

Short communication

## Stabilisation of composite LSF<sub>CO</sub>–CGO based anodes for methane oxidation in solid oxide fuel cells

A. Sin<sup>a</sup>, E. Kopnin<sup>a</sup>, Y. Dubitsky<sup>a</sup>, A. Zaopo<sup>a</sup>, A.S. Aricò<sup>b,\*</sup>, L.R. Gullo<sup>b</sup>,  
D. La Rosa<sup>b</sup>, V. Antonucci<sup>b</sup>

<sup>a</sup> *Pirelli Labs S.p.A., Viale Sarca 222, I-20126 Milan, Italy*

<sup>b</sup> *CNR-ITAE, Via Salita Santa Lucia Sopra Contesse 5, I-98125 Messina, Italy*

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### Abstract

A La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub>–Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub> (LSFCO–CGO) composite anode material was investigated for the direct electrochemical oxidation of methane in intermediate temperature solid oxide fuel cells (IT-SOFCs). A maximum power density of 0.17 W cm<sup>-2</sup> at 800 °C was obtained with a methane-fed ceria electrolyte-supported SOFC. A progressive increase of performance was recorded during 140 h operation with dry methane. The anode did not show any structure degradation after the electrochemical testing. Furthermore, no formation of carbon deposits was detected by electron microscopy and elemental analysis. Alternatively, this perovskite material showed significant chemical and structural modifications after high temperature treatment in a dry methane stream in a packed-bed reactor. It is derived that the continuous supply of mobile oxygen anions from the electrolyte to the LSF<sub>CO</sub> anode, promoted by the mixed conductivity of CGO electrolyte at 800 °C, stabilises the perovskite structure near the surface under SOFC operation and open circuit conditions.

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**Keywords:** LSF<sub>CO</sub>; Perovskite; CGO; Methane electro-oxidation; Intermediate temperature; Solid oxide fuel cells

### 1. Introduction

Solid oxide fuel cells (SOFCs) convert chemical energy into electrical energy with high efficiency and low emission levels of pollutants. Although the large-scale diffusion of this technology represents an attractive scenario, its implementation is beset with technical and economic difficulties. Common anodes materials for solid oxide fuel cells comprise nickel cermets (ceramic and metallic composite electrodes) where the ceramic component is usually yttria-stabilised zirconia (YSZ) [1]. Ni-cermets show suitable activity for hydrogen oxidation and allow internal steam reforming of hydrocarbons if sufficient amount of water is fed to the anode. As Ni catalyzes the formation of carbon deposits in dry methane, it is necessary to operate the anode at a steam/methane ra-

tio greater than 2 [2]. In addition, the poor redox tolerance of nickel cermets precludes many medium- and small-scale applications. Thus, there is a considerable interest in finding alternative anode systems [3].

Perovskite materials such as La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub> and La<sub>0.6</sub>Sr<sub>0.4</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> are known as efficient cathode electro-catalysts for SOFCs [4]. Although some attempts have been made to use these materials as anodes, only chromite-based perovskites [5] have shown good performance and stability in methane-fed SOFC devices in absence of Ni [6] or noble metal promoters [7]. Yet, methane electro-oxidation at the chromite-based perovskite seems promising at temperatures close or above 950 °C [5]. This precludes the SOFC cell to be operated at lower temperatures as necessary to replace ceramic housings by cheap ferritic steel interconnects [8]. A decrease of the operating temperature and the replacement of Ni cermets with stable oxide materials would result in a better tolerance towards thermal and redox cycles.

\* Corresponding author. Tel.: +39 090 624237; fax: +39 090 624237.  
E-mail address: [arico@itae.cnr.it](mailto:arico@itae.cnr.it) (A.S. Aricò).

