

Physicochemical properties of the Crofer 22 APU steel with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ protective-conductive coatings prepared by pulsed laser deposition

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Abstract

Commercial $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ powder was used for preparation of corresponding perovskite films on commercial Crofer 22 APU high chromium steel by pulsed laser deposition. The obtained films PLD1 and PLD2 with a thickness of 1.1 and 0.35 µm, respectively, were dense and homogeneous, with good adhesion to the polished surface. Oxidation studies of the samples were carried out in air at 800 °C for 200 h. The calculated parabolic rate constant k_p after isothermal oxidation for the PLD1 sample was $4.10 \times 10^{-14} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and was approximately four times lower than the oxidation rate determined for the PLD2 sample. As a result of the oxidation process, in both cases, a thin oxide layer of chromia and $Mn_{1.5}Cr_{1.5}O_4$ spinel was formed on the steel/film interface. In addition, small amounts of manganese-chromium spinel crystals were observed on the films' surfaces. Values of the specific electrical resistance at 800 °C after 100 h of the experiment were 0.06 and 0.038 $\Omega \cdot cm^2$ for PLD1 and PLD2, respectively. The results indicate that the applied coatings meet the criteria set upon protective-conductive layers for interconnect materials, for the IT- SOFCs (intermediate-temperature solid oxide fuel cells) applications.

Keywords: SOFC, interconnect, PLD, protective-conducting coating

I. Introduction

Solid oxide fuel cells (SOFCs) are energy devices that allow for the direct conversion of chemical fuels into electrical power [1]. A key component of the SOFC planar system is an interconnect, which constitutes the mechanical support of the cell stack. It is responsible for the oxygen-hydrogen separation between electrodes (anode and cathode) and ensures electrical contact between individual cells, as well as transferring electricity to external receivers [2–4]. Taking into account these requirements, for intermediate temperature SOFCs (IT-SOFC) operating in the range of 600–800 °C, ferritic stainless steels (FSS) are the most intensively studied materials for potential use as an interconnect [4–6]. However, using this type of steel leads to some undesirable phenomena, such as a gradual increase in areaspecific resistance (ASR) due to the growth of a Cr_2O_3 layer [4,6,7], as well as chromium species evaporation, which could affect the catalytic activity of the cathode and thereby lead to cell degradation [8]. An effective method of resolving these negative effects is the application of a protective-conducting coating on the steel [9]. Many papers show that $(Co,Mn)_3O_4$ or Cu-doped $(Co,Mn)_3O_4$ spinels seem to be good candidates for use as a protective-conducting coating on the oxygen side. Only a few works have been published concerning oxidation of Co₃O₄ or (La,Sr)MnO₃ (LSM) coatings in the fuel atmosphere [10-12]. Perovskite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF48) was usually applied as a coating, which is also commonly used as a state-of-the-art cathode material in IT-SOFCs technology [13-17,21-23].

Considering the chemical stability of electrolytic ma-

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terials such as gadolinium-doped ceria and the matching of the thermal expansion coefficient with the Crofer 22 APU steel, the use of LSCF as a protective-conducting coating material for metallic interconnect would be desirable. Typical X-ray diffraction analyses show that the LSCF ceramics have a near-cubic perovskite-type phase of the ABO₃ structure with a trivalent rare-earth ion on the A site and a trivalent transition metal ion on the B site and the R3c space group. Cobaltium ions on the B site indicate smaller binding energy for O_2 than that with Fe ions, enhancing the oxygen vacancy formation, and Sr ions on the A site lattice of LSCF act as an acceptor. This mechanism increases the electronic conductivity of LSCF. LSCF has good electrical conductivity (10^2 S/cm at 800 °C [18]), with a confirmed *p*-type electronic conductor. The oxygen diffusion parameters are as follows: oxygen surface exchange coefficient and oxygen self-diffusion coefficient (D^*) are 6×10^6 [19] and 5×10^7 cm²/S [20] at 800 °C, respectively. According to Alnegren et al. [13], the oxidation rates were not varied by increasing the O2 partial pressure. Whereas in the other studies [14] is claimed that the oxidation rates were significantly higher when annealed in pure oxygen compared to air. These discrepancies can be explained by the influence of factors such as differences in the pre-treatment of the steel substrate, different levels of humidification, or the use of different gas flow rates. These types of coating materials meaningly stop promoting the development of oxide layer and characterized a high value of conductivity even after a long time of oxidation in the fuel atmosphere. The thermal expansion coefficient *TEC* of LSCF is $14-15.2 \times 10^{-6}$ 1/K and matches the Crofer 22 APU $(11-15 \times 10^{-6} \text{ 1/K})$ [21,22]. One of the key advantages of LSCF coating is resistance to the cell's degradation caused by carbon contamination [23].

