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Enhanced Activity of Pr_6O_{11} and CuO Infiltrated $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ Based Composite Oxygen Electrodes

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Abstract

Operation of solid oxide fuel/electrolysis cells (SOFC/SOEC) at high temperatures ($T > 850\text{ }^\circ\text{C}$) is accompanied by degradation phenomena, which severely affect the operational life time of the cell. Degradation processes are expected to occur slower at low temperatures. However, significant reduction in electrocatalytic activity of the oxygen electrode, is one of the major challenges in decreasing the operating temperature down to $500\text{--}650\text{ }^\circ\text{C}$. Recently, Pr_6O_{11} infiltrated $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (CGO) based electrodes have been proposed to realize high electrochemical performance at intermediate temperature. In this study, Pr-oxide has been infiltrated into a well performing sub-micro $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (LSCF/CGO) composite electrode as well as a poorly performing $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3/\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (LNF/CGO) electrode. The results are compared with Cu-oxide infiltration. Formation of Pr rich oxide surface nanostructures, resulted

in a pronounced reduction of polarization resistances by a factor of 3 in state of the art LSCF/CGO electrodes. Even better performances were achieved in Pr_6O_{11} infiltrated LNF/CGO, demonstrating low polarization resistances of 0.074 ± 0.002 and $0.146 \pm 0.002 \text{ } \Omega \cdot \text{cm}^2$ at 600 and 550 °C, respectively. Low degradation rates were observed over a 200 hours durability test at 650 °C, illustrating the potential of Pr_6O_{11} infiltrated CGO oxygen electrodes for intermediate temperature SOFC/SOEC application.

Introduction

A desirable decrease in the operating temperature of solid oxide fuel cells (SOFCs) to a temperature regime of (550-650 °C) is accompanied by significant performance loss of the oxygen electrode. Therefore, developing cathodes with high catalytic activity in this temperature range is important [1]. Application of mixed ionic electronic conducting materials (MIECs) in the oxygen electrodes is one of the most applied approaches to enable a reduction of the operating temperature [1,2]. As an alternative to changing the material a significant increase in catalytic activity can be achieved through enhancing the surface area (or triple phase boundary (TPB) area) in the electrode. This can be done by infiltration of nano-sized catalyst particles into a pre-sintered backbone [3,4].

Enhanced electrochemical performance of infiltrated composite electrodes with respect to that of the bare backbones is related to the combination of a huge surface area of nano-sized catalyst particles as well as possibly a superior electro catalytic activity of the phase itself [3,4]. Thus, the ideal scenario is to use a precursor solution for infiltration which forms the desired phase at the lowest possible temperature in order to achieve the highest possible surface area. Many high performance electro catalyst phases for the oxygen reduction reaction (ORR), such as Pr_2NiO_4 (PNO), La_2NiO_4 (LNO), $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$ (LNC) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) crystallize at relatively

high temperatures (800 to 1000 °C) compromising achievable activity due to the accompanying decrease in surface area [5-7]. Recently, metal-oxide catalyst particles that can form at lower temperature, such as Pr_6O_{11} and CuO , were used to create highly efficient infiltrated oxygen electrodes for SOFC application [8,9].

A beneficial effect of Pr on both electronic and ionic conductivity in CeO_2 and super stoichiometric Ruddlseden-Popper type ($\text{LnNiO}_{4+\delta}$ based) structures has been well documented in the literature [10-15]. Especially Pr_6O_{11} has recently been getting attention for its characteristics as an oxygen electrode [16]. Sharma et al. [16,17] deposited a layer of Pr_6O_{11} on a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (CGO) electrolyte as an active catalyst layer. To ensure efficient current collection, different screen printed current collecting layers such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) or $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) were utilized on top which resulted in polarization resistances (R_p) as low as $0.022 \Omega\cdot\text{cm}^2$ at 600 °C [16,17]. Pr_6O_{11} was also employed in the form of infiltrated particles to produce an oxygen electrode. In one of the early studies, infiltration of $\text{La}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ with PrO_x reduced the overpotential from 330 to 175 mV ($50 \text{ mA}/\text{cm}^2$) at 600 °C [18]. Prominent reduction in R_p by approximately a factor of 10 was observed in different studies, via infiltrating Pr_6O_{11} into low performing $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) and LSM/CGO electrodes, demonstrating R_p values of $0.62 \Omega\cdot\text{cm}^2$ and $0.05 \Omega\cdot\text{cm}^2$ at 650 °C, respectively [19-21]. A very efficient oxygen electrode with a polarization resistance of $0.028 \Omega\cdot\text{cm}^2$ at 600 °C, was prepared by Nicollet et al [8] via infiltrating Pr_6O_{11} into bi-layer assembly of screen printed layers of CGO and LNF used as cathode backbone and for current collection, respectively. More recent studies have also reported on the good oxygen exchange properties of PrO_x and on its benefits in metal-supported SOFCs [22-24]. Cheng et al. [22], modified the surface of a porous $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{-\delta}$ (LSF) infiltrated yttria-stabilized-zirconia (YSZ) electrode via employment of an atomic layer deposited PrO_x thin film. This surface

decoration reduced the R_p by a factor of 2 [22]. In a series of studies by Dogdibegovic et al. [23,24], high performance metal-supported SOFCs were fabricated using Pr_6O_{11} infiltrated oxygen electrodes. Among different catalyst compositions such as perovskites and Ruddlesden-Popper nickelates, employment of Pr_6O_{11} resulted in the highest initial peak power density (1.3 W/cm^2 at 700°C) [24].

