

## CONTRIBUTIONS TO THE DEVELOPMENT OF A METHOD TO SEPARATE INTRA AND INTERGRANULAR CONDUCTIVITY OF IONIC CERAMIC MATERIALS USED TO MANUFACTURE THE LAMBDA SENSOR

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**Abstract:** *The lambda sensor with zirconium is one of the first types of lambda sensors used in the automotive industry. The electric conductivity of materials can be deduced by measuring the electric resistance and the geometric dimensions of a specimen. The electric resistance can be determined by methods which use either continuous or alternating electric current.*

**Keywords:** ionic ceramic materials, ionic conductivity, complex impedance spectroscopy

### INTRODUCTION

Pollution regulations require vehicle manufacturers still reduced emissions. The lambda sensor (also called the probe or the oxygen sensor) has special importance in connection to the reduction of emissions on vehicles. The lambda sensor with zirconium is one of the first types of lambda sensors used in the automotive industry. The working principle is based on the mode of operation of a fuel cell, called Nernst cell. This type of lambda sensor is a generating type of sensor, which produces an electric voltage without being connected to an external power supply. The electric voltage generated by the sensor is produced by the difference of oxygen molecules in the exhaust gas and atmospheric air [2]. Its operation is determined by the electric conductivity of the ceramic body made of zirconium dioxide doped or not with various elements. Therefore, in order to improve its operation it is required to improve the conductivity of the material from which the probe is made of.

The electric conductivity of materials can be deduced by measuring the electric resistance and the geometric dimensions of a specimen. The electric resistance can be determined by methods which use either continuous or alternating electric current.

The use of continuous current does not allow obtaining the real value of conductivity unless the phenomena of polarization of electric charges are negligible.

The measurement made for alternating current, at a given frequency, removes the polarization phenomenon, but does not guarantee the validity of the value obtained, since the real value of electric conductivity is obtained only at a certain frequency of the current and in its turn it depends on the type of material, the electrodes used, as well as on the temperature at which the determinations are made. This is why the method proposed will perform a frequency scan in a range as wide as possible, so as to obtain maximum of information on the material studied.

### PRINCIPLE OF THE METHOD

At first, this method was used in the field of electrochemistry of liquids. Its use was expanded also to other materials, such as solid electrolytes, ionic superconductors, mixed conductors and vitreous ceramics [1].

If you apply at the terminals of the system studied, an electric voltage of the form,

$$u(t) = U_0 e^{i\omega t} = U_0 \sin \omega t \quad (1)$$

frequency  $f = \frac{\omega}{2\pi}$  is crossed by a current  $i(t)$ . Within a linear approximation valid for low-amplitude signals, the answer is a sinusoidal function having the same pulsation, therefore, the form:

$$i(t) = I_0 e^{i(\omega t + \varphi)} = I_0 \sin(\omega t + \varphi) \quad (2)$$

The electric impedance  $Z(\omega)$  of an element of the circuit is given by the ratio between the voltage applied  $U = U_0 e^{i\omega t}$  and the resulting current  $I = I_0 e^{i(\omega t + \varphi)}$ .  $Z(\omega)$  is a complex number which can be represented in Cartesian coordinates by:

$$Z(\omega) = \text{Re}(Z) + i\text{Im}(Z) = |Z|(\cos \varphi + i \sin \varphi), \quad (3)$$

where  $\text{Re}(Z)$  and  $\text{Im}(Z)$  are the real part (resistance) and the imaginary part (reactance) of impedance  $Z(\omega)$ . The relations between these different values are the following:

