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Development and performance of MgFeCrO₄ – based electrodes for solid oxide fuel cells

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Abstract

Composite anodes for solid oxide fuel cells (SOFC) developed on yttria stabilised zirconia (YSZ) porous supports by infiltration of electrode materials has been successfully applied for various anode and cathode compositions, resulting in high performance SOFC devices. The focus of this study is the performance of

- ¹⁰ the chromium-rich spinel (MgFeCrO₄) as an electrode support material when used alone or impregnated. The composite anodes were prepared by aqueous infiltration of nitrate salts to produce (La_{0.75}Sr_{0.25})_{0.97}Cr_{0.5}Mn_{0.5}O_{3-δ}, Ce_{0.9}Gd_{0.1}O_{2-δ}, CeO₂ or Pd into a MgFeCrO₄ scaffold with 45% porosity and studied by electrochemical impedance spectroscopy in symmetrical cell configuration. The performance was evaluated in humidified 5%H₂/Ar in order to quantify their stability and performance up
- to 850 C with respect to the MgFeCrO₄ porous substrate. It was found that all the impregnated phases adhere very well to the spinel and considerably enhance performance and stability to a level required for SOFC applications. MgFeCrO₄/LSCM/CGO and MgFeCrO₄/LSCM/CGO/Pd showed the most substantial improvement in comparison to the scaffolds performance, with ASR values of 1.74 Ω cm² and 0.91 Ω cm², respectively.

20 1. Introduction

SOFCs are electrochemical devices which convert chemical energy stored in a fuel into electricity, via an electrochemical reaction at elevated temperatures (600-1000 °C).^{1,2} The development of fuel cell technology is encouraged by the clean

- ²⁵ production of electricity from a variety of fuels without the combustion step resulting in higher conversion efficiency and with low emissions of pollutants.^{3–6} However, for superior electrochemical performance, the material requirements for such devices are rather demanding and lead to expensive materials.
- ³⁰ The material requirements along with the tendency of decreasing the functioning temperatures for SOFCs encourage the development of new materials.

Thus, the application of ferritic stainless steels as interconnect materials in SOFCs is a desirable option for decreasing materials

- ³⁵ costs. These steels have several disadvantages when used in fuel cells, mainly chromium poisoning of electrodes and high temperature oxidation to form oxide scales such as chromia and $(Mn,Fe,Cr)_3O_4$ or $(Mn,Cr)_3O_4$ spinels.⁷⁻¹² . The compatibility of the interconnect with the electrode material is directly connected
- ⁴⁰ to their interface, where usually the materials may react, leading to performance degradation. Employing chromium-spinels at the interconnect/electrode interface might improve the compatibility as a transition layer between the metal and the electrode oxide materials. The interface interconnect/electrode is poorly ⁴⁵ optimised in a stack (optimisation of physical and chemical

nature), leading to much lower performance of the stacked fuel cells than individually tested cells.¹⁶ The use as a support material of a low cost, redox stable oxide that is compatible with high temperature steels, various electrode materials and YSZ would be ⁵⁰ of significant value.

We previously reported that several chromium-rich spinels displayed promising chemical stability and electrical conductivity in reducing conditions,¹⁷ leading us to investigate MgFeCrO₄ as an anode support material. Spinel MgFeCrO₄ has a chemical 55 composition and crystal structure closely related to the oxide scale formed on interconnect surfaces following oxidation of ferritic steels (FeCr alloy). However these materials would not be expected to be good electrodes, without the addition of extra materials to form composite electrodes. LSCM has been 60 previously studied and reported as an efficient stable electrode material in reducing and oxidizing conditions and enhances the electronic conductivity in composite anodes.18-21 Ionic conductivity is another desirable property for electrode materials, or composite electrodes so ionic conducting materials as CGO or 65 CeO₂²² can be added to improve the total performance of the cells. Pd is a well known catalyst to promote electrochemical reactions.23

Therefore the aims of this study were to fabricate MgFeCrO₄ ⁷⁰ scaffolds and to evaluate the electrochemical performance of symmetrical cells based on such scaffold impregnated with electrode materials $(La_{0.75}Sr_{0.25})_{0.97}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ (LSCM), $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO), CeO₂ or Pd.

