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LSCM–(YSZ–CGO) composites as improved symmetrical electrodes for solid oxide fuel cells

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Abstract

A new concept of solid oxide fuel cell (SOFC), recently proposed, using simultaneously the same material ($La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$, LSCM), as both, anode and cathode, has been verified. The performance of such new design, symmetrical fuel cells (SFCs), could be improved by using a YSZ/CGO-based composite. The optimum ratio to minimise the series and the polarisation resistances (R_p) under reducing conductions was 1:1. This composition renders improved R_p values by a factor of 2 at 950 °C in flowing H_2 in comparison to LSCM-YSZ composites. Thus, the use of a mixed composite (YSZ–CGO) will allow to extend the applicability of LSCM at temperatures lower than 850 °C. LSCM–(YSZ–CGO) based SFCs offer promising performances, e.g., 0.4 W cm^{-2} at 950 °C using humidified H_2 as fuel.

Keywords: Composites; Microstructure-final; Electrical properties; Fuel cell; Symmetrical fuel cell

1. Introduction

The never-ending rise in the oil-market prices has attracted growing attention towards the development of renewable energies. Under these circumstances, solid oxide fuel cell (SOFC) technology is one of the most promising options, in the medium and long-term, to produce energy with low environmental impact and more efficiently than the conventional processes based mainly on the traditional fossil fuel combustion.

SOFCs are devices that produce electricity from the electrochemical reaction of a gaseous fuel as hydrogen or hydrocarbons and an oxidant (oxygen or air), producing electricity, heat and, in the case of hydrogen fuelled cells, water as the only by-product.[1] Each single cell comprises at least three elements: an anode, a cathode and an electrolyte. Each of these components must fulfil some requirements such as stability of the microstructure during the preparation and operation; chemical and physical compatibility, i.e., thermal expansion coefficients (TECs) similar to those of the other cell components; adequate porosity and catalytic activity to achieve the highest performances. More specifically, the anode and the cathode must show high electronic conductivity and stability in reducing and oxidising conditions, respectively. In other words, the search for a specific material for each function and compatible with the other components is a hard task. Therefore, if one could reduce the number of different materials, the fabrication process of a fuel cell would be simpler and cheaper.

The state of art of SOFC electrolyte material is the yttria-stabilised zirconia (YSZ).[2] $La_{0.8}Sr_{0.2}MnO_3$ (LSM),[2] is a typical choice as cathode material due to its excellent electronic conductivity between 800 and 1000 °C and good catalytic behaviour towards oxygen reduction. As for the anode materials, the Ni/YSZ cermet[2] offers excellent catalytic properties, mixed conductivity and good current collection properties. However, such cermets present some disadvantages related to the low tolerance to sulphur, carbon build up and volume instability upon redox cycling.[3,4]

The use of the same material as both cathode and anode simultaneously would be ideal to reduce the classical three elements of the fuel cell to just two, producing a symmetric fuel cell

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(SFCs). The use of two elements could facilitate the assembly of a fuel cell in a single thermal treatment, minimising problems related with the interdiffusion between cell components. Another important advantage is related to suppression of the possible sulphur poisoning and carbon deposition, given that any loss of performance may be recovered after reversing the gas flow.

The concept of symmetric fuel cell (SFCs) has been recently proposed[5] and proved[6] on (La,Sr)(Cr,Mn)O_3 (LSCM)-based electrodes producing rather competitive performances, i.e., 0.5 and 0.3 W cm^{-2}, at 950 °C, under humidified H_2 and CH_4, respectively.

The main drawback associated to the use of LSCM as symmetrical electrode is that, under reducing conditions, the ohmic drop increases with decreasing the pO_2. On the other hand,[6] CGO has been proposed as a way to decrease the ohmic drop in reducing conditions and also as a complementary electrocatalytic agent to LSCM to promote methane oxidation.[7] In the communication presented herein, we have evaluated this option and found that the series resistances were improved in addition to lower R_p values under the same experimental conditions and, more important, at lower temperatures.