Several techniques were investigated for LSCF coating deposition on the interconnect: screen printing [24– 26], physical vapour deposition [27], spin coating [28], magnetron sputtering [29], electrostatic spray deposition [30,31], aerosol deposition method [32] or plasma spraying [33]. Previous studies [34] have discussed the physicochemical properties of uncoated Crofer 22 APU ferritic steel and the steel with the LSCF48 coating deposited by the PLD method. The LSCF48 coating significantly reduced the growth of the oxidation product on the metallic substrate and increased electrical conductivity. Pulsed laser deposition is a physical vapour deposition process, carried out in a vacuum system that shares some process characteristics common with molecular beam epitaxy and some with sputter deposition. Several features make PLD particularly attractive for complex material film growth: stoichiometric transfer of material from the target, generation of energetic species and hyperthermal reaction between the ablated cations and the background gas in the ablation plasma [35]. However, applying most of the above-mentioned methods does not allow for obtaining a coating that would be dense, homogeneous and reproducible simultaneously such a point of view, the PLD technique is an especially promising technique for obtaining protectiveconducting coatings on metallic interconnects.

The effectiveness of protective-conducting coating depends on the adherence of the layer to the alloy surface and the chemical stability of the layer [36]. PLD technique provides a good adherence of the coating to the substrate surface, which prolongs the longevity of LSM coating on metallic interconnects. An additional approach to realizing this condition is creating an interlayer between the LSCF coating and the substrate. It also provides a low thickness of the layer, which does not introduce an additional ohmic resistance [28,37].

The optical properties of LSCF film deposited on ferritic steels were studied by the total reflectance, the total integrated scatter method and the ellipsometry method. Analysis of the optical spectroscopic data reveals that the LSCF film produced by PLD technique has a uniform thickness and low surface roughness [38]. Preliminary studies have shown the need to improve the physicochemical properties of the obtained coating. The improvement of the uniformity and the quality of LSCF48 coatings deposited by the modified PLD technique was achieved. According to obtained results, the next series of LSCF48 coatings were improved and successfully deposited.

The main aim of this paper was to investigate the oxidation behaviour of the Crofer 22 APU with LSCF48 coatings under isothermal conditions, as well as its electrical resistance, testing both the protective and conductive properties of films. Samples with a coating thickness of 1.1 and 0.35 μ m were selected for investigations.

II. Experimental

The commercial $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ powder was supplied by Marion Technologies (Toulouse, France) and was synthesized by the auto-ignition method and calcined in air at 800 °C by 10 h. In order to obtain information about the chemical stability during the heating of the powder, thermal analysis was performed using the DTA and TG techniques. The tests were performed in the STA (simultaneous thermal analysis) apparatus of the SDT 2960 TA Instruments. At the same time, the chemical composition of gases released from the tested samples during their heating was analysed using a quadrupole mass spectrometer - QMS from Balzers Instruments, ThermoStar type, cooperating with the STA apparatus. The experiment was carried out in temperature range of 20–1100 °C. The sample was heated in a platinum crucible at a rate of 20 °C/min in synthetic air.

As a substrate material, the Crofer 22 APU highchromium stainless steel (ThyssenKrupp VDM GmBH, Germany) was selected. Table 1 shows the chemical composition of the steel. Samples with the following dimensions $20 \times 10 \times 0.5$ and $10 \times 10 \times 0.5$ mm were used for the oxidation studies and electrical measurements,

Table 1. The chemical composition of Crofer 22 APU alloy

	Chemical composition [wt.%]										
	Fe	Cr	Mn	Ti	Si	С	Р	S	La	Cu	Al
max.	Bal.	24.0	0.8	0.20	0.5	0.03	0.05	0.02	0.20	0.50	0.50
min.	Bal.	20.0	0.3	0.03	0	0	0	0	0.04	0	0

Table 2. Parameters of pulsed laser deposition

Parameter	Value
laser wavelength, λ	266 nm
energy density, ε	9.7 J/cm ²
laser pulse energy, E	100 mJ
frequency, f	10 Hz
substrate temperature, T	300 °C
oxygen partial pressure, p_{O_2}	5 mTorr
ablation pulses, PLD1	180 000
ablation pulses, PLD2	90 000
target-substrate distance	70 mm

respectively. The LSCF samples were ground with 1000 to 1200-grid SiC papers and finally polished with an alumina slurry. Two types of samples were prepared: PLD1 (as reference) and PLD2 with a film thickness of 1.1 μ m and 0.35 μ m, respectively. LSCF48 films were deposited on the steel by pulsed laser deposition. The dense target was obtained by compacting the LSCF48 powder under 300 MPa and then sintered at 1200 °C for 2 h in air. Films were deposited by an Nd:YAG laser (Continuum, Powerlite Precision II 9010 DLS). Detailed parameters of the films deposition are given in Table 2.

Measurements of oxidation kinetics are carried out in air at 800 °C for 200 h using the CI Electronics MK2-M5 microbalance heads characterized by a sensitivity of 10^{-6} g.

The phase compositions of the surface-modified steel were studied by means of X-ray diffraction (XRD) performed with a Panalytical X'PertPW3710, using monochromatic CuK α radiation and the HighScore Plus software. The scan range was from 10° to 90° with the 0.01° step size. To determine the crystallization temperature of the LSCF48 film, the high-temperature, *in situ* XRD measurements were performed in an MRI Camera (MRI TC) equipped with a platinum strip heating element. The sample was heated at a rate of 5 °C/min. to the desired temperature and then annealed for 20 min. Measurements were carried out in the temperature range of 30–600 °C.