2. Experimental

Symmetrical cells were produced by tape casting the $MgFeCrO_4$ electrode material with the YSZ electrolyte layer screen-printed on the green (un-sintered) tapes. The final structures were

- ⁵ obtained by laminating two green MgFeCrO₄/YSZ tapes. Green MgFeCrO₄ ceramic tapes were obtained by tape casting a slurry containing spinel powder, organic binder (poly(vinyl-butyrate)), dispersant (dibutyl(phthalate)), plasticiser (poly(ethylene-glycol)) and graphite pore former (~6 wt.% of total solids). MgFeCrO₄
- ¹⁰ was obtained by combustion synthesis and the experimental description is covered in our previous work.¹⁷ Laminated green tapes were sintered at 1400 °C for 12 h. In the final ceramic structure the 25 μ m thick dense electrolyte was enclosed between two porous spinel layers with 45% porosity and 200 μ m
- ¹⁵ thickness. The relative density of the sintered scaffold was determined from the measured diameter and thickness (from SEM micrograph), with the electrolyte weight, as estimated from sintering studies of different structures, subtracted from that of the sintered body.
- ²⁰ The porous layers were used as scaffolds for LSCM, with additions of CGO, CeO₂ and Pd, which were impregnated into the supports as nitrate solutions prepared with the reagents: La(NO₃)₃·6H₂O Alfa Aesar (>99.99%), Sr(NO₃)₂ Sigma Aldrich (>99%), Cr(NO₃)₃·9H₂O Sigma Aldrich (99.5%),
- ²⁵ Mn(NO₃)₂·4H₂O Alfa Aesar (99.98%), Ce(NO₃)₃·6H₂O Aldrich (99%), Gd(NO₃)₃·6H₂O Aldrich (99.9%). The desired loadings of electrode and catalyst material were obtained with the impregnation carried out as a multistep process, with intermediary calcinations steps at 500°C and final sintering steps
- ³⁰ at 1200 °C (4 h) for LSCM, 1000 °C (4 h) for CGO and 450 °C (1 h) for CeO₂ and Pd. The electrodes prepared in this study, with the specific component loadings, in wt. % are labelled as presented in Table 1.

Table 1.Composite electrodes prepared in this study by impregnating ³⁵ porous MgFeCrO₄ scaffolds and the nomenclature used for them throughout this paper.

Composition (wt. %)	Label
Support (MgFeCrO ₄)	MgFeCrO ₄
+ LSCM (31%)	MgFeCrO ₄ /LSCM
+ LSCM (27%) / CGO (15%)	MgFeCrO ₄ /LSCM/CGO
+ LSCM (27%) / CeO ₂ (6%)	MgFeCrO ₄ /LSCM/CeO ₂
+ LSCM (27%) / CGO (15%) / Pd(1%)	MgFeCrO ₄ /LSCM/CGO/Pd
+ LSCM (27%) / CeO ₂ (6%) / Pd (1%)	MgFeCrO ₄ /LSCM/CeO ₂ /Pd

MgFeCrO₄/LSCM/CGO and MgFeCrO₄/LSCM/CeO₂ were prepared by sequential impregnation of materials in order of ⁴⁰ decreasing required sintering temperature. The formation of perovskite phase inside the scaffolds was confirmed by X-ray diffraction.

Phase analysis for symmetrical cells was performed on a PANalytical Empyrean Diffractometer in reflection mode, while

⁴⁵ microstructure was observed on a JEOL JSM-6700F Scanning Electron Microscope (SEM).

