Mixed conducting materials for solid oxide fuel cells

by Domingo Pérez Coll

Summary

In today's globalized world, in which the energy demand is continuously growing, most of the consumed energy is focused on three primary sources such as oil, natural gas and coal. Whilst every effort has been paid in recent years to the development of different types of renewable energy, they still constitute a very small part of the energy used. On the other hand, large risks from nuclear power make it a kind of energy which can be problematic when implemented on a large scale. These factors lead to a global energy dependence based on limited energy sources, of a highly polluting nature, with very low efficiency and whose market value is highly speculative. Undoubtedly, these issues point to the need to promote a change in the energy model, which allows for a universal consumption without producing economically and environmentally devastating effects. One of the main drawbacks associated with a transition to clean renewable energy comes from the required wide network infrastructure not only for this generation but also for distribution to different points of consumption. In this regard, it is essential to make a gradual transition, which can take advantage of existing infrastructure, slowly decreasing the dependence on the dominant energy sources. At this point, fuel cells can play a crucial role as transitional technology due to their high efficiency, low pollution, fuel versatility and modularity, allowing them to be deployed in the place of consumption. These devices can produce energy within a wide range, from a few watts required for applications in mobile devices, to the megawatts needed for applications associated with large-scale stationary power.

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$$

Figure 1. Schematic representation of the energy conversion process in a fuel cell.

1. Introduction

Fuel cells are electrochemical devices with capability of directly converting chemical energy of a fuel and an oxidant into electricity and heat, without resorting to any intermediate stage [1]. The direct conversion of energy allows high energy efficiencies to be reached, which has the direct effect of decreasing the fuel consumption per unit of useful energy, but also lowers greenhouse gas emissions when fossil fuels are used. A fuel cell comprises *an anode*, where the fuel oxidation process takes place, *a cathode* where the reduction of the oxidant takes place, and *an electrolyte*, physically separating the anode and cathode, which is responsible for the transport of ionic species needed for the overall reaction to take place (Figure 1).
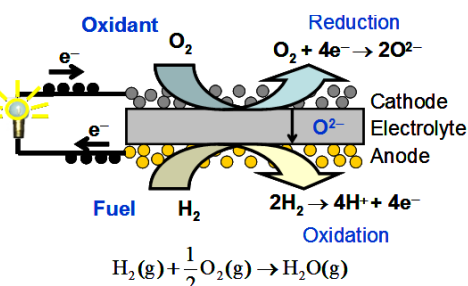
There are different kinds of fuel cells, mainly depending on the type of electrolyte, of which **solid oxide fuel cells (SOFC)** are comprised of ceramic component materials. These fuel cells need to operate at high temperatures to exhibit the appropriate electrical and electrochemical properties. Although this feature can be understood as an obstacle, it produces great advantages such as favoring the kinetics of electrochemical reactions, which increases performance and enables the use of different types of gaseous fuels such as hydrocarbons [2], in addition to hydrogen. While the high temperature produces better yields, the use in practical devices requires the lowering of temperature to extend the lifetimes of materials, reduce costs and allow for use in transportation applications and portable devices [3,4].

The **electrolyte** in a SOFC is an oxide-ion-conductor material by means of the defects introduced in the crystalline structure. These defects are generally composed by oxygen vacancies that have been generated by a charge-compensation mechanism in the crystal structure after doping with cations of lower oxidation state [5]. Ionic conduction processes in ceramic oxides must overcome a significant energy barrier which is overcome by working at high temperature. When a SOFC is submitted to a gradient of oxygen partial pressure (pO$_2$), the chemical potential is balanced by an electrical potential which lead to an electromotive force under open circuit conditions (OCV). This voltage difference will be present by maintaining the gas feed at both compartments that produce the chemical potential gradient of the active species. For a purely oxide-ion-conductor electrolyte the electromotive force under open-circuit conditions can be determined by the Nernst equation as follows [6]:

$$E_{th} = \frac{RT}{4F} \ln\left(\frac{pO_2'}{pO_2''}\right) \qquad (1)$$

where pO_2' y pO_2'' represent the oxygen partial pressure at the cathode and the anode sides, respectively, R, T and F are the ideal gas constant, the absolute temperature and the Faraday constant, respectively. The **cathode** material must stimulate the oxygen reduction process, but in turn should have a high electronic conductivity to facilitate both the collection of current and maximize the reaction active sites. Instead, the **anode** material will be subjected to the fuel environment, which, combined with the high operating temperature, may cause significant changes in its structural and transport proper-

ties. The main function of the anode is to catalyze the oxidation reaction of the fuel and, as in the case of the cathode, which requires the presence of electronic conduction to promote the process [5]. Under open-circuit conditions, the single-cell-output potential is maximum (OCV); however, under operating conditions, i.e. under current flow, a decrease of the useful voltage due to internal consumption associated to the total resistance occurs. The optimization of the internal resistance of the cell is an essential target to minimize the internal energy consumption and to reach suitable output-power values for practical applications.

