

# Methods for the measurement of transport numbers in mixed ionic and electronic ceramic conductors

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## Introduction

### Conductivity in ceramics

Ceramic materials are well-known since ancient times, they have been around as crockery, art pieces, and tiles, among others. They are identified as hard materials, which can withstand compression, even though they are brittle. Also, for being good thermal and electrical insulators. Nevertheless, there is always the exception to the rule, and the case of the electrical resistivity of ceramics is no different. There is a wide variety of conducting ceramics with different kind of applications. For example, indium tin oxide (ITO) is a transparent ceramic conductor [1], and it can be used as an electrode in solar cells; varistors usually made of silicon carbide (SiC) or zinc oxide (ZnO), are devices that can vary their electrical resistance in response to an applied dc-bias, and are used to protect integrated circuits from transient voltages [2]; another common application for conducting ceramics is as cathode materials in batteries as,  $\text{LiCoO}_2$  in lithium ion batteries.

### Types of conductivity

The electrical conductivity in a ceramic, as in any other material, can be classified as electronic and ionic. The first one is related with the motion of mobile electrons through the material. Ceramics have a crystalline structure, meaning that all the atoms are arranged in order; in addition. Therefore, if an impurity with a different valence or a transition metal or rare earth element with variable oxidation state is around, it can act as an acceptor or donor of electrons, as a result free electrons would be available inside the material [1]. Ionic conductivity, occurs if the crystal structure has enough space (channels, point defects) for ions to hop from one site to another; in the presence of ionic vacancies or interstitials. At room temperature the mobility of ions is low, but as the temperature increases so the mobility of ions, this is due to the atom's ability to crossover the energy barrier. The combination of these two types of conduction can be present in a solid, and it is called mixed conduction.

## Distinguishing between electronic and ionic conductivity, in mixed conductors

In the case of mixed conduction, it is of great interest to know which species (electrons, holes, anions or cations) are responsible for the conductivity and in what percentage, as some conduction can be more suitable than others, for a specific application. For example, for an electrolyte high ionic conduction and almost null electronic conduction is desirable, whereas and in a semiconductor, the opposite is desired. The parameter to describe the contribution of each species is called transport or transference number [3]. Therefore, it is important to find an accurate method to measure transport numbers.

### Transport numbers

Transport numbers could be defined as the partial current that is transported by a specific species when the material is subjected to a potential difference [3]. If only one kind of ions and electrons are considered, the ionic transference number  $t_i$  and the electronic transference number  $t_e$ , can be described in terms of current, impedance or even conductance, Table 1,

*Table 1. Ionic and Electronic transport numbers in terms of current, impedance and conductance [3].*

	<b>Ionic transport number (<math>t_i</math>)</b>	<b>Eq.</b>	<b>Electronic transport number (<math>t_e</math>)</b>	<b>Eq.</b>
current	$\frac{i_i}{i_i + i_e}$	(1)	$\frac{i_e}{i_i + i_e}$	(2)
impedance	$\frac{Z_e}{Z_e + Z_i}$	(3)	$\frac{Z_i}{Z_e + Z_i}$	(4)
conductance	$\frac{G_i}{G_i + G_e}$	(5)	$\frac{G_e}{G_i + G_e}$	(6)

where  $i_i$  and  $i_e$  are their corresponding currents;  $Z_i$  and  $Z_e$  are the related impedances in relation to the applied voltage; and  $G_i$  and  $G_e$  are the conductances related with the real part of the impedances. Therefore the sum of both transport numbers would be one.

$$t_i + t_e = 1 \quad (7)$$

An important consideration must be taken into account. Transport numbers are not a constant throughout the material, as they rely on the local composition and chemical potential of the material.