It has been reported [9,10] that perovskites containing Co, Ni or Cu are unstable in presence of hydrogen with significant precipitation of metal clusters. Moreover, CoO appears less stable than FeO in presence of hydrogen at 800–1000 °C, whereas MnO does not give rise to significant modifications under such conditions [9,10]. In the present work, a perovskite containing Fe/Co on the B-site has been investigated as anode in dry methane-fed SOFCs to assess its stability and electro-catalytic activity for methane electro-oxidation.

## 2. Experimental

The reactivity of the pure perovskite with respect to dry methane was investigated in an out-of-cell experiment. A pure  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$  powder (Praxair,  $\text{BET} = 5.5 \text{ m}^2 \text{ g}^{-1}$ ) was thermally treated at increasing temperatures in a tubular quartz reactor in the presence of a dry methane stream ( $40 \text{ ml min}^{-1}$  dry  $\text{CH}_4$ , 50 mg LSFCE powder, packed-bed reactor) and the outlet reaction products were analysed by quadrupole mass spectrometry (Fisons, VG). In another experiment,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$  powders were treated in dry  $\text{CH}_4$  at 800 and 900 °C for 2 h. Chemical and structural modifications occurring after these thermal treatments were investigated by X-ray diffraction using a Bragg–Brentano configuration (Philips X'Pert Cu K $\alpha$  diffractometer), FT-IR analysis in the transmission mode after dilution with KBr (Bruker Equinox 55 spectrophotometer, MCT detector, resolution set at  $4 \text{ cm}^{-1}$ ), CHNS-O analysis (Carlo Erba CHNS-O Elemental analyser) and transmission electron microscopy (TEM) observation (Philips CM12, operating at 120 kV with a LaB<sub>6</sub> filament).

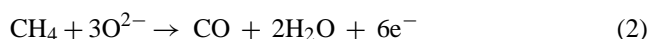
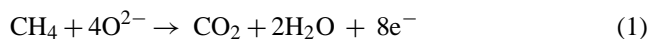
The  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  (CGO-20) powder, prepared from oxalic acid co-precipitation [11], was thermally treated at 1050 °C for 1 h, then uniaxially pressed at 300 MPa, and the resulting pellet was thermally treated at 1450 °C for 6 h. CGO-20 membranes with a thickness of 300  $\mu\text{m}$  and a relative density (experimental density/theoretical density) higher than 95% were obtained. The LSFCE powder was ground and homogenised by ball milling and dispersed in a solution of ethanol. Subsequently, the slurry was sprayed onto the electrolyte membrane and sintered at 1100 °C for 2 h in air to form the cathode. The anode was prepared in the same way by mixing the LSFCE powder with CGO-20 in a 70:30 weight ratio. The CGO added to the anode should provide benefits in terms of extension of the triple phase boundary zone [12]. Both anode and cathode layers were about 5  $\mu\text{m}$  thick. Gold wires were used for both current collectors and potential probes. The cell was mounted on an alumina tube and sealed with Aremco 516 paste. The cell active area was  $1 \text{ cm}^2$ . The anode was fed with a dry methane stream ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) whereas the cathode was exposed to static air. The cell was operated at 800 °C under both load and open circuit conditions (OCV). The anode layer of the SOFC cell was analysed after shut down in methane by using X-ray diffraction analysis both in the Bragg–Brentano configura-

tion and in the grazing angle mode. It was also subjected to elemental analysis by using a CHNS-O analyzer (Carlo Erba) to detect possible carbon traces. Morphology was investigated by scanning electron microscopy (SEM-EDAX, XL30 SFEG, FEI Company). Steady-state galvanostatic polarization curves and ac-impedance spectra were recorded by using a Metrohm Autolab 30 potentiostat–galvanostat, equipped with a FRA impedance analyser.