As already mentioned, Pr_6O_{11} surface decorated CGO shows very high electrocatalytic activity for oxygen reduction [8,16,17]. Due to extremely similar crystallographic structure of Pr_6O_{11} and CeO_2 , formation of some solid solutions in the form of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ (CPO) between these two phases can be expected [25,26]. CPO has higher electronic conductivity than that of the CeO_2 , due to mixed $4+/3+$ ionization states of Pr. The 2012 study by Chen et al. [27] assisted in bringing CPO into attention as a MIEC cathode material for SOFC application, and in a more recent study by Ma et al. [28] the oxygen surface exchange coefficient on CPO was directly measured via wafer curvature measurements. The dissolution of a redox active element is likely key to, that the compounds can show high surface exchange coefficients with values similar to those for LSCF [1,25,27,28]. Flura et al. [26] demonstrated a clear beneficial effect of using CPO as an interlayer in LNO based oxygen electrode instead of CGO. At 600°C , cells with a CPO interlayer showed a polarization resistance of $0.64 \Omega\cdot\text{cm}^2$ which was smaller than that of the cells with CGO interlayer ($0.88 \Omega\cdot\text{cm}^2$) [26]. Taguchi et al. [29] used several active layers such as CGO/LNF, CPO/LNF, Pr_6O_{11} /LNF composites as well as a single phase Pr_6O_{11} in combination with a LNF current collector. CPO/LNF composite active layers demonstrated better electrochemical performance compared to CGO/LNF. However, the lowest R_p value ($1 \Omega\cdot\text{cm}^2$ at 650°C) was measured in the cells with a single phase Pr_6O_{11} active layer [29].

LSCF/CGO is a robust and efficient composite oxygen electrode for intermediate temperature SOFC application [30-34]. It is a preferred choice among the industries developing SOFC/SOEC [30,32,33,35,36]. As reported in the literature, by infiltrating a "moderately performing" LSCF/CGO composite with CuO nanoparticles, R_p could be reduced from $0.62 \Omega \cdot \text{cm}^2$ to $0.32 \Omega \cdot \text{cm}^2$ at 650°C [9]. One should notice, on the other hand, that a well optimized sub-micro or standard nano-composite LSCF/CGO electrode can demonstrate an R_p down to $0.15 \Omega \cdot \text{cm}^2$ at the same temperature [31,32,37]. The sub-micro (grain sizes 100-500 nm) LSCF/CGO composites have significantly larger TPB area and consequently better electrochemical performance compared to coarse-grain (micrometer grain sizes) electrodes [30]. Even lower R_p values ($0.05 \Omega \cdot \text{cm}^2$ 650°C) can be achieved via developing highly optimized LSCF/CGO nano-composite electrodes [38]. To the best of our knowledge, the effect of CuO infiltration on the electrochemical performance of a "well performing" sub-micro LSCF/CGO composite has not been reported in the literature. It is relevant to determine whether this surface modification (CuO infiltration) can still be effective when it is implemented in an already "well performing" LSCF/CGO backbone.

LNF is a perovskite oxide with high electrical conductivity up to $580 \text{ S} \cdot \text{cm}^{-1}$ at 800°C . It has further, when applied as an electrode material, shown high resistance to chromium poisoning [1]. LNF, however, is an inferior electro-catalyst for oxygen reduction compared to LSCF, due to its significantly lower ionic conductivity [1]. The thermal expansion coefficient (TEC) of LNF matches better to that of CGO and yttria-stabilized zirconia (YSZ) than does the one of LSCF. Ni is also more abundant and cheaper than Co [1]. Hence, LNF has some distinct merits for use in SOFC and it is well suited to provide a network for electronic transport. It may thus be used as a part of a backbone composite structure which can further be modified with a nano sized decoration to boost performance.

In this work, inspired by the very low R_p values reported for Pr_6O_{11} infiltrated CGO backbones, Pr_6O_{11} was chosen as an infiltration compound to boost electrode performance. The results are also compared with the effect of CuO infiltration. The nano-particulate electrocatalyst decorations were realized via infiltrating suitable nitrate precursors in pre-fired composite backbone structures and heat treating. Two different composite backbone electrodes were applied in the study; the first one being a well optimized sub-micro LSCF/CGO composite electrode and the second one being a similar type of structure based on LNF/CGO (which in itself does not perform very well as an electrode). More detailed studies regarding, microstructural optimization, electrochemical performance and stability of this well optimized sub-micro LSCF/CGO composite can be found elsewhere [30-34,36]. Preliminary results from this study were recently published in Ref [39].

Experimental

Sample preparation.—In order to fabricate symmetrical cells, a 50/50wt% mixture of $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (Cerpotech) and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (Rhodia) (LSCF/CGO) as well as 35/65wt% of $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (Kceracell) and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (Rhodia) (LNF/CGO) were screen printed on both sides of dense CGO electrolyte (KERAFO), with a thickness of 200 μm . Fabricated LSCF/CGO and LNF/CGO cells were sintered at 1000 °C in air, for 5 and 4 hours, respectively. The weight fraction of LNF (~ 38/62 vol% LNF/CGO) was chosen to maximize electrolyte content whilst ensuring percolation of the electronic phase [40]. The resulting sintered porous backbones had thicknesses between 20 and 25 μm . 4x4 cm^2 cells were cut by laser into smaller 0.9x0.9 cm^2 symmetrical cells.

