Tailoring electrocatalytic properties of solid oxide fuel cell composite cathodes based on (La$_{0.8}$Sr$_{0.2}$)$_{0.95}$MnO$_{3+\delta}$ and doped cerias Ce$_{1-x}$Ln$_x$O$_{2-\delta}$ (Ln=Gd, La, Er, Pr, Tb and x=0.1-0.2)

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Abstract

Composites made of different doped cerias and (La$_{0.8}$Sr$_{0.2}$)$_{0.95}$MnO$_{3+\delta}$ were studied as potential solid oxide fuel cell cathodes. Tb, Pr, Gd and Er have been introduced as ceria dopants to enhance the electrocatalytic properties of (La$_{0.8}$Sr$_{0.2}$)$_{0.95}$MnO$_{3+\delta}$ composites fabricated within. Different electrochemical behaviors were observed for the studied composites depending on lanthanide cation nature, i.e., whether they can exhibit different oxidation states or not. Specifically, (La$_{0.8}$Sr$_{0.2}$)$_{0.95}$MnO$_{3+\delta}$/ceria composites with a mixed valence dopants (Tb and Pr) in the CeO$_2$ structure are the best performing and present a limiting step at low frequencies; whereas those with ceria-doping elements with fixed oxidation state (Gd and Er) exhibit the limiting processes at higher frequencies. This fact is related to the higher magnitude of the TPB enlargement in the composite cathode achieved thanks to the promotion of mixed ionic-electronic conductivity in the Pr/Tb-doped ceria phase. The best cathode performance was obtained with (La$_{0.8}$Sr$_{0.2}$)$_{0.95}$MnO$_{3+\delta}$_Ce$_{0.8}$Pr$_{0.2}$O$_{2-\delta}$ cathodes with the lowest values for both the polarization resistance in the 900-700 ºC temperature range.

Keywords: SOFC; cathode; composite; doped cerias; LSM; praseodymium

1 Introduction

Solid oxide fuel cells (SOFCs) are devices able to produce power from fuels with the highest efficiency. The performance of these devices depends on their capability to directly transform fuels into electricity at conditions suitable for the specific system integration and with improved durability. Research efforts have been focused on developing new materials with high electrochemical performance [1]. Specifically, the improvement of oxygen reduction reaction (ORR) electrodes (e.g. SOFC cathodes) requires adjusting the electrocatalytic properties in order to increase performance and/or reduce the operating temperature for future SOFC devices, as well as for other devices employing oxygen-ion based electrolytes and membranes.

One of the widest used SOFC cathode materials is the lanthanum strontium manganite ($La_{1-x}Sr_xMnO_{3+\delta}$ - LSM) due to its high electronic conductivity ($\approx$180 S·cm^{-1} at 1000 °C [2]), excellent catalytic properties [3] and high thermal [4, 5] and mechanical stability [6]. Moreover, LSM is thermo-chemically compatible with different electrolyte materials such stabilized zirconias [4, 7] and, doped cerias [8]. However, LSM has a negligible ionic conductivity [9] thus limiting its application as SOFC cathode at high temperatures (>850 ºC). In order to improve the performance of these cathodes, ion conducting materials are commonly added to form dual-phase composites, e.g. LSM/YSZ composites. As a consequence, the triple phase boundary (TPB), where the ORR can take place, is enlarged and the electrochemical reactions may occur not only on the interface electrode-electrolyte[10] but all along the cathode thickness. As a consequence, the introduction of the ionic phase results in cathodes with lower electrode resistance [11-13]. Usually, the same SOFC electrolyte ion conducting material is mixed with LSM. Different percentages of ion conducting compounds[14] and sintering temperatures have been studied[15] in order to further improve the electrochemical performance of these fabricated composite cathodes.

Doped ceria oxides[10] have been pointed as an alternative to state-of-the-art stabilized zirconia electrolytes, due to their higher ionic conductivity at low temperatures. In addition, different lanthanide-doped ceria materials have shown interesting catalytic redox properties and high ionic conductivity [16], and they have been tested both as electrolytes and composite electrodes [17, 18].

