Performance of cubic-(La,Sr)TiO_{3+δ} as SOFC anodes.

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The performance and potential application of the cubic members of the La₄Sr_{n-4}Ti_nO_{3n+2} series of compounds, i.e. n≥12, prepared by solid state reaction are discussed. Although these phases can be indexed as cubic perovskites by X-ray diffraction (XRD), there exists some oxygen beyond the ABO₃ stoichiometry accommodated in linear defects reminiscent to the oxygen rich layers in La₂Ti₂O₇. In the present work, we report preliminary fuel cell tests of the n=12,14 and 16 of the La₄Sr_{n-4}Ti_nO_{3n+2} series, which reveal moderate responses under hydrogen, but also some promising results implying activation favouring methane oxidation.

Keywords: Solid Oxide Fuel Cell, anodes, titanates, composites, current collector.

(La,Sr)TiO_{3+δ} en lugar de (La,Sr)TiO₃+d

En este trabajo se presentan las prestaciones y el potencial uso de las fases cúbicas de la serie homóloga con fórmula La₄Sr_{n-4}Ti_nO_{3n+2} (n≥12) preparadas por reacción en el estado sólido. A pesar de que estas fases pueden describirse como perovskitas cúbicas mediante difracción de rayos-X (DRX), existe una cantidad de oxígeno superestequiométrico respecto a la composición ideal de la perovskita ABO₃ localizado en defectos lineales análogos a las capas ricas en oxígeno en La₂Ti₂O₇. En el presente trabajo, se muestran ensayos en pilas de combustible realizados en las composiciones n=12,14 and 16 de la serie La₄Sr_{n-4}Ti_nO_{3n+2}, donde se muestran respuestas moderadas en hidrógeno, así como una cierta activación que favorece la oxidación del metano.

Palabras clave: Pilas de Combustible de Óxido Sólido, ánodos, titanatos, composites, colector de corriente.

1. INTRODUCTION

In the last years there has been a growing interest in the search of alternative anode materials for SOFCs. The disadvantages generally associated to the use of the state of the art Ni-YSZ cermets, i.e. formation of C-deposits in hydrocarbon-fuelled SOFCs, S-poisoning and agglomeration of Ni particles, might be overcome with the use of perovskite-based mixed oxides as recently shown by Irvine and co-workers [1] in (La,Sr)(Cr,Mn)O₃ or Goodenough and co-workers in the double perovskite Sr₂MgMoO_{6-δ} [2]. (La,Sr)TiO_{3+δ} phases have also been targeted as potential fuel electrodes due to their high electronic conductivity, stability under the most reducing conditions, tolerance to S-containing fuels and chemical compatibility with the commonly used electrolytes [3-11]. However, modest performances were reported in the first investigations by Marina et al [3]. Somewhat better results were obtained in the same phases, explained in terms of the very low redox kinetics of these titanates, which require long periods of time under H₂ atmospheres to achieve full reduction prior testing [4]. Chemical modification either via the use of CeO₂ composites [5] or cationic substitution [7-10] have been

attempted, rendering some materials with rather competitive performances. The most important result of those reports was the response under methane conditions, as both the power and current densities were very similar to those in hydrogen, which suggested a certain catalytic activity of the titanate-based anodes towards hydrocarbon oxidation. Indeed, recent investigations [10] claimed the discovery of a titanate-based anode material (La₄Sr₈Ti₁₁Mn_{0.5}Ga_{0.5}O_{37.5-δ}, hereafter termed LSTGM) with an enhanced stable OCV in excess of 1.2 V in methane, which in turn implied very high performances comparable to those of the state of the art materials in hydrogen fuelled SOFCs. Such phase owes its extraordinary performance to a new strategy in searching for advanced functional materials: the disruption of extended defects and further functionalisation through cation substitution.

It should be noted however that most of the results found in the literature only cover the composition La_{1/3}Sr_{2/3}TiO_{3+δ} or La₂Sr₄Ti₆O_{19.8} and derived phases, whilst the fuel cell performance of the other cubic members of the La₄Sr_{n-4}Ti_nO_{3n+2} series have not been reported to the best of our knowledge.