In order to infiltrate the sintered backbones; Pr and Cu nitrate aqueous solutions were utilized together with 5 wt% (metal ion basis) of surfactant Polyethylene-polypropyleneglycol so as to

achieve 0.5 M Pr_6O_{11} and CuO precursor solution for infiltration. The precursor solutions were infiltrated into the sintered backbones by simply immersing the symmetrical cells in the solution for several seconds. Excess solution was removed via using lab absorbent papers and consequently infiltrated cells were heat treated at 350 °C for 30 minutes to burn the desiccated nitrates. This procedure was repeated several times, until infiltrate amounts reached around 30 wt% and 10 wt% of the sintered LNF-CGO and LSCF-CGO backbones, respectively. These infiltrate loading values were established, comparing performance of electrodes with different loadings; at these levels no further improvement on increasing loading was achieved. Final calcination of the infiltrated precursors were conducted in-situ, inside the test rig (in air), at 600 and 650 °C for 2 hours. Designations for the different samples are listed in Table 1.

Microstructure and phase analysis.—Crystallographic phase analysis on calcined solutions as well as on the full symmetrical cells was conducted via a Bruker D8 X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Precursor infiltration solutions were calcined at 600 and 650 °C in air for 2 hours, mimicking the heat treatment inside the test rig. CGO powder was also mixed with grounded ash obtained from heat treating Pr-nitrate precursor solution at 400 °C for 2 hours, and the mixture was calcined at 600 °C in air for 2 hours. Diffraction patterns were analyzed by the Rietveld refinement method using the Maud program (Lutterotti, 2010) in order to determine the crystallographic structures [41].

Microstructural as well as Energy Dispersive X-ray Spectroscopy (EDS) elemental analysis on fractured surfaces of sintered and calcined symmetrical cells were performed using Scanning Electron Microscopy (SEM) (ZEISS Merlin, Carl Zeiss, Germany).

Electrochemical characterization.—Pt paste (64021015 Pt Paste, Ferro GmbH, Germany) was hand painted on both sides of the symmetrical cells as a current collecting layer. Previous studies demonstrate that the platinum grains do not have any significant contribution on the electrochemical reactions of the oxygen electrode, when used on such high surface area well performing electrodes [42,43]. The cells were sandwiched between two gold grids, which were loaded by a small weight so as to create proper contact for electrical measurements. Details of the EIS test rig and measurement setup can be found elsewhere [44]. EIS measurements were conducted using a Solartron 1260 impedance analyzer in the frequency range between 0.06 Hz and 1 MHz. The measurements were carried out under open circuit condition and an AC amplitude signal of 50 mV was applied. The impedances were normalized with the geometrical area of the electrodes and they were divided by two in order to account for two electrodes in the symmetrical cell configuration. Series resistance (R_s) as well as R_p were determined by measuring the high frequency intercept and difference between the low and high frequency intercepts of the real part of the impedance. The EIS measurements were analyzed by Elchemea Analytical (DTU Energy) [45], and an Equivalent circuit model; $LR_0(R_a//Q_a)(R_b//Q_b)(R_c//Q_c)$, was fitted to the measured data by Non Linear Least Squares (NLLS) method. R_0 signifies R_s which is the total ohmic loss in electrolyte, electrodes, current collectors and contact resistances [46]. The element L is attributed to the inductance in the wires and impedance analyzer [46]. The series of RQ elements model was utilized to represent process steps in the electrode reaction [46].

Results and discussion

Phase and microstructural analysis.—The X-ray diffraction (XRD) patterns of calcined precursor solutions (600 and 650 °C, 2 hours) are illustrated in Figure 1. At both temperatures, the solutions

crystallized into a cubic crystal structure with Fm3m space group and a monoclinic crystal structure with C2/c space group for Pr₆O₁₁ and CuO, respectively. The unit cell parameters of the two compounds were found to be, Pr₆O₁₁; (a = 5.4647 Å), and CuO; (a = 4.6840 Å), (b = 3.4250 Å), (c = 5.1290 Å), (β = 99.4700 °).

Figure 2 shows the XRD patterns of infiltrated backbones calcined at 600 and 650 °C for 2 hours in air. CGO and Pr₆O₁₁ have very similar diffraction patterns in their cubic form due to the identical symmetry and minuscule difference in cell parameter [15,16]. Due to small amount of infiltrate loading in the full cells, and the detection limit of the XRD technique, it's difficult to differentiate between CGO and Pr₆O₁₁ peaks in the patterns of the Pr-oxide infiltrated samples at 2θs below 40 °, and even more so for 2θs above 40 °, in which, Pr₆O₁₁ diffraction pattern overlaps with that of the both LNF and LSCF.

In order to elucidate the interaction between Pr and the CGO, XRD patterns of CGO powder mixed with the ash from calcined Pr-nitrate precursor were obtained. Results are reproduced in Figure 3. Two sets of mixtures (CGO powder and Pr-nitrate precursor) were considered here, targeting 30/70wt% as well as 10/90wt% Pr₆O₁₁/CGO composition, which are roughly the same amount of Pr precursor available to CGO (on wt% basis) upon infiltration in the LSCF/CGO and LNF/CGO composites, respectively (The powder has higher surface area than that of the sintered backbone, though). As can be seen in Figures 3 (a) and (c), two sets of diffraction peaks related to the Pr₆O₁₁ and CGO cubic Fm3m phases with unit cell parameters of (a = 5.4647 Å) and (a = 5.4189 Å), respectively, can be observed in both mixtures. However, diffraction peaks of CGO, especially the high intensity ones, such as the (111) reflection, also show shoulders which can be ascribed to a cubic Fm3m structure with a unit cell parameter of (a = 5.3975 Å) (Figures 3 (b) and (d)). Chiba et al. [25] has reported Pr-rich Ce_{0.1}Pr_{0.9}O_{2-δ} and Ce_{0.2}Pr_{0.8}O_{2-δ} solid solutions (here called CPO) to

have lattice constants in this range. As pointed to before, formation of solid solution between ceria and Pr_6O_{11} is feasible due to the very close crystallographic structure of the two phases [1,25,26,47] and mutual elemental solubility. Formation of a thin Pr-rich layer on CGO via infiltration with Pr-nitrate solutions and heat treatment has previously been demonstrated in a patent by Samson et al. [47].