With these premises, the present paper studies the electrochemical performance of several LSM-ceria composite cathodes, where the ionic conducting phase is composed of different ceria-based materials. Moreover, the oxygen reduction reaction mechanisms will depend on the electronic and/or ionic conductivity of both phases in the composite cathode. In the present work, different cations were incorporated in the fluorite phase to study the impact of working with composites made of (1) either pure electronic and ionic materials; or (2) pure electronic and mixed ionic-electronic materials. Thus, cations with a mixed valence (Pr and Tb) or a fixed valence were used (Gd and Er) with the purpose of changing the ceria properties. Ceria compounds used in this study have the general formula $Ce_{1-x}Ln_xO_{2-\delta}$, being Ln = Pr, Gd, Tb or Er and x = 0.1 or 0.2.

2 Experimental

Different $Ce_{1-x}Ln_xO_{2-\delta}$ (Ln = Pr, Gd, Tb or Er and x = 0.1 or 0.2) materials were synthesized by co-precipitation method [16]. The resulting precursor powders were dried overnight at 100 ºC after water filtration and rinsing. Finally, each precursor powder was calcined during 5 hours in air at 800 °C to decompose the residual nitrates and carbonates, and to favour the formation of the fluorite phase. $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3+\delta}$ (LSM) powder was purchased to Fuel Cell Materials (USA). A-deficient LSM in SOFCs exhibits better electrochemical performance although the deficiency promotes the densification of the material, which may cause loss of porosity over a long operation

Dense rectangular probes ($4 \times 0.4 \times 0.2$ cm^3) of ceria-based material were obtained by uniaxially pressing powders at 125 MPa during 1 min and subsequently sintering 5 h at 1300 °C in air. Electrical conductivity measurements were conducted by standard four-point DC technique. Silver paste and wires were used to ensure the electronic contact in the as-fabricated dense probes. A programmed current was supplied by a Keithley 2601 power source and the voltage was detected by a Keithley 3706 multimeter. Conductivity measurements were done under air and the total electric conductivity has been calculated.

The crystalline structure of the different materials was studied by X-ray diffraction (XRD). The measurements were carried out by a PANalytical Cubix fast diffractometer, using CuK$\alpha_{1,2}$ radiation and an X'Celerator detector in Bragg-Brentano geometry. XRD patterns were recorded in the 2θ range from 20° to 80° and analyzed using X'Pert Highscore Plus software.

Screen-printable inks made of LSM/ceria-based composite cathodes were prepared by three roll milling LSM powder, the corresponding ceria-based material and a 6% wt. ethylcellulose - terpineol solution in a 1:1:2 weight ratio. These inks were applied on both sides of 1 mm-thick fully-dense electrolytes made of Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ + 2% wt. of Co cations (GDC-Co), with regard to the total mass, provided by IKTS Fraunhofer (Germany). Porous electrodes were obtained after calcining screen-printed layers at 1150 °C for 2 h. A top screen-printed gold mesh was further applied on the electrodes in order to ensure proper current collection.

As-fabricated symmetrical cells were tested by means of electrochemical impedance spectroscopy (EIS) using a 0 V DC − 20 mV AC amplitude signal provided by a Solartron 1470E/1455 FRA device. Electrochemical measurements were performed in air and diluted air (5% vol.) in the 650-900 °C temperature range. The symmetric cell configuration provides polarization resistance of an electrode under the open-circuit condition. The cathode in full cells under DC load may exhibit lower polarization resistances depending on the specific

cathode material and the applied DC bias. The electrode microstructure was analyzed by SEM imaging in a JEOL 6360 microscope after electrochemical testing.

Voltamperometric measurements were carried out on fully assembled SOFC. Disk-shaped anode-supported cells with diameter 15.5 mm consisted of an anode substrate (averaged thickness of 1500 μm), an anode functional layer (thickness in the range 5–10 μm), and an 8YSZ electrolyte (thickness in the range 5–10 μm). The anode functional layer (NiO/8YSZ) and the electrolyte (8YSZ, Tosoh, Japan) were produced by vacuum slip casting and co-fired at 1400 ºC, resulting in a gastight 8 μm-thick electrolyte. On top of the electrolyte a ~30 μm cathode layer was applied by screen-printing. Electrochemical single cell testing was done as a function of temperature using humidified hydrogen (150 mL·min^{-1}) as fuel at the anode side and air (150 mL·min^{-1}) at the cathode side. Sealing was achieved using gold gaskets.

