

On the simultaneous use of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ as both anode and cathode material with improved microstructure in solid oxide fuel cells

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Abstract

A new concept of a solid oxide fuel cell (SOFC) using simultaneously the same electrode material at the anode and cathode sides with improved microstructure is proposed. We have found that $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM) can be considered as a good candidate for such configuration, symmetrical fuel cells (SFCs), due to its enhanced electrochemical properties in both reducing and oxidising conditions. LSCM-based SFCs offer promising performances, e.g., 0.5 and 0.3 W cm^{-2} at 950 °C using H_2 and CH_4 , respectively as fuels. Finally, the optimisation of the microstructure has been achieved via a novel facile procedure, using poly(methyl methacrylate) PMMA microspheres as templates.

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1. Introduction

Solid oxide fuel cell (SOFC) technology has experienced a growing interest in the last few years as means to generate energy more efficiently than the combustion of fossil fuels, limiting the emissions of greenhouse gases. SOFCs are solid devices that produce electricity from the electrochemical combination of a hydrogen-containing fuel and an oxidant such as oxygen or simply air [1]. Each single cell comprises two electrodes: an anode and a cathode separated by an electrolyte. Since the gases reach each electrode compartment separately, both materials must fulfil some general requirements: stability of the microstructure during the preparation and operation in a SOFC; chemical compatibility and 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 stabil-

ity in reducing and oxidising conditions respectively. Furthermore, some ionic conductivity is desirable, as it will help to extend the triple phase boundary (TPB) through the whole electrode material, hence decreasing the corresponding polarisation resistance.

The standard choice as electrolyte material is yttria-stabilised zirconia (YSZ) [2]. At lower temperatures, alternative electrolytes have been considered such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) discovered by Ishihara [3], and cerium oxide substituted with rare-earths [4], e.g., $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ or $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$.

Strontium-substituted manganites such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) [2] have been regarded as the most common cathode material for SOFCs due to their excellent electronic conductivities between 800 and 1000 °C and good catalytic behaviour towards oxygen reduction. At lower temperatures however, new cathode materials such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) render much better performances for IT-SOFC applications [5].

On the other hand, the state-of-the-art anode material is the Ni/YSZ cermet [2] which offers excellent catalytic properties, mixed conductivity and good current collection properties. However, such cermets present some disadvantages related to the low tolerance to sulphur [6], carbon build up when using hydrocarbon fuels [7] and volume

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instability upon redox cycling. Most of these problems have been overcome with the introduction of new materials based upon perovskite structures such as chromite–manganites [8], titanates [9] or double perovskites as $\text{Sr}_2\text{Mg}_{1-x}\text{Mn}_x\text{MoO}_{6-\delta}$ [10].

As mentioned above, a single fuel cell is assembled using at least three different elements, i.e., an electrolyte, a cathode and an anode. Obviously, there should exist good chemical and mechanical compatibility between the two electrodes and the electrolyte. It is also evident that the production of robust and reliable cells would be simpler reducing the number of components, e.g., using the same material as anode and cathode, considering that both the anode-electrolyte and the electrolyte-cathode interfaces would be similar. In other words, the development of symmetric fuel cell (SFCs) may simplify considerably the production of (future) commercial fuel cells. Nevertheless, there are numerous further benefits derived from this concept. Thus, the fuel cell could be assembled in a single thermal treatment, minimising problems related with the interdiffusion between cell components. Another important advantage is related to sulphur poisoning. It is generally agreed that the anodes may operate with very low S-levels [1] and any loss of performance may be recovered after using a S-free gas flow. Despite the engineering issues, working on a SFC would facilitate this procedure because the gases can be switched at the user's convenience. The working cathode with a clean microstructure runs now under fuel conditions, and the sulphur-contaminated anode works under oxygen, cleaning the microstructure. Similarly, any formation of carbon deposits can be removed easily from the anode simply by reversing the gas flow.