SEM images of fractured surfaces from pristine and infiltrated backbones are reproduced in Figure 4. Due to very low calcination temperature of 600 °C, a very fine microstructure was achieved for all infiltrated samples and nano sized catalyst particles properly covered the surface of the pre-sintered backbones. As seen in Figure 5, the formed nanoparticles are below 100 nm in diameter, with particle sizes between 20 to 90 nm.

EDS elemental mapping images for Pr and Cu in the infiltrated samples are shown in Figure 6. It is clear that the infiltrated compounds properly covered the electrode surface in all samples. Some Cu segregation was observed in the Cu-LNF/CGO electrodes (Figure 6 (d)), which was different from more uniform Cu distribution in Cu-LSCF/CGO samples.

Electrochemical performance: Pr versus Cu infiltration in LSCF/CGO.—Nyquist plots for Pr-LSCF/CGO and Cu-LSCF/CGO symmetrical cells at different temperatures are shown in Figure 7. Pr-LSCF/CGO electrodes show better activity than the pristine LSCF/CGO. Measured R_p values reduced from 0.147 ± 0.019 and $0.364 \pm 0.049 \text{ } \Omega \cdot \text{cm}^2$ to 0.056 ± 0.003 and $0.081 \pm 0.005 \text{ } \Omega \cdot \text{cm}^2$ at 650 and 600 °C, respectively. Electrode performance thus strongly improves after infiltration. It may be due to the catalytic activity of formed Pr_6O_{11} nanocrystals or an effect of surface doping of the CGO with Pr, both leading to increased areas available for the oxygen incorporation. The values

demonstrate that infiltration with Pr-oxide is an effective way to enhance the oxygen reduction activity even of already well performing LSCF/CGO electrodes. In contrast, Cu-oxide infiltration did not improve the performance and the R_p values slightly increased in these samples with respect to the as prepared LSCF/CGO. Performance degradation after infiltration has previously been reported in literature also for Co and Ba infiltrated $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ (LSM/CGO) electrodes [21]. From the results it is clear that enhanced surface area per unit cell area as created by CuO infiltration is not enough to improve performance of the already well performing electrode. The CuO nanostructures increased the R_p , probably due to partly covering the more active LSCF surface with CuO, which has inferior electrocatalytic activity for oxygen reduction.

Our findings are thus in contrast to what was reported by Gao et al. [9], who found improved performance of LSCF/CGO composites by CuO infiltration which they ascribed to 1) enhanced oxygen incorporation via changes in oxidation state of Cu ($\text{Cu}^{2+}/\text{Cu}^{1+}$) near CuO-LSCF/CGO interface, and 2) B-Site doping of LSCF with Cu^{2+} . Regardless of some similarities between our study and Ref [9], such as the same choice of composite (chemical composition and mass fraction) as well as similar calcination temperature, there are some noteworthy differences between these two studies. It seems that the LSCF/CGO composite electrodes in Ref [9] have larger grain sizes compared to our sub-micro samples (this might explain the higher R_p observed in Ref [9]). This different microstructure may increase the relative weights on how much oxygen incorporates via CuO surface decorated CGO and how much on the LSCF surface. Also lower infiltration loading in Ref [9] (1 wt%), compared to infiltrated LSCF/CGO electrodes in this study (10 wt%), may result in less coverage of active LSCF surface by CuO nano particles.

All samples show more or less the same summit frequencies as the LSCF/CGO backbone. Considering the performance degradation by Cu-oxide infiltration, the LSCF/CGO backbone is

still the main source of activity for oxygen reduction in these infiltrated electrodes. However, in case of Pr-LSCF/CGO electrodes, other processes with different characteristic frequencies affect the impedance. As can be seen in Figures 7 (f) and (e), infiltration of LSCF/CGO with Pr-oxide significantly decreases the impedance in the 1-100 Hz frequency range. This frequency range has in other studies of Pr_6O_{11} , Ln_2NiO_4 , CPO and LSCF/CGO been associated with the oxygen incorporation and ionic diffusion within the electrode [5,17,26,32,46,48]. Surface decoration cannot change charge transport inside LSCF, however, it can change incorporation kinetics and possibly add a second path, which consequently reduce the influence of ionic transport inside this phase. It seems that, regardless of the good electrocatalytic activity of LSCF, oxygen may in the infiltrated electrodes find a lower resistance incorporation path via the Pr_6O_{11} covered CGO surface; $\text{Pr}_6\text{O}_{11}(\text{CPO})/\text{CGO}/\text{air}$ TPB.

Electrochemical performance: Pr versus Cu infiltration in LNF/CGO.—Nyquist plots for Pr-LNF/CGO and Cu-LNF/CGO symmetrical cells at different temperatures are shown in Figure 8. The LNF/CGO backbones show very high R_p values as expected due to low electrocatalytic activity of LNF [1]. Significant reduction in R_p is observed after the LNF/CGO backbones have been decorated with the Pr- and Cu-rich oxides which have formed on the decomposition of the infiltrated nitrate precursors. R_p values substantially reduced from 7.6 ± 1.0 and $22.7 \pm 2.7 \text{ } \Omega \cdot \text{cm}^2$ in LNF/CGO composites to 0.058 ± 0.002 and $0.074 \pm 0.002 \text{ } \Omega \cdot \text{cm}^2$ in the Pr-LNF/CGO electrodes at 650 and 600 °C, respectively. As can be seen, very similar R_p values were achieved in LNF/CGO and LSCF/CGO electrodes, after Pr-oxide infiltration. This is ascribed to high electro catalytic activity of Pr_6O_{11} nanostructure on top of the CGO and/or formation of a thin CPO layer which results in very efficient oxygen electrodes [47]. The LNF and the LSCF phases in the infiltrated

electrodes do not seem to contribute to a large extent as catalysts for the oxygen reduction; they primarily act as a percolated phase for electronic conduction. The Pr_6O_{11} covered CGO surface for sure provides an additional surface for the exchange, and this appears to be even faster than the LSCF and LSCF/CGO TPB as the best performance was actually achieved with the Pr-LNF/CGO electrode.