Electrochemical performance was determined by electrochemical impedance spectroscopy (EIS) in the frequency range of 1 MHz-0.1 Hz with 20 mV AC perturbation amplitude using a

⁵⁰ Solartron 1260 frequency response analyser and SMaRT v2.8.0 (Solartron Analytical) and ZView v3.1c software (Scribner Associates). The geometric area of symmetrical cell electrodes was 1.2 cm² on either side of the dense electrolyte layer. Measurements were made in a single chamber, consisting of a ⁵⁵ quartz tube with one open end in which a two electrode alumina testing jig was inserted and closed gas tight. The alumina jig had inlet and outlet for gas flow (humidified (3%H₂O) 5%H₂/Ar) and platinum wires for electrical contact to the sample and a sample thermocouple. Measurements included temperature dependence ⁶⁰ and assessment of the reduction process at a constant temperature of 850 °C. The ohmic resistance of the testing jig and constituent Pt wires was measured and subtracted from the results obtained for symmetrical cells. In order to remove the contribution of the

thin YSZ electrolyte layer in the series resistance (R_s), a pellet of ⁶⁵ YSZ was measured by AC impedance and the resistance of the electrolyte layer was calculated and subtracted from the R_s value.

3. Results and discussion

3.1 Phase analysis and microstructure of MgFeCrO₄ scaffold

The requirements for the application of MgFeCrO₄ as electrode support on the fuel side of SOFCs comprise chemical and microstructural stability of the spinel under reducing conditions. We assessed the chemical stability of MgFeCrO₄ in dry and humidified 5%H₂/Ar at 1000 °C for 20 h. When reduced in dry 75 5%H₂/Ar, the MgFeCrO₄ decomposed, with segregation of metallic Fe and MgO The material reduced in humidified 5%H₂/Ar did not decompose, as the partial pressure of oxygen (p_{O_2}) was above the stability limit for which secondary phases did not segregate from the spinel (Fig. 1). When reduced at 850 °C so for 30 h in dry 5%H₂/Ar the MgFeCrO₄ showed no sign of decomposition which indicates stability in fuel environments

decomposition, which indicates stability in fuel environments when operated lower than 850 $^{\circ}\mathrm{C}.$

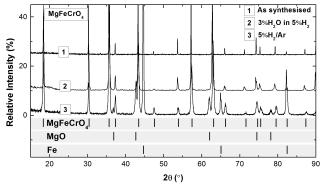


Fig. 1 X-ray diffraction pattern of MgFeCrO₄ scaffold reduced in dry $5\%H_2/Ar$ or humidified $5\%H_2/Ar$ at 1000 °C for 20 h.

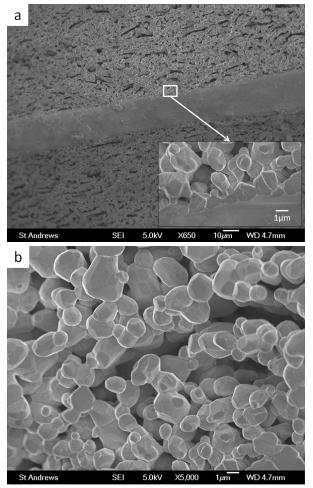


Fig. 2 Micrograph of MgFeCrO₄ / YSZ / MgFeCrO₄ scaffold, with detail of the spinel/YSZ interface and the spinel porous layer.

- ⁵ In Fig. 2 are illustrated SEM images in cross-section of the MgFeCrO₄ scaffold, with a general overview of the symmetrical architecture, the thickness of the YSZ electrolyte and the interface formed between YSZ and spinel. Sintered ceramic bodies were not cracked or curved after sintering, thus affirming that any difference in thermal expansion coefficient is small
- enough to not cause any significant mechanical damage. The spinel had particle size $1-5 \mu m$, good connectivity and open porosity for loading other materials by impregnation.

15 3.2 DC conductivity of MgFeCrO₄ scaffold

DC conductivity was measured at 850°C on a 63% dense pellet switching from static air to humidified 5%H₂/Ar (log $p_{O_2} \sim -18$). The conductivity increased significantly from 0.014 Scm⁻¹ to 0.36 Scm⁻¹ upon this reduction, indicating the n-type behaviour 20 for the material, as illustrated in Fig. 3.

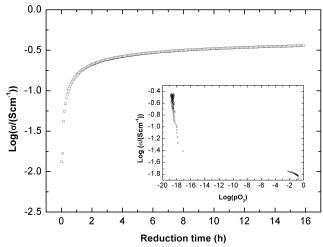


Fig. 3. DC electrical conductivity of a 63% dense MgFeCrO₄ pellet plotted as a function of time in reducing conditions at 850 °C. The inner plot shows the same data as a function of p_{O_2} .