$$|Z| = \sqrt{\text{Re}(Z)^2 + \text{Im}(Z)^2} \quad (4)$$

$$\varphi = \arctg \frac{\text{Re}(Z)}{\text{Im}(Z)} \quad (5)$$

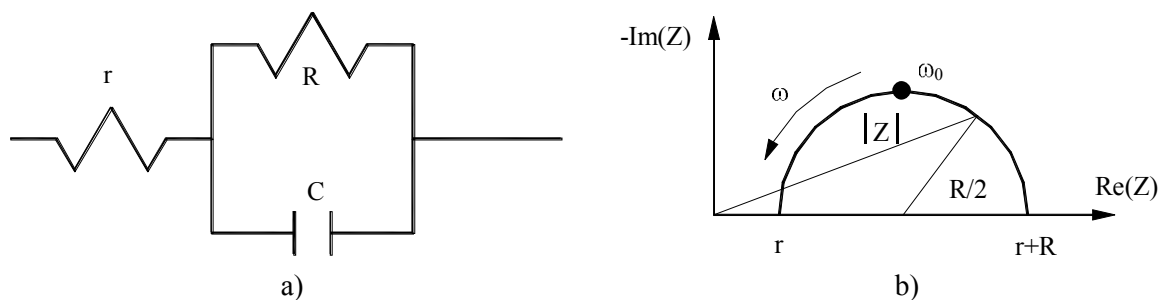


Figure 1. Representation of the complex impedance of a circuit a) electric circuit; b) corresponding complex impedance diagram

In the complex plan of the graphical representation in which there are marked the variations of  $\text{Im}(Z)$  depending on  $\text{Re}(Z)$  for different values of pulsation corresponding to a frequency scan represent a spectrum of complex impedance.

For example, we can mark the impedance of a basic electric circuit, presented in fig. 1.a), by a semicircle of radius  $R/2$ .

The impedance of this circuit can be written using formula:

$$Z(\omega) = \left[ r + \frac{R}{1 + (\omega\tau)^2} \right] - i \left[ \frac{R\omega\tau}{1 + (\omega\tau)^2} \right] = Z' - iZ'' \quad (6)$$

where  $\tau$  is the time constant of the parallel circuit RC.

By removing  $\omega\tau$  from the real and imaginary part of  $Z(\omega)$ , there can be obtained:

$$\left[ (Z' - r) - \frac{R}{2} \right]^2 + (Z'')^2 = \left( \frac{R}{2} \right)^2, \text{ that is} \quad (7)$$

$$\left[ (\text{Re}(Z) - r) - \frac{R}{2} \right]^2 + (\text{Im}(Z))^2 = \left( \frac{R}{2} \right)^2 \quad (8)$$

which is the equation of a circle with radius  $R/2$  with the centre on the real axis of abscissa  $(r + R/2)$ .

This semicircle intersects the real axis in the point of abscissa  $r$  when  $\omega \rightarrow \infty$  and in the point of abscissa  $(r + R)$  when  $\omega \rightarrow 0$ . The maximum amplitude of  $Z''$  has the value  $Z'' = R/2$  and this maximum value is reached for  $\omega_0\tau = \omega_0 RC = 1$ . Determining the characteristic pulsation  $\omega_0$  in the top of the semicircle allows us to calculate the capacity  $C_0$  of the circuit with formula:

$$C_0 = \frac{1}{\omega_0 R} = \frac{1}{2\pi f_0 R}, \text{ with} \quad (9)$$

$\omega_0 = 2\pi f_0$  ( $f_0$  = frequency of relaxation).

If we use a network consisting of two series-dipoles, each one made of a resistor in parallel with a capacitor, ( $R_i, C_i, i=1,2$ ) presenting different time constants  $\tau_i = R_i C_i = \omega_i^{-1}$ , we obtain a diagram as the

one presented in fig. 2. This manner of representation is interesting because it often enables a separation of the different kinetic stages of charge carriers in the interpretation of measurements. Therefore, depending on the form of the CIS obtained we can model the system electrode – sample – global impedance electrode  $Z(\omega)$  by a representative electric circuit, representing associations of passive basic dipoles containing resistive R, inductive L and capacitive C elements, regardless of the excitant frequency.

