procedure based on that presented in work [1]. The referred algorithm was slightly improved and the current resolution capabilities are demonstrated in Appendix A.

In practice, the best solution of Eq. (3) is obtained when computing 4 to 7 orders of frequency, centred around f_z. As can be seen in Fig. 2, the interfacial peak of $z''(f)$ is out of the measurement frequency

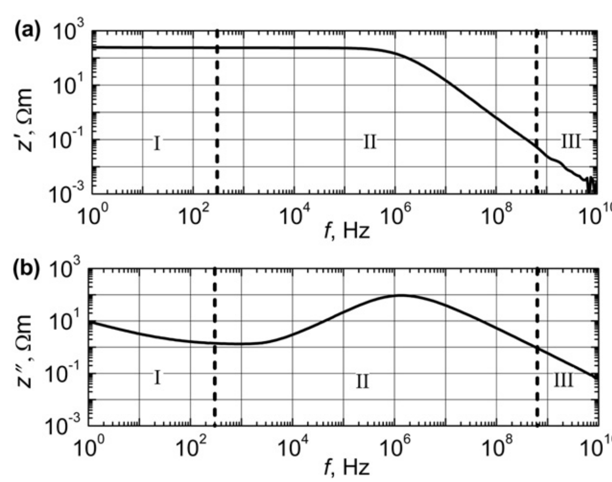

Fig. 2. The real (a) and imaginary (b) parts of impedance of the YSZ10 single crystal with Ag electrodes at 650 K, as a schematic example for selection of the frequency range for calculation of the DRT function.