Short communication

An all-in-one flourite-based symmetrical solid oxide fuel cell

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Abstract

A novel concept of solid oxide fuel cell (SOFC), the symmetrical SOFC, that uses simultaneously the same material as both anode and cathode has been investigated. Common materials typically used as anode components such as a combination of YSZ and CeO_2 plus a noble metal may be considered good candidates for such a configuration at relatively high temperatures (i.e. above 900 °C). These symmetrical electrodes exhibit enhanced electrochemical properties under both reducing and oxidising conditions, in part due to the catalytic properties of the noble metal used. In air the polarisation values are improved by a factor of four compared to electrodes without CeO_2, whereas under reducing conditions an improvement of two–three orders of magnitude has been observed. The best results correspond to cermets containing 50–60% of CeO_2.

This simple combination allows the assembly of all-in-one fluorite-based symmetrical fuel cells (SFCs): $YSZ–CeO_2/YSZ/YSZ–CeO_2$ plus a noble metal with good catalytic behaviour. Performances of 140 mW cm^{-2} at 950 °C were obtained when using H_2 as fuel and thick YSZ electrolytes. Interesting performances of 500 mW cm^{-2} are expected for thin YSZ electrolyte layer under identical experimental conditions.
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1. Introduction

Recently a new SOFC concept, the symmetrical solid oxide fuel cell, has been proposed [1,2] as a promising approach to overcome two of the main drawbacks associated to SOFC technology, e.g. reversible sulphur poisoning and carbon deposition when operating with hydrocarbons. Despite the engineering issues, working on a SFC would allow any formation of carbon deposits or sulphur-contamination to be easily removed from the anode simply by reversing the gas flow recovering any loss of performance.

Moreover, the production of robust and reliable SFCs would be simpler as the number of different components is reduced; hence the anode–electrolyte and the electrolyte–cathode interfaces would be similar, which would facilitate the assembly of a fuel cell in a single thermal treatment, minimising problems related with interdiffusion between cell components or asso-

ciated to thermal mismatch. In other words, the development of symmetric fuel cell (SFCs) may simplify considerably the production of (future) commercial fuel cells.

The requirements for candidate materials are rather restrictive as they should include all the conditions applicable to an anode and cathode simultaneously:

- The material should exhibit an acceptable electronic conductivity, in both oxidising and reducing atmospheres.
- It should be catalytically active towards oxygen reduction and fuel oxidation including hydrocarbons to avoid the use of external reformers.
- It should be stable and chemically and physically compatible with the other fuel cell components. This implies that no reactions should occur between the electrodes and the electrolyte and moreover the difference between the thermal expansion coefficients (TEC) should be negligible in a wide range of oxygen partial pressures.
- The porosity of the material should be precisely controlled to allow an optimum gas transient to the electrochemically active sites.

Despite the requirements over the materials choice are certainly demanding, the SFC concept has already been proposed and proved [1,2] using (La,Sr)(Cr,Mn)O$_3$ (LSCM)-based electrodes, producing rather competitive performances, i.e. 0.5 W cm^{-2} and 0.3 W cm^{-2}, at 950 °C, under humidified H$_2$ and CH$_4$, respectively [1]. Recently, the feasibility of the symmetrical SOFCs based on the same electrode material, LSCM, has also been confirmed by other research groups [3,4]. Nevertheless, several other systems have been explored in seeking for potential SFC electrodes such as La$_{0.7}$Ca$_{0.3}$CrO$_{3-\delta}$ [5], composites of chromium–manganites and gadolinium-doped ceria (CGO) [6] and titanates activated under oxidising conditions [7].

In the communication presented herein, we demonstrate that materials commonly used as anode components such as YSZ–CeO$_2$/noble metal [8] may operate as SFC electrodes at high temperatures.

2. Experimental

YSZ (Pi-KEM)–CeO$_2$ (Aldrich, 99.9%) composites were prepared in several ratios, i.e. 15%, 25%, 37%, 50%, 62%, 75% and 90% (w/w) of CeO$_2$. The powders were mixed with acetone in an agate mortar and left to dry at room temperature.

Phase purity was evaluated by X-ray diffraction (XRD) on a Philips X'Pert Pro automated diffractometer, equipped with a Ge(1 1 1) primary monochromator and a X'Celerator detector.

Dense YSZ pellets for symmetrical cell measurements and fuel cell tests, 1–2 mm thick and 15 mm diameter were obtained by uniaxially pressing YSZ powders at 1 ton for 1.5 min. The resulting pellets were sintered at 1500 °C for 10 h.

