Abstract—In the last years, the solid electrolyte fuel cells have been the subject of many researches, especially in order to remedy the problems relating to the environment. Although the solid electrolyte mostly used in industry, is the zirconium doped in yttrium, however a potential candidate can be the oxide of cerium non doped. Indeed this oxide presents, low-temperature, a conductivity higher than that of the zirconium oxide what should allow to lower the temperature of functioning of the electrochemical piles. Polycrystals have been elaborated of cerium oxide and cerium oxide pure non doped and studied the electrical behavior.

Index Terms—cerium oxide pure non doped, semiconductor type n, conductivity meters, transport properties

I. INTRODUCTION

Cerium oxide pure is a semiconductor type n. This material is an ionic conductor. The dopant materials have applications in electrical and chemical industry. Cerium oxide is used as a catalyst and it is a potential candidate for ammonium solid fuel cells and oxygen probes for example.

II. POINT DEFECTS AND ELECTRICAL CONDUCTIVITY OF CERIUM OXIDE

A. Point Defects

Oxides with fluorine structure, such as cerium oxide CeO\textsubscript{2-x}, represent an important family of materials where defects are present under chemical network of oxygen. These defects are on the stoichiometrically order (x). Their concentration may be important due to the effects of mixed valence of cation. The parameter x characterize whole atomic defects present in the majority defects of network formed after reaction (1):

\[ \text{O}_2 \rightarrow \frac{1}{2} \text{O}_2 + \text{V}_0^+ + 2\text{e} \]

where:

- O\textsubscript{2} is an atom of oxygen from oxygen network;
- V\textsubscript{0}+ is a lacuna of oxygen positively charged twice;
- e is a defect electronic.

The constant equilibrium thermodynamics is given by the relationship (2):

\[ K(T) = \frac{P_{O_2}^{\frac{1}{2}} \cdot [V_0^+] \cdot [e]^2}{\Delta H_f} \]

Equation 5 can be written:

\[ [V_0^+] = c \cdot K(T)^{\frac{1}{2}} \cdot P_{O_2}^{-\frac{1}{2}} = c \cdot P_{O_2}^{-\frac{1}{2}} \cdot \exp \left( \frac{\Delta H_f}{R \cdot T} \right) \]

where:
- \( \Delta H_f \) is enthalpy formation of a mol defects points;
- C is a constant;
- R is perfect gas constant (=8,314 JK\textsuperscript{-1} mol\textsuperscript{-1});
- T is the temperature [K].

B. Electrical conductivity of cerium oxide non doped

The electrical conductivity of a semiconductor-oxide to write:

\[ \sigma = n \cdot e \cdot \mu \cdot c \]

Where e is electron charge, n is valence, \( \mu \) is mobility and c is concentration.

Variation law of electrical conductivity in function of the partial pressure of oxygen at constant temperature can write:

\[ \frac{1}{\sigma} = \frac{\partial \log \sigma}{\partial \log P_{O_2}} \]

characterizes the degree of ionization of charged defects.

The law of electrical conductivity variation depending on
the temperature at constant pressure of oxygen and it can be written as:

\[
\left(\frac{\Delta H_e}{R}\right)_{P,O_2} = \frac{-\Delta H_e}{2.303}
\]  (9)

Where \(\Delta H_e\) is conductivity activation energy \(E_a\).

C. Cerium oxide non doped

In Figure 1 it is shown the results of Tuller et al. [1] concerning the influence of \(P_{O_2}\) on electrical conductivity for cerium oxide non doped obtained a sample of monocrystalline and in the Figure 2 it is shown the results of Popa E. obtained on a sample of polycrystalline prepared from powder Rhodia (HSA 5/lot 99159/01 \(\Phi\)grains~~6.4\(\mu\)m, \(SS = 137m^2/g\))

![Graph showing electrical conductivity vs. \(P_{O_2}\)](image)

Fig. 1. Results of Tuller et al. [1] obtained on a sample monocrystalline

![Graph showing electrical conductivity vs. \(P_{O_2}\)](image)

Fig. 2. Results of Popa E. [2] obtained on a sample polycrystalline

D. Cerium oxide doped in gadolinium

Figure 3 presents an comparing between the values obtained in the laboratory by Y. Aloui and the results obtained on two samples of cerium oxide, tempered uniaxial to 1300°C and prepared from two type of powder developed by Rhodia (LSA, HSA / doped 10 moles %Gd) and who has the grains diameter approximately 0.3\(\mu\)m.