## 3. Results and discussion

### 3.1. Chemical characterization

Fig. 1 shows the outlet composition and the reactor temperature as a function of time during the thermal treatment of the pure  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$  in dry methane. The variation of temperature as a function of time is shown in the inset. It is observed that the water physically adsorbed on the LSFCE surface is released below 200 °C, whereas the water produced by the reaction of dry methane with the perovskite surface is clearly observed at 350 °C simultaneously with the onset of the  $\text{CO}_2$  signal. The CO signal increases steeply up to reach a constant value just above 720 °C. This plateau is very likely associated to the diffusion of the lattice oxygen from the bulk to the surface as rate determining step. The  $\text{CO}_2$  signal shows some oscillations in the range 350–870 °C and it decreases significantly at 900 °C. The observed phenomena may thus be explained by a consumption of LSFCE surface and lattice oxygen by methane through two redox processes:



accompanied by the reduction of cations on the B-site (see below).

At high temperatures, the methane reforming process may occur.

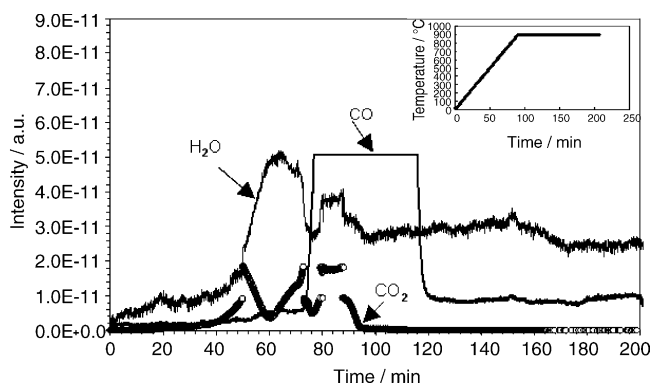
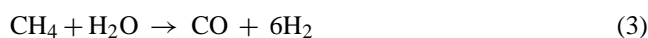


Fig. 1. Mass spectrometry analysis of the gas stream outlet during thermal treatment of LSFCE in a flow of dry methane. The inset shows the temperature program.

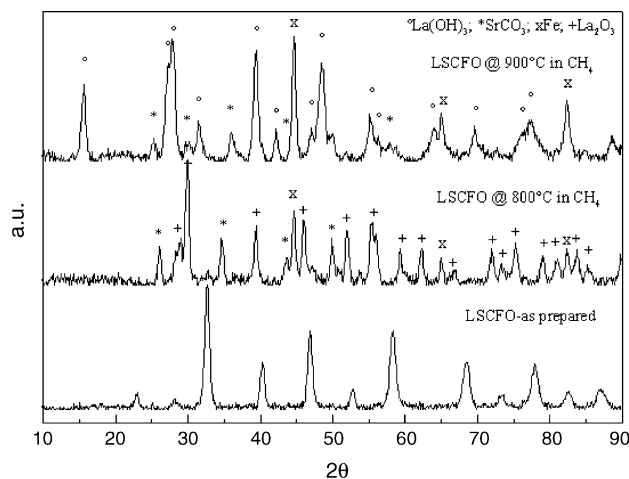


Fig. 2. X-ray diffraction patterns of LSCFO before and after thermal treatment in dry methane at 800 and 900 °C for 2 h.

Unfortunately, the employed mass spectrometry apparatus could not detect  $H_2$  in the outlet stream. However, it is clearly observed from the mass spectrometry analysis that the water signal does not decay dramatically but it slightly decreases to reach a constant value when the maximum rate of CO evolution is obtained. This is consistent with a prevailing occurrence of the first two reaction processes with a small contribution possibly due to the reforming.

At low temperatures and in excess of surface ionic oxygen, the  $CO_2$  formation appears to be favoured. Part of the  $CO_2$  reacts with the LSCFO surface forming carbonate species (see below). This probably reduces the availability of the ionic oxygen favouring the CO evolution process. The latter process might terminate when the surface is completely covered by a monolayer of carbonates or there is no more availability of mobile  $O^{2-}$  species.