Chromite-based materials have been generally employed as interconnect materials for SOFCs, although may also be regarded as potential anode materials due to their relatively good stability in both reducing and oxidising atmospheres at high temperatures, high electronic conductivity and a certain degree of ionic conductivity. However, the polarisation values are still far too high for efficient SOFC operation. On the other hand, the pure manganite (LaMnO_3) is the standard choice as cathode, but is unstable in anode conditions. Thus, a compromise between the two formulations with equal proportions of Cr and Mn on the B sites results on a potential anode material, LSCM. In addition, the introduction of Mn into the B-site of $\text{La}_{1-x}\text{Sr}_x\text{Cr}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ seems to improve the catalytic properties for methane reforming [11].

In the communication presented herein, we have found that LSCM can be considered as a suitable electrode material in SFC due to its good performance as both fuel electrode and, more importantly, cathode material at high temperatures. The latter is a relevant issue as LSCM shows performances comparable to several optimised LSM cathodes specifically prepared to work at temperatures as low as 650 °C [12]. Consequently, SOFCs using LSCM as cathode and anode simultaneously have been investigated, rendering promising performances as described hereafter. Additionally, the development of a novel procedure to optimise the microstructure [13] has been carried out rendering improved polarisation resistances in comparison to the values

previously reported under reducing conditions [8] as explained below.

2. Experimental

LSCM powders were prepared by conventional solid state reaction. Stoichiometric amounts of pre-dried high purity of the corresponding oxides were mixed and ground in zirconia ball mills for 30 min. and then fired at 1400 °C for 10 h. LSM was a commercial powder from Praxair (99.9%). YSZ used as electrolyte and in the composite mixtures was from Tosoh.

Dense YSZ pellets, for the symmetrical cell measurements, of 1.6 mm thickness were obtained after uniaxially pressing YSZ powders at 1 ton for 1.5 min. The resulting pellets were sintered at 1500 °C for 12 h.

The electrolyte for the fuel cell test was prepared via a modified tape-casting procedure described in the literature [14]. The slurry for the tape-cast contains YSZ powder, a mixture of trichloroethylene and ethanol as solvent, corn oil as dispersant, a mixture of benzyl butyl phthalate and polyethylene glycol as plasticisers and polyvinyl butyral as binder. The tapes were cut into disks and sintered at 1500 °C for 12 h. The final thickness was approximately 250 μm after firing.

Powders of YSZ and 500 nm PMMA microspheres were mixed in a 1:1 ratio following the procedure recently described [13]. The as-prepared powder was mixed with LSCM in a 1:1 ratio. A Decoflux(WB41, Zschimmer and Schwartz) binder was added to obtain a slurry, which was used to attach the electrodes onto the YSZ tape, in symmetrical configuration. The whole sample was fired at 1200 °C for 2 h. The porous electrode was impregnated with a Pt-based solution. After that, a Pt-based ink was used to paint a current collector in both sides and fired at 950 °C for 2 h. Platinum paste was chosen as current collector for testing purpose in the lab, helping to decrease the ohmic losses from the LSCM–YSZ composite and improving the electrical contacts between the components of the anode composite. The cell was introduced in a Macor[®] ring and sealed using a ceramic based material (Ceramabond 668, Aremco).

The polarisation measurements and fuel cell tests were performed on a two-electrode arrangement (Fig. 1). The ASRs were obtained under symmetric atmospheres. a.c. 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 a.c. 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. The Macor-supporting cell was sealed to the jig using a gold ring at 925–950 °C. *I*–*V* plots were recorded by cyclic-voltammetry at a scan rate of 4 mVs^{-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%. However, in the cathode compartment there are only dry gases as O_2 gas was bubbled through a sulphuric acid solution before entering the fuel cell setup. Consequently, water is not involved under oxidising conditions in our experiments.