25 3.3 Phase analysis and microstructure of impregnated MgFeCrO₄ scaffolds

XRD patterns corresponding to MgFeCrO₄/LSCM and MgFeCrO₄/LSCM/CGO are presented in Fig. 4 and the patterns for MgFeCrO₄/LSCM/CeO₂ in Fig. 5. All the peaks observed in ³⁰ the XRD patterns correspond to phases present in the samples: spinel and perovskite or spinel, perovskite and CGO, or CeO₂ respectively. The XRD pattern for MgFeCrO₄/LSCM/CeO₂ (Fig. 5) showed broad peaks corresponding to CeO₂ which is an indication that the Cerium nitrate has decomposed with the ³⁵ formation of CeO₂ with very small particle size.

In Fig. 6 cross-sectional SEM images from samples tested in humidified 5%H₂/Ar are presented. Cross-sectional SEM images confirm that infiltrated phases have good adherence and coverage to the scaffold, while images from the surface show mostly the ⁴⁰ microstructure of the infiltrated phases. In Fig. 6a, the micrograph for MgFeCrO₄/LSCM showed LSCM particles (500 nm – 1 µm) that adhere well to the spinel particles. MgFeCrO₄/LSCM/CeO₂ (Fig. **6**b) had a microstructure similar to MgFeCrO₄/LSCM samples and ceria nano-particles could be observed. The ⁴⁵ micrograph of MgFeCrO₄/LSCM/CGO (Fig. 6c) confirmed that additional thermal treatments at 1000 °C following the infiltration of CGO, led to densification of LSCM layer, while CGO particles of size 0.1-0.5 µm were apparently very well connected to the LSCM layer. For MgFeCrO₄/LSCM/CeO₂/Pd sample, CeO₂ and ⁵⁰ the assumed to be Pd nano-particles could be observed on the

- LSCM layer. In Fig. 6e,f is illustrated the microstructure of MgFeCrO₄/LSCM/CGO/Pd in cross section (e) and surface (f) suggesting the presence of Pd nanoparticles with size \sim 10-20 nm on top of larger particles of CGO. Pd nanoparticles are expected
- ss to behave as electrocatalytic sites during symmetrical cell electrochemical testing.

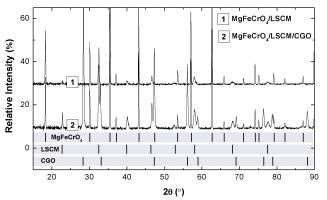


Fig. 4 X-ray diffraction pattern of MgFeCrO₄/LSCM and MgFeCrO₄/LSCM/CGO with LSCM sintered at 1200 °C (4 h) and CGO at 1000 °C (4 h).

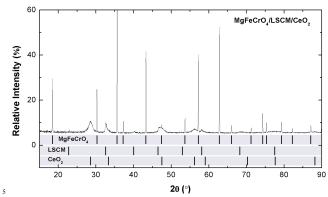


Fig. 5 X-ray diffraction pattern of MgFeCrO₄/LSCM/CeO₂ with LSCM sintered at 1200 °C (4 h) and CeO₂ at 450 °C (4 h).

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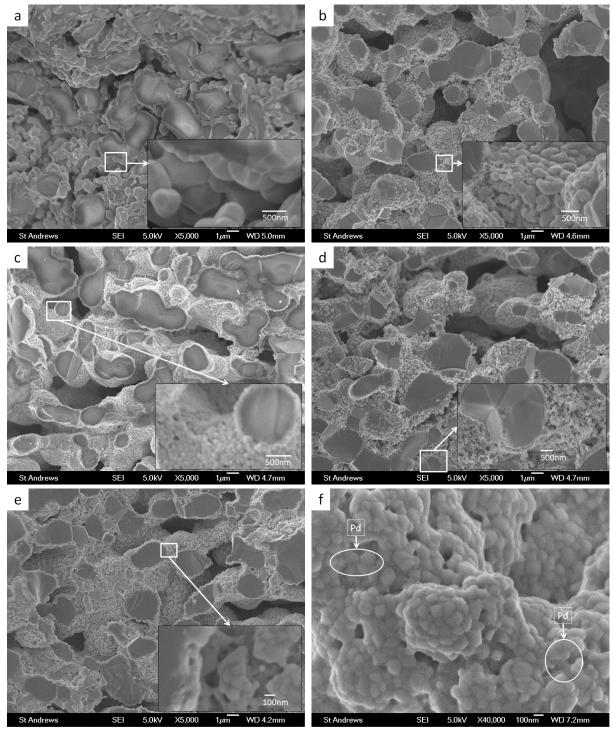