To gain more information on these mechanisms,  $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$  powders have been treated in dry  $CH_4$  at 800 and 900 °C for 2 h. It is observed from the XRD data (Fig. 2) that both samples are decomposed but in a different manner. The sample treated at 800 °C shows as main phases  $La_2O_3$ , Fe and  $SrCO_3$ , whereas the sample annealed at 900 °C also contains  $La(OH)_3$ . The Fe phase is more intense in the sample treated at higher temperature whereas the  $SrCO_3$  content appears to decrease. The previously observed decrease of water production above 800 °C in the mass spectrometry analysis could be preferably related to the formation of the  $La(OH)_3$  than a reforming process; detection of a small  $CO_2$  peak at high temperature (around 850 °C) in the mass spectrometry analysis could be related to the decomposition of  $SrCO_3$ . The presence of carbonate and  $La(OH)_3$  species were also detected by FT-IR analysis (Fig. 3). It is interesting to point out the absence of graphitic carbon (Bragg reflection at  $2\theta = 26^\circ$ ) in the XRD patterns of both LSCFO samples treated at 800 and 900 °C (Fig. 2). TEM observation of the LSCFO sample exposed to dry methane at 900 °C in a packed-bed reactor showed a change in the morphology

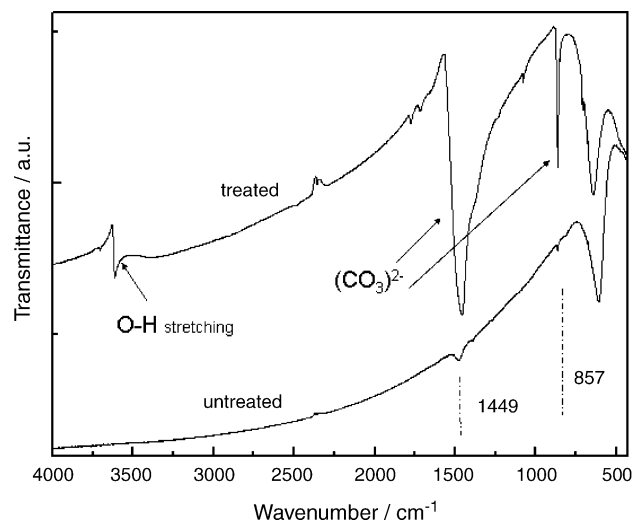


Fig. 3. FT-IR spectra of the LSCFO before and after thermal treatment in dry methane at 900 °C for 2 h.

of the primary particles (Fig. 4). This is attributed to the reactions occurred on the sample surface during exposure to methane. However, no carbon species such as whiskers-like or pyrolytic carbon were observed. Yet, it is not excluded that after prolonged treatment (e.g. 24 h in dry  $CH_4$  flux), when almost all lattice oxygen is consumed, some carbon deposits may occur due to the presence of metallic iron and cobalt. However, it is derived that no formation of metallic iron and carbonate phases would occur in the presence of a proper supply of oxygen ions, e.g. by an external oxygen source, replacing those on the perovskite surface consumed by reaction with  $CH_4$ . The stability of the LSCFO structure in an anodic SOFC environment was hypothesised by Weston and Metcalfe [13]. Furthermore, similar perovskite materials showed stable operation for methane partial oxidation in high oxygen permeability ceramic membrane reactors [14,15].

### 3.2. Electrochemical characterization

The electrochemical investigation was carried out by operating the cell at a temperature of 800 °C with dry  $CH_4$  at the anode and stationary air at the cathode.  $CH_4$  was fed at a flow rate significantly larger than the stoichiometric amount required by the electrochemical reaction to clearly assess the direct electrochemical oxidation, to avoid gas depletion and to enlarge any eventual catalyst degradation effect. In fact, the aim of the present work is to primarily investigate the mechanism of the electrochemical oxidation of methane at the perovskite-based anodes and not the fuel conversion efficiency [16]. In the presence of methane feed, the cell reached a constant OCV of 0.83 V (Fig. 5). Such low OCV was due to the presence of a small electronic conductivity contribution of the CGO electrolyte at 800 °C [8]. This determines an electron leakage through the electrolyte which reduces the process efficiency. An extra flow of  $O^{2-}$  ions through the electrolyte occurs with respect to the