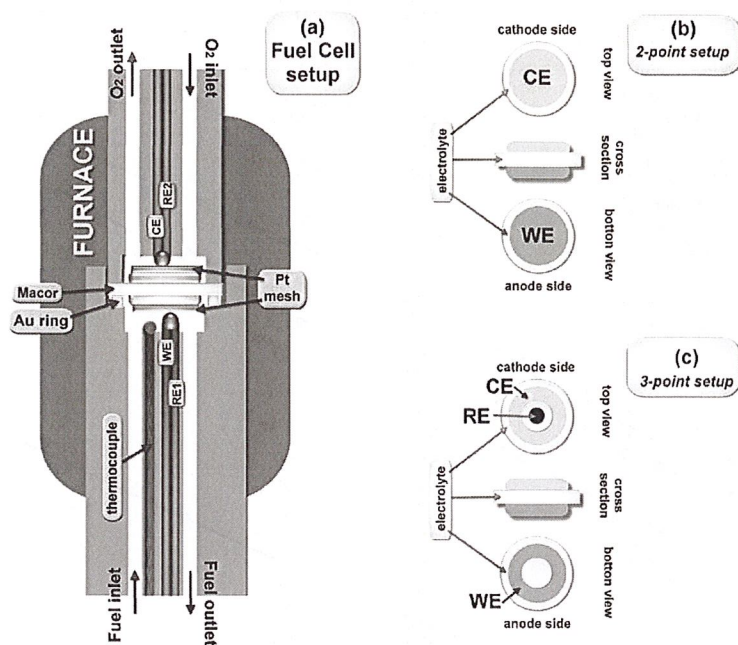


Fig. 1. (a) Scheme of a fuel cell setup. (b) two-point setup for symmetrical cell measurements and fuel cell tests. (c) three-point setup for the evaluation of the polarisation resistance on a single SOFC (WE: working electrode, anode; CE: counter-electrode, cathode; RE: reference electrode).

3. Results and discussion

The area-specific resistances (ASR) of LSCM in oxidising conditions were obtained using cells with symmetric configuration: (air, O₂), Pt/LSCM-YSZ/YSZ/LSCM-YSZ/Pt, (air, O₂) [15]. The use of the composite can be justified considering the benefits derived from the improved interfacial contact and the enlargement of the TPB through the electrode material. An additional factor is the likely increase of the BET-specific surface area (SSA). In other words, the use of YSZ with a much higher surface area than the electrode will produce a composite with an average surface area higher than the electrode on its own. For instance, the LSCM typically prepared by solid state reaction renders SSA values lower than 1 m²/g. Thus the combination of this LSCM with YSZ (Tosoh, SSA ≈ 13.6 m²/g) will produce a composite with higher SSA, i.e., 10 m²/g, than the LSCM on its own.

We have used the same experimental approach reported by several authors to study the system LSM–YSZ [12,16–19]. However special care should be taken interpreting the data collected from symmetrical cells measurements. McIntosh et al. [20] found that the data obtained in symmetrical configurations for LSM at 700 °C can be off by a factor of 50. However it is very likely that the differences will be narrow or negligible, at high temperatures. In any case, the source of such a difference in the ASRs is the symmetrical setup not the materials themselves. Therefore, the use of the same setup to verify whether one material performs better than another under the same experimental conditions should be a valid procedure, even if the absolute value of the ASR is not 100% correct as the final verification will come from the fuel cell test in asymmetric gases.

The ASR values obtained by a.c. impedance in O₂, were 0.06, 0.11, 0.24 and 1.6 Ω cm² at 950, 900, 800 and 700 °C. In air, at the same temperatures, the values were 0.09, 0.16, 0.43 and 2.4 Ω cm² (Fig. 2). The impedance plot in air consists of at least three arcs, with similar morphologies to those observed using LSM–YSZ composites [16]. The first two arcs, at high frequencies, are usually overlapped. Their relaxation frequencies were ≈ 10^{3.5} and ≈ 10^{2.2–2.6} Hz, respectively. These values are in good agreement with Arc A and B, described by Jorgensen et al. [16] and related with transport/transfer of oxygen intermedi-