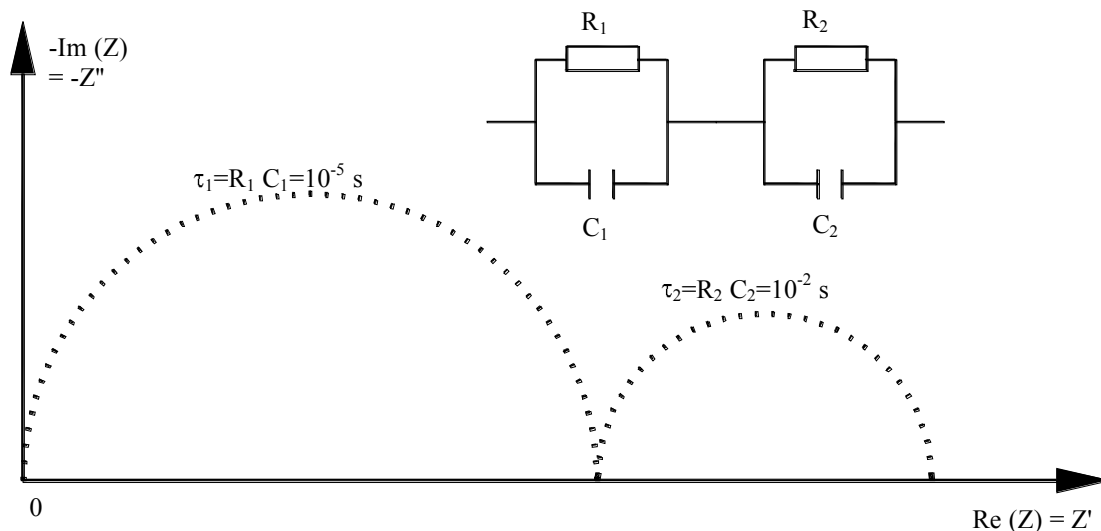


Figure 2. Impedance diagram corresponding to two circuits  $R_i, C_i$ , in parallel, connected in series

Therefore, a resistance R characterizes the migration of charge carriers undergoing the action of an electric field, inductance L expresses the idleness of charge carriers and capacity C takes into account the electrostatic interactions. In the case of ionic conductors, the complex impedance spectra (CIS) generally consist of a sequence of arcs of circle that point out the various phenomena which take place in the measurement cell (fig. 3).

This type of spectrum can be interpreted considering that:

- the first arc of circle (1), points out the transport phenomena which take place at the level of the grain (interior) volume of the sample. This is obtained when high frequencies are used;

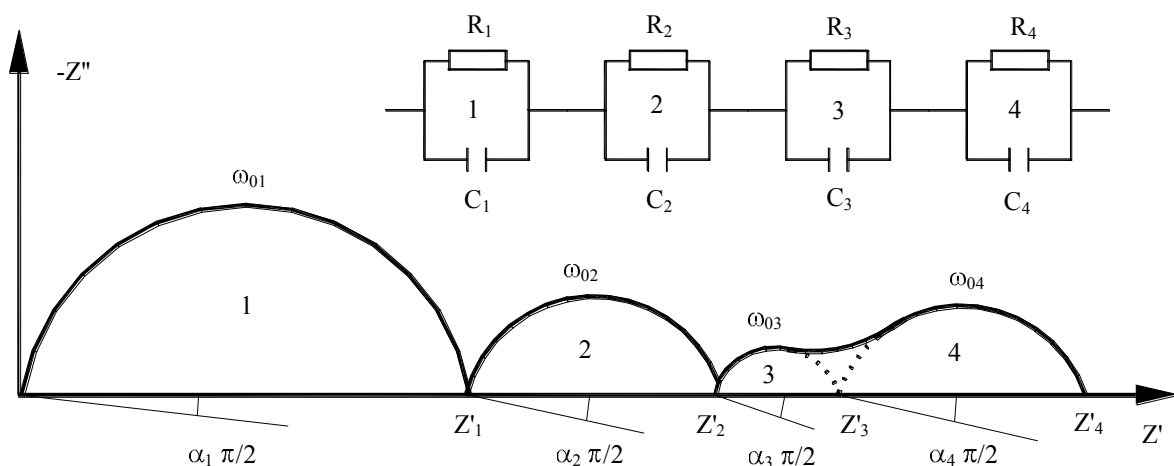
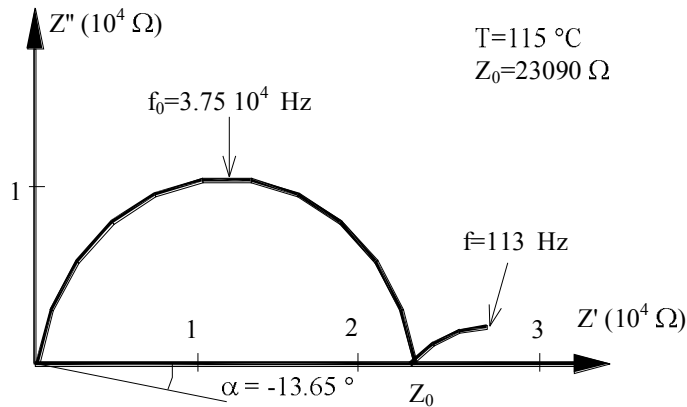