The aim of the work presented herein is to evaluate the potential of those phases ($n=12$ to $n=16$) as fuel electrode materials and compare their performance with other titanates reported in the literature.

2. EXPERIMENTAL

$\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ ($n=12, 14$ and 16) phases were prepared by conventional solid state reaction as described elsewhere [4]. Stoichiometric amounts of the starting materials (La_2O_3 , SrCO_3 , TiO_2 , Aldrich, >99%) were mixed in zirconia ball-mills for 30 minutes and then calcined at 1200°C for 6 hours. The resulting powders were uniaxially pressed at 2 ton. The cold-pressed pellets were then fired at 1400 – 1600°C for 48–96 hours, rendering the targeted phases.

X-ray diffraction (XRD) data were collected with a PANalytical X'Pert Pro X-ray diffractometer, using $\text{CuK}\alpha_1$ radiation in the range $2\theta=5$ – 70° in steps of 0.016° at a scanning rate of 100s/step. The resulting XRD data were indexed using a least-squares procedure. An intimate mixture of 1:1 YSZ: LST powders was fired up to 1350°C for several hours. After this thermal treatment, no chemical interaction was observed, which is consistent with previous reports [10,14c, 21].

TEM studies were carried out on a JEOL-JEM 2011 electron microscope operating at 200 kV and equipped with a side entry $\pm 20^\circ$ double tilt specimen holder. The homogeneity of the samples was tested by energy dispersive X-ray spectroscopy (EDS) microanalysis using an Oxford Link ISIS system. The specimens were prepared by making a suspension of the powders in acetone and depositing few drops onto a carbon coated Cu grid. HRTEM images were recorded at $\times 400$ K to $\times 1.2$ M magnification using a Gatan 974 CCD camera.

Preliminary electrochemical tests were carried out in symmetrical cells using two different current collectors Pt and Au to evaluate their effect on the cell performance. The as-prepared powders were mixed with commercial 8-YSZ (Tosoh) (1:1 ratio) and a Decoflux (WB41, Zschimmer and Schwartz) binder and attached as electrodes onto a YSZ dense pellet. The resulting assembly was fired at 1300°C to ensure a good adherence between the electrodes and the electrolyte. Finally, a Pt or Au-based ink was used to paint a current collector in both sides and fired at 950°C for 2 hours. YSZ dense electrolytes were prepared by uniaxially pressing commercial 8-YSZ into pellets that were sintered at 1400°C for 6 hours. The experiments were performed under both oxidising and reducing conditions and the polarisation values were obtained by a.c. impedance spectroscopy in a 2-electrode arrangement using a 1260 Solartron FRA measuring in the 10^6 – 10^{-1} Hz frequency range with an a.c. amplitude of 50 mV at open circuit voltage (OCV). Although these measurements may not provide 100% reliable data, they are very useful to compare among different phases analysed under the same experimental conditions. The series resistances (ohmic contributions) have been subtracted, leaving the polarisation resistances, which depend on both the electrocatalytic activity and the microstructure.

The anode response was investigated on a 3-electrode setup following the recommendations proposed by Primdahl to minimise interferences due to wire inductance in the high-frequency range [12]. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) was used as cathode material and $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ ($n=12$ – 16) as anode. The anodes were prepared by coating several layers of titanate-

based slurries mixed with YSZ in graded ratios, i.e. 2:1, 1:1 and 1:2 w:w. The resulting specimens were fired at 1350°C for 2 hours to ensure good adherence. Similarly, the cathode was prepared using graded LSM:YSZ composites, which were further coated with Pt Paste (Engelhard) and fired at 900°C for 1 hour. Gold mesh was used as current collector in the anode side to avoid any interference associated to the use of other precious metals such as Pt. The anode material was exposed to 5% H_2 /Ar for 48 hours prior to the fuel cell tests to ensure full reduction. As in the case of the symmetrical tests, the series resistances have been subtracted from the overall response.