## Impedance spectroscopy

Impedance spectroscopy is a technique used to characterize the electrical properties of electroceramics. Impedance measurements are obtained by applying an ac-bias to the sample over a wide range of frequencies. The different regions in the material can be represented as a parallel RC element. Therefore, a time constant that is characteristic of the region will be the product of

the resistance and the capacitance of the element. As a result of this, the regions can be identified at the frequency of maximum loss ( $\omega_{\max}$ ), by calculating the capacitance [4].

$$\tau = RC \quad (8)$$

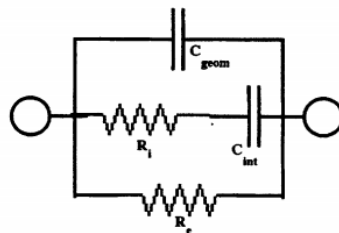
$$\omega_{\max}RC = 1 \quad (9)$$

The magnitude of the capacitance can be related with a phenomenon in the sample, due to the geometric relationship between the capacitance and the thickness and surface area of the sample. Table 2 gives typical values to these phenomena, which are not limited to be on this range [4].

*Table 2. Typical capacitance values for a range of effects [4].*

Capacitance (F)	Responsible effect
$10^{-12}$	Bulk
$10^{-11}$	Minor, second phase
$10^{-11}$ - $10^{-8}$	Grain boundary
$10^{-10}$ - $10^{-9}$	Bulk ferroelectric
$10^{-9}$ - $10^{-7}$	Surface layer
$10^{-7}$ - $10^{-5}$	Sample-Electrode interphase
$10^{-4}$	Electrochemical reactions

Once the experimental measurements are obtained, equivalent circuits can be proposed to fit the experimental values and try to represent the physical behaviour of the material. In the case of a mixed-conductor, two pathways could be found, the ionic and the electronic, Figure 1. [5]



*Figure 1. Basic equivalent circuit for a mixed conductor [3].*

From the experimental measurements different graphs can be plotted, such as complex planes of impedance and capacitance, or spectroscopic plots of capacitance, impedance and, electric modulus. Analysing the result with more than one plot can be useful to identify the different components, and the behaviour of the material, as only one graph might not reveal sufficient information, which can lead to misinterpretations [4]. This is important as the ions could travel through the different components of the material and a respective impedance will be related to it.

Therefore, in the case of the presence of bulk and grain boundary effects, the total ionic resistance would be the sum of the bulk resistance and the grain boundary resistance [6]. Assuming a series model to the current pathway.

$$R_i = R_b + R_{gb} \quad (10)$$

$$R_b = \frac{R_{b,i} R_{b,e}}{R_{b,i} + R_{b,e}} \quad (11)$$

$$R_{gb} = \frac{R_{gb,i} R_{gb,e}}{R_{gb,i} + R_{gb,e}} \quad (12)$$

Huggins [3], proposed to obtain the transport numbers by making use of the complex impedance plane. He mentions different scenarios. First the complex impedance plots of a high ionic conductor and a high electronic conductor are shown, Figure 2. Then, the plots for a mixed conductor with and without the presence of grain boundaries are shown in Figure 3.

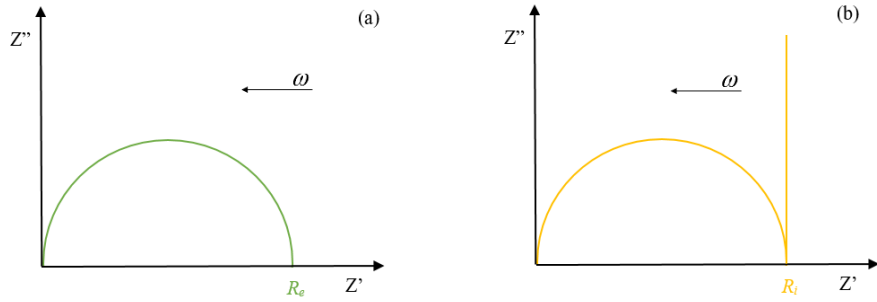


Figure 2. Complex impedance plane of a purely electronic (a) and ionic conductor (b) [3].