Figure 3. Impedance diagram of a cell of ionic conductors [1]

- the second arc of circle (2), noticed at average frequencies, is associated to transport phenomena specific to the grain boundary;

- the third (3) and fourth arcs of circle (4), obtained at low frequencies point out the phenomena specific to electrodes. These model the process consisting in the changes which take place at the level of electrodes, which are slower than the transport processes mentioned above. Experimentally, we notice that the centres of the arcs of circle are not on the real axis as presented in fig. 3 and fig. 4.



This phenomenon of decentring can be explained by the existence of a dispersion of the local value of conductivity due to a chemical inhomogeneity in the mass of the sample, around an average value  $\bar{\sigma}$ , given by formula:

$$\bar{\sigma} = \frac{1}{Z_0} \frac{l}{S} \quad (10)$$

**Figure 4. Complex impedance diagram obtained from the study of a vitreous sample where  $l/S$  is the geometric factor of the sample.**

As long as the spectra are well defined and the arcs of circle can be identified, the values  $Z_i$  can be determined either by extrapolating the part corresponding to low frequencies of the arc of circle  $i$ , or by extrapolating the part corresponding to high frequencies of the arc of circle  $i+1$ . The arcs of circle can be difficult or even impossible to identify in certain conditions (low or high measurement temperature).

The intragranular conductivity of the sample, which can also be called “bulk” conductivity, can be obtained with the help of the first arc of circle obtained at high frequencies, using the formula:

$$\sigma_{in} = \frac{e}{s} \frac{1}{Z_1' - Z_0'} \quad [\Omega^{-1} \text{ cm}^{-1}], \quad (11)$$

where,  $e$  = sample thickness [cm];  $s$  = sample section (surface) [cm<sup>2</sup>].

In the same manner, intergranular (or grain boundary) conductivity marked with  $\sigma_{jg}$  (“joints de grains”) is obtained with the help of the second arc of circle using the formula:

$$\sigma_{jg} = \frac{e}{s} \frac{1}{Z_2' - Z_1'} \quad [\Omega^{-1} \text{ cm}^{-1}] \quad (12)$$