Fig. 6 SEM images in cross-section of: (a) MgFeCrO₄/LSCM; (b) MgFeCrO₄/LSCM/CeO₂; (c) MgFeCrO₄/LSCM/CGO; (d) MgFeCrO₄/LSCM/CGO₂/Pd; (e) MgFeCrO₄/LSCM/CGO/Pd; (f) surface micrograph for MgFeCrO₄/LSCM/CGO/Pd - Pd particles . The micrographs were collected after the samples were tested in humidified 5%H₂/Ar.

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3.4 Electrochemical performance of impregnated $MgfeCrO_4$ scaffolds

The electrochemical performance of the impregnated scaffolds measured in 5%H₂/Ar suggests their suitability as SOFC anodes, ⁵ for realistic, fully humidified fuels. Comparative impedance spectra for the symmetrical cells at 850 °C in humidified SO(1/4).

- 5%H₂/Ar are displayed as Nyquist and Bode plots in Fig. 7a,b. Results obtained by fitting the experimental data to the equivalent circuit illustrated in Fig. 8, are summarised in Table 2. The ¹⁰ temperature dependence of ohmic resistances (R_s) and
- polarisation resistances (R_p) values are shown in Fig. 7c,d as Arrhenius plots. The ohmic resistance of the scaffold had a significantly lower value (R_s =0.47 Ω cm²), in comparison with the other impregnated samples (Table 2). The R_s value increased with
- ¹⁵ the infiltration of various phases, and the most for MgFeCrO₄/LSCM. Even after reduction the R_s value of MgFeCrO₄/LSCM remained the highest amongst the tested samples, 4.65 Ω cm². This may have been caused by two different contributions: first, the efficient reduction of the MgFeCrO₄ 20 scaffold was observed to have a major impact for the ohmic

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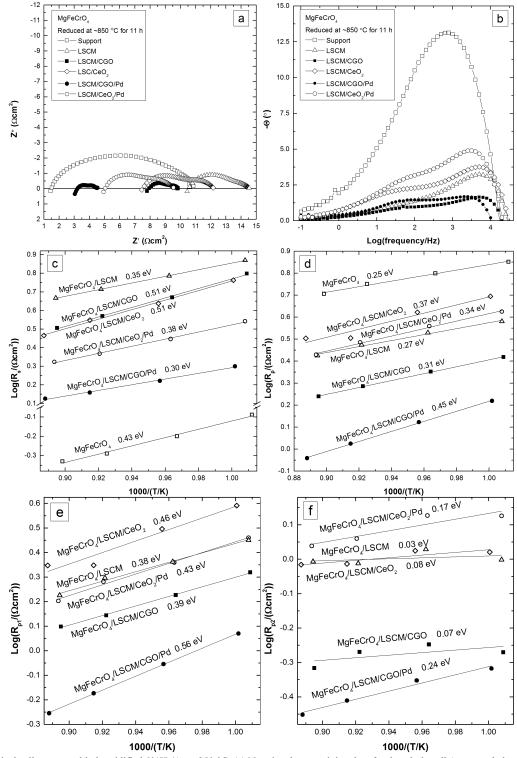
resistance, thus when infiltrated into the non-reduced scaffold, LSCM had a good adherence to the spinel particles and hindered the efficient reduction of the scaffold. Secondly, LSCM has ptype conductivity and in reducing atmosphere, its electronic 25 conductivity decreases,^{18,24} thus its contribution led to an increase of the the ohmic resistance. However, the infiltration of LSCM into the scaffold had a positive effect for the R_p value, as its electrochemical properties are superior to the spinel. The addition of CeO₂ or CGO further improved the cell performances, with 30 both Rs and Rp decreasing. Rs values for MgFeCrO₄/LSCM/CGO and MgFeCrO₄/LSCM/CeO₂ were about the same, while R_p values seemed to decrease in proportion to the quantity of ionic conducting material impregnated into the sample. MgFeCrO₄/LSCM/CGO/Pd and MgFeCrO₄/LSCM/CeO₂/Pd ³⁵ showed even better performance in R_s and R_p, as presented in Fig. 7a. Thus, the addition of catalysts contributed positively to the electrochemical tests, presumably by facilitating surface exchange reaction which is the initial step in the reduction of the scaffold. The reduced surface layer resulted in formation of a 40 conduction path with increased conductivity.