The quantitate phase composition of the studied materials was performed by comparing the obtained diffraction patterns with the data included in the ICSD database. The amount of each phase and its lattice parameter were determined using the Rietveld method.

The average crystallite size D_{XRD} of the ceramic films was calculated using the Scherrer equation [39]:

$$D_{XRD} = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \tag{1}$$

where D_{XRD} is the crystallite diameter [nm], K is the parameter equal to 0.9, λ is the wavelength of X-rays (for

CuK₁ is 0.15406 nm), θ is the diffraction angle of rays and β is corrected FWHM (full width at half maximum) of the diffraction peak.

Diffraction data were modelled using a pseudo-Voigt function and the FHWM value was calculated using Eq. 2, where B_{obs} is equal to FHWM and related to the sample, *B* is FHWM of reference material (corundum pure Al₂O₃):

$$\beta = \left(B_{obs}^2 - B^2\right)^{1/2} \tag{2}$$

The calculated minimum dislocation density δ of the particular structure using Eq. 3:

$$\delta = \frac{1}{D_{XRD}^2} \tag{3}$$

The morphology and chemical composition of the samples were studied using FEI Nova NanoSEM 200 and FEI Versa 3D scanning electron microscope. Chemical analysis was performed using an EDAX energy-dispersive X-ray spectroscopy (EDS) system. To evaluate the particle size of powder and density of films, SEM images were analysed using the free software ImageJ ver. 1.6. After image trimming cross section SEM images are transformed to the binary images to get the cracks and pores which formed in the layer.

Studies of changes in the electrical resistance of Crofer 22 APU/LSCF48 systems were carried on by applying different frequencies of an alternating current (AC) which goes through electrodes placed on both sides of samples under different temperatures. For an accurate measurement, a precise current source using 2 points 4wires to connect to the device under test has been created. Electrical resistance studies were performed with Zurich Instruments MFIA Impedance Analyzer, using the tetra-polar configuration to avoid the problem related to contact impedances, within 1 Hz to 1 MHz frequency range. Measurements were carried out in the air in the temperature range of 200–800 °C. Before measurements, platinum electrodes were deposited on both sides of studied samples using magnetron sputtering.

The evolutions of *ASR* were calculated using the data collected during conductivity measurements and using the following Eq. 4:

$$ASR = \frac{R \cdot A}{2} \tag{4}$$

where *R* is measured electrical resistance and *A* is the electrode surface area, $A = 0.78 \text{ cm}^2$. *ASR* of samples was calculated based on the direct current (DC) conductivity measured as a function of temperature in the range of 200–800 °C.

To determine the activation energy (E_a) and *B* parameter of the investigated samples, the Arrhenius plot (plot of $\ln(\sigma \cdot T)$ versus 1/T) was constructed and the activation energies E_a were computed by fitting a straight line to experimental data (Eq. 5):

$$\sigma = B \exp\left(-\frac{E_a}{k_B \cdot T}\right) \tag{5}$$

where σ is the specific conductivity (DC), E_a is activation energy, *B* is the pre-exponential factor, k_B is the Boltzmann constant (0.8617 × 10⁻⁴ eV/K) and *T* is temperature.

The *B* parameter was calculated as:

$$B = \frac{N \cdot e^1 \cdot a^2 \cdot v \cdot P}{k_B \cdot T} \tag{6}$$

where N is the total charge carrier density, e is the electric charge, v is the attempt frequency of the order of the lattice phonon frequency and P is the jump probability. The error of these calculations did not exceed 0.02 eV.

The Mössbauer spectrum was obtained using the MsAa-3 spectrometer with the commercial 57Co(Rh) source kept at room temperature. The study of the Mössbauer effect was carried out using the transmission technique on 57Fe atomic nuclei at room temperature. 57Co was used as the radiation source in the Rh matrix with an activity of approx. 17 mCi. Spectrum was obtained at room temperature. Data was processed within transmission integral approximation as implemented in the MOSGRAF software.

III. Results and discussion

3.1. Characterization of LSCF48 powder

Toward the comprehensive understanding of physicochemical properties of the LSCF48 powder provide better insights on their behaviour during the films deposition process. The measurement data analysis allowed to assess the suitability of the powder for use as a protective-conductive coating. Figure 1 shows the derivatographic analysis (TG/DSC/EGA curves) of the LSCF48 powder. As can be seen from the recorded curves the total weight loss of the sample falling within the temperature range of 20–1100 °C is about 2%. Below 100 °C, the loss of sample mass should be associated with the release of physically bound water, which confirms the presence of the H_2O peak in the mass spectrum of the ionic current. Then, as the temperature rises to 200 °C, the chemically bound water is released, which is in agreement with the observed peak on the EGA curve. This is confirmed by the presence of an endothermic peak on the DTA curve observed in the temperature range 900–1100 $^{\circ}\text{C}.$ The gaseous products evolved during the thermal decomposition of the LSCF48 in synthetic air by EGA-QMS technique and the curves are depicted in Fig. 1. It should be emphasized that there are no signals in the EGA spectrum