3 Results and discussion

Ceria-based compounds synthesized in this study[a] were completely obtained as single fluorite phase[19], excepting CeEr82, which show minor peaks related to Er_2O_3. The selection of lanthanides was done to bring enhanced conduction and electrocatalytic properties to the ceria phase, which serves as ionic component of the composite electrode. Gadolinium together with Samarium is the ceria dopant of choice for both SOFC electrolyte and composite electrodes due to its high pure ionic conductivity at moderate temperatures and oxidizing atmospheres. Erbium was chosen due to their trivalent oxidation state, which basically introduces oxygen vacancies into ceria in oxidant conditions [20], as gadolinium does. On the other hand, Pr and Tb are elements with a variable 3+/4+ oxidation state, depending on the temperature and oxygen partial pressure, and have a particular redox behavior. These cations

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[a] For simplicity, hereinafter $Ce_{1-x}Ln_xO_{2-\delta}$ ceria compounds will be named as CeLnXX depending on each lanthanide-dopant (Ln = Gd, Er, Tb or Pr) element and the corresponding percentage of substitution level (XX = 82 or 91)

were selected in order to add a particular electrochemical and redox behavior to the ceria phase on the cathode composite.

3.1 Ceria-based materials total conductivity

Arrhenius plots in Figure 1 show the total electrical conductivity and reveals that ceria-based materials with 20% molar lanthanide doping level exhibit higher total conductivity than 10% ones, excluding CeErXX compounds (diamond symbols in Figure 1). This is possibly due to the erbium oxide impurities in CeEr82 material, which may increase the resistivity of ceria [21].

For both Ln-doping levels (XX), the highest total conductivity at high temperatures was obtained for Gd doped ceria (CeGdXX data in Figure 1). However, the conductivity of CeGd82 is overwhelmed by CePr82 by decreasing the temperature (Figure 1a). Pr has been reported [22] to introduce electronic levels in the band gap of ceria, which enhance the electronic conductivity via small polaron hopping between Pr^{3+} and Pr^{4+}. This hopping reaches a maximum in conditions where the concentration of the two valence states is equal, which in air occurs at temperature around 700 °C. CePr91 does not show the same enhancement. The doping level seems to be insufficient to ensure the continuous electron hopping between the energy levels discretely introduced by Pr within the ceria band gap [22]. Finally, Tb-doped cerias exhibit a similar behavior [23] to CePrXX, i.e., CeTb82 is a mixed ionic electronic conductor, although CeTb82 and CeTb91 show the lowest total electrical conductivity among all the studied cerias (Figure 1).

3.2 LSM and ceria-based compatibility

With the purpose to optimize the electrocatalytic activity of the SOFC cathode made of LSM, LSM particles were physically mixed with different lanthanide-doped ceria particles. The resulting composite cathode comprised a 1:1 weight mixture of LSM and the corresponding ceria, including CeGd82 as a reference. This ratio has been studied previously and reported as the most performing for SOFC composite cathodes[10].

Powders of the different phases of the LSM/CeLnXX composite were mixed in order to check their compatibility at the electrode sintering temperature. After a treatment at 1150°C in air for 2 h, XRD measurements were performed to confirm the absence of other phases than ceria and LSM. As can be inferred from Figure 2, all peaks in each of the mixtures can be assigned to either the fluorite or the LSM perovskite structure (the patterns of both parent phases are added at the bottom of the Figure 2 for reference). The peak at 45° corresponds to the steel sample holder (stainless steel 434-L). Er_2O_3 impurity present in the ceria phase of LSM-CeEr82 sample cannot be detected within this measurements and at the scale of Figure 2, but it has been analyzed and reported [19].

3.3 SEM characterization of symmetrical cells

The microstructure of the fabricated symmetrical cell was characterized by means of SEM analysis on the fracture cross-section after electrochemical impedance spectroscopy (EIS) measurements. In Figure 3a, the high density of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (2% Co) electrolytes (bottom part of each micrograph in Figure 3a) can be observed while the thickness of representative electrodes is around 25 µm or higher. In addition, on top of the image corresponding to LSM_CeEr82 composite cathode, the gold screen-printed mesh for ensuring proper current collection is visible. This gold top layer is applied on top of both electrodes of all symmetrical cells. In Figure 3a the good attachment between electrodes and electrolyte after the 1150 °C firing step can be observed.