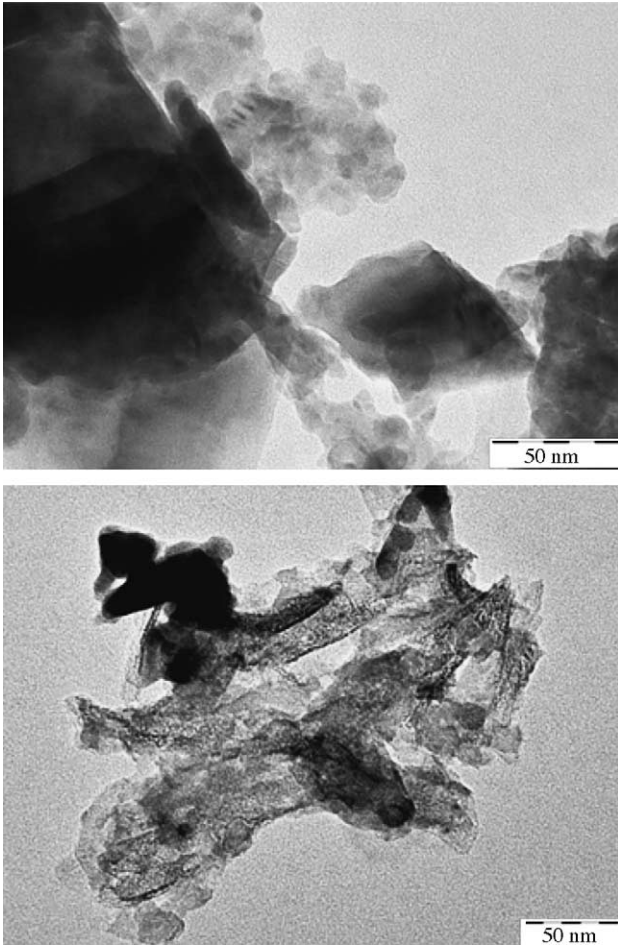


Fig. 4. TEM micrographs of the LSFCO before (top) and after (bottom) thermal treatment in dry methane at 900 °C for 2 h.

electronic current flowing in the external circuit to maintain the electro-neutrality. Such excess of oxygen ions produces an extra consumption of CH<sub>4</sub> molecules at the interface or other possible carbon-containing species [16]. This parasitic process can be reduced by decreasing the operating temperature of the SOFCs in the presence of an electrode-supported

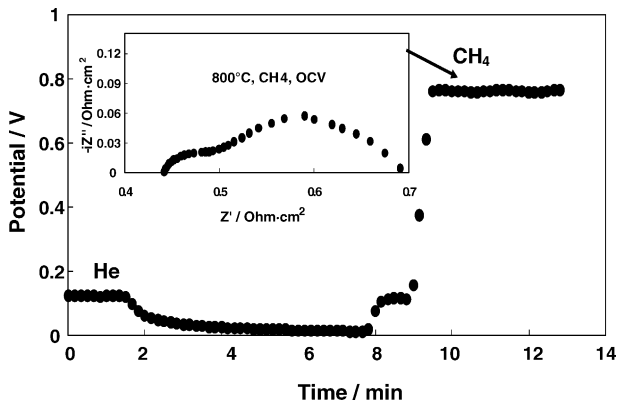


Fig. 5. Open circuit potential and ac-impedance profiles for a CGO–electrolyte supported SOFC based on LSFCO anode fed with dry methane at 800 °C.