3. RESULTS AND DISCUSSION

$\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ is the general formula that describes a family of layered perovskites which accommodate oxygen beyond the ideal ABO_3 perovskite. The members $n=4$ to $n=6$ exhibit ordered oxygen-rich layers (Figure 1 TEM 1) that become more sporadic with increasing n (Figure 1 TEM 2), until the structure in blocks is lost for the $n=12$ member [13] (Figure 1 TEM 3). $\text{La}_4\text{Sr}_8\text{Ti}_{12}\text{O}_{38}$ has been reported as an XRD cubic phase that accommodates extra oxygen in linear defects similar to the oxygen-rich planes characteristic of the layered phases ($n<12$) randomly distributed within a perovskite matrix. Therefore, phases with higher n values present a gradually smaller concentration of such defects as the ideal perovskite stoichiometry, i.e. SrTiO_3 , is approached. Consequently, one may predict that both the $n=14$ and $n=16$ members lie in the XRD cubic domain as shown in Figure 1.

Indeed, the XRD patterns corresponding to these phases could be indexed considering simple cubic perovskite unit cells (Figure TEM 2). The cell parameters vary slightly, decreasing as n increases, i.e. from $3.9049(2)$ Å for $n=12$ to $3.8975(1)$ Å for $n=16$ under oxidising conditions. Selected area electron diffraction (SAED) revealed the presence of superstructure reflections doubling the $(111)_p$ (Figure 2 TEM 2). This is typically explained in terms of a very common distortion in perovskites from cubic symmetry to tetragonal or orthorhombic rendering larger unit cells, i.e. $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$. However such distortion would result in broadening of the XRD peaks and/or the presence of extra reflection comparing to the ideal cubic unit cell and neither of these situations have been observed in the present work. Therefore, the unit cell of the $n=12, 14$ and 16 members of the $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ series may be better explained as a face centred cubic with cell parameter $a=2a_p$ [13].

3.1. Electrochemical characterisation.

The electrochemical studies performed on a symmetric configuration (1:1 YSZ:LST electrodes) revealed that the series resistance (R_s) values were similar to those corresponding to the YSZ electrolyte, which indicates that the ohmic losses associated to the electrode contribution are rather small and confirms that there is a good electrical contact between the electrode and the electrolyte. Contrary to what was expected the polarisation resistances (R_p) in air were smaller than under reducing conditions in all the compositions studied as shown in Table 1 and Figure 3. Despite titanates have been reported as SOFC anodes, these results suggest that these phases could also be regarded as SOFC cathode materials, although they require the presence of an adequate current collector (Pt or

Au in this case) as the overall conductivity under oxidising conditions is rather modest, e.g. 0.1 Scm^{-1} at 900°C [6], whereas under reducing conditions the conductivity is much higher, e.g. 60 Scm^{-1} at 900°C under $5\% \text{H}_2/\text{Ar}$ [4,6]. One would assume that the results observed might be a consequence of the titanate acting as an inert support of a Pt/Au-YSZ electrode and therefore the polarisation observed would not include any contribution from the titanate. However, the R_p values observed for a YSZ-Pt electrode (porous YSZ deposited onto a dense YSZ pellet with a thin layer of Pt paste on top) measured under identical conditions reveal that the polarisation becomes significantly smaller upon the addition of titanates under both oxidising and reducing conditions (Figures 3 TEAM 1 and 3 TEAM 2). The microstructure does not change in YSZ-Pt electrodes compared to YSZ-

Fig. 1- a) Schematic representation of the evolution of the structure in the $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ as a function of oxygen overstoichiometry (δ) compared to the ideal perovskite ABO_3 . The lower members (e.g. $n=6$) exhibit a layered structure (TEM1) which is gradually more difficult to produce fully ordered (TEM2). For $n>12$, the phases are XRD cubic (TEM3). The structural change is accompanied by a maximum in overall conductivity under reducing conditions (b).

Fig. 2- a) XRD patterns corresponding to the $n=12, 14$ and 16 members of the $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ series. (b,c,d) Typical SAED patterns showing the presence of weak reflections doubling the $\{111\}_p$.