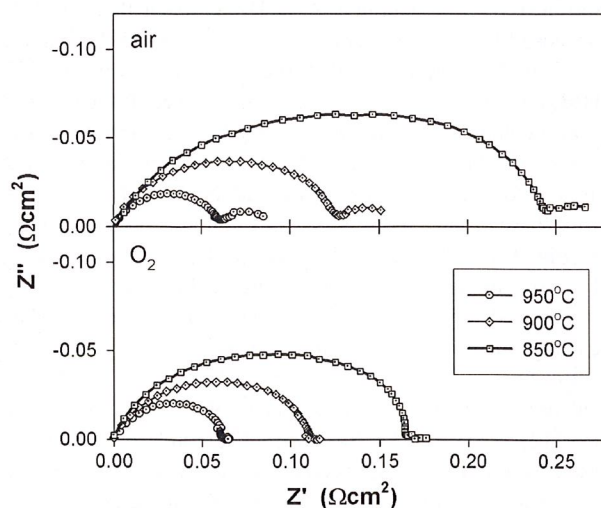


Fig. 2. Impedance plots for a LSM–YSZ composite showing low values of ASR in dry oxidising conditions at high temperatures. The spectra have already been divided by 2 due to the symmetrical configuration.

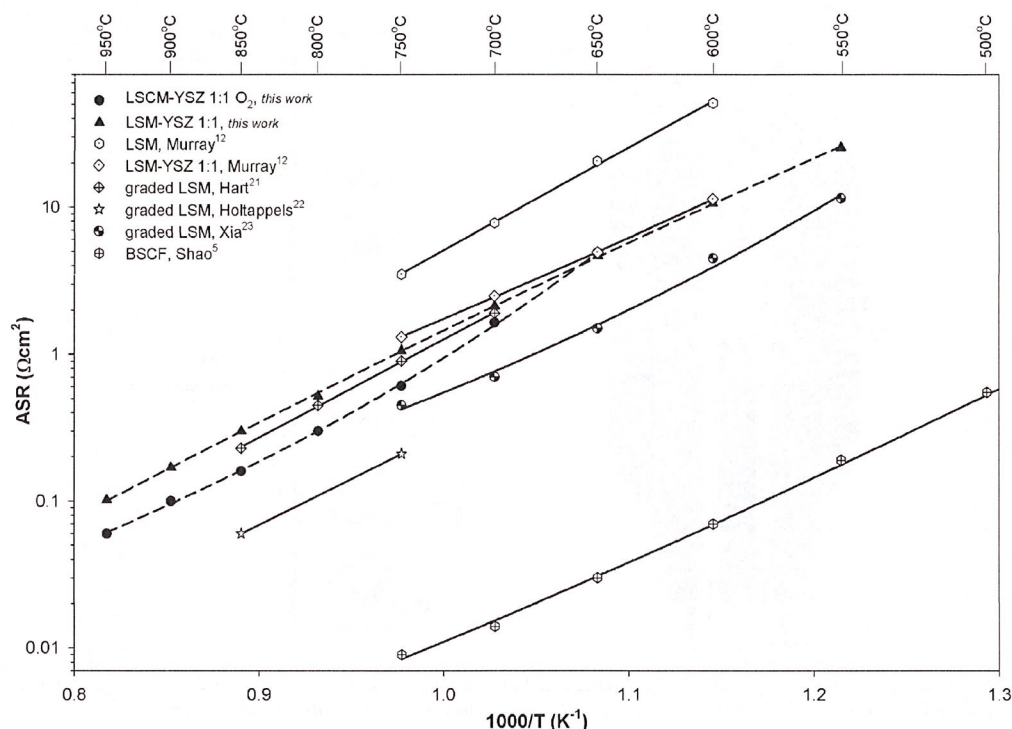


Fig. 3. Dependence of the ASRs values with the temperature for a LSCM–YSZ composite and compared to different LSM–YSZ composites. A very high performance cathode material, BSCF, is also shown. One should keep in mind that LSCM has been reported as a good anode material for SOFC operation at relatively high temperatures, thus the use of LSCM as symmetrical electrode should be restricted at 950–850 °C. Values showed at lower temperatures and with different materials are just for comparison. (The reader should note that we have just selected some of them as reference, not as a critical survey. ASR depends on several factors as composition of LSM, microstructure -porosity-, firing temperature, graded or ungraded microstructure with YSZ, ratio of the binder used to fix the material, etc. . .).

ates/oxide ions between LSCM and YSZ and through the YSZ of the composite.