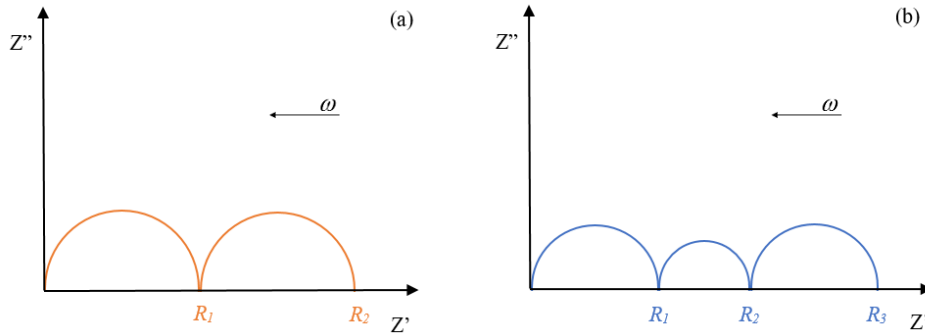


Figure 3. Complex impedance plane of a mixed conductor with 2 elements (a) and 3 elements (b) <sup>1</sup>[3].

The intercepts on the real axis of the complex impedance plane are related with the ionic and electronic resistances. Then, the ionic and electronic conductance (the real part of the admittance) are rewritten in terms of the ionic and electronic resistances, and therefore in terms of the resistance values from the intercepts. Once the partial ionic and electronic conductances are obtained, the transport numbers are found, by applying Equations 4 and 5, a full derivation of the equations can be found in the reference [3]. A summary of the interpretations of the intercepts on

<sup>1</sup> According to Huggins, Figure 3a corresponds to a mixed conductor without grain boundary effects, and Figure 3b, corresponds to a mixed conductor with grain boundary response. The definition of the resistances at the real axis of the plane can be found in Table 3.

the complex impedance plane, resistances and transport numbers, for an ionic, electronic and mixed conductor, is given on Table 2.

*Table 3. Interpretations of the intercepts on the complex impedance plane, resistances and transport numbers, for an ionic, electronic and mixed conductor [3].*

Type of Conduction	$R_1$	$R_2$	$R_3$	$R_e$	$R_i$	$t_e$	$t_i$
Electronic	$R_e$	-	-	$R_1$	-	1	0
Ionic	$R_i$	-	-	-	$R_1$	0	1
Mixed	$\frac{R_e R_i}{R_e + R_i}$	$R_e$	-	$R_2$	$\frac{R_2 R_1}{R_2 - R_1}$	$\frac{R_1}{R_2}$	$\frac{R_2 - R_1}{R_2}$
Mixed + gb	$\frac{R_e R_i}{R_e + R_i}$	$\frac{R_e (R_i + R_{gb})}{R_e + R_i + R_{gb}}$	$R_e$	$R_e$	$\frac{R_3 R_1}{R_3 - R_1}$	$\frac{R_2}{R_3}$	$\frac{R_3 - R_2}{R_3}$

It is also mentioned that in the case of only two semicircles, if the electronic transfer number dominates, the semicircle at high frequency would be larger than the one at low frequency. And the opposite behaviour would be found is the ionic transport number is larger than the electronic [5].

As mentioned before, to extract more information from the data two more graphs can be considered. The first one may show, capacitance versus frequency identifying the components of the material. The second could be an Arrhenius plot, in which the activation energy of the reaction can be related with the temperature. For an electronic conductor, the conductivity will decrease as the temperature increases, as the charge carriers will scatter one another, without following a conduction pathway. On the other hand, for an ionic conductor, as the temperature increases (reducing the energy barrier), the conductivity increases; making it easier for charge carriers to hop from one site to another. Therefore, a change in the slope might reflect some of this behaviour. Making use of these graphs, can back up the information from the impedance plot.

## Examples of types of conductivity

Impedance spectroscopy results showing electronic, ionic and mixed conducting behaviour, were kindly provided by researchers from the Functional Ceramics Group as part of the Materials Science and Engineering Department at the University of Sheffield.

### Electronic conductivity

To represent a highly electronic conductor a sample of TiO<sub>2</sub> doped with 15% of Cr, was quenched from 1000°C, and the impedance measurements were performed at 200°C. Figure 4a presents a semicircle on the complex impedance plane and Figure 4b shows only one plateau. It can be

deduced that only electronic conduction is taking place, as there is no spike at low frequencies, meaning that no charge is being retained on the ionic blocking electrodes.