YSZ and CeO$_2$ powders were mixed with a Decoflux^{TM} (WB41, Zschimmer and Schwarz) binder to obtain a slurry, which was used to paint symmetrical electrodes onto dense YSZ pellets. The samples were fired at 1200 °C for 2 h and then a Pt-based ink was deposited on top of the electrodes and fired at 950 °C for further 2 h; additionally, a gold-based ink was used to compare any extra catalytic activity effect derived from the use of Pt-based current collectors (please note that this does not rule out the possible effect due to differences in the microstructure of the current collectors).

The polarisation measurements and the fuel cell tests were performed on a two-electrode arrangement and all the experimental details could be found elsewhere [1].

Electron microscopy images were obtained on a Jeol JSM-6300 electron microscope after fuel cell testing to check microstructure, connectivity between electrodes and electrolyte, or any evidence of degradation. The samples were cut and the cross-sections were covered with a fine gold layer by sputtering to avoid charging problems.

3. Results and discussion

In SOFC research it is common practice to use ceramic-based electrodes as composites with YSZ to introduce ionic conductivity, to avoid thermal expansion mismatch and to expand the triple phase boundary (TPB) through the whole electrode material. Also, in most of the SOFC testing publications, the ceramic material under study is usually covered with a thin layer of an adequate current collector such as Pt, Au or Ag to ensure good electrical contact, although these metals may enhance the electrochemical responses due to their catalytic activity [9,10]. On the other hand, CeO$_2$ is commonly used to increase the catalytic activity towards hydrocarbon oxidation [11–13] and to introduce some additional electronic conductivity under reducing conditions. Additionally, the deposition of a noble metal – typically used as current collector – over a "reducible" oxide support such as CeO$_2$ may produce excellent catalysts for certain electrochemical reactions [14–16]. In theory, the combination of YSZ and CeO$_2$ plus a noble metal could be a potential candidate as symmetrical electrode, given that the combination of the three elements seems to enhance the catalytic properties under oxidising and reducing conditions.

It has been reported that CeO$_2$–YSZ forms a solid solution over a whole range of compositions [17–19], typically at temperatures above 1300 °C. In the present study, the XRD patterns of the YSZ–CeO$_2$ composites calcined at 1200 °C for 2 h show the typical diffraction peaks ascribed to the fluorite-type structures, although the diffraction peaks are shifted as the CeO$_2$ content is modified, Fig. 1(a) and (b). This trend is explained by some chemical reactivity between both materials [20]. As can be observed in Fig. 1(c), the cell parameter of YSZ varies significantly from 5.140 Å to 5.170 Å as the content of CeO$_2$ in the composites is increased. This indicates a possible migration of Ce^{4+} with larger ionic radii than Zr^{4+} into the YSZ phase or alternatively yttrium depletion from the YSZ, producing an expansion of the volume cell. On the other hand, the variation of cell parameter for CeO$_2$ decreases slightly as the content of YSZ increases, suggesting that Ce and/or Y are incorporated into the ceria structure, producing subtle cell shrinkages as reported in the ICSD database [21]. The reaction between YSZ and CeO$_2$ materials may affect the conductivity of both materials as reported in the literature [22–24] and explains the anomalous dependence of the series resistance of the cell with the CeO$_2$ content, under air, as explained below.

The impedance plots obtained under air show at least two rate limiting processes, with similar morphologies to those observed using LSM–YSZ [25] or LSCM–YSZ composites [1]. In reducing conditions, at least two arcs are observed, one of them is only noticeable at high frequencies and for CeO$_2$-based composites. The remaining spectra could be fitted with one or two overlapped arcs. Thus, an ideal equivalent circuit as LR$_s$(RQ)$_1$(RQ)$_2$(RQ)$_3$ was used to describe the experimental data in the whole range of temperatures. L is an inductive element, R_s includes all the ohmic resistances and is named series resistances, R_i and Q_i are the polarisation resistance and constant phase element, respectively of the electrochemical processes. The overall polarisation resistance (R_p) is given by the addition of the individual polarisations R_i. Under oxidising conditions, the polarisation resistances were estimated from the difference between the intercept with the real axis at high and low frequencies.