The last arc, which appears at very low frequencies, seems to be temperature-independent with a constant value of $0.03 \Omega \text{ cm}^2$. Under O_2 conditions, the contribution of this arc is negligible. The temperature-independent behaviour could be related with the interdiffusion in the gas phase [16], although the relaxation frequency obtained, $\approx 0.2 \text{ Hz}$, is lower than the values proposed for the LSM composites, i.e., 1.4–10 Hz. Taking into account this frequency value, the arc could be related with the TPB, i.e., with any of the processes involved in the oxygen reaction mechanism (in this case a dependence with the TPB thickness would be expected or alternatively with the presence of minor secondary phase segregation at the TPB [16]).

From these values and comparing to an average LSM electrode, (Fig. 3) [5,12,21–23] it is clear that LSCM is a relatively good cathode material at high temperatures. For practical applications, an ASR of $0.1\text{--}0.2 \Omega \text{ cm}^2$ or lower should be the target value at a given temperature. Using LSCM, this can be achieved down to 850 °C in O_2 . At lower temperatures, the ASRs are equivalent to the results proposed, for LSM or graded LSM, by Murray [12] and Hart [21]. Holtappels [22] rendering enhanced values by a factor of two, between 850 and 750 °C. These results are particularly relevant because they highlight the potential of LSCM as a good candidate as SFC electrode, especially because it has been reported as a good anode material [8] and now we prove that acts even better as cathode. The reader should note

that LSCM has been reported to date as a good anode material for SOFC operation at relatively high temperatures. Consequently, the use of LSCM as cathode in a symmetrical configuration should be applied in the same range of temperatures.

Accordingly, LSCM does not show any catalyst selectivity towards any gas because it performs really well in both oxidising and reducing environments. This would also explain the poor performances and low OCVs reported by Asahara et al. [24] using LSCM as anode in a single chamber configuration.

It should be noted that the values of the series resistances (R_s), in air and O_2 are almost identical (Table 1) matching the typical values for a YSZ pellet used as a blank, which indicates that the contribution to the ohmic drop is negligible when LSCM is employed as cathode in air or oxygen. On the other hand, the ASR values obtained under reducing conditions (Table 1) are somewhat lower than those reported by Tao

Table 1

Series (R_s) and polarisation (R_p) resistances (both in $\Omega \text{ cm}^2$) of symmetrical cells under symmetric atmospheres

T (°C)	Air		O_2		5% H_2		100% H_2		100% CH_4	
	R_s	R_p	R_s	R_p	R_s	R_p	R_s	R_p	R_s	R_p
950	1.62	0.09	1.64	0.06	1.85	0.29	2.18	0.18	2.05	0.26
900	1.90	0.16	1.92	0.11	2.20	0.43	2.70	0.23	2.40	0.39
850	2.30	0.27	2.30	0.16	2.96	0.59	3.40	0.34	3.00	0.67

The electrolyte was a dense 1.6 mm thick YSZ pellet.

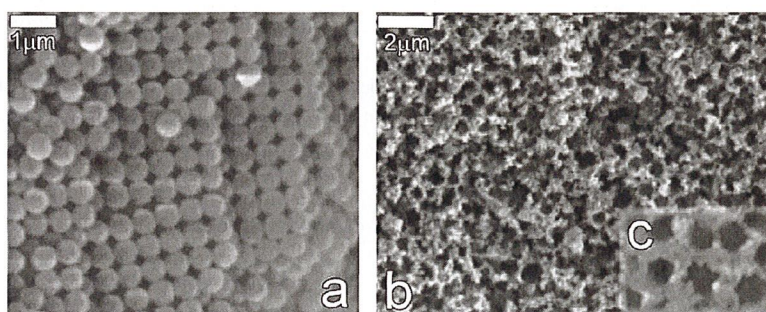


Fig. 4. SEM pictures of the (a) PMMA microspheres used as template to control the porosity in the LSCM-YSZ composite. (b) Optimised microstructure of a LSCM-YSZ composite after removal of organic template. (c) Higher magnification micrograph showing the distribution of pores in the microstructure.