2. Experimental

LSCM powders were prepared by solid-state reaction. Stoichiometric amounts of the corresponding pre-dried high purity of the corresponding oxides (Aldrich) were mixed and ground in acetone in zirconia ball mills for 30 min and then fired at 1400 °C for 10 h.

$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) was prepared following a precursors route. $Ce(NO_3)_3{\cdot}6H_2O$ and $Gd(NO_3)_3{\cdot}6H_2O$ were dissolved in the appropriate ratio in distilled water at 80 °C and then ethylene glycol and citric acid (Aldrich) were added under constant stirring until a gel was formed. The gel was then calcined at 300 °C rendering CGO powders with sub-micron particle size.

YSZ used as electrolyte and as a composite element was from Pikem. Dense YSZ pellets, for symmetrical cell measurements, 1.12–1.26 mm thick were obtained after uniaxially pressing YSZ powders at 1 tonne for 1.5 min. The resulting pellets were sintered at 1500 °C for 10 h.

The electrolyte for the fuel cell test was prepared via a modified tape-casting procedure described in the literature.[9] The green tapes were cut into disks and sintered at 1500 °C for 10 h. The final thickness of the ceramic was approximately 180 μm after firing.

Four LSCM–(YSZ–CGO) composites were prepared. The YSZ–CGO ratio was modified to produce different composites, i.e., 100:0, 80:20, 50:50 and 20:80 (w/w).

The powders were mixed together and a binder – Decoflux (WB41, Zschimmer and Schwartz) – was added to obtain a slurry. The slurry was used to paint symmetrical electrodes onto a YSZ thick-pellet for symmetrical measurements, and onto the YSZ thin-tape, in symmetrical configuration, for fuel cell test.[10]

All samples were fired at 1250 °C for 2 h. After that, a Pt-based ink was used to paint a current collector in both sides and fired at 950 °C for 2 h.

A ceramic-based material (Ceramabond 552-VFG, Aremco) was used to fix the sample to the fuel cell setup and to produce a gas-tight seal.

The polarisation measurements and the fuel cell tests were performed on a two-electrode arrangement. The ASRs were obtained under symmetric atmospheres. The ac impedance of the electrochemical cell was carried out using a Zahner IM6e, at open circuit voltage (OCV), in the frequency range 10^5–10^{-1} Hz. A 50 mV amplitude ac signal was used, obtaining reproducible spectra. Fuel cell tests were carried out using humidified 5% H_2, and pure H_2 and CH_4 as fuels and O_2 as oxidant. *I–V* plots were recorded by cyclic-voltammetry at a scan rate of 8 mV s^{-1}, using the Zahner IM6e unit. The water content was fixed by bubbling the gas through a humidifier thermostated at 20 °C. The concentration of water at that temperature was 2.3%.

3. Results and discussion

In a previous communication, the use of LSCM–YSZ composite was justified considering the benefits derived from the improved interfacial contact and the enlargement of the triple phase boundary (TPB) through the electrode material, in addition to the likely increase of the BET-specific surface area (SSA).[6] However, the p-type conductivity of LSCM in reducing conditions and the use of YSZ in the composite will produce an increase in the ohmic drop: the more reducing the more important will be this contribution and therefore the lower will be the fuel cell performance. The addition of CGO to this composite was proposed as an alternative to produce an increase in the electronic conductivity, thus removing the source of performance loss in the anode compartment. We decided to maintain the 1:1 eletrode:electrolyte ratio, as Murray and Barnett[11] found it rendered the smallest R_p values in air using similar composites (LSM–CGO in YSZ electrolyte).

The impedance plots in air (Fig. 1a), consist of at least three arcs, with similar morphologies to those previously observed,[6] and also similar when using LSM–YSZ composites.[12] The first two arcs, at high frequencies, are usually overlapped. Their relaxation frequencies were $\approx 10^{2.5\text{–}3.5}$ Hz. These values are in good agreement with those described by Jorgensen et al.[12] supposedly with transport/transfer of oxygen intermediates/oxide ions between LSCM and YSZ–CGO and through the ionic path of the composite. Under reducing conditions, the impedance spectra show at least two arcs (Fig. 1b) for the composites with lower CGO content, whilst an extra arc became visible for the composite with 80% of CGO. The first process, in the very high frequency, was usually negligible for the composite with lower CGO content and becomes more resistive as the CGO content increased. In any case, the introduction of CGO causes a marked decrease of the overall polarisation.