Irrespective of the ceria compound used, grains of both materials (LSM and $Ce_{1-x}Ln_xO_{2-\delta}$) are well connected and distributed for all electrodes, as deduced from Figure 3b, in which a SEM magnification for each electrode is shown. In fact, there are no big differences in the grain size between LSM and ceria-based compounds albeit the calcination temperature of both materials is different[8]. The open porosity of electrodes is enough for air percolating

3.4 Electrochemical characterization of symmetrical cells

Electrochemical Impedance Spectroscopy (EIS) measurements were performed on each symmetrical cell and impedance results were processed for obtaining the resistance assigned to electrodes: only the contributions in the negative imaginary part (capacitive and resistive) were taken into account as electrode contribution[24]. At the temperatures of the analysis, the contributions assigned to electrolyte and contacts appear as a real resistance in series with the electrode contribution, and they will not be taken into account. Then, the electrode related values were corrected by the area of the electrode and the resulting values were divided by two, since both electrodes are identical, obtaining the corresponding electrode polarization resistance (Rp) for each composite material.

3.4.1 Electrode polarization resistance

Figure 4 shows the electrode polarization resistance (Rp) in air as a function of temperature for the different analyzed composite cathodes. Values for symmetrical cells done with single LSM electrodes are placed on each plot for comparison. The addition of the different doped-cerias to LSM always produced an improvement of the electrode performance, i.e., the Rp drops in up to one order of magnitude, when compared to the parent LSM electrode (Figure 4). These lower Rp values confirm that the addition of an ionic conductor (and electrocatalytic) material to LSM leads to the enlargement of the active area and performance of the cathode.

One of the most surprising results, extracted from Figure 4, is the observation that LSM_CeGd82 and LSM_CeGd91 electrodes behave comparatively worse that the other electrodes comprising cerias doped with other lanthanides. The ORR activity of the electrodes containing Pr, Tb or Er seems to be enhanced despite the fact that the total conductivity ranking (Figure 1) is not directly followed. This may be an indication of the higher electrocatalytic activity of cerias doped with Pr, Tb and Er elements towards ORR. Thus,

alternative lanthanides other than gadolinium could be used for enhancing the performance of LSM-ceria composite cathodes, as it is purposed within this work.

Figure 4 shows the Rp dependence on the doping level for each lanthanide cation. Cathodes comprising Gd- and Er-doped ceria at 20% molar level exhibit lower Rp than the corresponding cathodes at 10% molar level (Figures 4c and 4d). This should be ascribed to the reduction of the ionic domain at higher dopant concentrations[25] and the increased ionic conductivity as a consequence of the higher concentration of oxygen vacancies. For the cathodes based on Pr- and Tb-doped ceria, this difference is much lower and, for the Tb-based cathodes, there is not a significant difference in Rp values (Figure 4b). In this case, the intrinsic mixed ionic-electronic conduction (MIEC) condition of the ceria based materials is good enough for ORR and no difference is observed within these two doping concentrations, as reported recently by Tuller et al [22] for Pr-doped ceria. The same conclusions can be extracted for Tb-doped ceria composites coming from the results in Figure 4.

Summing up for the tested electrodes, the higher the lanthanide dopant content the lower the electrode polarization resistance is, i.e. the best performing cathodes are LSM_CeX82 composites, with X = Pr, Tb, Er or Gd (Figure 4).

3.4.2 EIS analysis of the best composites

Detailed EIS analysis focuses on the best performing composite electrodes, i.e. 20% doping-ceria (LSM_CeLn82). Figure 5a shows the Nyquist plot for the EIS data measured at 750 °C in air for the different composite electrodes, while Figure 5b presents the Bode plot of the corresponding imaginary part. In order to easily compare the Rp exclusively related to the electrode, both electrolyte and minor contact (if any[b]) resistances have been subtracted in Figure 5.