Titanate-Pt electrodes; hence these results suggest that the combination of LST-YSZ-Pt facilitates both fuel oxidation and oxygen reduction. Therefore $(\text{La,Sr})\text{TiO}_{3+\delta}$ phases could also be regarded as electrode components for a recently proposed concept in SOFC technology: the Symmetrical Fuel Cells, where the same material is used simultaneously as anode and cathode [14], which may imply great advantages vs. more traditional SOFC configurations such as simpler fabrication process, minimisation of problems related to C-deposition, etc. Nevertheless, the use of these phases as cathode materials would always be restricted to the use of a current collector as already mentioned and/or deposited as very thin layers to minimise the ohmic contribution.

Figure 3 also shows the overall cell polarisation resistances in both air and $5\% \text{H}_2/\text{Ar}$ for the three compositions studied using Pt and Au as current collectors. Under air, the impedance spectra show at least 2 rate limiting contributions; one of the arcs appears in the low frequency range (5 Hz) and is temperature independent with an associated capacitance of 0.1 Fcm^{-1} (usually ascribed to absorbed charged species [20]). The second appears at 10-30 kHz (associated capacitance of $2-4 \mu\text{Fcm}^{-1}$) and is slightly temperature dependent. Under $5\% \text{H}_2/\text{Ar}$, the responses are more complex and defined by at least 3 processes occurring at low (5Hz), intermediate (100-300Hz) and high frequency range (10-30 kHz). Therefore, the equivalent circuit $\text{LR}_s(\text{RQ})_1(\text{RQ})_2(\text{RQ})_3$ was used to describe all the experimental data in the temperature range considered ($950-800^\circ\text{C}$). The polarisation values do not change largely as a function of the current collector and the composition. In the case of the cells with Au-based current collector, the best results in air were obtained for the $n=14$, whereas in the case of the cells using Pt, the same composition shows the poorest response (Figures 3 TEAM 1 and 3 TEAM 2). This could be due to a number of parameters affecting the microstructure, although the corresponding SEM images reveal that the microstructure is very similar in all cases in terms of porosity, and electrode thickness ranging $20-50 \mu\text{m}$, and should not cause a major change in the electrocatalytic response (Figure 4). The polarisation resistance depends strongly on both the microstructure and the catalytic activity and some previous reports suggest that other a priori "external" parameters such as the electronic conductivity may also play an important role [15,17]. Indeed in the present case, the series resistances (R_s) for cells using $n=14$ -based anodes where somewhat higher, which might explain the poorer electrocatalytic activity. Nevertheless, the electronic conductivity and the microstructure of the current collector do not change significantly and therefore one may assume that the fuel cell performance of the compositions investigated will not exhibit large variations as explained below. Previous investigations suggested that the $n=12$ member was the most interesting composition in the search for novel efficient SOFC materials as it exhibited the maximum overall conductivity of the $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ series, which in addition to further optimisation through changes in the chemical composition rendered outstanding performances [10]. The present results however point out that the other cubic members may also be considered as remarkable SOFC anodes upon further optimisation.

The use of Pt as current collector in fuel cell tests has been occasionally criticised especially when evaluating anode performance due to the catalytic activity of this noble metal towards hydrocarbon oxidation. Au is usually proposed as the most adequate alternative as is regarded as inert towards such

Fig. 3- Polarisation resistance (R_p) of symmetrical cells under static air (a) and 5% H_2 /Ar conditions at 900 °C for YSZ, $n=12$, 14 and 16 electrodes using Pt (b,c) and Au (d and e) as current collector. The use of titanate-based electrodes results on a marked decrease in the polarisation values in comparison to YSZ electrodes.

