

Short communication

## Fe-substituted (La,Sr)TiO<sub>3</sub> as potential electrodes for symmetrical fuel cells (SFCs)

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### Abstract

In the work presented herein, the potential use of La<sub>4</sub>Sr<sub>8</sub>Ti<sub>12-x</sub>Fe<sub>x</sub>O<sub>38-δ</sub> (LSTF) materials as electrodes for a new concept of solid oxide fuel cells, symmetrical fuel cells (SFCs), is considered. Such fuel cells use simultaneously the same material as anode and cathode, which notably simplifies the assembly and further maintenance of the cells. Therefore, we search for materials showing high conductivity in a wide range of oxygen partial pressures in addition to certain degree of catalytic activity for the oxidation of the fuel and reduction of the oxidant, respectively. The preliminary electrochemical experiments performed reveal that the overall conductivity increases notably upon Fe substitution, being the main contribution electronic n-type. The fuel cell tests indicate that LSTF composites with YSZ and CeO<sub>2</sub> perform reasonably well under H<sub>2</sub> conditions, although the performance in methane is rather modest and require further optimisation.

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### 1. Introduction

Fuel cells have generated considerable expectations over the last few decades due to the advantages associated to their use in the generation of energy with high efficiency and more environmentally friendly, limiting the emission of greenhouse gases.

These devices are rather simple and in the case of the solid oxide fuel cells (SOFCs), the typical cell consists of a dense ceramic electrolyte, i.e. an oxide-ion and/or proton conductor, with two electrodes attached, an anode and a cathode, where the electrochemical reactions, fuel oxidation and oxygen reduction, occur leading to the generation of usable electricity from the electrons liberated at the anode. Despite anode and cathode operate under completely different atmospheric conditions, they share most of the requirements for efficient

operation: high electronic conductivity, ionic conductivity, thermal and chemical stability, adequate porosity and catalytic activity.

Recent reports by Ruiz-Morales et al. and Irvine and co-workers have proposed and proved a novel concept in SOFC: the symmetrical fuel cells (SFCs) [1–3]. They consist in SOFCs using the same material simultaneously as anode and cathode (Fig. 1). The application of this concept would imply a number of advantages associated, such as the simpler fabrication process or the lack of problems related to C-deposition as the gas flow may be reverted without causing damage in the cell. Thus, the anode becomes the cathode and *vice versa*, which allows a simple removal of coke. Additionally, this new configuration might allow a higher tolerance to S-containing fuels in the cases of reversible S-adsorption at the anode.

The first SFCs used (La,Sr)(Cr,Mn)O<sub>3-δ</sub>/YSZ composites as electrode materials and rendered power densities of 0.5 and 0.3 W cm<sup>-2</sup> under humidified H<sub>2</sub> and CH<sub>4</sub> atmospheres, respectively at 950 °C [1,2]. These results proved the validity of SFCs compared to traditional configurations, which may open a new scope in fuel cell technology. However, there are still a num-

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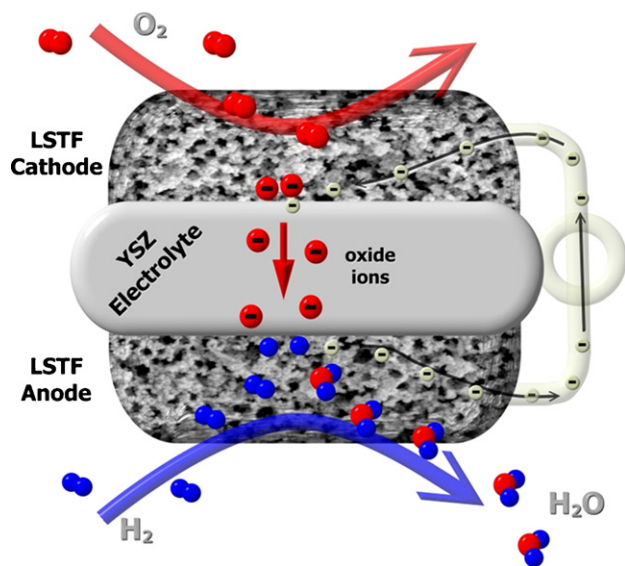


Fig. 1. Representation of the symmetrical fuel cell (SFC) concept. The same material is used simultaneously at both the anode and cathode sides.

ber of parameters that should be optimised before they become competitive.