Contrary to what was observed in the Cu-LSCF/CGO samples, the R_p with the LNF/CGO backbone decreased by a factor of 20 to $0.312 \pm 0.033 \text{ } \Omega \cdot \text{cm}^2$ at $650 \text{ } ^\circ\text{C}$ via Cu-oxide infiltration, which is thus an effective method to improve performance of this initially weakly performing backbone. However, this R_p value (in Cu-LNF/CGO-650) is still twice the value that was measured for the sub-micro composite LSCF/CGO backbones ($0.147 \pm 0.019 \text{ } \Omega \cdot \text{cm}^2$) in this study. CuO infiltration did not improve the electrochemical performance in the already well performing LSCF/CGO samples that we applied. In literature, Cu-oxide infiltration in LSCF/CGO backbones has been observed to improve performance [9]. Hence, there must be some differences between the surface chemistry or detailed microstructure between the LSCF/CGO backbones applied in our study and in the study by Gao et al. [9] that leads to the different effects of CuO decoration in the two studies. In Ref [9], R_p at $650 \text{ } ^\circ\text{C}$ reduced from $0.62 \text{ } \Omega \cdot \text{cm}^2$ to $0.32 \text{ } \Omega \cdot \text{cm}^2$ by infiltration, but the LSCF/CGO structure that we investigated already showed an R_p of half this value ($0.147 \pm 0.019 \text{ } \Omega \cdot \text{cm}^2$) prior to infiltration (and did not improve on CuO decoration).

In the LNF/CGO electrodes, the oxygen incorporation mechanism is significantly affected via Pr-oxide and Cu-oxide infiltration. Note that the activation energy in the infiltrated LNF/CGO and as prepared LNF/CGO are significantly different and also that the impedance spectra are completely different. Due to low activity of the LNF/CGO backbone, oxygen reduction in the infiltrated structures primarily occurs on Pr_6O_{11} or CuO nano particles, as evidenced by different summit

frequencies in the infiltrated electrodes (See Figure 8). Pr-LNF/CGO electrodes have significantly lower impedance than the Cu-LNF/CGO ones in the frequency range; 10-1000 Hz. It seems that the interface created between Pr_6O_{11} and CGO introduces a facile path for oxygen ion transfer, with major impedance contributions in the 1-100 Hz frequency range and low impedance at frequencies >1000 Hz. Low impedance at frequencies >1000 Hz has previously been suggested to be an indicator of better MIEC characteristic and a consequent reduction in charge accumulation at electrocatalyst/ionic conductor interfaces [7].

Recapitulating:

- 1) Cu-oxide infiltration is very effective for improving the poorly performing LNF/CGO backbone composites. It may also improve performance of a "moderately performing" LSCF/CGO composite as observed in Ref [9], but when used in a very well performing LSCF/CGO composite, as the one used here, it did not improve the performance.
- 2) Pr-oxide infiltration is very effective for improving performance, both of the LNF/CGO backbone and of the already well performing LSCF/CGO composites.

Variation of R_p with temperature.—The variation of R_p with temperature in all the cells is shown in Figure 9. Although, Pr-LSCF/CGO and Pr-LNF/CGO samples show more or less the same R_p values at 600 and 650 °C, at lower temperatures such as 500 and 550 °C, the Pr-LNF/CGO samples actually demonstrate a lower R_p . Most likely the fastest oxygen incorporation occurs at Pr_6O_{11} nanoparticulate decorated CGO and since there is more of this in the Pr-LNF/CGO compared to Pr-LSCF/CGO, R_p is smaller in the former especially at lower temperatures. One interesting observation is the opposite effects of calcination temperature between Pr- and Cu-oxide infiltrated electrodes. Increasing the calcination temperature from 600 to 650 °C, slightly increased the R_p in

all Pr-oxide infiltrated electrodes. This small increase is likely due to nano-particles coarsening. On the other hand, R_p somewhat reduced by the same small increase in calcination temperature in all Cu-oxide infiltrated electrodes. That might be attributed to more complete CuO formation via increasing in calcination temperature, which overcomes the negative effect of nano particles coarsening.

R_p , R_s and activation energies of R_p (E_a) deduced for all cells are summarized in Table 2. A very low E_a value of around 1 eV is deduced for the Pr-LNF/CGO oxygen electrodes. This as well as the lower R_p values points to this system as the preferred one among the studied ones for low temperature SOFC applications. Table 2 shows that all symmetrical cells have very similar R_s values at all temperature and the variation of the oxygen electrode has a negligible effect on this parameter, as expected (as the same type of electrolyte sheet was used for all and since the applied electrodes are thin and well-functioning, R_s is dominated by the resistance of the electrolyte sheet). As mentioned before, R_s is dominated by the internal resistance of oxygen ion conduction in the electrolyte with only minor contributions from limited ionic and electronic conduction in the oxygen electrode [46]. Since no R_s differences are observed between the samples, it is clear that the applied infiltration procedure does not create any significant current constriction effects, and that percolation of the electronic conducting phases of LSCF and LNF is sufficient.