Figure 1. TG and DSC curves of LSCF48 powder and selected EGA-QMS curves of gases evolved during thermal decomposition of LSCF48 powder, in air

attributed to gaseous CO₂ products, which confirms the high chemical stability of the tested powder during its preparation and operation in air (Fig. 1). No other phase transformations and product decomposition are observed. Above 570 °C, a slight mass loss of approximately 1% was observed due to the release of oxygen ions from of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} lattice and vacancies are created. The thermogravimetric study yielded an increase in values for the oxygen nonstoichiometry in the LSCF48 powder between 570 and 860 °C in synthetic air. It is well known that the higher concentrations of mobile oxygen vacancies significantly improve the ion conductivity process of LSCF48 coating. On the other hand, the total oxygen vacancy concentration would create a suppressing effect on the electron polaron hopping in the perovskite lattice. As a result, the electrical conductivity should decrease with increasing oxygen nonstoichiometry. This behaviour is often observed, because a low value of electrical conductivity introduces a large charge-transfer resistance.

In order to obtain structural information about the nature of phase in crystalline powder a XRD study was undertaken. Figure 2 shows X-ray diffraction pattern of the LSCF48 powder at room temperature. According to the analysis, all of the peaks can be indexed to a rhombohedral phase with *R3c* symmetry (ICDD XRD card. No. 01-082-1963). The observed diffraction peaks of the powder are sharp (the full width at half maximum peaks is narrow) which indicate that the investigated powder has a high crystalline characteristic. The LSCF48 powder does not exhibit a formation of secondary phase. The average grain size was calculated from the FWHM of 110 diffraction peak using the Debye-Scherrer formula, and indicated a value of 45 nm. The obtained value is similar to those reported elsewhere [40].

To achieve deeper insight into the structure of the in-



Figure 2. X-ray diffraction patterns of LSCF48 powder



Figure 3. Mössbauerabsorption spectra of LSCF48 powder recorded at room temperature

vestigated LSCF48 powder, a Mossbauer spectroscopic study was performed. It is necessary to emphasize, that this method is more sensitive and suitable for the study of the local atomic environments. Figure 3 displays the absorption Mössbauer spectrum (MS) of the LSCF48 powder, recorded at room temperature. The spectrum of the Mössbauer levels was obtained, caused by the hyperfine interactions of the atomic nucleus with the quadrupole electric interaction (doublet). The obtained spectrum was fitted using the least squares method. The results of MS and XRD show that iron is present only in octahedral coordination. The obtained spectrum of hyperfine interactions is consistent with typical for iron in the perovskite structure. A slight broadening of the MS curve in the region of low transmittance (close to the background) is related rather to structural disorder than local coordination environments.

SEM micrographs, at different magnifications, of the LSCF48 powder are shown in Fig. 4. These observations reveal that the LSCF48 powder consists only of irregularly shaped particles. However, fine powder tends to agglomerate due to the occurrence of inter-particle forces like cohesive force, attractive force, gravitational force and of course the Van der Waals force. The dimensions of the agglomerates formed are in the range from about $0.3 \,\mu\text{m}$ to $5 \,\mu\text{m}$. It should be highlighted that the advantage of PLD technique is that it does not require the use of a nano-sized powder to obtain dense layers.

3.2. Characterization of LSCF48 films after deposition

Figure 5 shows backscattered electron SEM images of surfaces of the PLD1 and PLD2 samples. In both samples, films obtained by PLD were homogeneous and dense, with small particles with dimensions varying from ~ 0.1 to $1.1 \,\mu\text{m}$ being visible on the surface. The presence of particles results from the specificity of PLD process. The ejection of micron-size particles in the ablation process is often observed when the penetration depth of the laser pulse into the target material is large. Whereas nanoparticles are formed in the gas phase when the background pressure is sufficiently high for heterogeneous nucleation and can become embedded in a depositing film [35]. During a mechanical polishing, the surface of the coating applied to the substrate becomes uneven (Fig. 5) because of the different distance from the surface and impurities of the grinding paper to the layer. The crucial characteristic of functionalized thin films is their porosity. Porosity estimated af-



Figure 4. SEM microphotographs of LSCF48 powder at different magnifications: a) 2500×; b) 50000×



Figure 5. Backscattered electron SEM microphotography of the surface of the LSCF48 layer on stainless steel: a) PLD1 and b) PLD2

ter digital binarization of series SEM microphotographs were $89 \pm 4\%$ and $79 \pm 4\%$ for the PLD1 and PLD2 samples, respectively. The thermal conductivity and the electrical conductivity increased with decreasing porosity because of effective phonon and charges particles scatterings by pores, respectively. High dense coating reduces the diffusion rate of oxygen particle and oxygen vacancy which are favourable for development of undesirable chromium oxide layer on the interconnector surface.