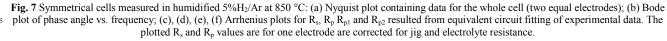
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Table 2. Relaxation frequencies and polarisation resistances for symmetrical cells tested in humidified 5%H₂/Ar at ~850 °C. R_s and R_p (R_{p1} , R_{p2}) are determined from equivalent circuits fitting and listed values are for one electrode.

Electrode	$R_s (\Omega cm^2)$	$R_p (\Omega cm^2)$	f _{max1} (Hz)	Process 1	f _{max2} (Hz)	Process 2	$R_{p1} (\Omega cm^2)$	$R_{p2} \left(\Omega cm^2\right)$
MgFeCrO ₄	0.47	5.09	1200	Charge transfer	132	Dissociative gas adsorption	0.80	4.29
MgFeCrO ₄ /LSCM	4.65	2.66	5250	Charge transfer	190	Dissociative gas adsorption	1.68	0.98
MgFeCrO ₄ /LSCM/CGO	3.20	1.74	6310	Charge transfer	76	Dissociative gas adsorption	1.25	0.48
MgFeCrO ₄ /LSCM/CeO ₂	2.92	3.19	5250	Charge transfer	30	Dissociative gas adsorption	2.23	0.96
MgFeCrO ₄ /LSCM/CGO/Pd	1.33	0.91	3020	Charge transfer	63	Dissociative gas adsorption	0.56	0.35
MgFeCrO ₄ /LSCM/CeO ₂ /Pd	2.10	2.68	3630	Charge transfer	63	Dissociative gas adsorption	1.60	1.10

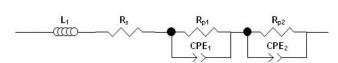


Fig. 8 Equivalent circuit used to fit experimental data, where L=inductor; R_s =series resistance; R_p =polarisation resistance and CPE=constant phase element.

Impedance spectra showed two arcs, one process distinguishable 10 at high frequency and one process at low frequency. The presence of two semicircles was observable for all the impregnated samples, while the scaffold showed a single bigger and depressed arc. The high frequency arc was always the largest and both processes were changing for different catalysts infiltrated into

- ¹⁵ scaffolds. The attribution of processes is based on relaxation frequency,^{25–27} which in this study were determined from equivalent circuits fitted to Bode plots (-Z"vs.f). The high frequency process corresponds to charge transfer and the low frequency process could be attributed to gas
- ²⁰ adsorption/desorption or association/dissociation. MgFeCrO₄ is not expected to be an ionic conductor, thus the high frequency process with f_{max1} =1200 Hz corresponds to electronic transfer, while the low frequency process with f_{max2} =132 Hz, is most likely gas adsorption/desorption. Relaxation frequencies determined for
- ²⁵ MgFeCrO₄/LSCM had similar magnitudes to the scaffold ones, 5250 Hz for high frequency process and 190 Hz at low frequency, corresponding probably to the same processes as previously described, charge transfer, at high frequency and gas adsorption/desorption, at low frequency. Table 2 summarizes
- $_{30}$ relaxation frequencies, the associated processes at high and low frequency and $R_{\rm p1}$ and $R_{\rm p2}$ values corresponding to each process. Scaffolds infiltrated with different materials showed the same trend, the resistance was higher for charge transfer than for gas adsorption/desorption and association/dissociation, while the
- ³⁵ uninfiltrated scaffold showed higher resistance for gas kinetic processes than for charge transfer. Activation energies (E_a) for R_s and R_p are included in Fig. 7c,d, where E_a for R_s is related to the

conduction activation and E_a for R_p is related to the electrochemical processes described by the impedance spectra in