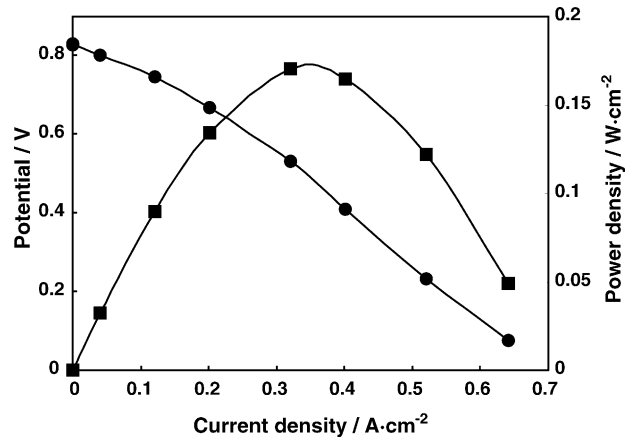


Fig. 6. Polarization and power density curves for a CGO–electrolyte supported SOFC based on a LSFCO anode fed with dry methane at 800 °C.

thin film electrolyte configuration. As clearly observed in the mass spectrometry analysis, the LSFCO is catalytically active for methane oxidation at temperatures as low as 350 °C.

The impedance spectroscopy (Fig. 5, inset) measured under OCV in dry methane shows a series resistance value ( $R_S$ ) of 0.42  $\Omega \text{ cm}^2$  and a polarization resistance ( $R_P$ ) of 0.25  $\Omega \text{ cm}^2$ . The results indicate that the ohmic resistance, mainly due to the electrolyte thickness (300  $\mu\text{m}$ ), is prevailing with respect to the electrode polarisation resistance. Thus, a significant increase of performance is expected in the presence of a thin electrolyte membrane. The electrode polarisation resistance is close to that observed for Ni-based cermets [16] indicating no significant loss of catalytic activity for the perovskite material. The polarization and the power density curves, obtained after 140 h of continuous operation with dry methane, are plotted in Fig. 6. At a working voltage of 0.6 V, the cell showed a current density close to 0.2  $\text{A cm}^{-2}$ . The maximum power density reached by this cell was 0.17  $\text{W cm}^{-2}$ . Finally, a chrono-amperometric measurement, during potentiostatic cell operation at 0.6 V with dry methane at 800 °C is presented in Fig. 7. The cell was working for 140 h in dry CH<sub>4</sub> and stationary air showing an increase of performance with time. The experiment was shut

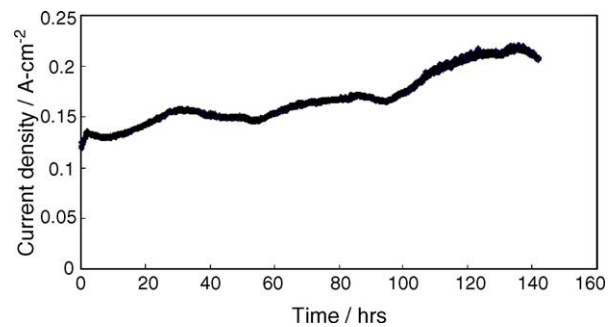


Fig. 7. Chrono-amperometric curves for the dry methane-fed SOFC during potentiostatic operation at 0.6 V.



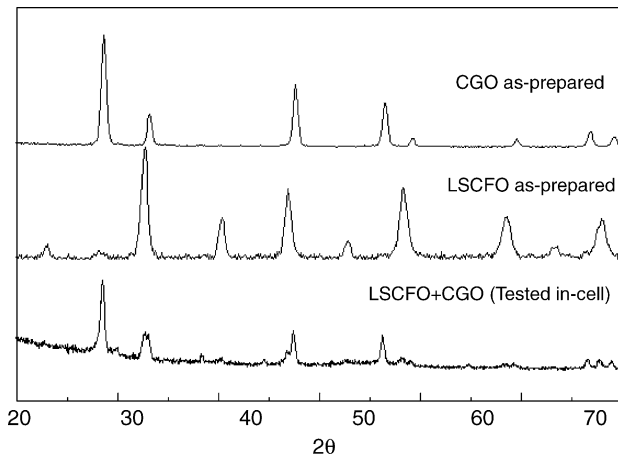


Fig. 8. XRD patterns of the raw LSCFO and CGO powders and LSCFO–CGO anode layer (grazing angle) after operation with dry methane at 800 °C for 140 h.

down by cooling the cell in dry methane under OCV conditions; afterwards, the anode side of the cell was analysed in terms of structure and composition.