Thin as-deposited film on steel substrates were investigated by *in situ* high-temperature XRD technique (HT-XRD) in order to analyse evolution of their phase composition during thermal treatment (Fig. 6). The primary α -Fe phase (ICDD XRD card. No. 98-062-5865), corresponding to the Fe-based metallic substrate was identified at room temperature. In addition, three peaks corresponding to the silicon phase (ICDD XRD card. No. 00-035-1158) were registered, most likely resulting from the presence of impurities, as the peaks appear throughout the whole series of diffraction patterns, without changing the position of 2θ and the intensity over the



Figure 6. X-ray diffraction patterns of the PLD2 heated at selected temperatures

entire measuring range. The presumed cause of these impurities seems to be the polishing process (SiC paper) rather than the presence of silicon in the substrate. Nevertheless, reflections overlapped with the reflection of the LSCF48 layer or Si-phase. The peaks of Si and α -Fe (ICDD XRD card No. 98-018-0970) phases are close to each other and difficult to distinguish. Nevertheless, HT-XRD results stay in agreement with data obtained by SEM-EDS analysis.

To determine the crystallization temperature of the film, the high-temperature, in situ X-ray analysis of the PLD2 sample was performed. A series of XRD patterns measured at an RT and in the temperature range of 300 to 600 °C with a 50 °C step are shown in Fig. 6. No reflection of the PLD1 and PLD2 phase are found in the films deposited, clearly indicated that films have an amorphous structure. HT-XRD patterns of the LSCF48 heated at 550 °C show (at $2\theta \sim 30^{\circ}$) the amorphous phase. DTA/TG results show that these structures are very stable up to 550 °C because the mass loss is negligible. Similar results are also observed for the PLD1 sample. The XRD peaks corresponding to the perovskite Co_{0.3}Fe_{0.7}La_{0.7}Sr_{0.3}O₃ phase (ICDD XRD card No. 98-008-6125) were observed between 550 and 600 °C. There is no ICDD XRD file matching the composition of LSCF48. The XRD analysis shows clearly that the $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ has the orthorhombic crystal structure. Therefore, this means that the crystallization of the LSCF48 film took place at a temperature between 500 and 550 °C, which corresponds to the literature data [41,42]. The crystallization of the (La,Sr)(Co,Fe)O₃ compounds is usually observed at 450 to 600 °C [41-43]. The LSCF48 phase is identified by a series of strong diffraction reflections. Major XRD peaks originating from the following lattice planes (101), (121), (220), (022) and (321) at 22.826°, 32.316°, 39.822°, 40.131° and 57.667°, respectively, according to ICDD 98-008-6125 XRD card (Fig. 6). The Si-phase and LSCF48 phase peaks located at around 38° and 48° overlap each other. Some reflections were too weak for reliable detection. X-ray crystallographic

		-		-	
	a [Å]	<i>b</i> [Å]	c [Å]	V [Å ³]	D_{XRD} [Å]
CrFe	2.891	2.891	2.891	24.162	-
α -Fe	2.887	2.887	2887	24.062	-
LSCF	5.526	7.810	5.521	238.276	280

 Table 3. Cell parameters obtained from Rietveld refinement of XRD pattern of the PLD2 sample

analysis revealed that LSCF48 films crystallized in an orthorhombic crystal system with space group *Pnma*. The α -Fe phase crystallized in the simple cubic type crystal system with space group $Im\bar{3}m$. Table 3 shows the lattice parameters for each phase and their relative concentrations in weight after the Rietveld refinements. The value is almost similar to the reference XRD card, a = 5.536 Å, b = 7.848 Å and c = 5.475 Å.

The theoretical density of the LSCF48 layer was calculated using a crystallographic density. For PLD1 and PLD2 samples, the theoretical density for the LSCF has been computed to be 6.35 g/cm^3 . These values are consistent with data reported in the literature for dense LSCF48 ceramics [44]. Calculated average dislocations density for the PLD1 and PLD2 samples reached $12.7 \times 10^{14} \text{ m}^{-2}$ and $11.5 \times 10^{14} \text{ m}^{-2}$, respectively.

3.3. High-temperature oxidation

The oxidation kinetics measurements of the Crofer 22 APU substrate with LSCF48 film were performed in ambient air at 800 °C for 200 h. Figure 7 depicted the isothermal oxidation kinetics of the PLD1 and PLD2 samples, expressed as a time-dependent mass change of the materials. The obtained results indicate that the oxidation kinetics of studied samples approximately follow the parabolic rate law. For the parabolic rate constant calculation, the Pilling-Bedworth equation was used [45]:

$$\left(\frac{\Delta m}{A}\right)^2 = k_p \cdot t + C \tag{7}$$

where Δm is the mass, A is the area, k_p is the parabolic rate constant, t is the time of reaction and C is an integration constant defining the onset of parabolic kinetics.