2. Increasing the performance of the SOFCs: tuning the mixed transport behaviour

The energy conversion process shown in Figure 1 comprises several consumption stages which affect the useful output voltage of the cell. Thus, the electromotive force available for use in an external circuit can be expressed as:

$$E = OCV - \eta \qquad (2)$$

where η is the **total voltage loss** of the system. Firstly, the **electrochemical processes** at the electrodes and the interface between the electrodes and the electrolyte are identified. These processes are divided into different stages, such as the charge-transfer process, the ion-transfer process between the interface and the electrolyte, and the diffusion and adsorption of different species at the surface. There is also an **electrical transport** of charged species through the whole device, resulting in the ohmic re -

sistance of the system. As the electrode conductivities are orders of magnitude higher than that of the electrolyte, the ohmic resistance of the single cell is mainly attributed to the electrical transport through the electrolyte. For this reason, the optimization of the ohmic transport requires the search for electrolyte materials with high ionic conductivity in the range of working temperatures.

APU unit
Auxiliary power unit for a commercial vehicle based on a SOFC.
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The **electrodes** should be electronic conductors and the **electrolyte** an oxide-ionic conductor. However the electrical transport properties are dependent on the defect chemistry of the materials, which are highly influenced by working conditions. In many cases, the search for materials with optimized ionic transport properties is followed by the presence of some electronic conduction, which impacts possible use as electrolyte. This is the case of **lanthanide-doped ceria** ($Ce_{1-x}Ln_xO_{2-\delta}$; Ln=Gd, Sm), which presents a higher oxide-ionic conductivity than that of **yttria-stabilized zirconia** (YSZ, $Zr_{1-x}Y_xO_{2-\delta}$), the classic electrolyte material, but which in turn presents considerable electronic conductivity under the reducing conditions of the fuel. The mixed transport properties of the electrolyte and the presence of a pO$_2$ gradient, created by the fuel and the oxidant, allow the electrochemical reactions at the

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electrodes to occur, followed by ionic and electronic conduction at the electrolyte under open-circuit conditions. This leads to an oxygen-electrochemical-permeability process as shown in Figure 2. As a consequence, the output electromotive force is decreased according to:

$$OCV_{mix} = OCV_{ion} \left(\frac{R_e}{R_{ion} + R_\eta + R_e} \right) \quad (3)$$

where OCV_{mix} (= E_{obs}) y OCV_{ion} (=E_{th}) represent the open-circuit potential of the cell for a mixed-conducting and a purely ionic-conducting electrolyte (Eq. 1), respectively; R_e and R_{ion} are the electronic and ionic resistances of the electrolyte, respectively, and R_η is the overall polarization resistance at the interfaces between the electrodes and the electrolyte.
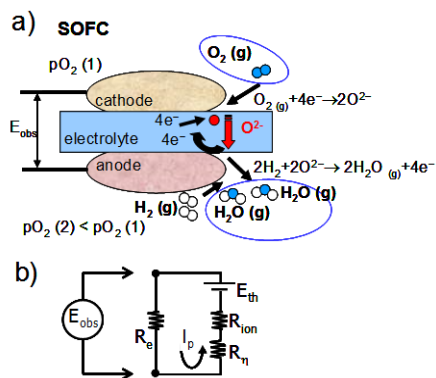

Figure 2. (a) Oxygen electrochemical-permeability process in a SOFC for a mixed conducting electrolyte; (b) equivalent circuit associated with the whole system under working conditions.

It should be noted that the presence of some *minor electronic conductivity at the electrolyte* could be beneficial for the improvement of the electrochemical

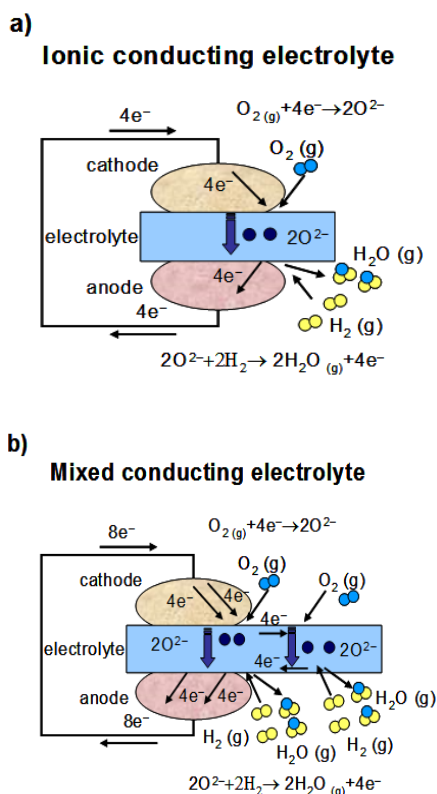processes at the electrodes [7], due to an enlargement of the active reaction zones (Figure 3).

