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Review on ceramic interphases by Transmission and Scanning Electron Microscopy

Soldati Analía¹, Montenegro-Hernández Alejandra¹, Baqué Laura¹, Troiani Horacio¹, Mogni Liliana¹, Schreiber Anja² and Serquis Adriana¹.

¹ CONICET – Centro Atómico Bariloche, CNEA-CONICET. Av. Bustillo 9500, S.C. de Bariloche (R8402AGP), Río Negro, Argentina

² Helmholtz-Zentrum Potsdam, Deutsches GeoForschungsZentrum GFZ, Sektion 3.3, Chemie und Physik der Geomaterialien, Telegrafenberg, C 120, D-14473 Potsdam, Germany

ABSTRACT

The Focused Ion Beam (FIB) technique was used to prepare site-specific samples from interfacial regions of different solid oxide fuel cells assemblies. Transmission and Scanning Electron Microscopy on the FIB foils combined with Electrochemical Impedance Spectroscopy (EIS) allowed the characterization of the electrode/electrolyte interphases and the determination of its influence on the cell performance after long-term operation conditions. This work reviews two cases: on one hand, $\text{Ln}_2\text{NiO}_{4+\delta}$ (Ln= La, Nd) cathodes deposited on both $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{1.96}$ and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ electrolytes, that react at 900 °C during the adhesion treatment and at temperatures higher than 650 °C during the EIS measurements. These samples present a reaction layer of 10 nm thickness, which contains elements of both phases and was found responsible of the cell performance degradation. On the other hand, $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ cathodes showed excellent performance on Ceria electrolytes, even after 1000 hours at operation conditions. In that case, the microscopic analyses of FIB foils showed a semi-coherent interphase growth.

INTRODUCTION

The fuel cell (FC) is an energy converter device that transforms chemical energy from gas fuels into electricity. Contrary to combustion chambers, the contact between the fuel and the oxidant is avoided by the presence of an electrolyte layer. The oxygen reduction reaction takes place on the cathode side, in an oxidizing atmosphere; while the oxidation of the fuel occurs on the anode side, in the presence of a reducing atmosphere. The electrolyte promotes the selective diffusion of species, favouring the electrochemical reaction but avoiding direct combustion processes.

Fig. 1: Schematic draw of a SOFC, showing its three main components: cathode, electrolyte and anode.

Among the different FCs that are being investigated, those made of solid oxides (SOFCs) assemblies are particularly interesting because they can generate electricity in intermediate to high power ranges (from 2 kW to several hundreds of MW) and are adequate for stationary and mobile applications [1]. However, a disadvantage of the SOFC technology is that the devices operate at high temperatures (between 800 and 1000 °C) for long periods of time, conditions that challenge materials and interconnectors. The bottle neck is to shift operation temperatures to 500-700 °C without performance detriment by developing new ceramics with better material and electrochemical properties.

Mixed conductors (MIECs) with tailored micro/nano structure allowed optimizing both cathode and anode functions [2-6]. However, bulk material properties and interphase characteristics are decisive in the transfer of the oxygen ions and electrons through the cell and need to be investigated and optimized to increase the device performance and life time.

Electrode/electrolyte interphases in SOFC assemblies present different phases of different composition, density, hardness and porosity in a submicrometer range. Therefore, preparation of microscopy samples of the interfacial zone is of greater importance. The Focused Ion Beam (FIB) technique uses Ga ions to release a sample foil of 15×10 μm and around 100 nm thickness from a specific site of the sample. In this way, the ions affect both materials in the same form [7], becoming an excellent option to study the SOFC interphases.

This work reviews two cases of MIECs used as SOFC electrodes on Ceria and Zirconia electrolytes. In the first case, LnNi_2O_4 (Ln = La, Nd) cathodes are studied assembled on the different electrolyte materials. Chemical reactivity is observed under operation conditions, with the consequent performance degradation. The second case comprises the interphase study between an optimum $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LSCFO) nanostructured cathode, deposited by spin coating on a Ceria electrolyte. No signs of degradation are observed, even after 1000 hours operation.