Pr-LNF/CGO-600 and Pr-LSCF/CGO-600 electrodes in this study demonstrate very low R_p at 450-600 °C, on par with some of the best high-performance cobaltite, Ruddlesden-Popper and fluorite infiltrated ceria based oxygen electrodes reported in the literature. A comparison of performance of fast oxygen electrodes is presented in Figure 10.

Schematic model for oxygen reduction.—A schematic model of the molecular, ionic and electronic fluxes is presented in Figures 11 (a) and (b) for Pr-LSCF/CGO and Pr-LNF/CGO electrodes, respectively. Gaseous oxygen $O_{2(g)}$ from air diffuses into the porous structure, and consequently is adsorbed and reduced on the infiltrated Pr_6O_{11} catalyst particles. Required electrons for these surface reactions are provided from Pr_6O_{11} catalyst particles that are connected to the LNF and LSCF backbones. No current constriction effect in the form of additional R_s was observed in the electrodes. In the Pr-LNF/CGO electrodes, infiltrate loading is approximately 30 wt% of the pristine backbone, thus the Pr rich infiltrate structure carries locally a part of the flow of the electrons [1,8,40]. However, LNF has an electronic conductivity of ~ 600 S/cm at 600°C that is 600 times higher than that of Pr_6O_{11} and CPO (~ 1 S/cm at 600°C) [8,25,56]. LSCF is also a much better electronic conductor (~ 300 S/cm at 600°C) than Pr_6O_{11} and CPO [57,58]. Therefore, the LSCF will be the main network for electronic conduction up to very close to the electrochemically active zone. It is fair to assume that all of the oxygen ions are passing through the CGO in Pr-LNF/CGO samples, owing to very low ionic conductivity of LNF. In Pr-LSCF-CGO, on the other hand, some fraction of the incorporated oxygen ions could be diffusing via LSCF grains. LSCF has relatively high ionic conductivity (~ 0.007 S/cm at 600°C) which is not far inferior to that of the CGO (~ 0.02 S/cm at 600°C) [58-60]. A schematic of the effects of both Pr-oxide and Cu-oxide infiltration on the active regions for oxygen reduction is presented in Figure 11 (c). The area specific resistance of the electrode will be inversely proportional to the width of the active zones as indicated in the Figure 11 (c). For LNF/CGO the active zone is a narrow zone around the TPB. Decorating the electrode structure with CuO will introduce new zones for oxygen incorporation as illustrated, as will decoration with Pr_6O_{11} , but this over a much larger part of the surface. Also illustrated are the effects of CuO and Pr_6O_{11} infiltration in LSCF/CGO. In the as

prepared state, oxygen incorporation occurs over wider TPB zones than in LNF/CGO due to the mixed conductivity in LSCF and its better electrocatalytic performance. When decorating with CuO, even though new areas for incorporation become available on the CuO coated CGO (as is the case with Cu-LNF/CGO) the exchange rates here are inferior to the one at the already highly active LSCF/CGO TPB zones (See Figure 11 (c)). With Pr_6O_{11} decoration one adds to the existing LSCF/CGO TPB zones, new areas of fast incorporation over the Pr_6O_{11} covered CGO surface. That this is in fact the area where reduction and incorporation is most facile which is deduced from the fact that the Pr_6O_{11} decorated LNF/CGO and LSCF/CGO electrodes have very similar overall performance; hence it is unlikely that it is the specific characteristics of the LSCF that are decisive for the overall performance.

R_p Stability.— Limited long-term stability is one of the major concerns in infiltrated electrodes. R_p is likely to increase due to coarsening of the infiltrated nano particles and consequent decrease in surface area [7,8,44]. The "long-term" stability of all the infiltrated electrodes as well as the reference LSCF/CGO was tested over 200 hours at 650 °C. Results are reproduced in Figure 12. Both Pr-LNF/CGO and Pr-LSCF/CGO electrodes exhibited stable R_p at 650 °C for more than 200 hours. A slight degradation is observed with a rate of approximately 17 $\text{m}\Omega\cdot\text{cm}^2/\text{hr}$ (29 %/hr) and 31 $\text{m}\Omega\cdot\text{cm}^2/\text{hr}$ (55 %/hr) in Pr-LNF/CGO and Pr-LSCF/CGO electrodes, respectively. This is smaller than the degradation rate of 130 $\text{m}\Omega\cdot\text{cm}^2/\text{hr}$ (88 %/hr) measured for the LSCF/CGO backbone at 650 °C (linear interpolation). 200 hours is not long enough to prove technological feasibility of the prepared electrodes. However, several studies have shown that a major part of the degradation in infiltrated oxygen electrodes, occurs during the first 200 hours [44,49,53] and that degradation rates decrease over time reflecting the underlying character of a coarsening process.

