

Potential electrode materials for symmetrical Solid Oxide Fuel Cells

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Chromites, titanates and Pt-YSZ-CeO₂ cermets have been investigated as potential electrode materials for an alternative concept of Solid Oxide Fuel Cell (SOFC), the symmetrical SOFCs (SFC). In this configuration, the same electrode material is used simultaneously as anode and cathode.

Interconnector materials, such as chromites, could be considered as potential SFC electrodes, at least under pure hydrogen-fed at relatively high temperatures, as they do not exhibit significant catalytic activity towards hydrocarbon oxidation. This may be overcome by partially substituting Cr in the perovskite B-sites by other transition metal cations such as Mn. La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) is a good candidate for such SFCs, rendering fuel cell performances in excess of 500 and 300mW/cm² using pure H₂ and CH₄ as fuel, at 950 °C.

Similarly, typical n-type electronic conductors traditionally regarded as anode materials, such as strontium titanates, may also operate under oxidising conditions as cathodes by substituting some Ti content for Fe to introduce p-type conductivity. Preliminary electrochemical experiments on La₄Sr₈Ti_{12-x}Fe_xO_{38-δ}-based SFCs show that they perform reasonably well under humidified H₂ at high temperatures.

A third group of materials is the support material of any typical cermet anode, i.e. YSZ, CeO₂ plus a current collector. It has been found that this combination could be optimised to operate as SFC electrodes, rendering performances of 400mW/cm² under humidified pure H₂ at 950°C.

Keywords: Solid Oxide Fuel Cell, Symmetrical electrodes, Titanates, Chromites, Cermet.

Potenciales materiales de electrodo para Pilas de Combustible de Óxido Sólido simétricas

Cromitas, titanatos y cermets de Pt-YSZ-CeO, han sido investigados como potenciales materiales de electrodo para un concepto alternativo de Pilas de Combustible de Óxidos Sólidos (SOFC), las pilas SOFC simétricas (SFC). En esta configuración, el mismo material de electrodo se utiliza simultáneamente como ánodo y cátodo.

Materiales utilizados de interconector, como las cromitas, podrían ser considerados como potenciales electrodos SFC, al menos con hidrógeno puro como combustible y a temperaturas relativamente elevadas, debido a que no presentan una actividad catalítica relevante hacia la oxidación de hidrocarburos. Esto puede ser superado mediante la sustitución parcial del Cr, en el sitio B de la perovskita, por otro metal de transición como Mn. La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} (LSCM) es un buen candidato para SFCs, generando rendimientos superiores a 500 y 300mW/cm² empleando hidrógeno y metano puro como combustibles, respectivamente, a 950 °C.

De igual manera, conductores electrónicos comunes, tipo-n, tradicionalmente considerados como materiales de ánodo, como los titanatos de estroncio, podrían también funcionar bajo condiciones oxidantes como cátodos, substituyendo parte del contenido en Ti por Fe para introducir conductividad tipo-p. Estudios electroquímicos preliminares en SFCs basadas en La₄Sr₈Ti_{12-x}Fe_xO_{38-δ} muestran que pueden funcionar razonablemente bien bajo hidrógeno húmedo a alta temperatura.

Un tercer grupo de materiales lo constituye la base típica de cualquier material cermet de ánodo, esto es YSZ, CeO₂ más un colector de corriente. Se ha encontrado que esta combinación puede ser optimizada para funcionar como electrodo SFC, dando lugar a rendimientos del orden de 400mW/cm² en hidrógeno puro húmedo a 950°C.

Palabras clave: Pila de Combustible de Óxidos Sólidos, Electrodos simétricos, titanatos, cromitas, cermet

1. INTRODUCTION

Solid Oxide Fuel Cells (SOFCs) (1,2) are electrochemical devices that operate at high temperature, facilitating hydrocarbon reforming and hence avoiding the use of costly and bulky external reformers. However operating at high temperature has also some drawbacks as the number of candidate materials for efficient operation is notably reduced. A typical SOFC comprises three components: a porous anode,

a porous cathode and a dense electrolyte which separates the different gas atmospheres. The oxide ions produced at the cathode diffuse through the dense electrolyte towards the porous anode, where they participate in the electrochemical fuel oxidation, producing electricity, heat and water as final by-product of the overall reaction when hydrogen is used as fuel. The high working temperatures are in the range of

850-1000°C, mainly imposed by the low ionic conductivity of the electrolyte at lower temperatures.