![Graph comparing electrical conductivity of doped and undoped cerium oxide](image)

Fig. 3. Results of Aloui Y. [3] on the sample P5 (LSA tempered 1300°C/1h, \(p=25MPa, d=97\%\)) et P6 (HSA tempered 1300°C/1h, \(p=25MPa, d=96.1\%\))

Mention that different authors have studied cerium doped in gadolinium (Gd, 20% and 10% \(Gd_2O_3\)) [4-6]. It has been demonstrated that cerium doped in gadolinium is an excellent conductor and is considered as ionic conductivity of cerium oxide doped 20 moles% \(Gd_2O_3\) is higher than of cerium oxide doped 10 moles% \(Gd_2O_3\). [4,5,6]

III. EXPERIMENTAL TECHNIQUES

A. Preparation of the sample

The samples are prepared from cerium powder, purity of 99.5%. The powder has been compacted, isostatic pressure less than 4000 bar, after which it was tempered. In table 1 are presented the conditions of tempered, material density obtained and the size of the average grains. It was observed that the gadolinium limited growth of grains and the thermal treatment in the presence of argon leads to a more proper densification. This result is coherent with the increasing concentration of defects points (lacunes of oxygen) because when the partial pressure of oxygen diminishes it favors the process of transportation.

B. Processing and microstructure control

After tempered process, the samples are cut in the parallelepiped or cylinder shape using a micro cutting machine. Using EDX analysis to observe the homogeneity of the materials obtained and can estimate the size of grains (table 1). Note that the samples of cerium oxide non doped have the grains tails between 20-40 microns.

In figure 4 is presented the structure of cerium oxide non doped tempered to 1600°C, time 15 hours in air by EDX analysis and the sample is noted A.
TABLE I
TEMPERED CONDITIONS FOR CERIUM OXIDE NON DOPED

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Tempered cond.</th>
<th>Density</th>
<th>φgrains</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1600°C/15 h/air</td>
<td>99%</td>
<td>30-50μm</td>
</tr>
<tr>
<td>E</td>
<td>1600°C/30 h/air</td>
<td>96%</td>
<td>~10μm</td>
</tr>
<tr>
<td>P4</td>
<td>Uniaxial to 1300°C/1 h/25MPa</td>
<td>94%</td>
<td>0.5-1 μm</td>
</tr>
</tbody>
</table>

![Fig. 4. Cerium oxide opaline micronized, tempered 1600°C/15 h/air](image1)

In figure 5 is presented the structure of cerium oxide opaline tempered to 1600°C, time 30 hours in air by EDX analysis and the sample is noted E.

![Fig. 5. Cerium oxide opaline, tempered 1600°C/30 h/air](image2)

C. Electrical conductivity measurement of cerium oxide non doped

Cerium oxide is a semiconductor with electrical conductivity. It has been used the method "4 points", that allows to eliminate the contacts wires because they are negligible, since cerium has relatively low electrical resistance. Measurements were made at alternating current with frequency 1.5 kHz, using a Kelvin bridge, as in Fig. 6.

![Fig. 6. Montage double Kelvin bridge](image3)

R is a variable resistance R_{ch} is sample resistance studied (between electrical connections 3 and 4) and G is a synchronic detector which allows to control the balance Kelvin bridge (the null balance Kelvin bridge).

The resistances R_1, R_2, R_3, R_4 are the resistances of the Kelvin bridge. These resistances are chosen in order to:

\[ \frac{R_1}{R_2} = \frac{R_3}{R_4} = k \]  \hspace{1cm} (10)

With R<<R_1, R_2, R_3, R_4

When the Kelvin bridge is equilibrium using Kirchoff's law, we can write:

\[ R_3 \times I_1 = R_{ch} \times I + R_2 \times I_2 \]  \hspace{1cm} (11)

\[ R_5 \times I_1 = R \times I + R_4 \times I_2 \]  \hspace{1cm} (12)

With I>>I_1, I_2

\[ \frac{R_{ch}}{R} = \frac{R_3}{I_1} \times \frac{R_2}{I_2} \]  \hspace{1cm} (13)

Result is the variable resistance depends on the Kelvin bridge to be at equilibrium:

\[ R_{ch} = k \times R \]  \hspace{1cm} (14)

Precision device to measure resistance sample is about one centime of ohm.