## INFLUENCE OF TEMPERATURE ON THE FORM OF SPECTRA

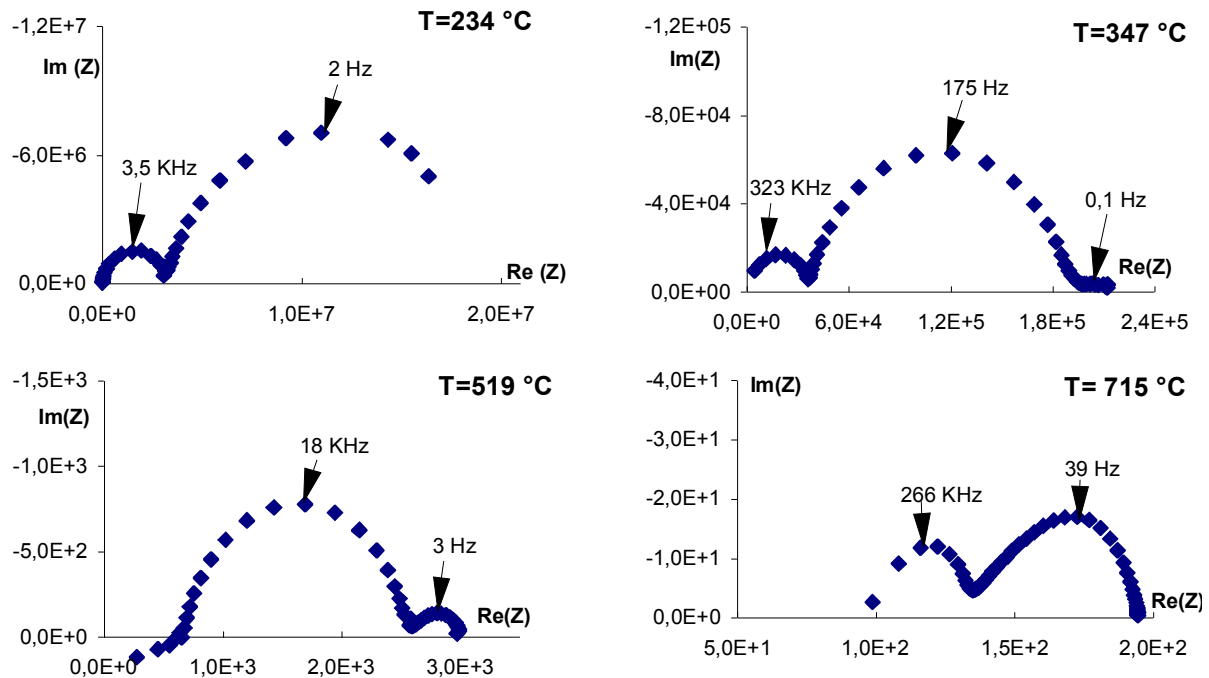
Considering the facts mentioned above, the method used to determine the value of electric conductivity of samples consists in measuring the electric resistance of these samples as well as the geometric factor. The measurements of electric resistance were made by complex impedance spectroscopy. The measurement cells had a cylindrical form with thickness (height)  $e$  and diameter  $D$  ( $1.5 \leq e \leq 3.5$  [mm] and  $3.5 \leq D \leq 6.5$  [mm], respectively). The two electric junctions consist of deposits of platinum or silver lacquer. For the complex impedance spectroscopy, the measurements are made in a furnace with kanthal resistance, whose temperature is controlled by a regulator that allows obtaining stable temperatures up to 1200 °C, the operating limit temperature of the furnace. The experimental assembly includes an experimentation room where the measurement cell is placed inside an alumina tube.

Five polycrystalline samples having the same chemical composition  $\text{ZrO}_2 + 9$  moles%  $\text{Y}_2\text{O}_3$ , but sintered at five different temperatures:  $T_{f1}=1350^\circ\text{C}$  for 5 hours;  $T_{f2}=1400^\circ\text{C}$  for 5 hours;  $T_{f3}=1500^\circ\text{C}$  for 5 hours;  $T_{f4}=1600^\circ\text{C}$  for 5 hours;  $T_{f5}=1600^\circ\text{C}$  for 40 hours, were studied with this method, in the temperature range  $230 \div 700$  °C and the partial pressure of oxygen range  $1 \div 10^{-22}$  atm (the measurements were generally performed under air; argon and oxygen were very rarely used, especially

to separate the results corresponding to polarization at the level of electrode from those due to the properties of solid electrolyte).

For each one of the values of couple (sample – temperature - partial pressure of oxygen) the impedance of the samples was measured for about 50 values of frequency between 10 MHz and 10 mHz using a voltage equal to 10 mV.

Fig. 5. presents the evolution of the complex impedance spectra with temperature obtained under air for a sample sintered at 1500 °C for 5 hours.



**Figure 5. Evolution of impedance spectra with temperature, for a sample of  $ZrO_{2-0.91}Y_{2O_{3-0.09}}$ , sintered at 1500°C for 5 hours**

It is noted that at a given temperature, a single part of the theoretic diagram in fig. 3 is actually noticeable; only two of the four arcs of circle are visible.

We also notice that this visible part moves toward the left side of the diagram (mass phenomena), while temperature decreases, and toward the right side (interface phenomena), respectively, when the operating temperature increases. The arcs of circle (1) and (2) are always well separated (the ratio of time constants  $\omega_0$  remains in order  $10^3$  Hz), while arcs (3) and (4) are generally overlapped.