[8] in pure hydrogen and under pure methane. Such enhancement can be attributed to the optimisation of the microstructure using poly(methylmethacrylate) PMMA microspheres as template [13]. In this process, the porosity of the materials is controlled through the simple combination of oxide powders, polyvinyl alcohol and PMMA microspheres. The size of PMMA microspheres, Fig. 4a, will control the size of the pores in the electrode microstructure, Fig. 4b–c, after the appropriate thermal treatment.

Another conclusion from Table 1 is that the contribution of the LSCM-YSZ composite to the ohmic drop in reducing conditions is important. Thus, the increase in the ohmic drop were: 0.21, 0.28 and 0.66 $\Omega \text{ cm}^2$ in 5% H_2 ; 0.54, 0.78 and 1.10 $\Omega \text{ cm}^2$ in 100% H_2 ; and 0.41, 0.48 and 0.70 $\Omega \text{ cm}^2$ in 100% CH_4 at 950, 900 and 850 $^\circ\text{C}$, respectively. Thereby, the more reducing the atmosphere is, the higher the ASR. This increase can be easily explained as being due to the p-type conductivity of LSCM under reducing conditions [8], which in turn is a common feature in perovskite manganites. However, if the electronic conductivity were higher enough, the nature of the charge carrier would have a negligible effect on the performance. We believe that the drop in the anode conductivity comes from the use of a composite with 50% of YSZ. Thus a composite with lower YSZ content might help to improve the conductivity of the anode material.

These results also suggest that the performance in fuel cells with thin film-electrolyte will be largely affected by this contribution. These values were obtained for a 50 μm -thickness film of electrode material; hence the use of thinner layer will not produce much better results. Consequently, a good current collector should be incorporated to the electrode material to improve the conductivity under reducing conditions. The production of NiO cermets might be a possible solution, although this is not feasible in a SFC as NiO will be exposed to oxidising conditions. A second alternative is to impregnate the porous electrode material with a noble metal-based solution. The ohmic contribution under reducing conditions has been proved to be negligible, after performing the aforementioned procedure with a Pt-based solution. Alternatively, a gold-based solution could be used to avoid some extra catalytic effects from the platinum.

From a technological point of view, a composite with doped ceria could be an acceptable solution for practical applica-

tions. Some of the best polarisations results for LSM have been obtained using SDC or GDC-based composites [12]. Another advantage is the increase of the electrical conductivity under reducing conditions due to the partial reduction of Ce^{4+} to Ce^{3+} , which in turn compensates the low conductivity of the LSCM. Additionally, a very thin layer of anode should be deposited to minimise the ohmic drop. Nevertheless, this is currently under investigation in our laboratory and the results will be published elsewhere.

It should be noted that LSCM does not seem to degrade under wet conditions. This was evaluated considering the impedance spectra collected from a symmetrical cell measured under wet fuel conditions. Any degradation should affect the values of both, the series resistances (R_s) and the polarisation resistances (R_p). None of the mentioned values showed evidence of drifting with the time, at least after 24 h. However long-term tests should be performed in order to discard any possible degradation. Additionally, the stability of LSCM under wet conditions has been studied by Tao and Irvine [8b] and they did not find evidences of degradation after ageing the material for 120 h under 3% of H_2O at 900 $^\circ\text{C}$, which is in agreement with our results.