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[b] It should be taken into account the top gold mesh layer applied on the electrodes to ensure a high electron collection

Despite the overall electrode Rp values are quite similar for the four analyzed cathode composites (Figure 5), two different behaviors depending on the ceria dopant nature can be easily distinguished in Figure 5b. Tb- and Pr-based electrodes present limiting contributions at high frequencies (HF) while Gd- and Er-based composites are limited by low frequencies (LF) processes (Figure 5b). The two different behaviors appear, as for the conductivity measurements of single ceria-based compounds, depending on the possible valence of the lanthanide dopant. Gd and Er present exclusively 3+ oxidation state under the testing conditions whereas Pr and Tb can adopt mixed oxidation states, i.e. 3+ and 4+. Accordingly, the different electrochemical behaviors stated by EIS analysis may stem from the different redox behavior of the lanthanide cations[19] and the derived electrochemical properties, i.e., the degree of mixed ionic-electronic conduction introduced by the ceria phase.

In a previous work[8], composite cathodes comprising LSM and co-doped ceria-gadolinia materials were tested and up to five different contributions were identified[26] in the impedance spectra, depending on the specific ceria composition. The three most important contributions were: two occurring at HF and another one at LF. The processes occurring at high/medium frequencies are related with the transport of oxygen ion/intermediates species through the LSM/Ce-doped material interface as well as their transport from the composite particles to the electrolyte[26]. On the other hand, the LF processes are related with the dissociation of oxygen species at the TPB competing with surface diffusion, as it happens on mixed ionic-electronic conductors.

In the present work Tb- and Pr-containing composites exhibit LF limiting processes (Figure 5b), in contrast with Gd- and Er-based electrodes limited by processes at HF. One may conclude that the addition of Tb/Pr allows the strong enhancement of HF processes and therefore the remaining LF contributions become prevailing. HF processes are ameliorated due to the generation electron percolating pathways along the electrode.

Taking into account the main processes identified previously for composite cathodes[26], Gd- and Er-based composites seems to suffer from transport limitations through the electrode. On the contrary, Tb- and Pr-ceria composites have limited processes related to competitive dissociation and diffusion of oxygen species.

The introduction of Tb and Pr in ceria-based material, assuming that Ce maintains the oxidation state at operation condition [16], produces a mixed valence of 3+ and 4+ in the structure, and consequently electronic conductivity is added to the ionic one [27]. That change in the oxidation state is temperature dependent [27]. This thermochemical reduction induces mixed ionic-electronic conduction in the ceria materials[25]. Therefore, the ORR takes place not only in the TPB but all along the ceria surface and the oxygen transport through the MIEC to the electrolyte is enhanced, making surface processes become limiting, [26] i.e., the oxygen dissociation and incorporation of oxygen species[28, 29], which appear at low frequencies in the EIS data. Furthermore, the enhanced performance observed for LSM_CePr82 is attributed to the higher oxygen exchange rate of CePr82 with respect to CeTb82 [23] due to the lower activation energy obtained (1.25 eV for CePr82 and 1.46 eV for CeTb82).

On the other hand, Er or Gd cannot change their valence. Thus, the ceria phase in LSM_CeEr/Gd82 provides only ionic conductivity at this operation conditions (electronic paths are negligible thus blocking the transport of oxygen in the grain boundaries)[25] and the oxygen reduction reaction is limited to TPB. Thus, the oxygen transport itself is limiting the whole electrode performance, and the main contribution in the EIS plots appears in the high frequencies range[26].

3.4.3 Influence of oxygen partial pressure on EIS measurement

In order to corroborate the preceding analysis of the impedance results, symmetrical cells of selected composite cathodes were additionally tested at 5% air in Ar (pO_2 = 0.01 atm) and EIS data were compared to the corresponding measurements under air.

The lack of pO$_2$ dependence shown in Figure 6 for all composites at the highest frequencies can be directly assigned with the oxygen ion transfer [30, 31] from the composite to the electrolyte. Since the electrolyte is the same for all tested symmetrical cells it is right to assume that the same behavior should happen for all electrodes.

On the contrary, when the amount of oxygen is reduced, the processes appearing at LF become more limiting, i.e., the impedance values increase and, in general, the spectrum shifts towards lower frequencies (Bode plots in Figure 6), irrespective of the cathode composition. Neither new limiting processes nor substantial changes in the limiting steps of each group of composite cathodes can be observed, i.e., Tb- and Pr-containing composites still have limiting processes placed at lower frequencies while Er- and Gd-mixtures do so at higher frequencies, with certain oxygen partial pressure dependence related to the origin of each process [30].