For higher temperatures the inductive impedances ( $Z'' > 0$ ) of current threads (silver threads in this case) become important in relation to the capacitive impedances of the sample (the same order of size, or sometimes superior to those of the electrolyte). This phenomenon was always observed during measurements. Still, we can delay the apparition of this phenomenon to higher temperatures by increasing the geometric factor of the sample. Fig. 6 presents a full spectrum (including the inductive effect) for a sample of YSZ sintered at 1500 °C for 5 hours, studied at a temperature of 603 °C under air.

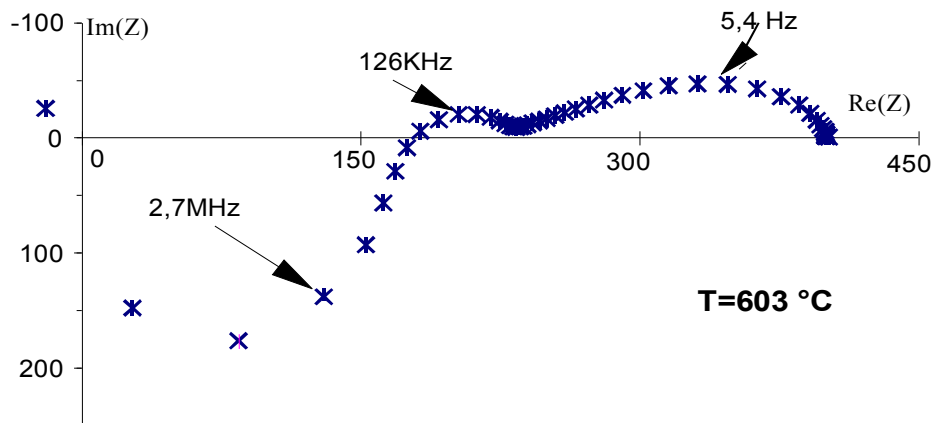


Figure 6. CIS for a sample of YSZ sintered at 1500 °C for 5 hours; measurement temperature  $T=603^{\circ}\text{C}$

In conclusion, as the temperature increases, we notice a displacement of the spectra toward the left (from the mass phenomena toward the electrode phenomena). For this reason, it is necessary to identify the arcs of circle observed, that is to succeed in making the correspondence between each of the physical phenomena specific to the grain volume, the grain boundary and the electrode phenomena.

### INFLUENCE OF POLARIZATION VOLTAGE ON THE EVOLUTION OF SPECTRA

In the case of the samples studied, the representation of complex impedance points out time constants characterizing more or less separated arcs of circle, depending on the experimental conditions. In order to differentiate the phenomena specific to the samples from those interfering at the level of the interface, a continuous voltage ranging between 0 and 0.5 V was overlapped to the measurement voltage and the evolution of CIS was followed according to this continuous polarization. (fig. 7.)

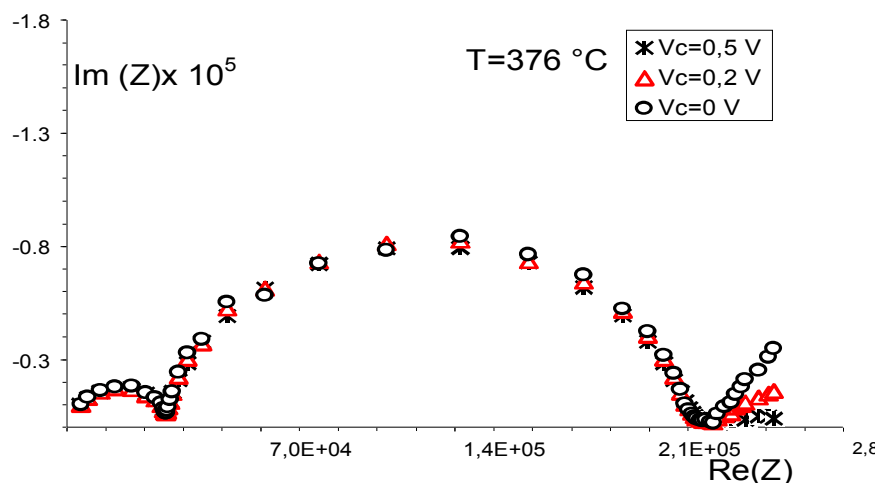


Figure 7. Evolution of spectra depending on the continuous polarization, for a sample of  $\text{ZrO}_2_{0.91}\text{Y}_2\text{O}_3_{0.09}$  sintered at 1600°C for 40 h