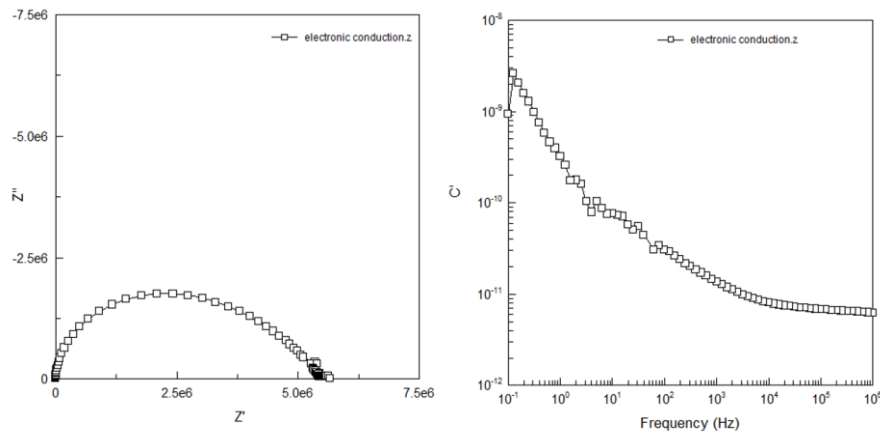


Figure 4. Impedance plot (a) and Capacitance vs frequency plot (b) of a high electronic conductor.

### Ionic conduction

The sample representing ionic conductivity is  $\text{Li}_5\text{SiO}_4\text{F}$ . On the complex impedance plot, Figure 5a, has the shape of a distorted semicircle with an almost vertical spike at low frequencies. The spike is due to build up charge at the interphase with the electrode. When looking at the capacitance plot, Figure 5b, three plateaus can be observed. According to Table 1, the first one at  $10^{-6}\text{F}$ , could correspond to the sample-electrode interface, the second one around  $10^{-11}\text{F}$  could correspond to grain boundary effects, and the one at the highest frequency might represent the bulk. As both, bulk and grain boundary effects are present, which might be the reason of the non-perfect semicircle, as it looks like two been really close together. This appears to be an example of Li ion conduction.

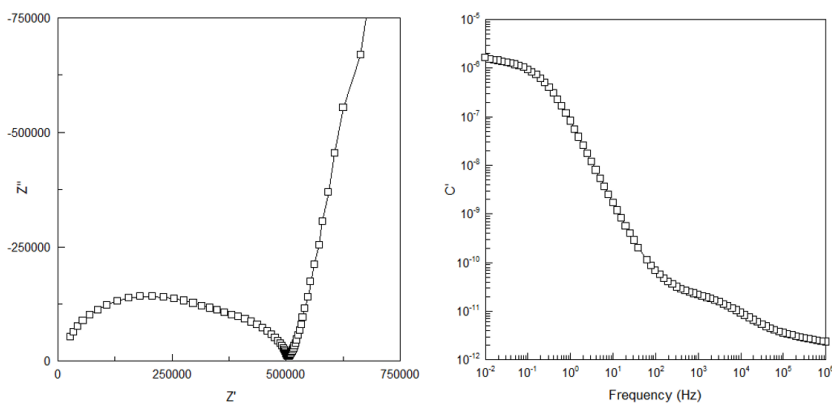


Figure 5. Impedance plot (a) and Capacitance vs frequency plot (b) of a high ionic conductor.

An example of oxide ion conduction is given by a sample of  $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ ,  $x=0.08$ , better known as YSZ. Impedance measurements were performed at  $356^\circ\text{C}$ . The complex impedance plot, Figure 6a, shows two semicircles and a spike with an angle of 45 degrees. Corroborating with the capacitance plot, Figure 6b, the high frequency semicircle could correspond to a bulk response,

the low semicircle correspond to the grain boundary, and the low frequency spike could represent the sample-electrode interface with some ion-diffusion, showing a rate limiting step.