As a consequence of the high operation (and fabrication) temperatures, the fuel cell components must fulfill some requirements. The electrodes must show high electronic conductivity and high catalytic activity in the corresponding gas-environment. Both electrodes should exhibit an adequate degree of porosity; the higher limit is controlled mainly by the mechanical properties and the lower value is controlled by the good transient of gaseous species. All the elements must show chemical and dimensional stability during cell operations and the fabrication process and compatibility with the other cell elements. The electrolyte should be a gas-tight material to avoid contact between the reactant gases and should be a pure ionic conductor with negligible electronic conductivity to avoid short-circuits across the cell, which in turn would result in poorer fuel cell performances.

The state-of-the-art SOFC materials are the Ni-YSZ cermet as anode, yttria-stabilised zirconia (YSZ) as electrolyte and substituted manganites such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) as cathode material (1,2). All of them are really cost-effective, which facilitates the implementation of these materials for mass-scale production. An additional component is necessary to connect several cells in series to produce a stack, i.e. the interconnector (1,2). A commonly used material is a substituted lanthanum chromite.

The same electrode material could be used simultaneously as cathode and anode in a SOFC, to create a symmetrical Solid Oxide Fuel Cell (SFC) and consequently replacing the traditional SOFC configuration. The development of SFCs would notably simplify the production of fuel cells, minimising compatibility problems between components (there would be two identical electrode-electrolyte interfaces in comparison with the typical anode-electrolyte and cathode-electrolyte interfaces in traditional SOFCs), decreasing the fabrication costs derived from the simpler fabrication process and address problems related with reversible sulphur poisoning and carbon deposition by simply reversing the gas flows. This alternative concept, where the same electrode material is used, simultaneously, as cathode and anode in a Fuel Cell, replacing the traditional SOFC configuration, has been recently proposed and verified by our research groups in 2006 (3-6). The fuel cell tested in this new configuration (3) have rendered promising performances, e.g. ~ 550 , ~ 330 and ~ 350 mW/cm², at 950°C, using H₂, 5% H₂ and CH₄ as fuel respectively, and O₂ as oxidant. Later on, S. P. Jiang et al. (7,8) obtained 275 mW/cm², at 850°C under pure H₂ using the same configuration.

In the work presented herein, we summarise the main results and strategies followed in the procedure of testing several potential electrode materials for SFCs: Lanthanum chromites, lanthanum chromium-manganites, Fe-substituted strontium titanates and YSZ-CeO₂ based cermets.

2. EXPERIMENTAL

2.1. Materials preparation

$\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$ (LCC), $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) and $\text{La}_4\text{Sr}_8\text{Ti}_{12-x}\text{Fe}_x\text{O}_{38-\delta}$ (LSTF) powders were prepared by conventional solid state reaction. Stoichiometric amounts of pre-dried high purity reactants were mixed and ground in acetone using zirconia ball mills for 30 min and then fired

at 1100-1200°C for 6-10 hours (occasionally this process was repeated twice). The powders were pressed into pellets and finally fired at 1300-1500 °C for 5-48 hours. Phase purity was evaluated by X-ray diffraction (XRD) on a Philips X'Pert Pro automated diffractometer, equipped with a Ge(111) primary monochromator and a X'celerator detector.

YSZ used as electrolyte and in the composite mixtures was from Tosoh and /or Pi-KEM. Dense YSZ pellets for symmetrical cell measurements and fuel cell tests, 1-2 mm thick and 20 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-based composites of LCC, LSCM or LSTF were prepared in a 1:1 (w/w) ratio. The powders were mixed with acetone in an agate mortar and left to dry at room temperature. Several ratios were used for the YSZ-CeO₂ composites, i.e. 15, 25, 37, 50, 62, 75 and 90% of CeO₂.