In both cases, under air and H$_2$ atmospheres, the composites with high CeO$_2$ load exhibit much higher polarisation resistances. This is related with the poor adherence between CeO$_2$ and YSZ electrolyte in the experimental conditions considered,
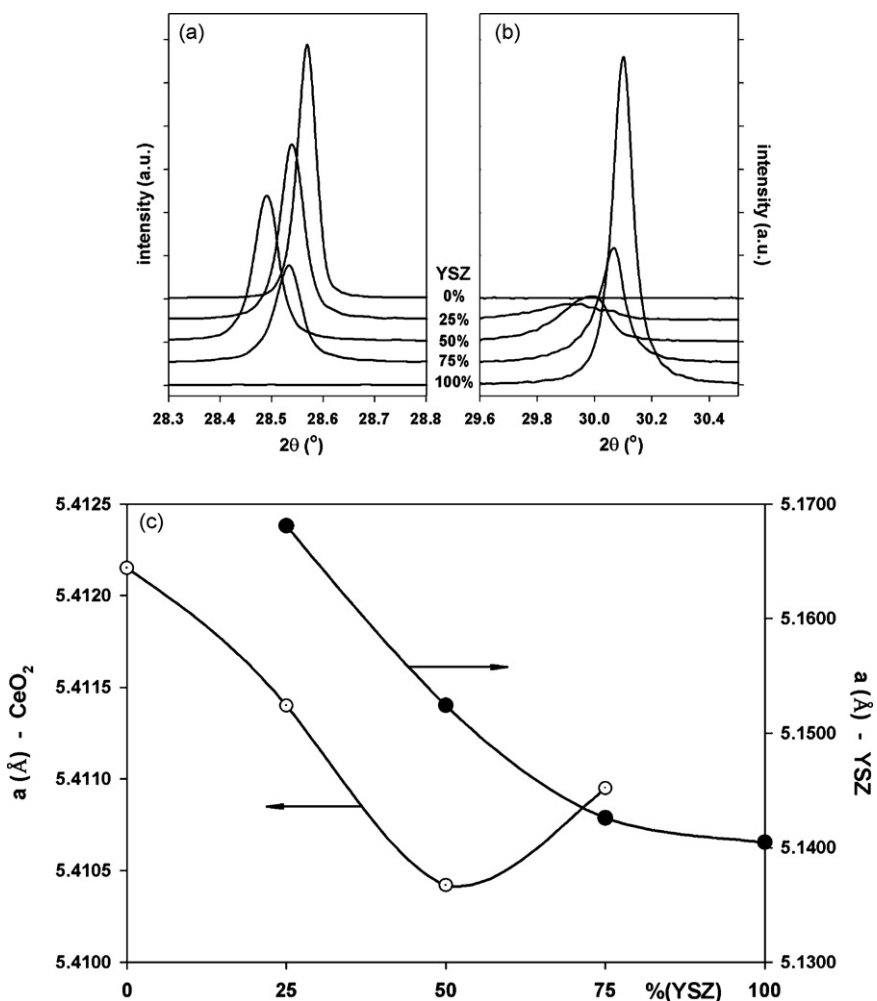
Fig. 1. Selected regions of XRD patterns of YSZ–CeO$_2$ composites, fired for 2 h at 1200 °C, under static air. (a) A magnification of the (1 1 1) diffraction peak of CeO$_2$, (b) magnification of the (1 1 1) diffraction peak of YSZ and (c) evolution of the cell parameters with the YSZ content, showing evidence of phase reaction.

decreasing the electrolyte–electrode contact surface area and hence increasing the polarisation values. Temperatures well above 1200 °C are typically required to properly fix the CeO$_2$ to the dense YSZ electrolyte, which in turn may result in further complications derived from the reaction between these two fluorites.

3.1. Behaviour of Pt–YSZ–CeO$_2$ as cathode

Fig. 2(a) shows the dependence of the polarisation resistance values with the temperature in static air for several cathode materials and the combination Pt–YSZ–CeO$_2$. The polarisation values under air improve upon increasing the CeO$_2$ content, reaching a minimum value for 30–50% of CeO$_2$ as shown in Fig. 2(b). The same behaviour has been observed for typical cathode materials used as composites of LSM and modifying the CGO content [26].