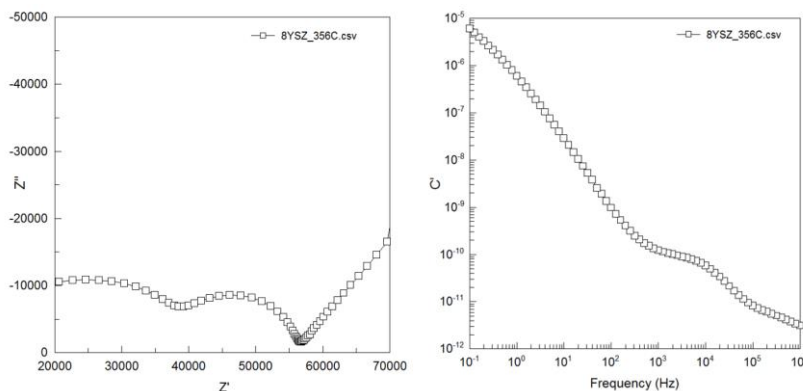


Figure 6. Impedance plot (a) and Capacitance vs frequency plot (b) of an oxygen ion conductor.

### Mixed conduction

To represent mixed conduction the YSZ sample was used again. The sample was heated up to 409°C, and impedance measurements were taken. The shape of the plots looks very similar to the ones at 356°C, Figure 6. Nevertheless, the magnitude of the resistance and the capacitance decreases Figure 7a and 7b. Then, the same sample was subjected to a dc-bias of 8V for 10 minutes, and the low frequency spike reduces in such way that it becomes a small semicircle. This represents electronic conduction. Therefore, the mixed conducting behaviour is observed.

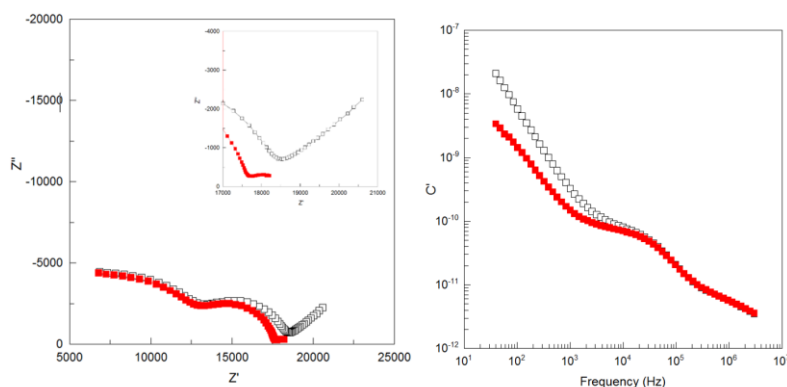


Figure 7. Impedance plot that shows the transition from ionic to electronic conduction (a) and Capacitance vs frequency plot (b) of mixed conductor.

### Effect of oxygen partial pressure on conductivity

Semiconducting oxides can be classified as intrinsic or extrinsic. The first one, has an equal concentration of holes and electrons. For the second one, an element is introduced to the structure (it can be on purpose or not), and the charge carriers are either electrons or holes. If the new element is electron deficient, it would be called an acceptor; the charge carriers would be holes, and the material would be classified as a p-type conductor. On the other hand, if the new element

is electron rich, it would be called a donor; the charge carriers would be electrons, and the material would be classified as an n-type conductor [7].

To distinguish between p-type and n-type conduction, measurements of conductivity as a function of oxygen partial pressure can be performed. If the slope turns out to be positive, the material would be a p-type conductor, and if is negative the material would be n-type. Usually the slope is of the magnitude of  $1/4$ . This can be deduced by writing the point defect reaction for the compensation mechanism on the Kroger-Vink notation, and then writing the equilibrium constant of this reaction to obtain the relation between the charge carrier concentration and the oxygen partial pressure [8].

The conductivity of an oxide ion conductor would be independent of oxygen partial pressure. Therefore a diagram with the conductivity domains of an n-type, p-type and an oxide ion conductor as function of oxygen partial pressure, can be built up, as shown in Figure 8.