2.2. Fuel Cell assembly and electrochemical measurements

The as-prepared powders of LCC, LSCM, LSTF, YSZ and CeO₂ were mixed with a Decoflux™ (WB41, Zschwimmer and Schwartz) binder to obtain a slurry, which was used to paint symmetrical electrodes onto a YSZ dense pellet. Typical active areas were ranging between 0.75 and 1cm², though the polarisation values measured were conveniently normalised. The samples were fired at 1200°C for 2 hours and then a Pt-based ink was deposited on top of the electrodes and fired at 950°C for 2 hours; sometimes a gold-based ink was used to avoid any extra catalytic activity effect derived from the use of Pt-based current collectors.

Nevertheless, one should keep in mind that in all cases the Pt-ink should be considered as a part of the electrode given the good electrocatalytic properties showed by this noble metal under oxidising and reducing conditions. Moreover, the thicknesses of the electrode layer were rather small 10-30 micros to minimise ohmic drops. Consequently, the overall performance is probably affected by the noble metal used as current collector.

The polarisation measurements and the fuel cell tests were performed on a two-electrode arrangement (3). The polarisation resistances were obtained under symmetric atmospheres. a.c. impedance spectroscopy of the electrochemical cell was carried out using a Solartron 1260 FRA, at open circuit voltage (OCV), in the 10⁰-10¹ Hz frequency range using a 50 mV of a.c. signal amplitude.

Fuel cell tests were carried out using humidified 5% H₂, pure H₂ and CH₄ as fuels and O₂ as oxidant at temperatures ranging between 850 and 950°C. The sample was sealed using a ceramic-based material from Aremco. The measurements were carried out using a Zahner IM6ex unit at open circuit voltage conditions in the 0.1-5x10⁵ Hz frequency range using a 50 mV perturbation. j-E plots were also performed using the same equipment. The water content was fixed by bubbling the gas through a humidifier thermostated at 20 °C. The concentration of water at that temperature was estimated to be 2.3 %.

2.3. Scanning Electron Microscopy (SEM)

Electron Microscopy images were obtained on a Jeol JSM-6300 electron microscope after fuel cell testing to check

microstructure and 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.

3. RESULTS AND DISCUSSION

The requirements for a material to be considered as a symmetrical electrode for SOFC are rather restrictive as they should include all the conditions applicable to an anode and a cathode simultaneously, that is:

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

3.1. Lanthanum Chromites

A priori, the chromites generally used as interconnector material (1,2) fulfill almost all the conditions required for a potential symmetrical electrode. The main problem of the chromites is related to their rather modest catalytic activity towards hydrocarbon oxidation (9,10). Preliminary studies in this type of materials (6), with a Ca-substituted lanthanum chromite, $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$ (LCC), reveals an interesting performance under humidified pure hydrogen, approximately $110\text{mW}/\text{cm}^2$, in a thick electrolyte-based cell, at 950°C , Figure 1.

However the performance under methane was rather modest, i.e. $25\text{mW}/\text{cm}^2$ at 950°C , possibly due to two

factors: firstly, the poor catalytic activity of simple chromites towards hydrocarbon oxidation (9,10). The second factor could be a very poor microstructure. Indeed, a SEM image corresponding to the electrode-electrolyte interface reveals a very dense electrode material that could certainly explain the low performances obtained under hydrocarbons as the transient of gases to the active sites may be notably hindered, Figure 1(b). The H_2 molecule is much smaller than CH_4 or any of the other gas molecules produced during the oxidation, e.g. CO , CO_2 or H_2O , and therefore it can easily diffuse even through a relatively dense microstructure. The same process is much more complicated for larger molecules and hence the corresponding polarisations are considerably worse. Thus the material is open to further improvement by optimising the microstructure, especially for hydrocarbon fuels.

Regarding compatibility, XRD studies reveal that the main diffraction peaks of LCC-YSZ composites do not shift significantly and moreover there are no extra peaks, which seem to indicate that no reactions occur between the electrolyte and the electrode at least up to 1400°C . Although no degradation of LCC was observed in our short-term experiments under reducing conditions, further investigations after long-term operation are highly demanded to clarify this issue as reported by Primdahl et al. (11), and to check potential problems related with the volatilisation of chromium species.