In the figure it is noted that the points belonging to the two arcs of circle (obtained at high frequencies) do not depend on the polarization conditions (they merge), while the points belonging to the other arcs of circle (obtained at low frequencies) depend very much on these conditions (the arcs are different). According to these results, we can conclude that the arcs of circle obtained at high frequencies identify to the theoretical arcs (1) (representative for the intragranular – volume phenomena) and (2) (representative for the intergranular – grain boundary phenomena), while the other arcs of circle identify to arcs (3) and (4) (representative for the electrode phenomena).

## INFLUENCE OF ATMOSPHERE ON THE EVOLUTION OF SPECTRA

In order to point out the influence of the atmosphere in which the measurements are made, several measurements were performed (under identical temperature conditions) by varying the oxygen concentration. Fig. 8 presents the evolution of impedance diagrams with  $P_{O_2}$ , for  $T=346^\circ\text{C}$ . These show that in the case of stabilised zirconium oxide the influence of partial pressure of oxygen provides an answer similar to the previous case: circles (1) and (2) do not depend on this parameter, while circles (3) and (4) depend very much on it. These results show that the conductivity of YSZ polycrystals is extrinsic ionic.

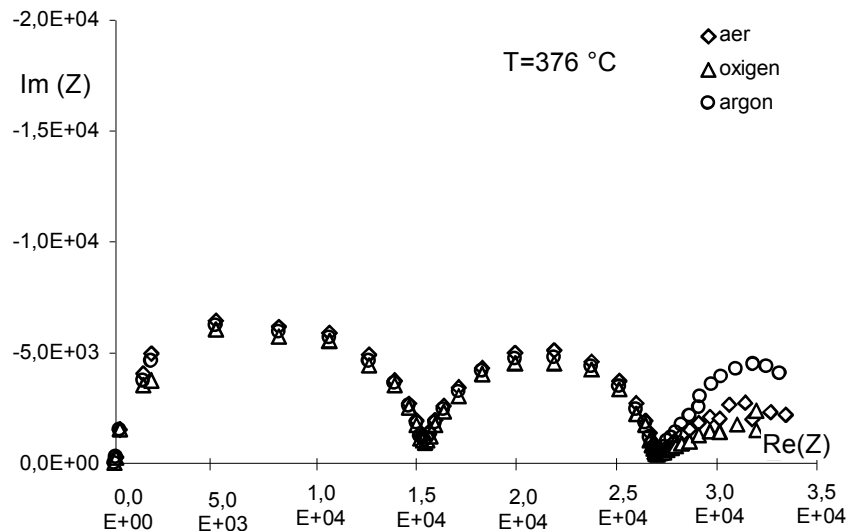


Figure 8. Evolution of CIS depending on the partial pressure of oxygen for a sample of yttrium zirconium oxide

## CONCLUSIONS

Considering the facts presented above the following conclusions can be drawn:

- in order to separate the transport phenomena at mass level, grain and electrode boundary, a frequency scan within a wide spectrum is required;
- at a certain measurement temperature, the 4 theoretical spectra (volume, grain boundary and interfaces with electrodes) are not all visible;
- in order to have access to all these a temperature scan is required. As the temperature increases, the spectra move to the left (from the mass phenomena to the electrode phenomena);
- the first two arcs of circle do not depend on the continuous polarization voltage and the measurement atmosphere, which leads us to the conclusion that these are specific to the material to be measured.
- the last two arcs of circle depend on the continuous polarization voltage and the measurement atmosphere, which leads us to the conclusion that these are specific to the phenomena which take place at the level of electrode.

In conclusion, Complex Impedance Spectroscopy (CIS) enables obtaining the value of conductivity both of the grain (intragranular), the grain boundary (intergranular), the electrodes and the total one.

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