Perovskite-based phases with general formula  $\text{La}_4\text{Sr}_8\text{Ti}_{12-x}\text{M}_x\text{O}_{38-\delta}$  ( $\text{M} = \text{Sc}, \text{Ga}, \text{Mn}$ ) have been recently reported as highly efficient anodes for direct methane SOFCs, exhibiting extraordinary performances [4–7]. On the other hand, ferrites substituted with Ti in the B-site have been proposed as mixed conducting oxide membranes and/or SOFC cathode materials [8–10] due to their high mixed (ionic-electronic) conductivity and chemical compatibility with YSZ electrolytes.  $\text{La}_4\text{Sr}_8\text{Ti}_{12-x}\text{Fe}_x\text{O}_{38-\delta}$  phases could be potential SFC electrodes and therefore, we have evaluated their potential in the work presented herein.

## 2. Experimental

$\text{La}_4\text{Sr}_8\text{Ti}_{12-x}\text{Fe}_x\text{O}_{38-\delta}$  (LSTF $_x$ ) phases were prepared via the traditional solid-state reaction. Pre-dried stoichiometric amounts of  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$  (>99%, Aldrich) were milled in zircona ballmills using acetone as solvent for 30 min and then fired at 1200 °C for 6 h. The resulting powders were further ballmilled for 30 min and pressed uniaxially into pellets at 1 metric ton. The pellets were then fired at 1300–1500 °C for 48 h, showing relative densities >90% after sintering.

Phase purity was evaluated by XRD diffraction on a PANalytical diffractometer with monochromatic  $\text{Cu K}\alpha_1$  radiation and equipped with a X'Celerator detector. The stoichiometry was evaluated by EDS analysis on a JEOL 2011 TEM electron microscope operating at 200 kV.

The overall conductivity in addition to the analysis of the different contributions were analysed by impedance spectroscopy in dense as prepared LSTF pellets coated with cured Pt paste acting as electrode. Polarisation studies were performed using YSZ electrolytes coated with 1:1 LSTF:YSZ electrodes under different atmospheres. These studies were carried out on a 1260

Solartron frequency response analyser in the 0.1–1 MHz range applying a 50 mV signal.

Polarisation studies and fuel cell tests were performed using 1–2 mm thick fully dense YSZ disks, prepared after pressing commercial YSZ powders (Pi-KEM) at 1 metric ton and sintering at 1400 °C for 12 h.

SFC electrodes were prepared using two different configurations. The first consists on applying a thin layer (typically 50  $\mu\text{m}$ ) of 1:1:1 LSTF:YSZ: $\text{CeO}_2$  composites mixed with binder (Decoflux WB41, Zschimmer and Schwartz) on both sides of the YSZ electrolyte and fired at 1200 °C for 2 h to ensure good adherence. The second is a two-layer configuration, i.e. first of all a 1:1 YSZ:LSTF layer is fixed onto the electrolyte and then a 1:1  $\text{CeO}_2$ :LSTF layer is added on top. The two approaches will be termed hereafter as non-graded and graded composites, respectively.

A fine layer of Au and Pt was used at the anode and the cathode, respectively to act as a current collector. Au was used to avoid any possible catalytic activity as Pt favours the electrochemical oxidation of methane. Occasionally, Au acted as current collector at the cathode side to work in a true symmetric configuration.