3.2. Lanthanum Chromium-manganites

The substitution of Cr for Mn was suggested by Sfeir et al. (9) as a way to improve the lack of catalytic activity of simple chromites toward the hydrocarbon oxidation. Therefore the possibility of use of any Mn-substituted chromites as symmetrical electrode was explored (3). $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) has been proposed as a good anode material (12,13), and also as a good symmetrical material (3,4). Indeed LSCM has been the first material tested in such configuration rendering high performances exceeding $500\text{mW}/\text{cm}^2$ under pure hydrogen at 950°C and $300\text{mW}/\text{cm}^2$ in methane (3). Moreover, Jiang et al. (7) recently obtained $275\text{mW}/\text{cm}^2$ using this approach, under pure H_2 at 850°C .

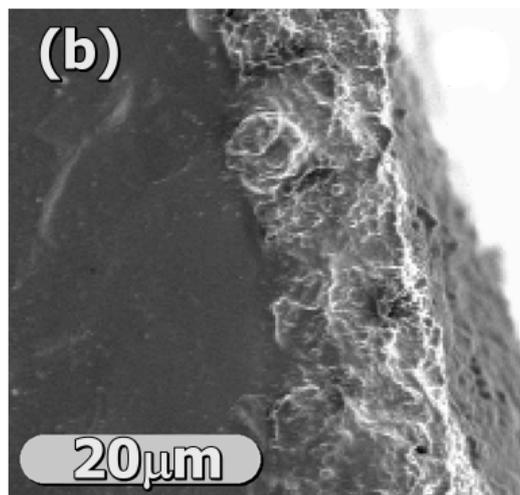
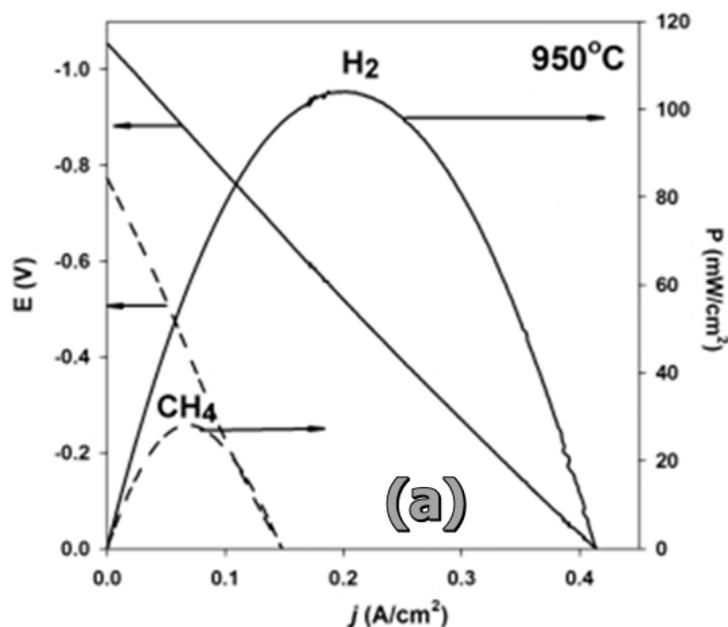


Fig. 1. a) Fuel Cell test performances using $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$ (LCC) as SFC electrode, at 950°C , with different gases, b) SEM image of the interface.