MATERIALS AND METHODS / EXPERIMENTAL PROCEDURE

The electrode samples ($\text{Ln}_2\text{NiO}_{4+\delta}$ and $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$) were synthesized by HMTA (hexamethylenetetramine) method [6, 8]. The synthesis of electrode powders was performed by dissolving the precursors into a solution of acetic acid, HMTA and acetylacetone and by using a ligand to metal molar ratio of 3:1. Nickelates powders were synthesized from La_2O_3 or Nd_2O_3 and $\text{Ni}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$, while LSCFO powders were obtained from La_2O_3 , SrCO_3 , $\text{Fe}(\text{CH}_3\text{COO})_2$ and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. Each obtained solution was heated until forming a gel, which later was fired at 400 °C and calcined afterwards. In the case of nickelate powders, the calcination was performed at 950 °C for 12 hours, while this procedure was carried out at 750 °C during 6 hours for the LSCFO powders.

Symmetric cell assemblies (cathode/electrolyte/cathode) were prepared by spin coating technique. YSZ and CGO electrolyte pellets of 2-4 mm thickness were covered with a layer of slurry containing the electrode powders and organic additives [9]. The pellets were let dry at 100 °C for 20 min and the treatment was repeated four times at each side, until reaching an electrode thickness of 10-50 μm . After that, the assemblies were thermally treated to favor adhesion and sintering. Ln_2NiO_4 ($\text{Ln}=\text{La}, \text{Nd}$) /electrolyte cells were heated at 900 °C for 1 hour, while LSCFO/CGO cells were heat treated at 800 °C for 6 h. With the aim of studying the interphases behavior at the cathode side during long periods of time, the electrochemical performances were monitored by using EIS. The experiments were performed by simulating cathode operation conditions under synthetic air flow (Ar_2 -20% O_2). On one hand, La_2NiO_4 (LNO) and Nd_2NiO_4 (NNO) cathodes were tested in a temperature range from 500 to 800 °C during 400 hours. On the other hand, LSCFO cathodes were also tested at 500 °C for 1000 hours.

After the EIS measurements the samples were analyzed by Transmission (TEM) and Scanning (SEM) Electron Microscopy. A Focused Ion Beam (FIB) device FEI-FIB 200 (Geo-Forschungs-Zentrum Potsdam, Germany) was used to prepare site-specific samples of the interphases. For that, the cells were broken in pieces and mounted in a SEM sample holder, with their interphases or their cathode side upwards. A layer of $15 \times 0.2 \mu\text{m}$ of Pt was deposited on their surfaces to avoid the material sputtering on the selected areas and a Ga-ions gun (operated at 30 kV) was used to extract $10 \times 15 \times 0.1 \mu\text{m}$ slabs. The foils were lift-out with help of a micromanipulator, and the samples were mounted in a Cu holey Carbon TEM grid allowing easier manipulation. The FIB foils were studied at the Centro Atómico Bariloche (Argentina) with a NovaFEI Field Emission Gun (FEG) SEM and two TEM instruments: a Philips CM 200 UT and a TECNAI F20 FEG TEM-STEM microscope equipped with a High-Angle Annular Dark Field (HAADF) detector for STEM imaging. In addition, the three devices were coupled to Energy Dispersive Spectroscopy (EDS) detectors of the company EDAX®, that allowed material identification and quantification.

RESULTS AND DISCUSSION

Case 1: Interphases showing chemical reactivity

One problem associated with SOFC assemblies operation is the appearance of chemical reactivity between the cell components due to the intermediate (500 °C) to high (1000

°C) temperatures necessary for their proper function. Diffusion, migration and new phases formation at the material's interphases, that degrade the cell integrity, are reported as consequence of long-term operation. These changes are often responsible of the cell life span reduction and their electrochemical performance detriment. The combination of FIB preparation and microscopy analyses at the interfacial areas help to evaluate the assembly evolution after specific operation conditions.