Fuel cell tests were performed to prove that LSCM can work as both anode and cathode *simultaneously* in a SFC. The fuel cell (Fig. 1) was assembled as described in the experimental section. Fig. 5 shows the current-voltage plots obtained at 950 $^\circ\text{C}$ for a

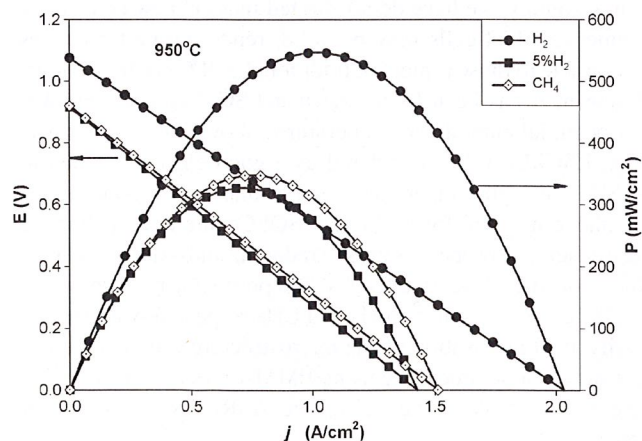


Fig. 5. Voltage (E) and power density (P) vs. Current density (j) plots of a SFCs based on LSCM obtained at 950 $^\circ\text{C}$ using three different fuels.

SFC with a 250 μm -thin YSZ tape under different fuel conditions. Maximum power densities of 546, 326 and 347 mW/cm^2 were obtained under humidified pure H_2 , 5% H_2 and pure CH_4 . These results demonstrate that a symmetric fuel cell may render high performances from a rather simple device. The performance is equivalent to the reported previously with LSM as cathode and LSCM as anode [8].

Preliminary work carried out in a SFC using LSGM as electrolyte and LSCM as electrode for its application at lower temperatures (IT-SOFC), rendered larger polarisation resistances (R_p) than the expected values, i.e., ASR above $3.5 \Omega \text{cm}^2$ at 950°C . Considering that during fuel cell operation we could not observe any evidence of chemical reaction, we believe that the elevated firing temperatures during the preparation of the cell (using LSGM as electrolyte) could lead to the formation of new non-conducting secondary phases. We have verified [26] that the highest limit to avoid the formation of secondary phases is 1600 K. The firing temperature in the present work was close to this limit and therefore it is quite likely that minor secondary phases may have formed. Nevertheless, the presence of the minor secondary phases does not seem to be important under reducing conditions. In the other hand, Irvine et al. [8a] showed that no reaction takes place between LSCM and YSZ firing both in air at 1300°C for 80 h by XRD. The same conclusion can be extracted from the EDS studies [8b] performed to monitor La, Sr, Cr and Mn, showing that there was no significant diffusion or local reaction. Even the reactivity of LSCM with similar electrolytes, as LSGMCo, has been recently probed to be negligible by Kilner et al. [25] by ICP mass spectrometry. They show again that the diffusion of Cr and Mn into LSGMCo is insignificant.

On the other hand, LSGM-based fuel cells performed reasonably well, with ASR values of $0.4 \Omega \text{cm}^2$ (at 925°C), when using LSM as cathode and LSCM as anode measured on a three electrode setup to evaluate the anode contribution in isolation. Performances exceeding $550 \text{mW}/\text{cm}^2$ at 800°C under H_2 , were achieved in this last configuration [26].

4. Conclusions

In summary, we have demonstrated that the new concept of symmetrical fuel cells may be valid, rendering performances comparable to those typical of traditional SOFC configurations. Moreover, it has been found out that LSCM can be regarded as a potential cathode at temperatures above 850°C . Furthermore, LSCM can be considered as a good electrode material for SFCs at high temperatures, rather than just a good anode or cathode material for traditional SOFCs due to its enhanced electrochemical properties in both reducing and oxidising conditions. Indeed, LSCM-based SFCs offer promising performances, e.g., 0.5 and 0.3W cm^{-2} in H_2 and CH_4 respectively at 950°C . Finally, the optimisation of the microstructure can be achieved via a novel facile procedure using PMMA microspheres, which leads to a notable reduction of the ASRs, especially under methane.

The development of SFCs would simplify notably the production of fuel cells, minimising compatibility problems between

components. The most important advantage from the application point of view is the likely reduction of costs per kW produced, derived from the simpler fabrication process and the elimination of problems related with sulphur poisoning and carbon deposition by simply switching gases.

Acknowledgments

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