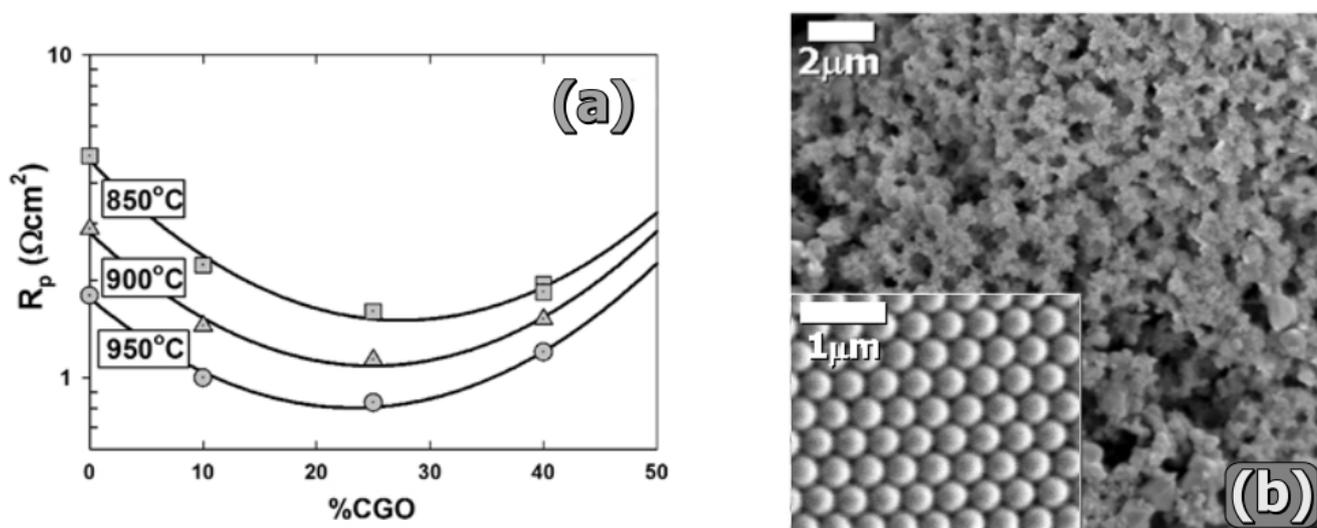


Fig. 2. (a) Dependence of Polarisation Resistances (R_p) with the CGO content in (LSCM-YSZ-CGO)-based symmetrical cells, at different temperatures (3). (b) SEM image of the microstructure of LSCM-YSZ symmetrical electrode prepared using PMMA microspheres (15).

The main drawback of LSCM is the modest electronic conductivity under reducing conditions. However this could be solved by using LSCM composites with gadolinium-doped ceria (CGO) (14). The performed studies in (LSCM-CGO-YSZ)-based composites (5) showed that a 2:1:1 (w/w) composite results in improvements of the polarisation resistances, at least by a factor of 2, compared to the YSZ-based composites, Figure 2(a). Furthermore the series resistances were also improved due to the increase of the CGO electronic conductivity in reducing conditions.

The (CGO-YSZ)-based composites could allow the applicability of LSCM at temperatures lower than 850°C. (CGO-YSZ)-based fuel cells render values of 400mW/cm² at high temperatures using humidified pure hydrogen (5).

On the other hand, a novel method to optimise the microstructure of the electrode materials using Polymethyl methacrylate (PMMA) microspheres as pore formers (15,16) was applied to overcome the problems of poor microstructure previously observed with the microstructure of simple chromites. This method allows a better control of the porosity, Figure 2(b), and produce better values of polarisation resistances specially when working with hydrocarbons (5).

3.3. Substituted Strontium titanates

The substituted strontium titanates typically proposed as anode materials (17-22) usually exhibit high electronic conductivities under reducing conditions and generally they can operate with sulphur-containing fuels (23,24). Furthermore, very recently it has been shown that the introduction of different elements in the perovskite B-sites, e.g. Sc (19), Mn (20) and (Ga,Mn) (21,22), seems to promote catalytic activity toward the hydrocarbon oxidation. Thus, it could be interesting to convert these SOFC stable anode materials into symmetrical SOFC electrodes.

Considering that titanates show mainly n-type electronic conductivity almost in the whole $p\text{O}_2$ range, the strategy consists on replacing some Ti for another transition metal that could introduce p-type conductivity in oxidising conditions.

One of the most obvious candidates is Fe to form $(\text{La,Sr})(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$. This system shows both n-type and p-type conductivity (25-28) and rather promising performances under pure hydrogen (29).

Measurements in symmetric configuration (i.e. symmetric atmospheres) reveal that the series resistances (R_s) do not significantly change with the Fe content and they remain stable with time under both oxidising and reducing conditions. Furthermore, the R_s values are very close to the YSZ electrolyte contribution indicating a good lateral contact, which implies that the overall electronic conductivity of the material is high enough and does not contribute significantly to the overall cell ohmic drop, in agreement with the results reported in the literature in similar systems (25,26). The best results are obtained for $x > 5.0$ in the $\text{La}_4\text{Sr}_{8-12-x}\text{Fe}_x\text{O}_{38-6}$ series.