- electrochemical processes described by the impedance spectra in 40 Fig. 7a. The E_a with regard to R_s (0.35 eV) for MgFeCrO₄/LSCM was smaller than E_a value of 0.56 eV measured for LSCM in 5% H_2/Ar^{18} and the E_a value 0.43 eV determined for the scaffold. E_a values for R_s generally remained value below 0.51 eV, that corresponded 45 MgFeCrO₄/LSCM/CGO and MgFeCrO₄/LSCM/CeO₂. In air, the reported E_a values for CGO are 0.60 eV²⁸ and 0.64 eV²⁹, for which the conductivity is mostly ionic. However, in reducing conditions mixed ionic-electronic conductivity may arise due to the reduction of Ce⁴⁺ to Ce³⁺. The conductivity mechanism for 50 the electrons is considered to be small polaron activated hopping process which implies low mobility.²⁹ These contributions explain to certain extent, the increase in E_a with CGO and CeO₂ infiltration. The E_a values for R_p showed an increase from the scaffold (0.25 eV) to the composite electrodes, with a maximum 55 value of 0.45 eV observed for MgFeCrO₄/LSCM/CGO/Pd. As illustrated in Fig. 7e, f, the activation energies for R_{p1} and R_{p2} components of the R_p values indicate that the charge transfer process is more temperature dependent and has a larger resistance than the gas adsorption process.
- 60 The best achieved electrochemical performance was for MgFeCrO₄/LSCM/CGO/Pd, which was comparable to results reported for LSCM used as an SOFC anode material. In humidified 5%H₂/Ar at 850°C, R_p of 0.59 Ωcm^2 has been observed,^{18,20} while at 900 °C R_p values of 0.51 Ωcm² (ref ¹⁸) and $_{65}$ 0.43 Ω cm² (ref ²⁰) have been measured. In humidified H₂ at 900 °C, D.M Bastidas et al¹⁹ reported an R_p of 0.3 Ω cm², while S.P. Jiang et al³⁰ reported R_p values for a 1:1 composite LSCM-YSZ, with LSCM obtained by gel-casting or solid state reaction of 1.1 Ω cm² and 1.9 Ω cm², respectively. The comparable results 70 obtained here relative to results reported in the literature are encouraging since the MgFeCrO₄ scaffold is not ionically conducting and since the amount of loaded perovskite was limited. Furthermore, E_a values for R_p included in Fig. 7d were lower than E_a values of between 0.70-0.90 eV reported by S.P. 75 Jiang et al³⁰ for LSCM/YSZ composite anodes.

3.5 Influence of prolonged reduction of impregnated MgFeCrO₄ scaffold upon electrochemical performance

The electrochemical performance of the symmetrical cells after ⁵ prolonged exposure to humidified 5%H₂/Ar is relevant for evaluating the stability of the tested SOFC anodes. The reduction process was performed on symmetrical cells heated to ~850 °C in humidified 5%H₂/Ar. Once constant temperature was reached, impedance measurements were taken after 1 h and 11 h. Nyquist ¹⁰ plots for measurements after 1 h and 11 h are compared in Fig. 9a-f, to estimate the influence of reduction upon tested scaffolds infiltrated with different catalysts.

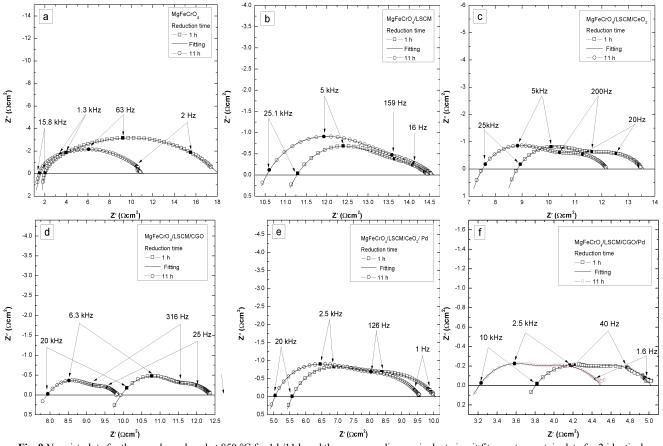


Fig. 9 Nyquist plots for the samples reduced at 850 °C for 1 h/11 h and the corresponding equivalent circuit fit; spectra contain data for 2 identical electrodes.