Figure 7. Oxidation kinetics of PLD1 and PLD2 samples in air for 200 h at 800 °C expressed as mass change in a function of time

The estimation values of k_p parameter for the PLD1 and PLD2 layered systems, with time intervals in which the parabolic rate law is obeyed, are provided in Table 4. The value of k_p for the PLD2 sample was calculated as 1.71×10^{-13} g²/cm⁴s and is of the same order of magnitude as k_p of bare Crofer 22 APU steel [26,46]. However, in the case of the PLD1, the parabolic rate constant is approximately four times lower and equals $4.10 \times 10^{-14} \text{ g}^2/\text{cm}^4$ s. Take under consideration only k_p parameter, the LSCF48 ceramic layer with a thickness of 1.1 µm (the PLD1 sample) more effectively decreases the speed of the oxidation of investigated steel at 800 °C. In contrast, a thinner film (the PLD2 sample), seems to be not an effective barrier against oxidation in the studied conditions. To improve the physicochemical properties of the PLD2 layer, it was necessary to increase the density of layer by the further increase in the sintering temperature. The doping strategy involves free electron in the lattice, then promotes the electric conductivity of oxides. The effect of active element additions in the case of PLD2 may be amplified by increasing the concentration of the active element in the surface layer of the material either via ion implantation. Figure 8 presents the surface morphologies of the PLD1 (Fig. 4a) and PLD2 (Fig. 4b) samples after 200 h of oxidation at 800 °C in air, together with the results of EDS point analysis. In both cases, on the surface of the film, isolated spinel crystals were visible, which means that during the oxidation process the transport of manganese and chromium ions through the LSCF48 film took place. From the EDS analysis (point 1) it follows, that spinel has high manganese to chromium ratio. In the case of the PLD1 sample, crystals were about $0.5-2\,\mu m$ in size. On the contrary, the PLD2, spinel crystals were much smaller (about $0.2-1 \,\mu m$) and were present in a greater amount. For the PLD1 layered systems, EDS analysis of the LSCF48 film (point 2) shows that the chemical element ratios of Sr : La and Fe : Co are 0.44 : 0.56 and 0.79 : 0.21, respectively. In the case of the PLD2, the element ratios of Sr : La and Fe : Co are 0.40 : 0.60 and 0.79: 0.21, respectively. In the case of a perovskite, (La,Sr)/(Co,Fe) ratio must be close to 1, whilst reported EDS data show a large excess of La and Sr compared with Co and Fe for the PLD1 ((La,Sr)/(Co,Fe) = 2.25) and a slight excess of (La,Sr)/(Co,Fe) = 1.1for the PLD2 sample. Thus, the obtained results prove that the stoichiometry of the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite was preserved for the PLD2 but not for the PLD1. The crucial characteristic of functionalized thin films is their porosity.

Figure 9 illustrates the microstructure of crosssections of the samples after 200 h oxidation in air at 800 °C, together with the results of EDS point analysis (after the polished procedure). From the SEM observation of the PLD1 (Fig. 9a) it follows that underneath the LSCF48 film an oxide layer with a thickness of about 0.9 μ m has formed. The chemical mappings by SEM-EDX measurements allow for a distinction between the



Figure 8. SEM microphotographs of the sample surface with EDS point analysis after 200 h of isothermal oxidation in air at 800 °C: a) PLD1 and b) PLD2 sample



Figure 9. SEM microphotographs of the polished cross-section with EDS point analysis of the samples after 200 h of isothermal oxidation in air at 800 °C: a) PLD1 and b) PLD2

Table 4. The computed values of k_p of PLD1 and PLD2 with time intervals in which the parabolic rate law is obeyed

Sample	$k_p [{\rm g}^2 {\rm cm}^{-4} {\rm s}^{-1}]$	Time interval [h]
PLD1	4.10×10^{-14}	50-170
PLD2	1.71×10^{-13}	55-180

main phases preliminary observed in the XRD studies. The SEM-EDS observation confirms the appearance of a two-layered structure, consisting of Cr_2O_3 (at the steel surface) and the $Mn_{1.5}Cr_{1.5}O_4$ spinel (outer layer). However, the contrast of dark grey between spots 2 and 3 is uniform, there is likely a transition of composition from Cr_2O_3 to $Mn_{1.5}Cr_{1.5}O_4$.

Such a composition of the oxide layer is observed in the case of the bare Crofer 22 APU after oxidation at 800 °C and is well reported in the literature [25,26,47]. On the oxide/steel interface, the presence of SiO₂ was detected. In addition, in the metallic core, Al_2O_3 precipitates were observed. These oxides were formed as a result of the internal oxidation of silicon and aluminium. The cracks observed in the film are a result of the film crystallization process.

In the case of the PLD2, the chemical composition of the layer was comparable to the inner layer consisting of chromia and the outer layer was built of the Mn–Co– O spinel. The appearance of an internal oxidation zone with SiO₂, Al₂O₃ and TiO₂ participles was also noticed. In the LSCF48 film, based on SEM observations of the PLD2 surface, it seems to be a less visible cracks compared to the PLD1. On the film surface, crystals of the spinel with a higher ratio of Mn to Cr, compared to the spinel in the oxide layer (Mn_{1.5}Cr_{1.5}O₄), were observed. The enrichment of the spinel phase with manganese is likely associated with a higher Mn diffusion coefficient compared to Cr in both the oxide layer and the LSCF48 perovskite [48,49].