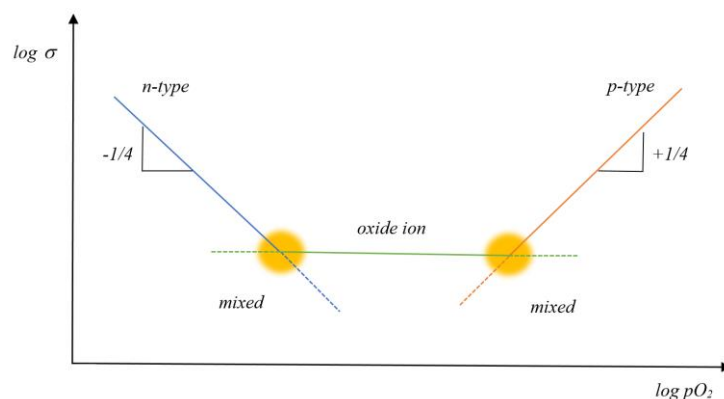


Figure 8. Electronic and oxide ion conductivity as function of oxygen partial pressure [9]

As shown in Figure 8, regions of mixed conductivity can be found on the intercepts of the electronic and electrolytic domain<sup>2</sup> [9]. It is of great interest to know where the holes are located on the p-type region. Could it be on the oxygen or on the metals? [9].

## Other methods

### Tubandt DC method

This method is used primarily to obtain the ionic fraction of the current in a mixed conductor. DC-bias is applied to the sample which is placed between non-blocking electrodes, meaning that the ions and electrons could pass through it. A change in the weight of the electrodes appears, one been heavier than the other one. Taking the measurements of the weight of the electrodes, the time and magnitude of the bias, the atomic weight of the ionic species that is being transported, and assuming Faraday's Law; the number of moles of the ionic species that are transferred can be

<sup>2</sup> It has to be taken into account that this approach is valid when the mobile ionic species is oxygen.



calculated. Then, comparing it with the number of Faradays that flows through the arrangement, the ionic transport number can be found, and therefore also the electronic transport number [3].

### **DC asymmetric polarization or Hebb-Wagner method**

The determination of a small portion of electronic conduction for high ionic conductors is determined by this method. The aim of this experiment is to polarize the cell, and measure the current as function of the voltage between electrodes. For this purpose dc-bias is applied to the system and two types of electrodes are used; one ionic blocking electrode and the other is a reversible electrode (which allows both electronic and ionic conductivity to pass through) [10]. There exist variations to this experiment as four point measurements, which uses three ion blocking electrodes (one of them being a voltage probe to avoid overpotential effects), and one reversible [11]. Another configuration, adds a second reference electrode which is a mixed conductor; this will allow the partial electronic conductivity to vary as its potential can be controlled [3][12]. The transport numbers are determined by the partial conductivities of the sample.

### **DC open circuit potential on concentration cells**

This method is usually applied in mixed conductors where the mobile ions are oxygen. The sample is placed between two reversible electrodes [13], but also is exposed to different oxygen partial pressures at each side, creating a chemical gradient that needs to be balanced by an electrical voltage and an internal current [14]. Therefore, the voltage is measured as a function of the partial pressures of the gases (different types of gases can be used such as air, oxygen, nitrogen, etc), and making use of Nernst equation the transport number can be calculated. This method can also be used when the ionic conducting species are protons by using a gradient of hydrogen partial pressure [14][15][13].

### **Charge-discharge measurements**

This method can be used when the mobile ionic species are metallic. For making these measurements the sample is placed between metal electrodes, and dc-bias applied. The method assumes that the discharge current comes from an electrochemical reaction, and not from a double layer or Schottky barrier charge storage effect. Therefore, the ratio of discharge/charge, will be related to the ionic and electronic transport numbers. Ideally, if the sample presents only electronic conduction the discharge/charge ratio would be zero. On the opposite case, if the sample has purely ionic conduction, the discharge/charge ratio would be one (as the efficiency of electrochemical reactions is less than 100% and is hard to recover all the charge, this ratio would be less than one). Thus, this method can be used to estimate the electronic and ionic transport numbers [16].

# Conclusions

There are ceramics, which can have ionic, electronic or mixed conduction. It is important to differentiate the type of conductivity present as the applications rely on the type of conductivity. Transport numbers are a parameter to indicate the amount of electronic and ionic conduction present in the material. When dealing with mixed conductors, there are several methods that are used when the ionic transport number is predominant, as the Tubandt, DC-asymmetric polarization, and even more specific ones that deal with oxygen and hydrogen mobility, as concentration cells. The challenge is to determine the transport numbers in mixed conductors in the presence of high electronic conduction. Therefore, alternative methods such as impedance spectroscopy are proposed for the determination of transport numbers. This technique reveals important information about the material structure and behaviour in the presence of a dc-bias.