The fuel cell tests were performed on a two electrode setup (Fig. 2) using humidified 5%  $\text{H}_2/\text{Ar}$ ,  $\text{H}_2$  and  $\text{CH}_4$  as fuels and  $\text{O}_2$  as oxidant at the cathode (flow rates 150–200  $\text{ml min}^{-1}$ ). The polarisation measurements were carried out using a IM6e Zahner unit at open circuit voltage conditions in the 0.1–3  $\times 10^5$  Hz frequency range using a 50 mV perturbation. Cyclic-voltammeteries at 4–12  $\text{mV s}^{-1}$  were also performed using the same equipment.

## 3. Results and discussion

$\text{La}_4\text{Sr}_8\text{Ti}_{12}\text{O}_{38-\delta}$  is the first XRD cubic phase in the  $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$  series and accommodates the extra oxygen beyond the ideal  $\text{ABO}_3$  stoichiometry in local oxygen-rich defects randomly distributed within the perovskite framework [11–12]. The substitution of Ti by lower valence cations also renders XRD cubic phases, although in the case of Mn, the unit cell distorts to rhombohedral ( $R\bar{3}c$ ) [6]. In the present case, the introduction of up to 20% Fe in the B-site does not affect notably the structure, exhibiting cubic unit cells ( $Pm\bar{3}m$ ). Higher levels of substitution cause distortions to orthorhombic unit cells [8,9].

Preliminary electrochemical studies reveal that the overall conductivity in air increases notable at Fe contents above 33%, i.e.  $x=4.0$  (Fig. 3), whereas under reducing conditions the change is less marked. At low Fe contents, the conductivity under oxidising conditions largely depends on the concentration of charge carriers (mainly electrons), which in this case is given by the amount of Fe cations. Therefore, larger Fe contents result on higher conductivities. On the other hand, under reducing conditions a fraction of  $\text{Ti}^{4+}$  is reduced to  $\text{Ti}^{3+}$ , causing a drastic increase of the conductivity in the non-substituted phases. Hence the presence of Fe at low oxygen partial pressures has a much smaller effect on the conductivity. The observed changes in the activation energy at high Fe contents are probably due to a change in the conduction mechanism as typically occurs in ferrites. Additionally, Fe is prone to be partially