LNO and NNO nanostructured cathodes of Ruddelsden Popper phase, deposited by spin coating on dense YSZ and CGO electrolytes, and operated at intermediate to high temperatures during 400 hours, showed slight to very degraded interphases. Actually, the degradation was predicted by the EIS measurements reported previously [10, 11]. Those analyses demonstrated that the cell specific resistances increased with time in all cases, deteriorating the assemblies electrochemical properties. Thus FIB-TEM analysis appears as the key to understand these processes in the four cases studied.

S-TEM imaging (Fig. 2) revealed the accumulation of some material between the cathode nano-particles and the dense electrolyte, covering a high percentage of the LNO/YSZ interphase, this material is named reaction layer. A magnified detail of this layer is showed in Fig. 2 b) and c). EDS analyses showed that this material was composed of Ni, La and Zr, and electron diffraction studies were in accordance with a polycrystalline structure. These results are in agreement with previously reported X-Ray Diffraction (XRD) data, that allowed the identification of the insulating phase $\text{La}_2\text{Zr}_2\text{O}_7$ [8]. In consequence, FIB-TEM analyses resulted in precise information about the location and extent of this new phase and its composition.

Fig. 2. a) STEM image of the reaction zone in a LNO/YSZ assembly after 400 hours at operation conditions in an oxidative atmosphere. b) and c) Magnified detail of the reaction zone observed between both materials. This reaction layer might be the cause of the degradation observed in the cell electrochemical properties [10].

On the other side, the LNO/CGO interphase (Fig 3) showed much higher chemical reactivity than the LNO/YSZ assembly. The reaction product, named as amorphous in Fig. 3, was observed not only at the interphase (Fig. 3 b)), but also surrounding all LNO grains (Fig. 3 c)). This clearly contrasts with the LNO/YSZ cell, which showed

reactivity only at the cathode/electrolyte interphase. EIS analyses demonstrated that the specific resistance values for the LNO/CGO assembly were 20 times higher than those of the LNO/YSZ cell [11], thus, supporting a greater degradation in that assembly.

Fig. 3. Bright field TEM images of the reaction zone in a LNO/CGO assembly after 400 hours at oxidative operation conditions. (b) Enlarged images showing of the LNO/CGO interface and (c) a LNO grain boundary in the cathode region.

For the NNO/YSZ and the NNO/CGO interphases (Fig. 4) the presence of chemical reactivity is less evident than for the LNO cathode. This observation was also supported by EIS measurements, which detected slower electrochemical degradation in NNO cathodes operated at 700 °C as compared with the observed for LNO cathodes [11, 12]. Again, TEM and STEM on the FIB foils helped to find the predicted degradation zone.

Fig. 4. a) and b) STEM images of the reaction zone in the NNO/YSZ assembly after 400 hours at oxidative operation conditions. c) and d) STEM images of the NNO/CGO reacted interphase.

Case 2: A semi-coherent interphase

Contrary to the reaction layer described in the former section with the LNO and NNO cathodes deposited on YSZ and CGO electrolytes, there are other materials that do not show chemical reactivity when working at typical SOFC operation conditions. An interesting example of this type is obtained when an ink done with nano-sized LSCFO powder is deposited on a CGO dense pellet by the spin coating method.

This case is worth to mention because of two reasons: first, despite of the simplicity of the deposition method, the interphase obtained presented an atomic order, close to that observed in samples deposited by complicated and expensive methods, such as Pulsed Laser Deposition [2]; and second, because the assembly tolerated intermediate (500 °C) temperatures under long periods of time (1000 h) without evidence of mechanical degradation or growth of a reaction layer [7].