The phase composition and unit cell parameters of the phases of the PLD1 and PLD2 samples, obtained by using X-ray diffraction technique, after 200 h of isothermal oxidation are presented in Fig. 10. The phase composition of the PLD1 revealed the presence of oxida-



Figure 10. X-ray diffraction patterns of the PLD1 obtained at 25 °C: before a) and after b) the long-time treatment (200 h) at 800 °C in air



Figure 11. X-ray diffraction patterns of the PLD1 and PLD2 obtained after long-time treatment (200 h) at 800 °C in air

tion products, i.e. $Co_{0.1}Fe_{0.9}La_{0.4}Sr_{0.6}O_3$ (ICDD card No. 98-015-8800), $Cr_{0.7}Fe_{0.3}$ (ICDD card No. 98-010-2754), $Mn_{1.5}Cr_{1.5}O_4$, (ICDD card No. 98-000-9573). The long-time treatment (200 h) at 800 °C in air contributed to the observed XRD pattern to shift toward higher angles demonstrating that a decrease of cubic cell parameter took place (Fig. 11). The significant peak related to the CrFe and Si phase totally disappeared, due to the rapid formation of LSCF48 and Mn-Cr spinel thin layers of the surfaces on stainless steel substrates. It is an obvious fact that there are residual stresses in an asdeposited layer, which change its lattice parameter. The short thermal treatment is one of the most common ways to decrease semi-residual stresses from the layer resulting modifying of the lattice parameters.

In the case of PLD2, the following phases were detected: $Co_{0.1}Fe_{0.9}La_{0.4}Sr_{0.6}O_3$ (ICDD card No. 98-015-8800), $Cr_{0.7}Fe_{0.3}$ (ICDD card No. 98-010-2754),

 $Mn_{1.5}Cr_{1.5}O_4$ (ICDD card No. 98-000-9573) and residual α -Fe phase from the metallic substrate. These additional phases confirmed the interaction between the LSCF48 coating and steel.

The calculated values of the lattice parameters of the PLD 1 and PLD2 specimen after heat treatment experiment are presented in Tables 5 and 6, respectively. The experimentally determined lattice parameters are close to the standard lattice parameter for a bulk LSCF48 [44]. However, the crystalline structure values depend on the chemical route synthesis method as also the atmosphere, temperature and time of the duration of thermal treatment. Estimated average dislocations density for annealed PLD1 and PLD2 samples reach values $2.26 \times 10^{14} \text{ m}^{-2}$ and $2.5 \times 10^{14} \text{ m}^{-2}$, respectively. The increasing of the average dislocations density (after the heat treatment) is related to the transformation of phases as well as reducing in a spacing of the level crystal as the temperature increase with time.

Table 5. Crystallographic data obtained from Rietveld refinement of XRD pattern of the PLD1 after a long-time thermal treatment (200 h) at 800 °C in air

	a [Å]	<i>b</i> [Å]	c [Å]	V [Å ³]	D_{XRD} [Å]
$Mn_{1.5}Cr_{1.5}O_4$	8.466	8.466	8.466	606.785	-
LSCF48	5.492	5.492	13.397	404.081	210

Table 6. Crystallographic data obtained from Rietveld refinement of XRD pattern of the PLD2 after a long-time thermal treatment (200 h) at 800 °C in air

	a [Å]	<i>b</i> [Å]	c [Å]	V [Å ³]	D_{XRD} [Å]
$Mn_{1.5}Cr_{1.5}O_4$	8.501	8.501	8.501	614.314	-
α-Fe	5.561	5.561	15.375	475.467	-
LSCF48	3.876	3.876	3.876	58.231	200

3.4. Electrical resistance

Figure 12 illustrates the temperature dependence of ASR for the PLD1 and PLD2 samples. In both cases, it should be noticed that with temperature increases, the resistance and related ASR parameter of the studied ceramic-steel composites systematically decreases. Electrical properties manifest in the low and hightemperature range semiconducting character. Nevertheless, within the high-temperature region the slope of the line of ASR vs. T is going to higher values. In terms of ASR values, it is clearly demonstrated that the PLD1 and PLD2 at 800 °C reach values 0.019 and $0.012 \,\Omega \cdot cm^2$, respectively. These computed parameters for the high chromium stainless steels with LSCF coatings are similar to the data reported elsewhere [25,26,32]. All mean values obtained after heat treatment are significantly under the ASR limit (ASR = $0.1 \Omega \cdot cm^2$ [2]. Linearity character ASR(T) confirmed that electrical conduction in the ceramic-metal composite layers is a thermally activated process, so conductivity (the directed charge transport) is dominated by the small polaron hopping mechanism.



Figure 12. Temperature dependence of the area-specific resistance for the PLD1 and PLD2 samples



Figure 13. Arrhenius plots of $\ln \sigma$ as a function of 1000/T for PLD1 and PLD2

Based on the slope of the Arrhenius plot depicted in Fig. 13, activation energies E_a of electrical conduction and pre-exponential factor B for the PLD 1 and PLD2 samples are obtained (Table 7). From these results, it was observed that PLD1 has the lowest activation energies. Regarding the two-layer ceramic/steel systems, PLD1 exhibited the highest E_a value, and PLD2 was characterized by the lowest pre-exponential factor. The values of E_a for the investigated layers are higher than the E_a value (0.028 eV) of the LSCF48 bulk sample material (sinter T = 1200 °C) synthesized by the traditional ceramic route in the paper of Wu et al. [50] and also the E_a value of the LSC bulk sample after heating at 1100 °C achieve higher E_a value (0.049 eV) than the cathode lanthanum strontium cobalt oxide cathode material ($T = 1100 \,^{\circ}$ C) prepared by the wet chemistry route [51].