The symmetrical measurements (Fig. 2a) show that the series resistances (R_s) in humidified 5% H_2, reach a minimum for the 1:1 CGO:YSZ composition, in the whole temperature range. However, the R_s values rise again for larger CGO contents. A possible explanation could be rather poor microstructure

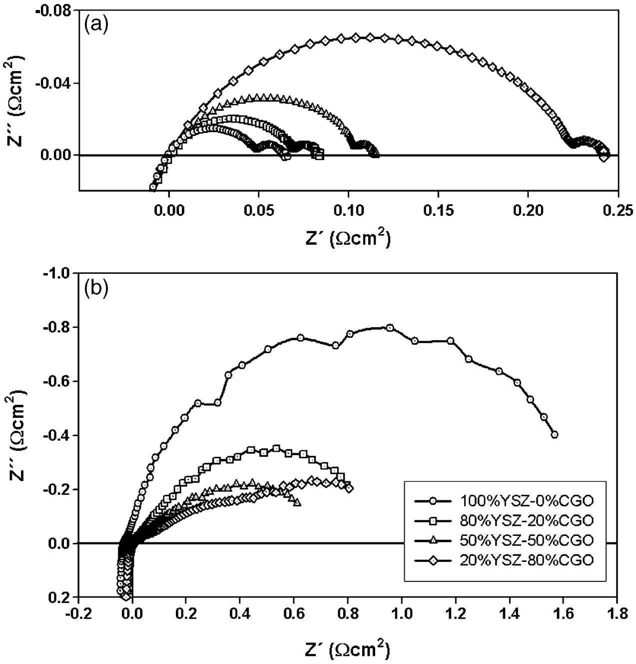

Fig. 1. Impedance plots under (a) air and (b) humidified 5% H_2, for four LSCM–(YSZ–CGO) composites, at 950 °C. (One should note that the inductance elements were not corrected, hence the final R_p values would be higher.)

observed for this composite (Fig. 3d). In air, the series resistances almost match the values obtained for a YSZ pellet used as a blank (Fig. 2a, dash line).

Additionally, the polarisation resistances (R_p) under 5% H_2, show a marked improvement for the 50:50 (YSZ:CGO) composite (Fig. 2b). At 950 °C, the polarisations values are reduced from 1.8 Ω cm^2 to approximately 0.8 Ω cm^2. Such improvement is even more remarkable at 850 °C, with a reduction from ~5 Ω cm^2 to just 1.6 Ω cm^2. Even the use of 20% of CGO reduces the R_p values to a half. A large increase of the CGO content, e.g., 80%, produces slightly worse values compared to the 50:50 samples. This can be attributed again to the poor microstructure (Fig. 3d) which in some places shows large holes in the interface electrolyte–electrode, decreasing the active surface and hence increasing the polarisation values.

On the other hand, the most unexpected result is the increase with the CGO content of the polarisation values under oxidising conditions (Fig. 2b). This could be explained in terms of the very small particle size of the CGO prepared by sol–gel, and during the production of the composite, it gets distributed around the LSCM particles. Thereby, the LSCM particles lose connectivity within the composite, causing a disruption of the electronic paths, which in turn explains the polarisation curves presented in Fig. 2b, since for an electrode it is very important to maintain the electronic paths well-connected through the electrode material.

All these results show that the addition of CGO may improve the polarisation values under reducing conditions. It should be noted that the microstructure was not optimised in this work (Fig. 3). Consequently, the use of the recently proposed method[8] using poly(methylmethacrilate) (PMMA) microspheres as template could produce a further enhancement of the fuel cell responses.

The potential use of these composite was tested in a fuel cell device under humidified H_2 and CH_4 as fuels and air as oxidant, rendering performances in the order of 400 mW cm^{-2} in H_2 (Fig. 4).