The polarisation resistance values (R_p) are mainly related with the electrocatalytic response of the electrode materials and with the mass-transport through the material, i.e. the microstructure. In the present case, the microstructure was almost identical in all the compositions investigated, and the results pointed out that LSTF electrodes performed better in air than under reducing conditions in addition to a notable improvement of the polarisations resistances with increasing the Fe content under reducing conditions, Figure 3(a). Therefore, Fe substitution in these phases has a double benefit: the overall electronic conductivity increases and, more important, the catalytic activity of the electrodes improves notably.

The polarisation values of the whole cell at 950 °C in H_2 were approximately 3.0 Ωcm^2 for both LSTF50 ($x=5.0$) and LSTF60 ($x=6.0$). Under methane feed, the R_p values were larger, indicating a rather limited application of these composites in direct methane fuel cells.

Graded composites were prepared to increase the effective Triple Phase Boundary rendering R_p values down to 50% lower than in the previous configuration, especially under methane. The performance in symmetric configuration and using a fine layer of Au, in both sides, as current collector, led to quite remarkable power densities of 100 mWcm⁻² under

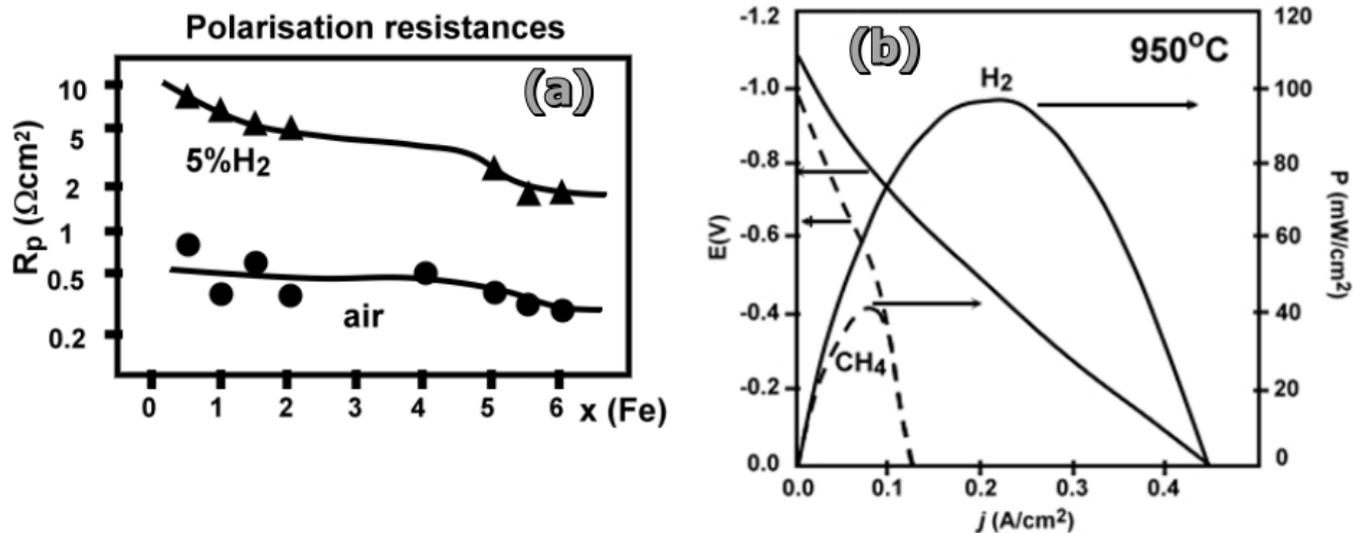


Fig. 3. (a) Dependence of Polarisation Resistances (R_p) with the Fe content, at 900°C, in the $\text{La}_4\text{Sr}_5\text{Ti}_{12-x}\text{Fe}_x\text{O}_{38.8}$ system (29). (b) Fuel Cell test performances using LSTF symmetrical electrode, at 950°C, with different gases.

humidified H_2 at 950 °C. Additionally, it should be pointed out that stable open circuit voltages (OCV) of approximately 1.0 V were obtained under methane at 950 °C, Figure 3(b).