The frequency factor (B parameter in Eq. 5) describes the frequency at that molecules collide with the cor-

Table 7. E_a and pre-exponential factor *B* for PLD 1 and PLD2

	E_a [eV]	E_a [eV]	В	В
	<500 °C	>500 °C	<500 °C	>500 °C
PLD1	0.389	0.213	174555	4732669
PLD2	0.358	0.212	126753	2213310

rect orientation to allow initializing a chemical reaction. When both series of samples are taken into account, the most desirable electrical properties were observed for the PLD2 sample.

Figure 14 shows ASR for the PLD1 and PLD2 samples as a function of time, measured at 800 °C in air. In both cases, a gradual, slight increase in ASR was observed. However, ASR values obtained after 120 h of the experiment were ~0.06 and $0.038 \Omega \cdot \text{cm}^2$ for the PLD1 and PLD2 samples, respectively, are still well within the previously mentioned limit of $0.1 \Omega \cdot \text{cm}^2$.



Figure 14. Time evolution of *ASR* for the PLD1 and PLD2 samples at 800 °C in air

The lower ASR values of the PLD2 sample are likely due to the following reasons. The thickness of the LSCF48 film, when compared to the PLD1 sample was about three times smaller. After the isothermal oxidation of the PLD2 sample, a slightly thinner chromium oxide layer was formed. After oxidation at 800 °C for 200 h, the thickness of the Cr₂O₃ layer was approximately 0.6 µm and 0.4 µm for the PLD1 and PLD2, respectively. According to the literature, the growth of the chromia layer negatively affects the electrical properties of the steel [2]. Another aspect is the formation of the manganese-chromium spinel due to the oxidation on the LSCF48 film surface, which was observed in the case of the PLD2 in a larger amount. At the selected temperature (800 °C), the electrical conductivity of the manganese-chromium spinel is approximately orders of magnitude higher than LSCF48 [52,53].

The high-temperature oxidation data were analysed by fitting it to the theoretical model which was selected from many models during the model selection process. This model allows the best fit of theoretical and experimental data and can be represented by the equations presented below:

$$y = 0.0134 \exp\left(\frac{-x}{10.5996}\right) + 0.03715 +$$

$$+ 0.0002364x$$
 (8)

 $y = 0.013 + 0.028 \cdot \ln(x + 252.105) \tag{9}$

Interconnect lifetime can be precisely predicted because the experimental results are consistent with the hypothesis. As it can be seen from Fig. 14, in the case of the PLD1 sample an increase in ASR value is described by an exponential curve, in contrast to the PLD2 sample which is fitted by a logarithmic law. When carrying out calculations based on Eqs. 8 and 9, the value of ASR for PLD1 and PLD2 will exceed $0.1 \Omega \cdot cm^2$ after ~280 h and ~5000 h, respectively. Thus, the LSCF48 coating deposited by the PLD technique can be considered as a possible protective-conducting surface modification for the target SOFC. The designed SOFC cell with LSCF48 coating in cross section is presented in Fig. 15. Generally, single component fuel cell is composed of a homogenous layer made of electrolyte (e.g. YSZ) and electrode (e.g. anode - Ni-YSZ and cathode -LSF) materials.



Figure 15. Schematic representation of SOFC cell with LSCF48 coating

IV. Conclusions

Perovskite $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ films with a thickness of 1.1 (PLD1) and 0.35 µm (PLD2) were deposited on Crofer 22 APU steel by the pulsed laser deposition. In both cases, the deposited LSCF48 film was dense, homogeneous and characterized by an amorphous structure. The *in situ* HT-XRD measurements show that the crystallization of the LSCF48 film takes place at a temperature between 500–550 °C.

The results of high-temperature oxidation studies indicate that the LSCF48 film with a thickness of 1.1 μ m (PLD1 sample) effectively reduced the oxidation rate of Crofer 22 APU steel at 800 °C. It was also confirmed that an interlayer between the LSCF48 film and substrate was formed after oxidation and it consists of Cr₂O₃ (inner layer) and the Mn_{1.5}Cr_{1.5}O₄ spinel (outer layer). In both cases, spinel crystals were observed by SEM. It should be noted that after oxidation in studied conditions, in both cases no secondary phases were identified that would indicate an interaction of the LSCF48 coating with steel and/or the layer (e.g. $SrCrO_4$, LaCrO₃).

Values of the area-specific resistance measured after 100 h of heat treatment at 800 °C in the air were 0.06 and $0.038 \,\Omega \cdot \text{cm}^2$ for the PLD1 and the PLD2, respectively. The obtained physicochemical analysis results of the PLD2 sample show potential as the protective-conducting coating material for IT-SOFC applications.

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