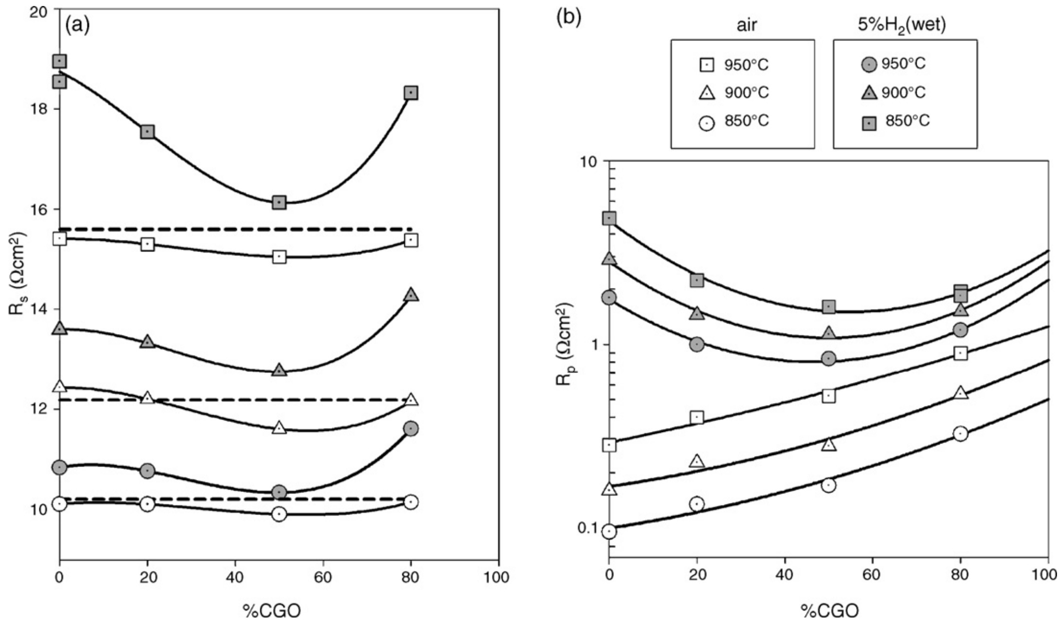

Fig. 2. Polarisation and series resistance values performed in symmetrical configurations under symmetric atmosphere. (a) Dependence of the series resistances, measured under reducing and oxidant gases, with the CGO content in the (YSZ–CGO) mixed composite. (b) Dependence of the polarisation resistances, measured under reducing and oxidant gases, with the CGO content in the (YSZ–CGO) mixed composite. The spectra have already been divided by two due to the symmetrical configuration. Humidified 5% H_2 (filled symbols), air (empty symbols), 950 °C (circles), 900 °C (triangles) and 850 °C (squares).