3.4.4. Overall discussion

The different behavior presented above for the composite electrodes can be explained by means of clusters formation in the electrode microstructure. Different types of interfaces should appear when electronic and ionic phases are mixed in the same electrode, since each well-dispersed phase forms a cluster (Figure 7): Type I is an interface formed between two clusters both ends of them are connected to both ends of the composite, i.e., current collector and electrolyte. In Type II interface, clusters are connected to their corresponding bulk phase but not to the other. Type III interface presents at least one of the phases not connected to the corresponding bulk phase[32]. Types I and II will reduce the overall electrode resistance[33], but Type III will increase the polarization resistance of the electrode. Specifically, the last type can be related with the high frequency contribution in the impedance spectrum [32, 33].

It is presumable that the main interfaces found in the studied composites should be like Type III or Type II because of the high degree of distribution for both LSM and ceria-based particles in the composite cathodes (Figure 3).

Sunde [33] studied the influence of different parameters on the impedance spectra of composite materials by computer modeling, taking into account the different types of interfaces presented above. These calculations were carried out for anode composites, but the general remarks can be extrapolated to any electronic/ionic composite electrode, like the cathodes presented in this work. As it can be appreciated in the Figures 5 and 6, for both Gd- and Er-based composites a HF arc is overlapping the main impedance arc, which is the typical shape for electronic/ionic composites with an electrode particle volume fraction around 0.4 and 0.5, as it is the case. As one phase of composite has (mainly) ionic conductivity and the other, i.e. LSM, presents electronic conductivity, the presence of Type III interface seems the most probable. The main HF contribution in the Bode plot (Figure 5 and 6) fits with the occurrence of Type III interfaces in these Er- and Gd-based composites. As a consequence, the transference of charged species or ion transport to the electrolyte is limited and it leads to HF limiting processes on impedance spectra.

On the other hand, the 20% molar doping level on the ceria compounds for Pr- and Tb-based cathodes provides mixed conductivity to these ceria-based materials. It produces extra electron transport paths and changes the nature of the composite electrode interface. The assumed Type III interface configuration for the LSM-CeLn82 composites is kept for CeEr82 and CeGd82 materials, but it changes when CePr82 or CeTb82 are used instead. With the addition of an ionic material (the ceria phase) with also electronic conduction (coming from Tb and Pr cations) Type III cluster interface is diluted. As a consequence, HF processes related to Type III interfaces are reduced and other limiting processes appears at lower frequencies (Figure 5), as for MIEC electrodes. The MIEC behavior of the LSM_CePr82 or LSM_CeTb82 composites allows for higher electron/ion transferring and then the dissociation coupled with surface diffusion (occurring at LF) becomes the limiting process of these cathodes. Besides, the intrinsic catalytic redox properties of Pr and Tb elements for the surface reaction due to the mixed valence [34, 35] could also take part in reducing the electrode Rp for the ORR in these composite cathodes.

3.5 Fully-assembled Solid Oxide Fuel Cells

A 30 µm-thick cathode of the best performing cathode comprising LSM and CePr82 was screen printed on a YSZ/Ni anode supported fuel cell. The electrochemical results are depicted in Figure 8a using wet (2.5% vol.) hydrogen as fuel and air as oxygen source.

Fully-assembled fuel cell composed LSM-YSZ/YSZ/Ni-YSZ was tested by Leng. et al.[36], and they obtained a maximum power density of 267 mW·cm^{-2}. In addition, Tsai el al. [37] studied LSM/YSZ composite as cathode with an interlayer of $(CeO_2)_{0.84}(Y_2O_3)_{0.16}$ (YDC) and the power density of LSM-YSZ/YSZ/YDC/Ni–YSZ fuel cell at 700 °C was 250 mW·cm^{-2}. In the present work, reasonably good results are obtained for these cathodes at relatively low SOFC temperatures. Nevertheless, further improvements are necessary to achieve higher performance with these tailored composite cathodes, e.g. changing electrolyte/anode composition to ceria-based materials and/or optimizing cathode microstructure. SEM analysis of the tested cell (Figure 8b) shows the good cathode attachment to the YSZ electrolyte, as well as the cathode microstructure. The top gold current collector layer applied on the sintered cathode is also visible.