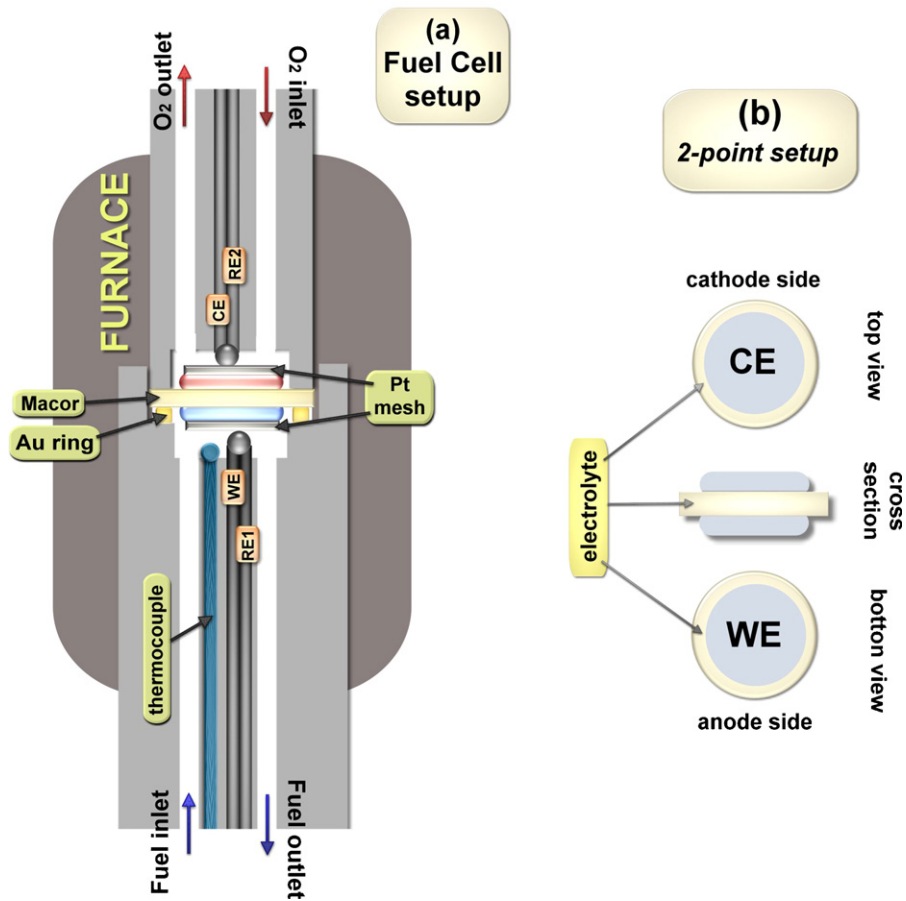


Fig. 2. (a) Schematic representation of the fuel cell setup. (b) Two-point setup for symmetrical cell measurements and fuel cell tests. (WE: working electrode; CE: counter-electrode, cathode; RE: reference electrode).

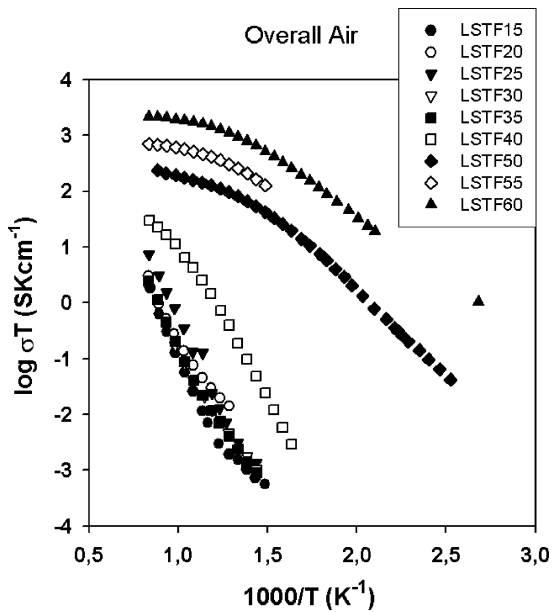


Fig. 3. Arrhenius plot corresponding to the overall conductivity in air for the  $\text{La}_4\text{Sr}_8\text{Ti}_{12-x}\text{Fe}_x\text{O}_{38}$  series. The conductivity increases with increasing the Fe content.

reduced at relatively low temperatures (i.e.  $600^\circ\text{C}$ ), which may cause a significant change in the number of charge carriers, which in turn results in an effective change in the conductivity values.

Measurements in symmetric cells under symmetric atmospheres revealed that the series resistances ( $R_s$ ) do not change significantly with the Fe content and they remain stable with time under both oxidising and reducing conditions, which indicates that no undesirable electrode–electrolyte reactions take place in addition to good electrode–electrolyte adherence (Fig. 4). It is very important to note that the  $R_s$  values are very close in every case to the YSZ electrolyte contribution, which implies that these values are dominated mainly by the electrolyte. It should be pointed out however that at Fe contents below 50%, the  $R_s$  under oxidising conditions are larger than under reducing conditions, whereas at  $x > 5.0$  the  $R_s$  values under air become smaller than under 5%  $\text{H}_2/\text{Ar}$ . This apparently agrees with the overall conductivity observed under a range of atmospheric conditions (Fig. 5), exhibiting higher conductivities under more oxidising conditions, which in turn coincides with the results reported in the literature in similar systems [8,9].

The polarisation resistance values ( $R_p$ ) are related to the electrocatalytic response of the electrode materials in addition to several other parameters such as the microstructure.