The performance of the cells improved with increasing reducing time consistently: for MgFeCrO₄ the reduction had a significant ²⁰ contribution in decreasing the R_p value (3.26 Ω cm²), decrease in resistance that corresponded to the low frequency process, possibly due to improvements in the gas surface exchange kinetics after reduction. MgFeCrO₄/LSCM showed a decrease in R_s and an increase in R_p corresponding to an increase in

- ²⁵ resistance of both high and low frequency processes: 0.12 Ωcm^2 for R_{p1} and 0.21 Ωcm^2 for R_{p2}. MgFeCrO₄/LSCM/CeO₂ had a small decrease of R_p and an important decrease of R_s of about 0.55 Ωcm^2 after 11 h of reduction. Reduction of MgFeCrO₄/LSCM/CGO showed a significant improvement in R_s
- ³⁰ (~1 Ω cm² decrease) and R_p (~0.22 Ω cm² decrease in R_{p1} and ~0.08 Ω cm² decrease in R_{p2}). MgFeCrO₄/LSCM/CeO₂/Pd and MgFeCrO₄/LSCM/CGO/Pd had similar improvement in the cells performance after reduction with a decrease of R_s values (~0.3 Ω cm²), while R_p did not change. The values reported above ³⁵ are for one electrode. The reduction in R_s and R_p could be

attributed mostly to the reduction of the support material. Only

MgFeCrO₄/LSCM showed an increase in R_p that could be explained by the p-type semiconductor behaviour of the LSCM, with the reduction of its conductivity in 5%H₂/Ar.³¹ The ⁴⁰ reduction process had positive effects for cell performance and this contribution was more important than the negative effect corresponding to sintering of ceria nano-particles,³² a process that cannot be noticed here.

The modelled data are in a good agreement with the measured ⁴⁵ points indicating a good fit of the equivalent circuit with the electrochemical processes identified for the samples.

4. Conclusions

Porous scaffolds of MgFeCrO₄ were prepared in symmetrical configuration by combining tape casting and screen printing ⁵⁰ techniques. MgFeCrO₄ was stable when reduced in dry 5%H₂/Ar, at 850 °C and in humidified 5%H₂/Ar, at 1000 °C. Thus, the material could be applied as support material in a number of other high temperature devices that do not need to operate at extreme very low p_{O_3} values (e.g. electrolysers – steam or CO₂, ammonia

fuel cells, direct carbon fuel cells etc.)

In terms of chemical stability, the results presented above suggest ^{19.} that there is no or limited reactivity between MgFeCrO₄ and other₂₀. cell materials. MgFeCrO₄ had satisfactory performance as anode

- ⁵ electrode support, as the infiltrated materials had a good²¹. adherence to the spinel particles. The formed coating diminished²². the scaffolds reduction, thus leading to an increase in R_s for tested 23 samples. However, the insertion of electrode materials into the scaffolds decreased polarisation resistances of the cells, as it²⁴.
- ¹⁰ formed a new conducting path and their electrochemical activity 25.75 M. J. Jørgensen and M. Mogensen, J. Electrochem. Soc., **148**, A433– was superior to the spinel. Further catalyst insertion facilitated the reduction of the scaffold and, as expected, enhanced the26. performance of symmetrical cell as new electrocatalytic sites²⁷. were active during electrochemical tests. The reduction process 28.80 C. Xia and M. Liu, Solid State Ionics, 2002, 152–153, 423–430.
- 15 had a positive influence for the symmetrical cells performance $\frac{29}{29}$. even if hindered by infiltrated electrode materials. Overall, both 30. reduction process and increase of electrocatalytic activity 31. determined improvements in the electrochemical performance.

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