4 Conclusion

Different ceria-based materials synthesized by co-precipitation method as pure fluorites were added as ionic phase in composite SOFC cathodes based on LSM. The electrochemical performance of 1:1 CeLnXX/LSM composites was carried out by electrochemical impedance spectroscopy in symmetrical cells. The results show a reduction of the polarization resistance when Ln=Pr, Tb or Er are used as dopants in the ceria phase in composite cathode, compared to state-of-the-art LSM/$Ce_{1-x}Gd_xO_{2-\delta}$ cathodes.

The mixed valence of Pr and Tb elements induces mixed ionic and electronic conduction in the ceria phase. The introduction of mixed conductivity allows the transport of oxygen along the whole electrode and thus changes the nature of the interfaces within the composite. Then limiting processes are shifted to low frequencies in impedance spectra. They are related to oxygen dissociation and surface diffusion like in MIEC materials. However, the addition of Gd- and Er-doped ceria to the LSM composite still presents limiting processes on impedance spectra occurring at higher frequencies. These are related to transport of oxygen ions to the electrolyte. Furthermore, all tested electrodes have a component independent on pO_2 at high frequencies which can be attributed to the oxygen ion transfer resistance in bulk materials.

In terms of polarization resistance, Pr- and Tb- doped-ceria composites have achieved the lowest polarization resistance values at the tested temperature range, and the LSM/$Ce_{0.8}Pr_{0.2}O_{2-\delta}$ combination showed the comparatively lowest values when decreasing temperatures. Finally the best performance material (LSM_CePr82) was tested as cathode in fully-assembled fuel cell obtaining a maximum power density of 162 mW/cm^2 at 750 °C. Although the LSM_CePr82 showed the best electrochemical performance in the symmetrical cell configuration, the low power density achieved indicates that further improvement should be done in the fully-assembled fuel cell configuration.

Acknowledgements

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Figure captions

Figure 1. Total conductivity of ceria-based materials in air with different doping contents: (a) CeLn82 and (b) CeLn91. Plots are arranged in an Arrhenius configuration

Figure 2. XRD patterns for the composite materials after 1150 ºC calcination. Patterns of CeO_2 fluorite and LSM perovskite are showed at the bottom as reference

Figure 3. SEM images of (a) cross section of selected symmetrical cells and (b) different composite electrodes microstructure after calcination at 1150 ºC

Figure 4. Electrode polarization resistance of LSM/ceria-based composites compared to the single LSM electrodes at different temperatures. (a) $LSM\_Ce_{1-x}Pr_xO_{2-\delta}$, (b) $LSM\_Ce_{1-x}Tb_xO_{2-\delta}$, (c) $LSM\_Ce_{1-x}Er_xO_{2-\delta}$ and (d) $LSM\_Ce_{1-x}Gd_xO_{2-\delta}$ (where x= 0.1 or 0.2). Plots are arranged in an Arrhenius configuration

Figure 5. Nyquist (left) and imaginary Bode (right) plots for the different LSM_CeLn82 tested electrodes at 750 ºC in air and in diluted air: (a) $LSM\_Ce_{0.8}Pr_{0.2}O_{2-\delta}$, (b) $LSM\_Ce_{0.8}Tb_{0.2}O_{2-\delta}$, (c) $LSM\_Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and (d) $LSM\_Ce_{0.8}Er_{0.2}O_{2-\delta}$. Logarithm of selected frequencies is provided on the Nyquist plot

Figure 6. Electrochemical impedance spectra for selected composite electrodes in air and under diluted air (pO_2 = 0.01 atm) at 750 ºC. Logarithm of selected frequencies is provided on the Nyquist plot (left). Bode plots of the imaginary part are showed at the right side of each Nyquist plot

Figure 7. Schematic illustration of different interface types present in a composite electrode with clusters of electronic and ionic particles

Figure 8. Fully-assembled fuel cell test: a) voltamperometric curves of a full LSM_CePr82/YSZ/NI-YSZ hydrogen fed fuel cell, with the calculated power density values at 700 and 750 ºC; and b) Back-Scattered SEM image of the cross-section of the SOFC. Inset: Higher magnification SEM images of cathode and anode.