Fig. 4- SEM images corresponding to cross-sections of typical measured cells, i.e. $n=14$ (a) and $n=16$ (b). The porosity and final thickness (45 μm approximately) of the anode is very similar in every case and there seems to be a good electrolyte-electrode adherence.

electrochemical reactions, although there are reports stating the contrary [16]. One could argue that Au partially melts and tends to sinter at the working temperatures, which would result in large clusters blocking the electrode pores, hence impeding the transient of gases as shown in Figure 5 TEAM 1. However, the cells using Pt as current collector exhibited an almost identical distribution of large metal clusters impeding the access of the fuel to the porous electrode (Figure 5 TEAM). Therefore the differences observed in the present study may be attributed to the better catalytic activity of Pt compared to Au. In the case of $n=14$ the polarisation using Au as current collector is lower possibly due to a better electrical contact, as the polarisation is not completely independent of the ohmic losses [15, 17], and we observed an anomalously high series resistances (50-60% larger) for this composition as mentioned above.

3.2. Fuel cell tests.

Fuel cell tests were carried out to evaluate the response of these phases as SOFC anodes. Previous reports on $\text{La}_{1/3}\text{Sr}_{2/3}\text{TiO}_3$ or $\text{La}_2\text{Sr}_4\text{Ti}_6\text{O}_{19.5}$ ($n=12$) [3,4] highlighted that titanates exhibited potential as alternative SOFC anode, although the polarisation values were far too large to consider their use in practical SOFCs. The use of graded composites rendered much better results possibly due to YSZ allowing certain oxide ion transport beyond the electrolyte, thus extending the triple phase boundary. Consequently the anode polarisation resistance was notably decreased compared to our previous studies on $n=12$, e.g. R_p in humidified pure H_2 at 900°C ranges from 0.9 to $1.2\ \Omega\text{cm}^2$ in the present study in comparison to approximately $3\ \Omega\text{cm}^2$ using pure titanate as anode material [3] (figure 6). This effect is more pronounced in methane as can be observed in Figure 6 TEAM 1 and Table 2. The R_p values are very similar for the three compositions studied, although it is somewhat lower for higher n values under hydrogen atmospheres. Nevertheless, the response under methane does not change significantly with changing the composition.

As already mentioned titanate-based anodes have been

Fig. 5- SEM images corresponding to a top view showing the anode topography in the case of Au (a) and Pt (b) current collectors. As can be observed, both Pt and Au tend to agglomerate impeding the access of the fuel to the porous anode.

recently reported as exhibiting rather high performances in direct methane fuel cells, with very high stable open circuit voltages (OCVs) and power densities. Such responses were explained in terms of the disruption of the oxygen rich planes in the $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ series. As the phases studied in the present work, e.g. $n=12, 14$ and 16 , lie on the cubic domain, one would expect some hints of catalytic activity towards hydrocarbon oxidation.

Preliminary tests carried out in $5\%\text{H}_2/\text{Ar}$ and H_2 rendered OCV values matching the Nernst equation, indicating good sealing (Figure 7). The performance did not vary significantly with the composition despite the overall conductivity exhibits a maximum for the $n=12$ composition (Figure 1) [10]. The power density was $100\text{--}120\ \text{mWcm}^{-2}$ at 900°C in the three compositions studied, which is quite promising taking into account the rather thick YSZ electrolyte ($\sim 2\ \text{mm}$). Moreover, these results may indicate that most of the cubic phases of the $\text{La}_4\text{Sr}_{n-4}\text{Ti}_n\text{O}_{3n+2}$ series have certain potential use as SOFC anodes and therefore the $n=14$ and $n=16$ compositions may also enhance their performance upon appropriate cation substitution as largely reported for the $n=12$ member [7-10].

In the case of methane (Figure 8), the performances were relatively modest and the OCV values lower than $1.0\ \text{V}$ at 925°C ($t=0$), which is common in other perovskite-based systems [1,3,5-6]. However, these phases usually present rather slow kinetics and it is desirable allowing the system to stabilise for prolonged periods of time. Thus, the best responses under hydrogen require at least 24 hours to achieve full reduction prior testing. Analogously, the system may evolve under methane even if it has been switched directly from pure hydrogen. Figure 8 also shows the evolution of the cell performance with time, highlighting a certain activation

Fig. 6- Polarisation resistance (R_p) corresponding to the anode response in a complete fuel cell measured at 900°C under methane (a) and hydrogen (b). The use of graded LST-YSZ compositions results on highly improved results.