Surprisingly the sample used as reference with 0% CeO$_2$, Fig. 2(a), exhibits low R_p values, just 0.2 Ω cm^2 at 950 °C, although the series resistances, Fig. 2(b), were considerably larger. This sample was prepared using YSZ powder coated with a thin layer of noble metal paste to produce similar porous

structure comparable to the other samples. This is a clear evidence of the good behaviour of Pt–YSZ towards oxygen reduction. When replacing 50% of YSZ by CeO$_2$, the polarisation values are improved by a factor of 4, Fig. 2(b), and the series resistances almost match the value obtained for a YSZ pellet used as reference, at least at high temperature, Fig. 2(c). Most surprisingly, the polarisation values obtained for the Pt–(50% YSZ–50% CeO$_2$) cermet are similar, Fig. 2(a), or even in some cases, better than the values reported for commonly used high temperature cathode materials such as LSM or LSM–YSZ/GDC composites [26–28], LSCM–YSZ [1,3,4] composites, LCC–YSZ composites [5] or LSTF–YSZ [7]. Another noble metal, Au, was used to evaluate the catalytic effect of Pt in these electrodes. In this case, the polarisation response increases by a factor of up to 30 when using Au (∼1.4 Ω cm^2). Nevertheless the microstructural optimisation of the gold layer allows decreasing the starting polarisation from ∼1.4 Ω cm^2 to 0.6 Ω cm^2, which demonstrates that the effect is in part due to the microstructure and not only to the difference in catalytic activity.

On the other hand, an important contribution to the series resistances (R_s) is expected from the electrode material under
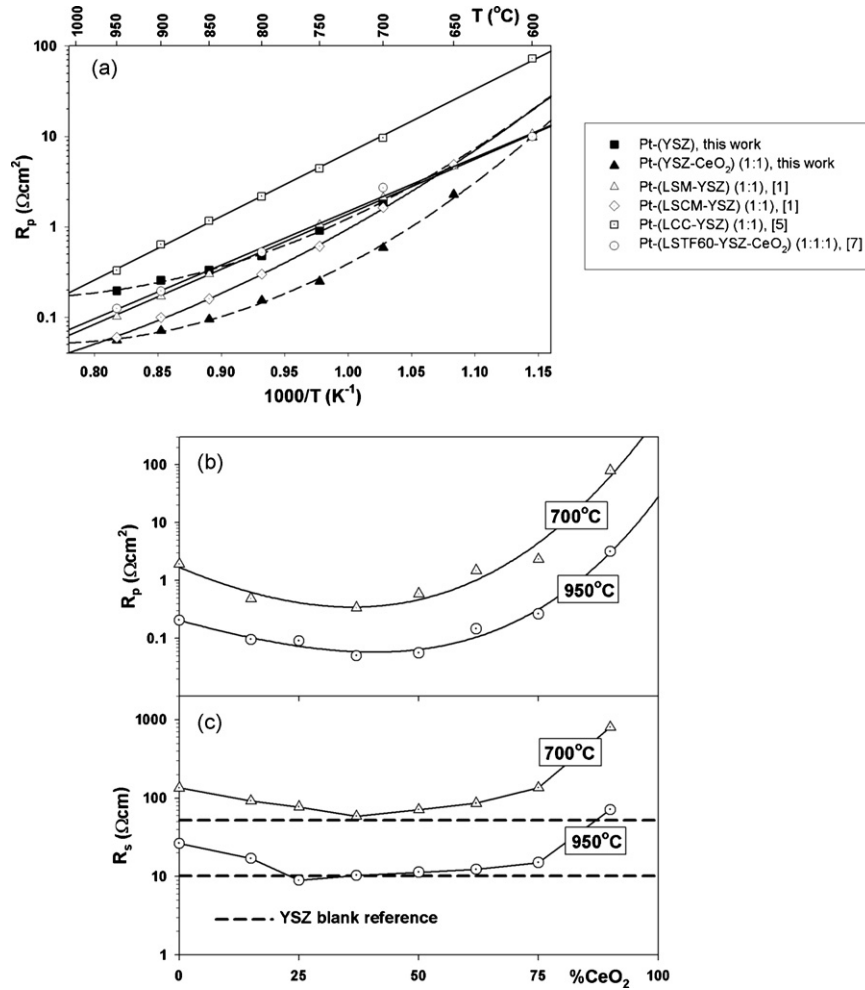
Fig. 2. (a) Dependence of the polarisation resistance values (R_p) with the temperature for different cathode materials tested under the same configuration in air (LCC: $La_{0.7}Ca_{0.3}O_{3-\delta}$, LSTF60: $La_4Sr_8Ti_6Fe_6O_{38-\delta}$), evolution of the (b) polarisation resistances, R_p and (c) series resistances, R_s, with the CeO_2 content in cermets Pt–YSZ–CeO_2 tested under air in symmetrical cells.