The resistance measured is related to the conductivity according to the relationship:

\[ \sigma = \frac{L}{S \times R} \]  \hspace{1cm} (15)

Where:
- \( \sigma \)– conductivity;
- \( R \)– measured resistance;
- \( L \)– useful length of the 2 electrical connections;
- \( S \)– sample section.

In figure 7 is presented the measuring cell. In figure 8 is presented the montage of sample.

![Fig. 7. Measuring cell](image4)

Apply platinum varnish to the extremities of sample to ensure a better contact with the electrical connections of platinum and to have the current parallel lines in the sample.
Experiences are made in a tube sealed in aluminum that circulates gas and containing electrochemical gauge and port tube sample.

Sample contacts/electrical connections are secured by a ressort screw, who exerse an adjustable pressure on the sample through an aluminum tube inside which there are electrical connections and wires of platinum thermocouple Pt-Pt Rh 10%, designed to accurately measure the temperature of the sample's neighborhood.

Aluminum screens arranged conveniently permit in the improvement of the thermal profile allow in the work area.

Partial oxygen pressure control is performed in the sample with a probe of the zirconium like in figure 9.

It has been demonstrated that the measured voltage at the terminals of the probe is related to partial pressure of oxygen to gaseous phase and the zirconium tube through the relationship:

\[ E = E^i - E^f = \frac{R}{4F} \ln \frac{P_{O_2}^i}{P_{O_2}^f} \]

\( P_{O_2}^i \) is the partial pressure of oxygen in the balance of the cerium oxide;

\( P_{O_2}^f \) represents the partial pressure of oxygen of reference (air/0.21 atm).

Electromotive force is measured with the help of a mini voltmeter Tacussel with input impedance 10^{12} ohm.

Conductivity measurement of cerium oxide is accomplished by complex impedance spectrometry using a Schlumberger impedance meters (series 1), in the frequency range 10^{-2}-2*10^{7} Hz.

**IV. EXPERIMENTAL RESULTS**

Electrical conductivity measurements have been realized on two samples compacted isostatic cold, pressing to 4000 bar, then tempered (samples A and E) and a sample pressed and tempered uniaxial (sample P4).

Electrical conductivity measurements have been carried out in the temperature range 700°C-1400°C and partial pressures ranging from 10^{-15} and 1 atm.

For the same sample, checked the reproducibility of the results, realized measurements in breeder and descending sense of temperature and of partial pressure of oxygen.

A fissure was observed around the temperature of 954°C. This effect may be attributable to the prevailing influence of the impurities at low temperature.

In figures 10, 11, 12 are reported values of electrical conductivity measured depending on the partial pressure of oxygen, for temperatures between 700°C and 1400°C, for sample A, E, P4.
This result can be attributed mainly to the role of joints of grains at low temperature.

The density of joints of grains is higher due to the finer powder used and to lower temperatures tempered and shorter duration of tempered process.

In figure 14 results of sample A are compared with Popa's [2].

In figure 15 are compared the results obtains on sample A and E.

In figure 16 results were compared with those obtained in the laboratory sample A with the Tuller's [1] and Popa's [2].

In figure 17 are compared the results obtains on sample E and Tuller's [1].

In figure 18 are compared the results obtains on sample A and sample P4.
V. CONCLUSION

It was noted that non-doped cerium oxide is a semiconductor of type n, as the majority of defects are the lacunes of oxygen. The results obtained on non-doped cerium oxide has enabled us to put in evidence the influence of joints of grains on the electrical conductivity, when the temperature diminishes, leading to an increase of conductivity. Electrical conductivity of grains is not influenced by the way of obtaining the samples, but the electrical conductivity of the joints of grains increases when sample density increases. The activation energy is not influenced by tempered conditions.

REFERENCES