Figure 3. Schematic representation of the electrochemical reactions at the interfaces between the electrolyte and the electrodes for a purely oxide-ionic-conducting electrolyte (a) and for a mixed-conducting electrolyte (b).

For this reason, the performance of the overall devices could be improved by the introduction of a minor electronic component into the electrolyte, which should be orders of magnitude lower than the ionic conductivity, to avoid damaging the open-circuit voltage of the system, but in turn improving the performance of the electrodes.

For ceria-based materials, the decrease of the open-circuit voltage is less pronounced for lower temperatures, because of the greater decrease of the electronic conductivity compared to the ionic conductivity, associated with the higher activation energy of

the electronic process. As a consequence, ceria-based materials are very interesting candidates for use in the intermediate range of working temperatures of 500-700 ºC. On the other hand, decreasing temperature has the effect of increasing the ionic resistivity, which indicates the need for reducing the electrolyte thickness. For this reason, new research is mainly focused on anode supported single cells, in which the enlargement of the anode thickness has a low impact on the overall ohmic resistance of the system. Regarding this, different technologies of film deposition are receiving increasing interest as a key factor for the development of suitable designs for several applications. Regarding the electrodes, while presenting electronic conductivity is necessary for the electrochemical reactions to take place, the presence of some ionic conductivity generally increases the performance of the whole system. The reason for the improvement is the enlargement of the active sites of reaction to the whole surface of the electrode (Figure 4), whereas for purely electronic-conducting electrodes the electrochemical reactions take place at the three-phase boundary where oxygen, electrode and electrolyte meet.

As presented above, the optimization of the mixed-conducting properties is considered a very interesting strategy for the improvement of the performance of SOFCs. This requires modification of the properties of the materials with the objective of producing the desired effects without affecting other parameters.
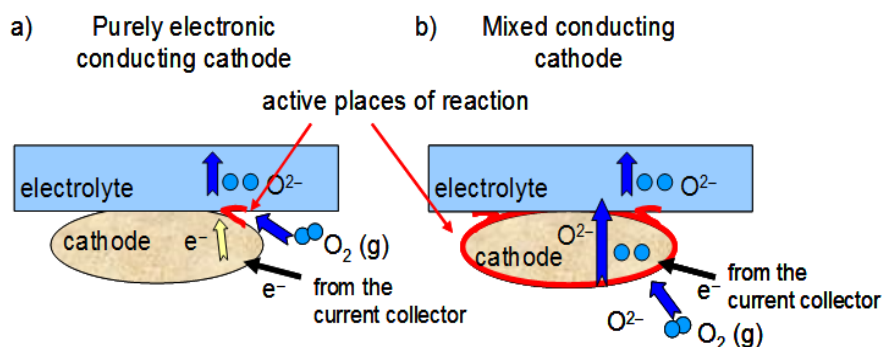
Figure 4. Representation of the active places for the reduction electrochemical reaction for a purely electronic-conducting cathode (a) and for a mixed-conducting cathode (b).

3. Evaluation of the mixed-transport properties: characterization techniques.

Classical techniques for characterization of the electrical-transport properties of the materials are focused on the relation between the voltage to which they are submitted and the current flowing through the sample. These techniques include the use of alternating current or direct current signals, or even several configurations for the electrode arrangement, such as 2-probe or 4-probe methodologies. In the latter arrangement, the application of the electrical field is located away from the electrodes for the evaluation of the response of the sample in order to avoid a contact resistance. However, the evaluation of mixed-conducting materials by classical methodologies leads to a parallel transport of charged species. As a consequence, the transport through the minor conducting species could be obscured by the transport through the main conducting carriers, thereby masking information about the minor conducting component. Moreover, if both conductivities are of the same order of magnitude, the total current consists of the addition of the two contributions, which prevents the separation between the components.