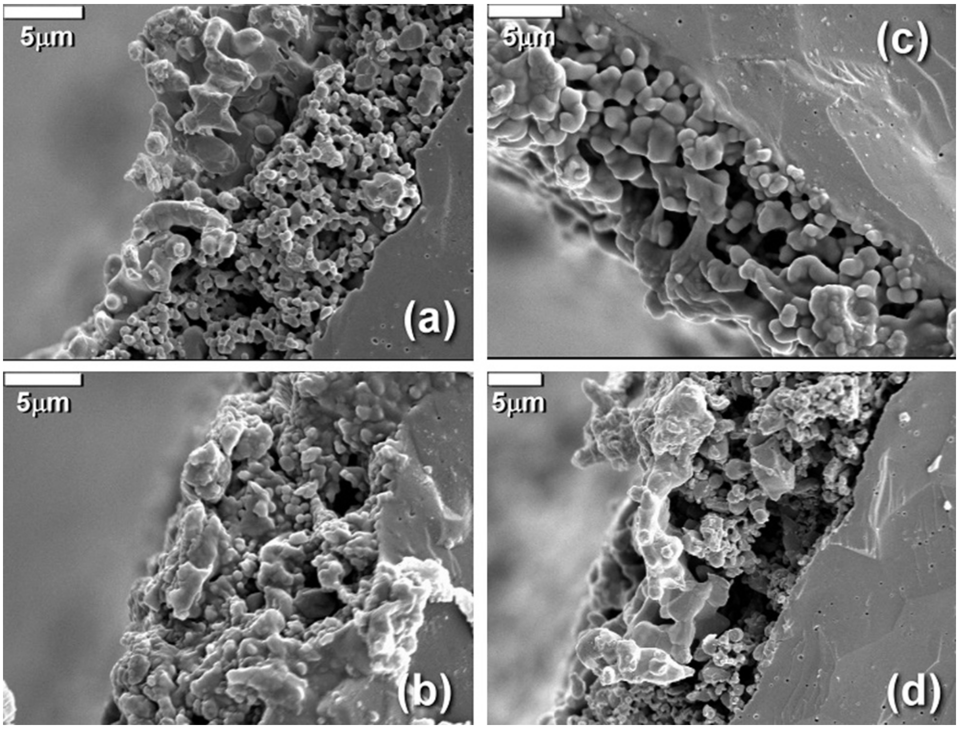

Fig. 3. SEM pictures of the cross-sections of four composites after testing. Ratio YSZ:CGO = (a) 100:0, (b) 80:20, (c) 50:50 and (d) 20:80. (a) Shows a homogeneous distribution of the grain size. However, the rest of the composites do not seem to exhibit an optimal microstructure. Particularly (d) shows big holes that could explain the high series resistances and polarisation values obtained for this particular composite. On the other hand, one should note that the electrode thickness ranges from 5 to 10 μm, to minimise the ohmic losses. However, in such a situation the platinum current collector should be considered as a part of the electrode material itself.

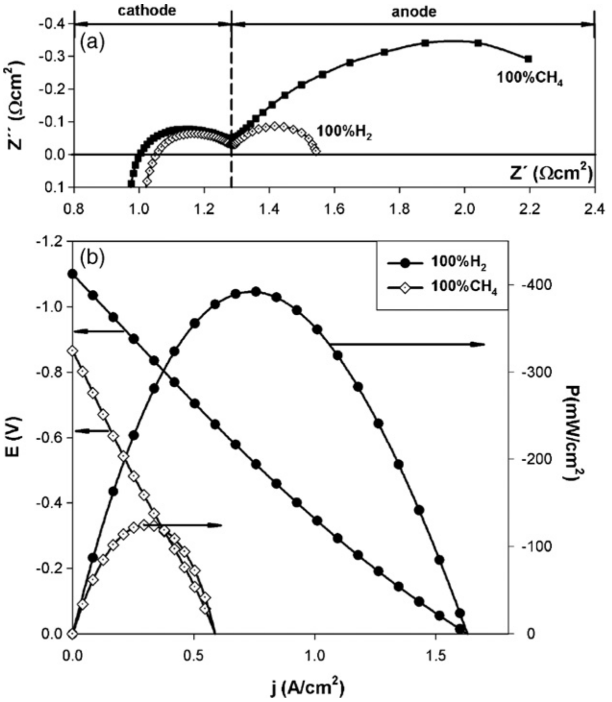

Fig. 4. (a) Typical impedance spectra of the whole fuel cell, under hydrogen, and methane, at 950 °C. (b) Voltage (*E*) and power density (*P*) vs. current density (*j*) plots of a SFC based on LSCM–(50% YSZ:50% CGO), obtained at 950 °C using two different fuels.

4. Conclusions

In summary, the new concept of symmetrical fuel cells was proved to be a valid alternative to the traditional SOFC configurations. It has been found out that the addition of small quantities of CGO to the LSCM–YSZ composite could further improve the performances as the series resistances and the polarisation values diminish under reducing conditions.

In air, the series resistances remain constant but the polarisations increase. However this increase could be considered negligible compared to the improvement obtained from the values in anode compartment. SFCs using LSCM-based composites offer interesting performances, e.g., 0.4 W cm^{-2} in H_2 at 950 °C.

Acknowledgments

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