The significantly smaller R_p of these infiltrated electrodes with respect to state of the art LSCF/CGO as well as their modest degradation rate shows the promising nature of Pr_6O_{11} infiltrated LNF/CGO and LSCF/CGO composite electrodes for intermediate-temperature SOFC/SOEC application. That this type of architecture can be brought to work well has already been shown by the demonstration of a stable single cell potential of 0.82 V (600 °C, 0.5 A/cm²) over more than 800 hours, in tests of full anode supported SOFCs with Pr_6O_{11} infiltrated CGO oxygen electrodes [8]. It seems that the reduction of specific surface area for oxygen reduction via nano particle coarsening does not significantly affect the overall electrochemical performance of Pr_6O_{11} infiltrated CGO based electrodes when used at low temperatures such as 600 and 650 °C. This reduced sensitivity to nano particles coarsening might be attributed to improved electronic conductivity at the surface of CGO via Pr doping [1,25,26,47], or establishing a percolated electronically conductive network via high infiltration loading (in case of Pr-LNF/CGO) [8,40] (Coarsening reduces the surface area but the particles are more likely to stay a part of the electronically percolating network). Moreover, the Pr-LNF/CGO electrodes are Co-free and do not contain any alkaline-earth elements such as Sr. Thus, their electrochemical performance will not be affected by detrimental phenomena associated with alkaline-earth elements, such as Sr segregation or formation of Sr-chromites after Cr exposure [1,8,61]. Contrary to what was observed in Pr-LNF/CGO, Cu-LNF/CGO showed a severe performance degradation after 100 hours, and these electrodes were strongly sensitive to nano particles coarsening (and further loss of active area by particles detaching from the percolating network upon coarsening). An activation phenomenon was observed in both Pr-LSCF/CGO and Cu-LSCF/CGO electrodes in the first 100-150 hours, which was followed by a performance degradation at 650 °C. This activation was stronger in Cu-LSCF/CGO than in Pr-LSCF/CGO, and interestingly Cu-LSCF/CGO demonstrated

slightly better electrochemical performance than the reference LSCF/CGO after 200 hours of aging at 650 °C. However, this performance improvement is not strong enough for Cu-oxide infiltration to be considered a practical modification of well performing LSCF/CGO electrodes.

Conclusions

In this study LNF/CGO and LSCF/CGO backbones were successfully infiltrated by Pr- and Cu-nitrate which after thermal treatment lead to formation of Pr_6O_{11} and CuO nano particulate decorations on the electrode surface. CuO nano particles significantly reduced the R_p of LNF/CGO composite electrodes, however, contrary to what has been reported in literature, this compound was not effective in improving the electrochemical performance of an already well performing LSCF/CGO composite. On the other hand, Pr_6O_{11} infiltrated nanostructures significantly enhanced the electrocatalytic activity of a state of the art LSCF/CGO by reducing the R_p from 0.147 ± 0.019 and $0.364 \pm 0.049 \text{ } \Omega \cdot \text{cm}^2$ to 0.056 ± 0.003 and $0.081 \pm 0.005 \text{ } \Omega \cdot \text{cm}^2$ at 650 and 600 °C, respectively. Hence, simply modifying already proven and well performing technological LSCF/CGO electrodes, where the manufacturing route is in place, by a Pr-oxide infiltration seems a simple way of reducing losses and enabling a reduction in operation temperature. Interestingly, Pr_6O_{11} infiltrated LNF/CGO showed similar or even better electrochemical performance than the Pr_6O_{11} infiltrated LSCF/CGO, exhibiting low R_p values of 0.074 ± 0.002 and $0.146 \pm 0.002 \text{ } \Omega \cdot \text{cm}^2$ at 600 and 550 °C, respectively. It is postulated that regardless of the higher electrochemical performance of LSCF compared to LNF, in the infiltrated electrodes, both perovskite oxides mainly serve as paths for electronic conduction and the high electrocatalytic activity of Pr_6O_{11} covered CGO is responsible for the low R_p achieved in the infiltrated electrodes. The Pr-oxide infiltrated LNF/CGO results show that highly performing electrodes for low temperature SOFC/SOEC application can

indeed be prepared without use of Sr and Co as also previously shown by Nicollet et al. [8]. Both Pr_6O_{11} infiltrated electrodes, demonstrated fairly stable R_p over 220 hours further emphasizing the promising nature of these electrodes for intermediate-temperature SOFC application. In summary;

- 1) Even well performing LSCF/CGO composite electrodes can be improved via Pr_6O_{11} surface decoration.
- 2) By Pr_6O_{11} surface decoration good electrochemical performance can be realized with composite backbones made of a pre-dominant electronic conductor and an electrolyte as found here with the LNF/CGO composites.
- 3) By the documented route one can expand the temperature of operation of yttria-stabilized zirconia based cell down to 600-550, where with the modified electrode, one is not limited by the oxygen electrode [59,60,62].
- 4) Good electrode performance can be achieved in Sr- and Co-free formulations.

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Tables

Table 1. Designations for different symmetrical cell samples

Designation	Precursor aqueous solution for infiltration	Type of Backbone	Maximum calcination temperature (°C)
Pr-LSCF/CGO-600	Pr nitrate	LSCF/CGO	600
Pr-LSCF/CGO-650	Pr nitrate	LSCF/CGO	650
Pr-LNF/CGO-600	Pr nitrate	LNF/CGO	600
Pr-LNF/CGO-650	Pr nitrate	LNF/CGO	650
Cu-LSCF/CGO-600	Cu nitrate	LSCF/CGO	600
Cu-LSCF/CGO-650	Cu nitrate	LSCF/CGO	650
Cu-LNF/CGO-600	Cu nitrate	LNF/CGO	600
Cu-LNF/CGO-650	Cu nitrate	LNF/CGO	650

Table 2. R_p , R_s and E_a values (average values calculated from 4 to 6 measurements as well as corresponding standard of deviation) measured in all symmetrical cells.