### 3.3. Phase and chemical characterization of the composite perovskite anode after operation

Fig. 8 shows the XRD pattern (c) of the anode material after 140 h operation. This pattern was obtained in the grazing angle mode ( $0.5^\circ$  incidence angle,  $1^\circ$  mask) to enhance the structural information from the anode layer and to reveal more precisely any trace of carbon deposition. The X-ray pattern in Fig. 8 shows the presence of large intensities for the CGO reflections indicating a significant contribution from the electrolyte underlayer to the total X-ray scattering. From the XRD analysis, it can be observed that the LSCFO–CGO anode does not show any significant degradation after 140 h operation. Moreover, there is no presence of carbon deposition which usually appears at  $2\theta = 26.7^\circ$ . The possible presence of carbon was also investigated by an elemental CHNS–O analyzer. The carbon content in the anode layer fed with dry methane was similar to that observed before operation and it is close to the lower detection limit of the instrument; as opposite, the sample treated in methane in the out-of-cell experiment revealed a significant content of carbon due to the carbonate phase formation.

The anode morphology before and after SOFC operation was investigated by SEM–EDAX analysis (Fig. 9). The LSCFO phase, identified by EDAX analysis, showed fine particles and lower degree of agglomeration with respect to CGO grains. A decrease of porosity for the anode layer was observed subsequently to SOFC operation in dry methane. However, the morphology of the LSCFO and CGO grains did not change significantly. The absence of fibers or whiskers-like carbon species was confirmed from high magnification analysis.

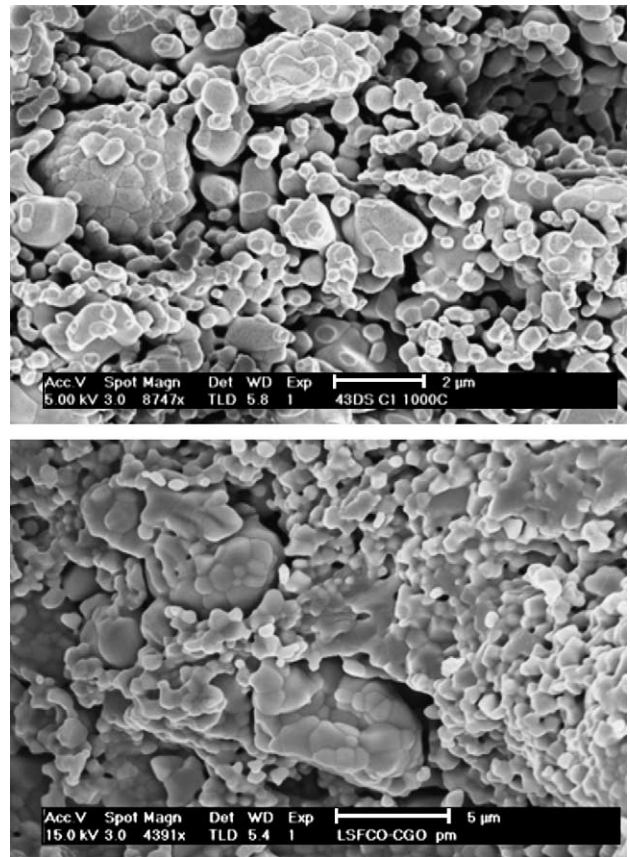


Fig. 9. SEM micrographs of the anode layer before (top) and after (bottom) SOFC operation in dry methane.

### 3.4. Stabilisation of the LSCFO perovskite anode in a methane-fed SOFC device

It was pointed out in the previous sections that the degradation of the LSCFO perovskite in dry methane was only observed in out-of-cell experiments. In fact, no chemical or structure modifications were observed after operation in a SOFC of the LSCFO layer. It is worth to note that the cell was operated both under OCV and electric load for a period significantly larger than that selected to evaluate the material stability in out-of-cell conditions.