air as YSZ is a pure ionic conductor, Pt is on top of the electrode layer and the overall conductivity of CeO_2 in air is two orders of magnitude lower [22] than the conductivity of YSZ. However, the partial formation of a solid solution in YSZ–CeO_2 system presumably results in improved values of the series resistances, considering that the conductivity of these solid solutions is higher than the conductivity of pure CeO_2 but lower than YSZ depending on the CeO_2 content [23]. At CeO_2 contents above 60%, the ionic component (YSZ) becomes minor and hence the low conductivity of CeO_2 prevails, giving rise to larger series resistances.

3.2. Behaviour of Pt–YSZ–CeO$_2$ as anode

The temperature dependence of the polarisation resistances, under humidified 5% H_2 feed, is shown in Fig. 3(a). The apparent activation energy is 1.46 eV for the Pt–YSZ sample used as reference, which is in agreement with the larger values reported for Ni–YSZ cermets ranging between 1.0 eV and 1.5 eV [29,30], or for other Cu–YSZ-based cermet anodes as $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM) and

$La_4Sr_8Ti_{11}Mn_{0.5}Ga_{0.5}O_{37.5-\delta}$ (LSTMG) with apparent activation energies ranging between 1.05 eV and 1.09 eV [31]. When introducing 10% of CeO_2, a drastic improvement in the activation energy is observed, i.e. decreasing from 1.46 eV to 0.68 eV, this value remains constant up to 50% of CeO_2 and then increases slowly to reach 0.83 eV for cermet with 90% of CeO_2, Fig. 3(b). Such an improvement is mainly related with the good catalytic behaviour of CeO_2 towards fuel oxidation, given that the cermet microstructures remain fairly similar in the whole range of tested compositions and the noble metal used was always the same.

Such an enhancement as a function of the CeO_2 additions is even more noticeable when analysing the R_p values. Replacing 50% of YSZ by CeO_2 produces a very important decrease of the polarisations of up to three orders of magnitude at 700 °C. For instance, the R_p values change from 63.5 Ω cm^2 to 0.42 Ω cm^2, at 950 °C, whereas at 700 °C the R_p varies from 1516 Ω cm^2 to 1.74 Ω cm^2, Fig. 3(c).

Under reducing conditions and/or temperatures above 600 °C, Ce^{4+} is partially reduced to Ce^{3+}, leading to a significant increase of the electronic contribution to the overall
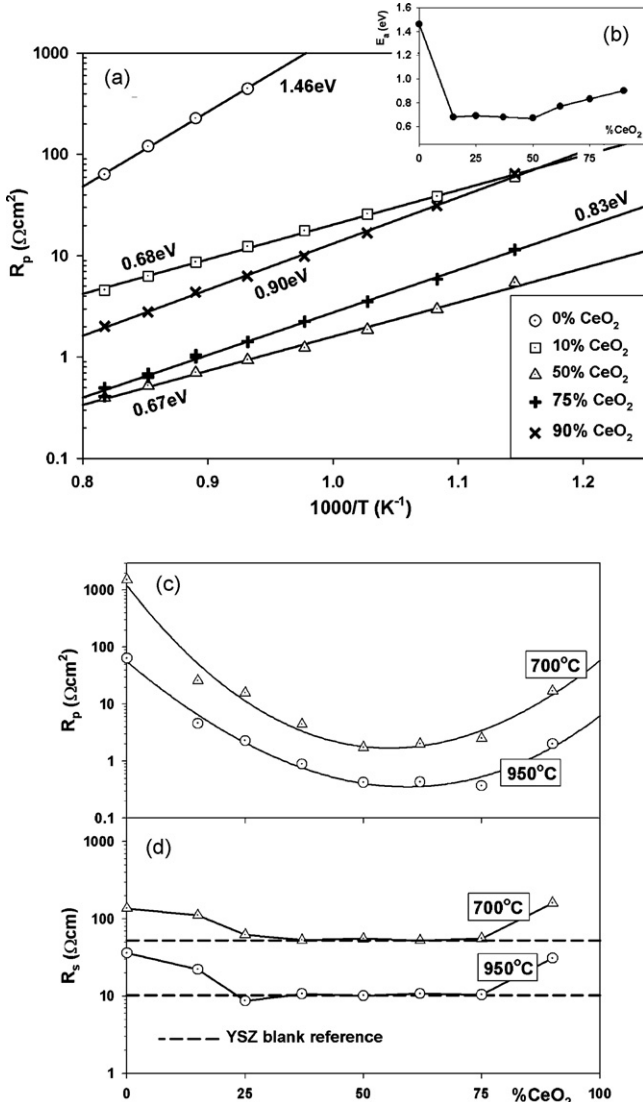
Fig. 3. (a) Dependence of the polarisation resistances values (R_p) with the temperature, for several CeO_2 contents in Pt–YSZ–CeO_2 composites under humidified 5% H_2, (b) evolution of the overall activation energy with the CeO_2 content. Plot of the (c) polarisation resistances, R_p and (d) series resistances, R_s, with the CeO_2 load in Pt–YSZ–CeO_2 cermets tested under humidified 5% H_2 in symmetrical cells.