TABLE I. POLARISATION RESISTANCES IN Ωcm^2 (R_p) OF 1:1 YSZ:LST ELECTRODES DEPOSITED ON YSZ THICK ELECTROLYTES MEASURED AT 900 °C AND USING PT AND AU AS CURRENT COLLECTORS. THE R_p OF YSZ ELECTRODES USING PT AS CURRENT COLLECTOR WAS APPROXIMATELY 0.70 Ωcm^2 .

	Au			Pt			
	n=12	n=14	n=16	YSZ	n=12	n=14	n=16
Static Air	0.60	0.35	0.80	0.70	0.30	0.46	0.42
5% H ₂ /Ar	15.3	16.1	11.6	55.8	14.5	30.3	12.7

Fig. 7- j-E plots of the titanate-based anodes at 900 °C in 5% H₂/Ar (a) and pure H₂ (b). The response is very similar in all compositions. The YSZ electrode refers to a simulated j-E curve from the R_p values in Table 1 for comparison purposes.

of the titanate-based anode with time and rendering higher OCV values, which in turn implies higher current and power densities, in clear agreement with the results reported for LSTGM. It should be noted however that such activation does not affect the polarisation resistances at the OCV, which remain constant with time. In other words, the electrocatalytic activity of the anode does not change, although the mechanism for the electrochemical oxidation of methane may be changing including steps that result in higher OCVs.

The OCV of a fuel cell depends on the partial pressure of

Fig. 8- j-E plots corresponding to the n=16 member measured at 925 °C in methane at different times. The material response improves notably in the first few hours before achieving complete stabilisation.

the different gaseous species generated, mainly H₂, CO, CO₂ and steam [18]. In the case of hydrogen, the OCV depends exclusively on the partial pressure of H₂ and steam. In the case of methane, the situation is far more complex, as several reactions may occur simultaneously affecting the OCV such as steam methane reforming, direct oxidation, or partial oxidation in addition to gas shift and cracking. Therefore titanate-based anodes could favour a complex mechanism with several reactions competing, hence leading to high voltages. Nevertheless, this effect has also been observed when precious metal is added to Cu-CeO₂ based anodes as reported by McIntosh et al. [19]. In our experiments, the anode current collector is a fine layer of gold that could certainly promote the anode activation, although other perovskite-based systems investigated under identical experimental conditions did not present such high OCVs. Consequently further work is required to discern the precise cause of the activation observed in this system and the results will be published elsewhere.

4. CONCLUSIONS

The XRD cubic members of the La₄Sr_{n-4}Ti_nO_{3n+2} series have been investigated as potential SOFC materials. The preliminary electrochemical tests revealed that titanates exhibit certain electrocatalytic activity under both oxidising and reducing conditions, which suggests that these materials might be used as components of SOFC cathodes or even electrodes for Symmetrical Fuel Cells, although their use is conditioned by the presence of an adequate current collector. Indeed, the current collector may also play a crucial role in the catalytic activity of the electrodes, as both Pt and Au [16] promote the electrochemical oxidation of hydrocarbons. Moreover, McIntosh et al. have suggested that precious metal nanoparticles may favour oxygen reduction [19]. The fuel cell tests show that the use of anodes with graded composition

results on highly improved performances, e.g. polarisation resistances 2-3 times smaller than in previous reports in 5% H₂/Ar, H₂ and CH₄. It should be noted however that titanates require prolonged periods of stabilisation under working conditions to produce the best results as a consequence of their very slow kinetics. Thus, the performance under methane improves for the first few hours of operation before complete stabilisation, resulting in enhanced OCV values, hence higher power and current densities, e.g. an improvement in excess of 10% in the OCV values for n=16-based anodes is observed after just 3 hours of operation under methane.

Despite most of the research work reported in the literature has been focused in the performance of n=12-based anodes, the results observed in the present work suggest that several other cubic members of the La₄Sr_{n-4}Ti_nO_{3n+2} series may also operate efficiently as SOFC fuel electrodes.

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