# Further work

The next step would be to apply Huggins method [3] to samples with different types of conductivity and compare the results with the theoretical conductivity of each mobile species. Then, try to refine the method if the results are not coherent, or find an alternative solution.

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# References

- [1] "Conductive ceramics", Encyclopedia Britannica, 2017. [Online]. Available: <https://www.britannica.com/technology/conductive-ceramics>. [Accessed: 22- Mar- 2017].
- [2] I. Reaney, "Varistors", Sheffield, Mappin Building, 2016.
- [3] R. Huggins, "Simple method to determine electronic and ionic components of the conductivity in mixed conductors a review", *Ionics*, vol. 8, no. 3-4, pp. 300-313, 2002.
- [4] J. Irvine, D. Sinclair and A. West, "Electroceramics: Characterization by Impedance Spectroscopy", *Advanced Materials*, vol. 2, no. 3, pp. 132-138, 1990.
- [5] V. Thangadurai, R. Huggins and W. Weppner, "Use of simple ac technique to determine the ionic and electronic conductivities in pure and Fe-substituted SrSnO<sub>3</sub> perovskites", *Journal of Power Sources*, vol. 108, no. 1-2, pp. 64-69, 2002.
- [6] N. Masó and A. West, "Electronic Conductivity in Yttria-Stabilized Zirconia under a Small dc Bias", *Chemistry of Materials*, vol. 27, no. 5, pp. 1552-1558, 2015.
- [7] D. Sinclair, "Functional Materials (electrical), Topic III: Principles of solid electrolytes and mixed conductors", The University of Sheffield, Mappin Building, 2016.

- [8] D. Sinclair, "Functional and Structural Ceramics, Topic II: Thermodynamic treatment of defects and conduction models", The University of Sheffield, Mappin Building, 2016.
- [9] A. West, H. Beltran, M. Jovani and E. Cordocillo, "Mixed conduction in yttria-zirconia ceramics", National Physical Laboratory, 2017.
- [10] I. Riess, "Review of the limitation of the Hebb-Wagner polarization method for measuring partial conductivities in mixed ionic electronic conductors", *Solid State Ionics*, vol. 91, no. 3-4, pp. 221-232, 1996.
- [11] I. Riess, "Four point Hebb-Wagner polarization method for determining the electronic conductivity in mixed ionic-electronic conductors", *Solid State Ionics*, vol. 51, no. 3-4, pp. 219-229, 1992.
- [12] W. Preis and W. Sitte, "Theory of galvanostatic processes in mixed conductors with arbitrary electronic transport numbers", *Journal of the Chemical Society, Faraday Transactions*, vol. 92, no. 7, p. 1197, 1996.
- [13] J. Guan, "Transport properties of  $\text{BaCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\alpha}$  mixed conductors for hydrogen separation", *Solid State Ionics*, vol. 100, no. 1-2, pp. 45-52, 1997.
- [14] D. Pérez-Coll, G. Heras-Juaristi, D. Fagg and G. Mather, "Methodology for the study of mixed transport properties of a Zn-doped  $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  electrolyte under reducing conditions", *J. Mater. Chem. A*, vol. 3, no. 20, pp. 11098-11110, 2015.
- [15] N. Bonanos, "Perovskite solid electrolytes: Structure, transport properties and fuel cell applications", *Solid State Ionics*, vol. 79, pp. 161-170, 1995.
- [16] H. Sumathipala, M. Disssanayake and A. West, "Novel  $\text{Li}^+$  Ion Conductors and Mixed Conductors,  $\text{Li}_{3+x}\text{Si}_x\text{Cr}_{1-x}\text{O}_4$  and a Simple Method for Estimating  $\text{Li}^+/\text{e}^-$  Transport Numbers.", *ChemInform*, vol. 26, no. 47, p. 2138-2143, 2010.