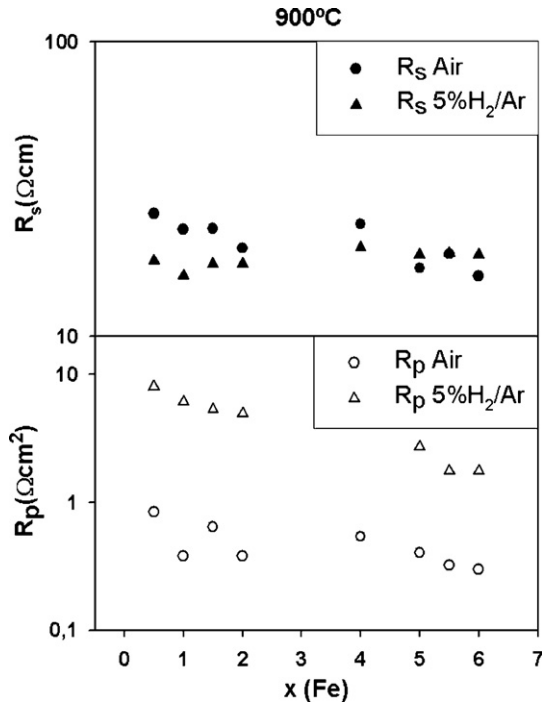


Fig. 4. Variation of the series ( $R_s$ ) (top) and polarisation ( $R_p$ ) (bottom) resistances with the Fe content. Although the  $R_s$  remains constant, the  $R_p$  values decrease at higher Fe contents in both reducing and oxidising conditions at 900 °C. The dotted line in the  $R_s$  graph represents the YSZ electrolyte contribution (1 mm thick).

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 performance with increasing the Fe content under reducing conditions (Fig. 4b). Under oxidising conditions the changes were less significant. This is quite remarkable, as the non-substituted and related phases have been considered as anode

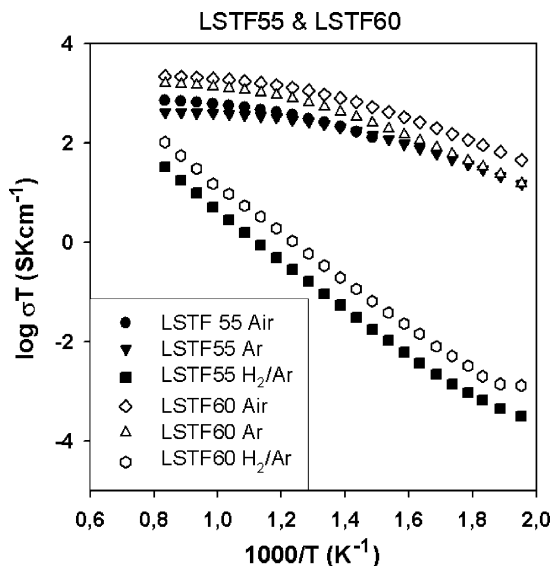


Fig. 5. Arrhenius plot corresponding to LSTF55 and LSTF60 under static air, Ar and 5%  $H_2$ /Ar.

materials, whereas in the present case the catalytic activity highlights certain potential as air electrode and moreover the activity under reducing conditions improves upon Fe introduction. Therefore, Fe substitution in these phases has a double benefit: the overall electronic conductivity becomes higher and, more important, the catalytic activity of the electrodes improves notably.

As a consequence of their better electronic conductivity under both reducing and oxidising conditions and the apparently better catalytic activity, we decided to evaluate the potential of composites of the higher Fe content phases ( $x=5.0, 5.5$  and  $6.0$ ) as SFC electrodes. The non-graded composites, i.e. 1:1:1 LSTF:YSZ:CeO<sub>2</sub> rendered some good results, although somewhat poorer than those reported for LSCM electrodes [1]. The polarisation values of the whole cell at 950 °C in  $H_2$  were 3.0 and