Sample	R_p at 650 °C ($\Omega.cm^2$)	R_p at 600 °C ($\Omega.cm^2$)	R_p at 550 °C ($\Omega.cm^2$)	R_p at 500 °C ($\Omega.cm^2$)	R_s at 650 °C ($\Omega.cm^2$)	R_s at 600 °C ($\Omega.cm^2$)	R_s at 550 °C ($\Omega.cm^2$)	R_s at 500 °C ($\Omega.cm^2$)	E_a (ev) (Corresponding to R_p)
Pr- LNF/CGO- 600	-	0.074±0.002	0.146±0.002	0.413±0.018	-	0.866±0.028	1.297±0.015	2.188±0.010	1.00±0.04
Pr- LNF/CGO- 650	0.058±0.002	0.092±0.002	0.205±0.006	0.684±0.022	0.549±0.003	0.805±0.017	1.271±0.013	2.213±0.027	1.01±0.03
Pr- LSCF/CGO- 600	-	0.081±0.005	0.210±0.008	0.724±0.030	-	0.805±0.032	1.261±0.034	2.248±0.005	1.27±0.02
Pr- LSCF/CGO- 650	0.056±0.003	0.101±0.005	0.249±0.009	0.868±0.024	0.620±0.009	0.868±0.031	1.331±0.019	2.274±0.020	1.13±0.06
Cu- LNF/CGO- 600	-	0.839±0.081	2.080±0.192	5.774±0.301	-	1.020±0.044	1.509±0.012	2.511±0.031	1.12±0.03
Cu- LNF/CGO- 650	0.312±0.033	0.736±0.075	1.991±0.095	6.370±0.386	0.624±0.007	0.833±0.012	1.358±0.038	2.328±0.036	1.24±0.03
Cu- LSCF/CGO- 600	-	0.449±0.051	1.232±0.224	4.182±0.600	-	0.736±0.012	1.187±0.012	2.114±0.022	1.12±0.03
Cu- LSCF/CGO- 650	0.164±0.022	0.404±0.036	1.193±0.297	4.255±0.312	0.508±0.003	0.755±0.009	1.204±0.015	2.146±0.019	1.34±0.05
LNF/CGO	7.575±1.005	22.694±2.665	-	-	0.612±0.002	0.870±0.033	-	-	1.59±0.08
LSCF/CGO	0.147±0.019	0.364±0.049	1.190±0.211	4.185±0.547	0.556±0.002	0.834±0.010	1.254±0.029	2.275±0.017	1.26±0.03

Figure Captions

Figure 1. Room temperature XRD patterns of the powders formed after calcination of the aqueous nitrate solutions (a) Cu nitrate at 650 °C, (b) Cu nitrate at 600 °C, (c) Pr nitrate at 650 °C and (d) Pr nitrate at 600 °C for 2 hours in air.

Figure 2. Room temperature XRD patterns of (a) Cu-LNF/CGO-600, (b) Cu-LNF/CGO-650, (c) Cu-LSCF/CGO-600, (d) Cu-LSCF/CGO-650, (e) Pr-LNF/CGO-600, (f) Pr-LNF/CGO-650, (g) Pr-LSCF/CGO-600 and (h) Pr-LSCF/CGO-650 full symmetrical cells.

Figure 3. Room temperature XRD pattern for CGO powder mixed with Pr nitrate precursor (a) target composition 30/70wt% Pr_6O_{11} /CGO, (b) (111) reflection in target composition 30/70wt% Pr_6O_{11} /CGO, (c) target composition 10/90wt% Pr_6O_{11} /CGO, (d) (111) reflection in target composition 10/90wt% Pr_6O_{11} /CGO, heat treated at 600 °C for 2 hours in air as well as (e) CGO powder and (f) (111) reflection in CGO powder.

Figure 4. SEM images of fractured surfaces from (a) LSCF/CGO, (b) LNF/CGO, (c) Pr-LSCF/CGO-600, (d) Pr-LNF/CGO-600, (e) Cu-LSCF/CGO-600 and (f) Cu-LNF/CGO-600.

Figure 5. SEM image of a fractured surface in a Pr-LNF/CGO-600 electrode. Some of the formed nano particles are marked by orange arrows.

Figure 6. EDS elemental mapping images for (a) Pr-LSCF/CGO-600, (b) Pr-LNF/CGO-600, (c) Cu-LSCF/CGO-600, (d) Cu-LNF/CGO-600.

Figure 7. Nyquist plots for (a) LSCF/CGO measured at 650 °C, (b) LSCF/CGO measured at 600 °C, (c) Cu-LSCF/CGO-650 measured at 650 °C, (d) Cu-LSCF/CGO-650 and Cu-LSCF/CGO-600 measured at 600 °C, (e) Pr-LSCF/CGO-650 measured at 650 °C and (f) Pr-LSCF/CGO-650 and Pr-LSCF/CGO-600 measured at 600 °C.

Figure 8. Nyquist plots for (a) LNF/CGO measured at 650 °C, (b) LNF/CGO measured at 600 °C, (c) Cu-LNF/CGO-650 measured at 650 °C, (d) Cu-LNF/CGO-650 and Cu-LNF/CGO-600 measured at 600 °C, (e) Pr-LNF/CGO-650 measured at 650 °C and (f) Pr-LNF/CGO-650 and Pr-LNF/CGO-600 measured at 600 °C.

Figure 9. The variation of R_p with temperature in all symmetrical cells.

Figure 10. Comparison between Pr-LNF/CGO electrodes with some of the best high-performance oxygen electrodes reported in the literature. (Guidelines for reading the legend: A-B (A infiltrated B), A/B (A and B micron sized composite)).

Figure 11. A schematic model for molecular, ionic and electronic fluxes in (a) Pr-inf-LSCF/CGO and (b) Pr-inf-LNF/CGO electrodes. (c) Schematics for the effect of Pr- and Cu-oxide infiltration on the active regions for oxygen reduction.

Figure 12. Variation of R_p with time at 650 °C under air in all infiltrated electrodes as well as LSCF/CGO.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12