conductivity and therefore, the R_s values match the values of the YSZ blank, for composites with CeO_2 content ranging between 30% and 75%, Fig. 3(d). For larger CeO_2 contents, the electrode–electrolyte adherence becomes poorer under the same fabrication conditions and consequently the R_s values increase.

3.3. Fuel cell test and SEM characterisation

A prediction regarding the best composition to assemble a fuel cell with symmetrical materials can be estimated once the series and polarisation resistances have been fully characterised. The overall losses should be minimised given that the voltage drop is related to the ohmic losses from both, electrolyte and electrodes, and the polarisation resistances
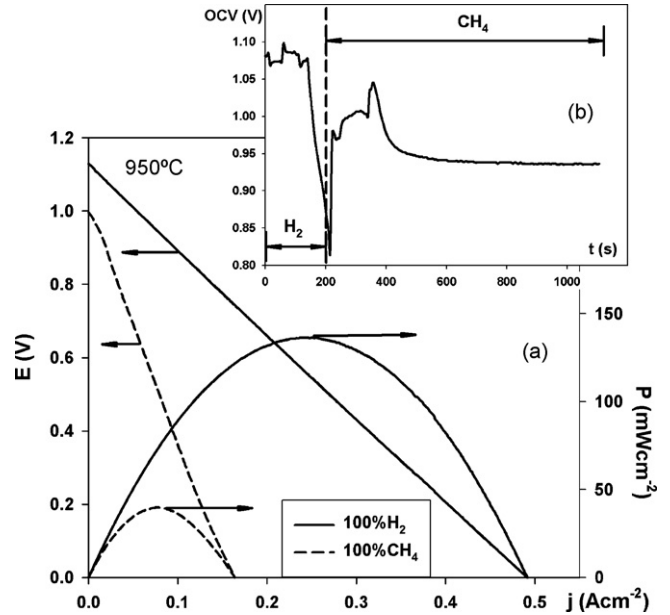

Fig. 4. (a) Fuel cell test of the symmetrical fuel cell: Pt–YSZ–CeO_2/YSZ/YSZ–CeO_2–Pt, (YSZ:CeO_2) ratio = (1:1), 1.21 mm thick YSZ electrolyte, tested under humidified pure H_2 and CH_4, at 950 °C and (b) evolution of the OCV with time when changing from humified pure H_2 to humidified pure CH_4.

from electrodes:

$$E = OCV - iR_{s,overall} - \eta_{overall}$$
$$= OCV - i(R_{s,electrolyte} + R_{s,anode} + R_{s,cathode})$$
$$- i(R_{p,anode} + R_{p,cathode}) \tag{1}$$

The best composites contain 50–60% of CeO_2, which allows to minimise the overall polarisations resistance ($R_{p,overall}$) to approximately 0.5 Ω cm² and also the R_s contribution from electrodes are minimised, which implies that the ohmic losses would be just given by the resistance of the dense electrolyte. The expected performances may be approximately predicted [32] for thick and thin YSZ electrolytes with these values, Eqs. (1) and (2):

$$P = \frac{OCV^2}{4R_{overall}} = \frac{OCV^2}{4(R_{s,YSZ} + R_{p,overall})} \tag{2}$$

After these considerations, one may predict performances of ~160 mW cm⁻² and ~500 mW cm⁻², at 950 °C, for 1.2 mm (equivalent to the tested fuel cell) and 100 μm thick YSZ electrolytes, respectively and taking into account that the OCV under humidified pure H_2 is 1.09 V.