These considerations point to the need for specific electrochemical methodologies of characterization to evaluate the different components of conductivity, which should be used to complement conventional techniques to have a broad knowledge of electrical and electrochemical properties

As remarked above, an electrochemical-oxygen-permeability process is observed when an oxide-ion-electron mixed-conducting material is exposed to a gradient of pO_2, leading to the transport in series of ionic and electronic species, according to Figure 2. Under these conditions, the overall conduction process is determined by the ambipolar conductivity as follows:

$$\sigma_{amb} = \frac{\sigma_{ion} \cdot \sigma_e}{\sigma_{ion} + \sigma_e} \qquad (4)$$

where σ_{ion} y σ_e represent the oxide-ionic and electronic conductivities, respectively. From Eq. 4, it is directly deduced that the electrochemical permeability process is governed by minor species when both conductivities are separated by several orders of magnitude. This interesting feature allows the identification of the minor electrical transport component in mixed-conducting oxides by means of the oxygen flux produced by *electrochemical permeability* [8,9].

On the other hand, the existence of the mixed-conducting properties produces a decrease of the electromotive force of the system when it is submitted to a gradient of pO_2 in order to produce the current flux. According to Eq. 3, there is a direct relation between the mixed transport properties and the open-circuit potential of the mixed conducting material. Hence, the evaluation of the *electromotive force* of the sample after being submitted to a gradient of pO_2 could be used for determination of different components of the electrical conduction [10].

Another interesting methodology is *faradic efficiency*, which is focused on the analysis of the ionic current that is flowing through the mixed-conducting material when a total current is set. The determination of the ionic flux is performed by driving the oxygen transported by the mixed conducting sample through a purely ionic-conducting sample [10].

These methodologies are mainly used for the analysis of the transport properties under moderately oxidizing conditions. In the range of low values of oxygen partial pressure, that is under reducing conditions, the *Hebb-Wagner ion-blocking* method is suitable for determination of minor elec-

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tronic conductivity. For the application of this technique, one of the electrodes should act as an ion-blocking electrode. For this purpose, the cell design involves the establishment of a small sealed chamber in contact with one of the electrodes of the sample, which has an oxide-ion blocking effect after steady-state conditions are reached. Under the ion-blocking conditions, the evaluation of the transport properties are related to the electronic properties [11].

The electrochemical methodologies listed above require the design of specific electrochemical cells capable of tuning the operation conditions to obtain information concerning the mixed-conducting components.

Knowledge of the contributions associated to the electrical transport is a key factor which allows the corresponding properties to be understood and thereby to produce an enhancement of the overall performance of the devices.

Bloom Box
SOFC system based on YSZ electrolytes and natural gas as fuel.
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Conclusions

Solid Oxide Fuel Cells are an interesting solution as a transitional technology for the future implementation of efficient, renewable and emission-free energy systems. The electrical and electrochemical properties of the constituent materials are responsible of the generation of an electromotive force when the anode and the cathode are submitted to a fuel and an oxidant, respectively. This electromotive force is exploited to produce an electrical current with a high degree of energy efficiency. As essential issues, the electrodes should possess high catalytic activity towards electrochemical reactions and high electronic conductivity under working conditions, whereas the electrolyte should be an oxide-ion conductor. In this regard, controllable introduction of mixed conduction in the materials could be decisive for the enhancement of the performance of the systems due to a lower internal resistance. For the proper tuning of the transport properties, the determination of the specific components involved in the whole conduction process is required. For this purpose, the development of appropriate electrochemical cells, specifically made to produce the required working conditions and to assess the corresponding magnitudes, is essential.

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CHP unit
Heat and power combined system for residential use based on SOFCs.
www.cerespower.com

Most of his career has been focused on the study of solid oxide materials for application in high temperature electrochemical devices, such as solid oxide fuel cells and, in particular, the analysis of the electrical and electrochemical properties of ionic, electronic and mixed conducting materials. During his research career he has worked at the University of La Laguna, the Polytechnic Institute of Viana do Castelo, the University of Aveiro, the Center of Energy, Environmental and Technological Research (CIEMAT) and the Institute of Ceramics and Glass (ICV-CSIC), where he has worked since 2009. His research has been mainly funded by the "FPU", "Juan de la Cierva" and "Ramón y Cajal" programs.

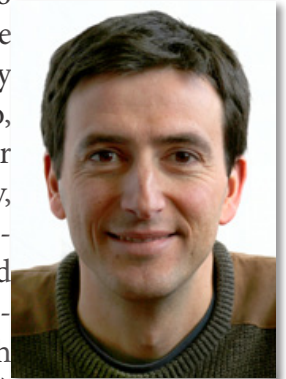# References

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