The processes occurring during LSCFO exposure to methane in out-of-cell conditions (excluding carbonate phase formation) are similar to those in a SOFC anode during the direct electrochemical oxidation of methane; however, in the latter case, the ionic oxygen was continuously provided by the reduction of oxygen molecules to  $O^{2-}$  at the cathode–electrolyte and their transport to the anode–electrolyte interface. As a logic consequence, it is observed that if ionic oxygen is efficiently supplied to the LSCFO anode under SOFC operation conditions, no degradation of the perovskite structure would occur. On the other hand, under open circuit conditions, being the device operated at a temperature where a mixed conduction (ionic and electronic) domain exists for the electrolyte membrane, the system also

acts as a pressure driven oxygen pump. Thus, a flow of oxygen ions towards the anode (counterbalanced by a flow of electrons to the opposite direction) is also present. Such a condition, besides protecting the anode, generally causes both a reduction of electrical and fuel efficiency. However, it is observed that the OCV does not represent a practical operating condition, but generally the cell is left under OCV for short transition periods, e.g. during start and up-shut down cycles. Furthermore, the ionic domain of ceria depends, beside the temperature, also on the electrical potential; in fact, the reduction process of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  inside the ceria lattice, which is responsible of the electronic conductivity, is favoured by strongly reducing conditions for the anode as those occurring close to the OCV. Thus, the current loss occurring under conditions close to the OCV (low current density values) is suitably decreased by operating the SOFC at potentials where this reduction process is less favoured (high current densities) compatibly with the electrical efficiency and power density requirements.

To further corroborate the present findings, it is observed that the stability of the LSFCE perovskite in the anodic atmosphere during SOFC operation was previously hypothesised by Weston and Metcalfe [13]. These authors observed, in out-of-cell experiments, that the filling of oxygen vacancies in LSFCE, in the presence of oxygen supply, proceeds at much greater rate than their generation during the reduction process. Furthermore, similar perovskite materials (e.g. BSCFO) showed stable operation (500 h) for methane partial oxidation in a high oxygen permeability membrane reactor [14,15]. It was inferred such stability under reducing conditions is due to both high oxygen permeation flux and excellent phase reversibility. It was observed, in reduction–reoxidation experiments, that all Co and Fe metallic species originated during reduction were reincorporated into the perovskite structure after subsequent oxidation [14].

Another important aspect that should be taken into consideration, in view of a possible applications, is the architecture of the SOFC cell. It has been previously evidenced that to increase the performance, a reduction of the ohmic drop limitations appears necessary. A thin film electrolyte configuration would represent a possible solution. However, it may be hypothesised that the anode layer near the three-phase boundary, close to the electrolyte membrane where the oxygen supply is more effective, is properly stabilised by the transported oxygen ions. Thus, the perovskite anode layer should be sufficiently thin as in the present case. This requires that a cathode-supported configuration is adopted. In any case, a thin oxide-based anode layer would also, in principle, provide benefits in terms of tolerance to redox cycles for SOFC devices.

#### 4. Conclusions

The catalytic activity of LSFCE towards methane electro-oxidation appears to be associated with a high surface mobility and availability of ionic oxygen in this material [10]. The continuous supply of mobile  $\text{O}^{2-}$  ions to the LSFCE anode also promoted by CGO under both SOFC operation and OCV conditions, due to the mixed conduction properties of the CGO electrolyte at 800 °C, protects the surface from degradation. The latter would otherwise occur through lattice oxygen consumption in absence of external oxygen ion source. Out-of-cell catalytic experiments in dry methane may represent a fast and reliable method to assess the intrinsic catalytic activity of perovskites, but they cannot be assumed as a valid test to prove the catalyst degradation which should be properly verified by electrochemical operation. Such evidence could open new perspectives for the use in SOFCs of materials previously ruled out on the basis of ex situ stability requirements.

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