A fuel cell was assembled considering the estimated optimum composition of 50% of CeO_2 and was prepared in a single thermal treatment. A dense 1.21-mm thick YSZ was used and the performance obtained under pure hydrogen was ~140 mW cm⁻² which corresponds to 90% of the previously predicted value, Fig. 4(a). This indicates that the SFC-based on Pt–YSZ–CeO_2 may be an interesting choice at high temperatures (>900 °C) and probably for small devices and flat configurations.

A reduction in the electrode thickness to $10\,\mu m$ would be desirable to reduce the ohmic drops from the electrodes, especially for the cathode layer. If we use a thickness limit of $150\,\mu m$ to consider a fuel cell as an electrolyte-supported [33] then the performance under hydrogen would be approximately $450\,mW\,cm^{-2}$ at $900\,°C$.

Another option would be anode-supported, given that the R_s values remain constant with the CeO_2 content (25–65%) under reducing conditions, matching the value from an YSZ blank. At $700\,°C$, the overall R_p reaches a value of $\sim 1.6\,\Omega\,cm^2$. The expected performance under humidified pure H_2 is about $275\,W\,cm^{-2}$ at $700\,°C$; for a YSZ deposited layer few microns thick.

On the other hand, the performance under methane was rather modest, just below $\sim 50\,mW\,cm^{-2}$, although the OCV was stable with the time around $0.95\,V$ at $950\,°C$, Fig. 4(b). Such modest results may indicate that the preparation via solid state routes does not take full advantage of the reported catalytic activity of CeO_2 towards hydrocarbon oxidation, as a consequence of the lower surface area compared to CeO_2 obtained via wet methods, e.g. impregnation.

The SEM images corresponding to the electrode–electrolyte interface, Fig. 5(a) and (b), reveal similar microstructures despite changing the CeO_2 content from 0% to 90%. Thus, in the present case, the microstructure does not seem to be responsible for the dependence of the overall electrochemical response with the CeO_2 content.

The performance of this new symmetrical system is in the range of the best electrodes tested in the same symmetrical configuration, Table 1. For instance, at $950\,°C$, using air as oxidant and 5% wet H_2 as fuel, the best overall polarisation resistance measured at the OCV corresponded to the Pt–(LSCM–YSZ) (1:1) system [1] with $0.38\,\Omega\,cm^2$. Under the same experimental conditions the Pt–(YSZ–CeO$_2$) (1:1) system renders R_p values
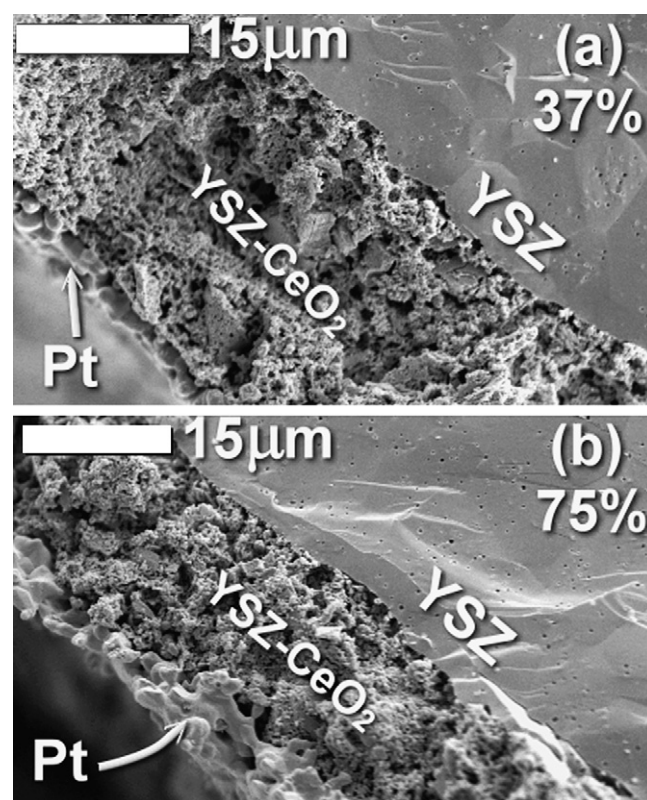

Fig. 5. Cross-section SEM images of two symmetrical system with (a) 37% and (b) 75% (w/w) of CeO_2 in the corresponding cermets. The microstructure remains fairly similar in the whole range of analysed compositions.

of $0.5\,\Omega\,cm^2$. Other candidate symmetric electrode materials such as calcium-doped lanthanum chromite [1], typically used as interconnector material, shows an overall polarisation close to $1\,\Omega\,cm^2$.