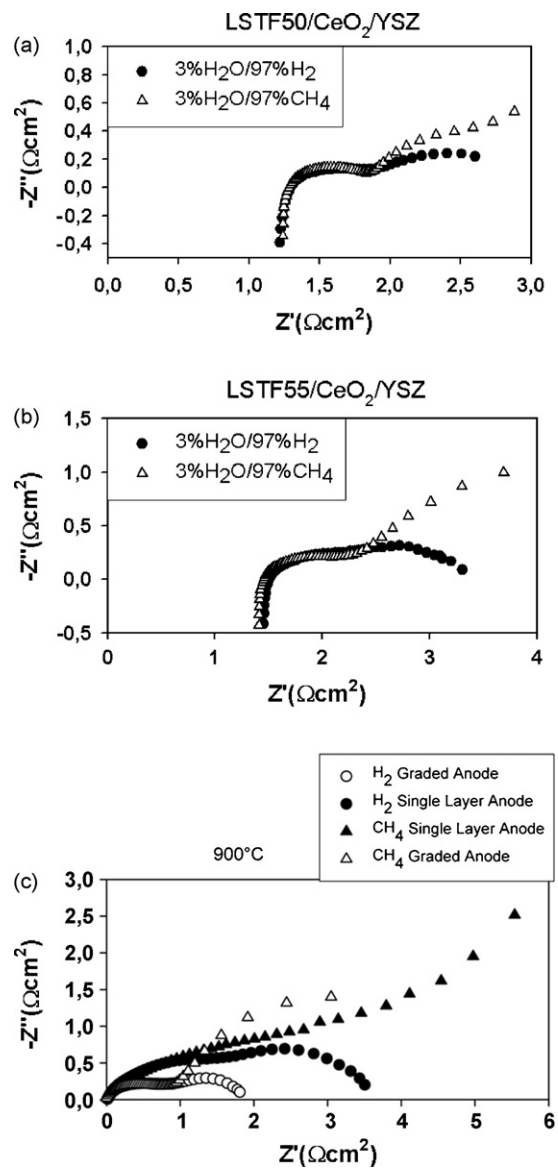


Fig. 6. Cell polarisation for LSTF50:YSZ:CeO<sub>2</sub> (a) and LSTF55:YSZ:CeO<sub>2</sub> (b) under humidified  $H_2$  and methane at 900 °C. The use of a two-layer configuration ensures better results under both humidified  $H_2$  and  $CH_4$  (c). The electrolyte was a 2 mm thick dense YSZ disk.



$3.8 \Omega \text{ cm}^2$  for LSTF50 ( $x = 5.0$ ) and LSTF55 ( $x = 5.5$ ) composites, respectively (Fig. 6a and b). Similar values were obtained in the case of 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 (two layers) rendered an enhancement of the responses, i.e. the  $R_p$  were up to 50% lower than in the previous configuration (one layer), especially under methane (Fig. 6c). Consequently, we evaluated the performance considering the graded composites and decided to work in a true symmetric configuration. A fine layer of Au was used at both the anode and the cathode as current collector to avoid any interference given by Pt. The responses under humidified  $\text{H}_2$  are quite remarkable, rendering power densities of  $90\text{--}100 \text{ mW cm}^{-2}$  at  $950^\circ\text{C}$ . Additionally, it should be pointed out that stable open circuit voltages (OCV) of approximately  $1.0 \text{ V}$  were obtained under methane at  $950^\circ\text{C}$ , which is higher than the values reported in the literature for LSCM composites (Fig. 7). This can be explained considering a number of factors such as the

higher  $\text{CeO}_2$  concentration at the electrode surface, favouring the electrochemical reactions at the electrodes and also due to a higher electronic conductivity as the LSTF concentration is also higher at the surface in this particular configuration. One should note that the  $E$ - $j$  curves deviate from linearity specially in the case of diluted hydrogen and methane. We believe such trend is mostly due to a relatively poor microstructure as the increase in the slope occurs at high current density values. This effect is more important when using diluted fuels or larger molecules (e.g. methane), as the access to the active sites may be severely restricted.

The most important issue however is that these electrodes are open to further improvement via optimisation of the composite grading or the control of the electrode microstructure [13]. This latter issue also affects the current collector as gold sinters easily upon heating at the operation temperatures, blocking a large number of pores at the electrode surface, hence decreasing the active area. This would explain the polarisation losses observed in the corresponding  $j$ - $E$  curves.