Coherent SOFC interphases are especially interesting when using mixed conductors (MIECs) as electrodes such as LSCFO. These materials conduce both electrons and ions, thus improving the whole cell performance. The SOFC function involves the transfer of oxygen ions (O^{2-}) from the electrode to the electrolyte through the interphase, by an oxygen vacancy diffusion process. Because the cathode material itself is a MIEC, it can transport oxygen ions through its bulk towards the electrolyte. In consequence, it is enough to have good connection between the cathode grains and a large cathode/electrolyte interphase, thus avoiding the need of a triple phase boundary (TPB). Clearly, under these conditions diffusion is favored when the electrode and the electrolyte atoms are semi-coherently oriented and both cell parameters coincide, as is the case observed for LSCFO and CGO.

On one hand, electrode/electrolyte interphases can be tailored to fulfill these conditions. A useful technique to accommodate layers of atoms is the Pulsed Laser Deposition (PLD). In this case, a cathode dense core of desired composition is ablated by Laser pulses at controlled energy and frequency. The sputtered material is deposited on the electrolyte pellet, layer by layer, promoting a coherent growth. Moreover, it allows shaping the cathode with special nano-structured morphologies, which can improve the assembly performance. An example are the vertically aligned nano-pores (VANP), which enhances oxygen reduction reaction kinetics [2, 13]. The drawback of this technique is that it requires complicated and expensive instrumentation. On the other hand, cheaper and less complicated methods are often preferred to assemble SOFCs. Wet methods based on inks, for example, are the most extended ones. However, the interphases obtained in these cases are very dependent on the electrode and the substrate characteristics, involving factors such as ink composition and viscosity, electrolyte texture and surface characteristics, grain sizes, deposition speed, and subsequent thermal treatments [9]. Unlike the PLD technique, the big advantage of these methods is that they are simple, cheap and industrially scalable.

Fig. 5 (a) shows a FEG-SEM image of the FIB foil obtained in this sample. The LSCFO nanostructured cathode can be observed well stacked at the dense CGO grains. The Pt used to protect the material from the Ga-ions sputtering is observed as a brighter dense zone on the right side, as a product of the enhanced Z-contrast. Fig. 5 b) shows a magnified image of the interphase. Some zones of poor adhesion can be detected; however, their presence did not affect the assembly mechanical integrity [6, 7]. TEM bright field images (Fig. 5 (c)) were obtained from places where the LSCFO grains were well adhered to the substrate. The interphase there appears totally covered and smooth. A High-Resolution image (Fig. 5 d)) showed that LSCFO atoms are semi-coherently oriented with CGO atoms. Indeed, this is possible because the CGO crystals have cell parameters close to those of the LSCFO material.

Regarding the possible chemical reaction between LSCFO and CGO, the fact that the atoms of both materials are in close contact could facilitate species migration and reaction. However, no chemical reaction or mechanical degradation of the interphase was detected, even after 1000 h at operation conditions in a cathode-side atmosphere (synthetic air at 500 °C).

Fig. 5: (a) FEG-SEM image of a LSCFO/CGO FIB foil, showing the interface. The brighter layer on the right side corresponds to the Pt deposited to avoid sputtering in the cut process (b) Magnified zone of the interphase. (c) and (d) High Resolution images at the LSCFO/CGO interphase, after 1000 h at oxidative operation conditions. The arrows show the interface, where LSCF atoms are semi-coherently oriented with the CGO substrate.

SUMMARY

The FIB technique has demonstrated to be adequate as a preparation method for investigating the interfacial properties of SOFC assemblies by electron microscopy. With help of a SEM the electrode/electrolyte interphases can be carefully selected with sub-micrometric resolution and a Ga-ion beam can be used to cut thin slabs suitable for detailed SEM and TEM analyses. It is worth to mention that even a heterogeneous zone as is the electrode/electrolyte interphase can be successfully prepared in this way, despite of the different compositions, textures, microstructures, densities and hardnesses that are present at both sides.

SEM and TEM imaging and the use of complementary techniques (EDS, STEM) allows the complete identification of interfacial characteristics and signals of deterioration after long-term operation conditions, even when minor phases are in such low concentrations that could not be detected by other usual techniques such as X-ray diffractometry.

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