Table 1
Overall polarisation resistances of several electrodes tested in symmetrical configurations

System	Polarisation resistances, R_p ($\Omega\,cm^2$)			
	Air	Wet 5% H_2	Overall	Reference
Pt–(LSCM–YSZ)[a] (1:1)	0.09	0.29	0.38	[1]
Pt–(YSZ–CeO$_2$) (1:1)	0.05	0.45	0.50	This work
Pt–(LCC–YSZ)[b] (1:1)	0.30	0.89	1.19	[1]
Pt–(LSCM–YSZ–CGO)[a] (1:1:1)	0.52	0.80	1.32	[6]
Pt–(LSTF6–YSZ–CeO$_2$)[c,d] (1:1:1)	0.30	~1.8	2.10	[7]
Au–(LST16–YSZ)[d,e] (1:1)	0.80	11.6	12.4	[34]
Pt–(LST16–YSZ)[d,e] (1:1)	0.42	12.7	13.1	[34]
Pt–(LST12–YSZ)[d,f] (1:1)	0.30	14.5	14.8	[34]
Au–(LST12–YSZ)[d,f] (1:1)	0.60	15.3	15.9	[34]
Au–(LST14–YSZ)[d,g] (1:1)	0.35	16.1	16.5	[34]
Pt–(LST14–YSZ)[d,g] (1:1)	0.46	30.3	30.8	[34]
Pt–(YSZ)	0.20	~60	60.2	This work

Data typically obtained at $950\,°C$, using air as oxidant and 5% wet H_2 as fuel (the values were obtained at open circuit voltage conditions).

[a] LSCM: $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$.

[b] LCC: $La_{0.7}Ca_{0.3}CrO_{3-\delta}$.

[c] LSTF6: $La_4Sr_8Ti_6Fe_6O_{38-\delta}$.

[d] Obtained at $900\,°C$.

[e] LST16: $La_4Sr_{n-4}Ti_nO_{3n+2}$ ($n = 16$).

[f] LST12: $La_4Sr_{n-4}Ti_nO_{3n+2}$ ($n = 12$).

[g] LST14: $La_4Sr_{n-4}Ti_nO_{3n+2}$ ($n = 14$).

Several lanthanum-substituted strontium titanates were also tested in similar conditions, using Pt and Au as current collectors [34] to evaluate the role of the current collector. It is worth noting that the differences observed in the responses were far from being significant. Nevertheless, the polarisations obtained considering titanate-based electrodes were in all the cases rather high, preventing their potential use as highly efficient SFC electrodes. However replacing some Ti for Fe in the perovskite structure and optimising the chemical composition via the partial replacement of YSZ by CeO_2 resulted in polarisations values improved by a factor of 6–8 compared to the doped-free titanates and YSZ-based composites [7].

Nevertheless further investigations, especially long-term tests, are required to evaluate the effect of the formation of solid solutions in the CeO_2–YSZ system and their effect upon the electrochemical performance of the YSZ–CeO_2/current collectors proposed. Another issue will be the replacement of the current collector for cheapest option such as silver or perovskite-based materials as chromites.

4. Conclusions

In summary, it has been shown that the combination of YSZ–CeO_2 typically used as SOFC anodes plus noble metals fulfill all the requirements to be considered as a symmetrical material.

CeO_2 introduces catalytic activity for fuel oxidation in reducing conditions in addition to some electronic conductivity, whereas the ionic conductivity is mainly given by the YSZ. The noble metal provides electronic conductivity and catalytic activity in both environments and the combination of the three elements seems to exhibit enhanced catalytic activity towards oxygen reduction and fuel oxidation, e.g. the polarisation resistances under air can be improved by a factor of four, and up to three orders of magnitude under reducing conditions, by modifying the YSZ:CeO_2 ratio. Nevertheless long-term tests are required to evaluate the effect of crucial parameters such as TECs mismatch between the oxidised and reduced ceria that may be rather important in composites with high CeO_2 content and the effect of the formation of YSZ–CeO_2 solid solutions upon the electrochemical response.

Preliminary tests on 50:50 YSZ:CeO_2/(noble metal) cermets showed rather promising performances in thick YSZ electrolytes, e.g. $140 \, mW \, cm^{-2}$ at $950 \, °C$ using H_2 as fuel.

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