#### 4. Conclusions

In the present work,  $\text{La}_4\text{Sr}_8\text{Ti}_{12-x}\text{Fe}_x\text{O}_{38-\delta}$  (LSTF) phases have been investigated as symmetrical fuel cell (SFC) electrodes. The introduction of Fe in the perovskite B-site is beneficial as causes a marked increase in the overall conductivity under both reducing and oxidising conditions and also favours the catalytic activity at the electrodes.

The fuel cell tests performed in (thick) electrolyte-supported configuration revealed that these phases have certain potential as SFC electrodes, showing performances comparable to LSCM electrodes in  $\text{H}_2$  conditions. The best results were achieved considering a two-layer configuration, i.e. depositing a 1:1 LSTF:YSZ layer and a 1:1 LSTF: $\text{CeO}_2$  layer on top. The responses under methane are especially interesting as the OCV values were approximately  $1.0 \text{ V}$  at  $950^\circ\text{C}$ , which could indicate certain activity towards methane oxidation. The development of an SFC electrode exhibiting an adequate catalytic activity towards hydrocarbon oxidation would imply competitive SFC compared to more traditional SOFC configurations.

The use of techniques allowing a precise control the microstructure, e.g. using PMMA microspheres as template, can certainly result in enhanced performances [13]. Moreover, composite optimisation via the introduction of other additives or improved grading could also produce better results and further research is highly demanded to address these issues.

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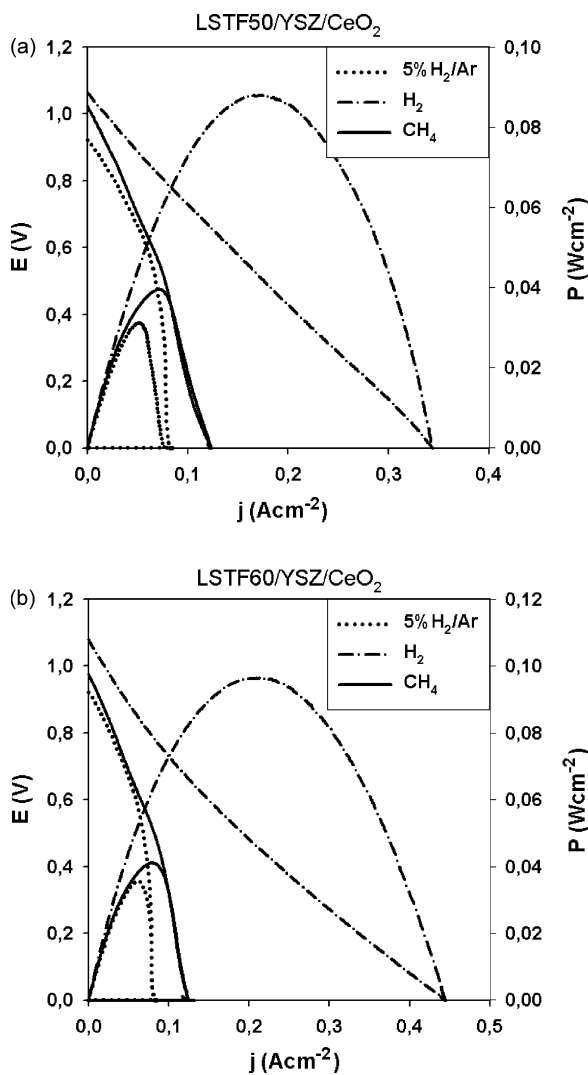


Fig. 7. Fuel cell tests corresponding to two-layer LSTF50:YSZ: $\text{CeO}_2$  (a) and LSTF60:YSZ: $\text{CeO}_2$  (b) electrodes at  $950^\circ\text{C}$ . The electrolyte was a 1 mm thick dense YSZ disk.

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