3.4. Pt/Au-YSZ-CeO₂ cermets

The combination of YSZ-CeO₂, used in many anode materials and Pt or Au, typically used as current collectors, fulfil all the requirements to be considered as a symmetrical material.

CeO₂ introduces catalytic activity in reducing conditions and some additional electronic conductivity, whereas the ionic conductivity is mainly given by the YSZ. The current collector provides electronic conductivity in both environments and the combination of the three elements seems to enhance the catalytic properties under oxidising and reducing conditions, e.g. the polarisations resistances under air can be improved

by a factor of two, and by a factor of three under reducing conditions, Figure 4, just modifying the ratio YSZ:CeO₂.

Preliminary test of this simple combination showed rather promising performances, e.g. 400mW/cm² at 950 °C using H_2 as fuel (30). This allows the assembly of all-in-one fluorite symmetrical SOFC, Figure 4(b), plus a current collector, which could be typical noble metals or common interconnector materials (30, 31).

4. CONCLUSIONS

It has been shown that Mn-substitute chromites, Fe-substituted titanates or (current collector)-YSZ-CeO₂ cermets can be considered as potential electrodes for symmetrical Solid Oxide Fuel Cells. In all cases the corresponding fuel cell tests render promising performances, especially under

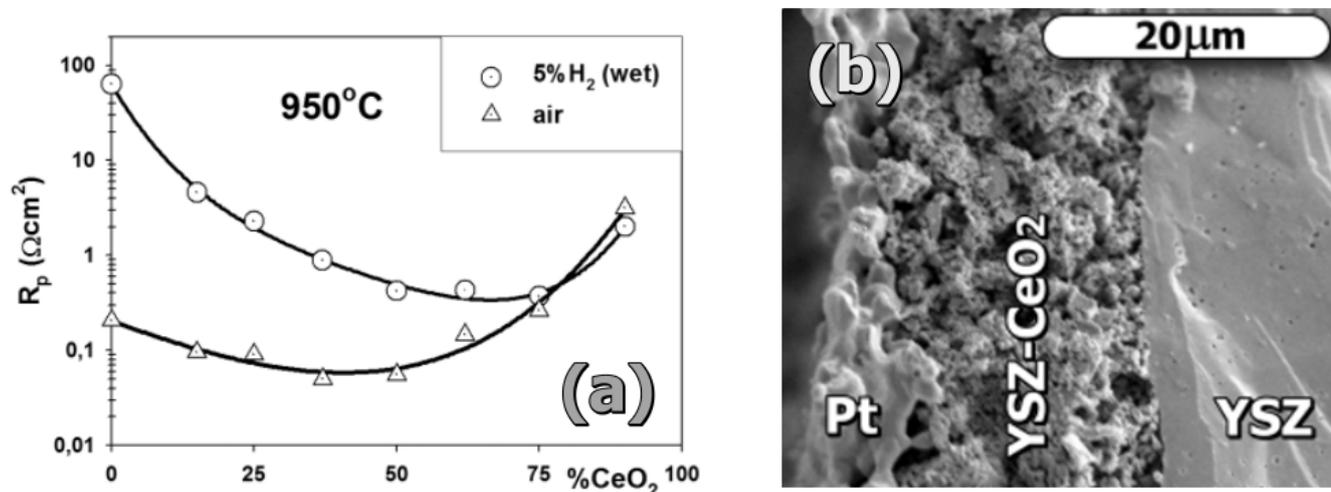


Fig. 4. (a) Dependence of the Polarisations Resistances (R_p) with the CeO₂ content, at 950°C, for the cermets Pt-YSZ-CeO₂ under air and humidified 5% H_2 . (b) SEM image of a cross-section of a Pt-YSZ-CeO₂ based symmetrical SOFC (30).

hydrogen at high temperatures, reaching 500mW/cm² in the best case. Moreover, Mn-substituted chromites exhibit interesting performance under humidified methane compared to the values obtained in classical configuration. In all the cases enhanced fuel cell performances may be expected by further optimisation of the microstructure, i.e. using PMMA microspheres as template. However, the use of Pt-ink as current collector probably is affecting the overall performance given that the good electrochemical properties of the Pt under reducing and oxidising conditions and therefore should be considered as a component of the electrodes evaluated.

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