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Electrochemical performance of intermediate temperature micro-tubular solid oxide fuel cells using porous ceria barrier layers

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Abstract

We describe the manufacture and electrochemical characterization of micro-tubular anode supported solid oxide fuel cells (mT-SOFC) operating at intermediate temperatures (IT) using porous gadolinium-doped ceria (GDC: $Ce_{0.9}Gd_{0.1}O_{2-\delta}$) barrier layers. Rheological studies were performed to determine the deposition conditions by dip coating of the GDC and cathode layers. Two cell configurations (anode/electrolyte/barrier layer/cathode): single-layer cathode (Ni–YSZ/YSZ/GDC/LSCF) and double-layer cathode (Ni–YSZ/YSZ/GDC/LSCF–GDC/LSCF) were fabricated (YSZ: $Zr_{0.92}Y_{0.16}O_{2.08}$; LSCF: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$). Effect of sintering conditions and microstructure features for the GDC layer and cathode layer in cell performance was studied. Current density–voltage (*j–V*) curves and impedance spectroscopy measurements were performed between 650–800 °C, using wet H_2 as fuel and air as oxidant. The double-cathode cells using a GDC layer sintered at 1400 °C with porosity about 50% and pores and grain sizes about 1 μm, showed the best electrochemical response, achieving maximum power densities of up to 160 mW cm^{-2} at 650 °C and about 700 mW cm^{-2} at 800 °C. In this case GDC electrical bridges between cathode and electrolyte are preserved free of insulating phases. A preliminary test under operation at 800 °C shows no degradation at least during the first 100 h. These results demonstrated that these cells could compete with standard IT-SOFC, and the presented fabrication method is applicable for industrial-scale.

Keywords: A. Dip coating; C. Electrochemical properties; D. GDC; E. Micro-tubular SOFC

1. Introduction

Currently there is a special interest in developing micro-tubular solid oxide fuel cells (mT-SOFC) for their use in portable energy systems. A rapid start-up and shut-down, an increase in the volumetric power density, a better thermal shock resistance together with a low thermal mass allows mT-SOFC devices to compete advantageously with other SOFC geometries [1–4]. Furthermore, mechanical robustness and long-term stability of these micro-tubular cells are also an advantage [5,6]. Therefore, all these features combined with the fact that mT-SOFCs are smaller, lighter, cleaner and even cheaper than lithium batteries [7], makes them stand out as a highly attractive technology for transportable devices. Their properties, performance and manufacturing techniques of mT-SOFCs have been recently reviewed [8–12].

The current challenge is to reduce the working temperature of mT-SOFCs from 800 °C down to an intermediate-temperature range of between 500 and 750 °C (IT-SOFC), which would prevent many of the inconveniences associated with operation at high temperatures. Low-temperature operation would allow the use of inexpensive conventional metals for the stack components, the minimization of thermal degradation and also the deleterious effects of chemical reactions between cell components [7–13]. However, operating at low temperatures has some drawbacks. Firstly, it decreases cell performance due to the increase in the polarization

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resistance of the electrodes, as well as a decrease in the ionic conductivity of the electrolyte. In order to reduce the operating temperature, traditional YSZ ($Zr_{0.92}Y_{0.16}O_{2.08}$) electrolyte has been proposed to be replaced by alternative solid electrolytes such as doped ceria, which presents higher ionic conductivity [14]. Another alternative is reducing the thickness of the YSZ electrolyte layer. The main advantage YSZ presents, in addition to its good chemical and mechanical stability, is that YSZ is cheaper than any doped ceria, because it is a material more used in industry. Moreover, ceria-based materials display relatively lower open circuit voltage (OCV) due to high electronic conductivity at the reducing atmosphere [12]. Bearing in mind also that YSZ thin layers can be mass produced reliably using relatively cheap ceramic production routes [15–17], it seems reasonable to continue developing YSZ-based SOFCs for IT applications. From there, its intrinsic resistance increases substantially [16], and the use of hydrocarbon fuels such as propane, methane, diesel or syngas would require a preliminary stage reforming [18].

Secondly, at low temperatures, the increased polarization on the cathode side might decrease cell performance. In order to reduce cathode polarizations, mixed ionic–electronic conductors (MIECs) have been considered as alternative cathode materials [19–21]. In fact, LSCF ($La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$) has been regarded as a promising alternative cathode material because it provides higher ionic–electronic conductivity than LSM (Sr-doped $LaMnO_3$), currently being used at high temperatures [22–24]. The properties of these cobalt-ferrites depend on their composition. $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ seems to be the preferred composition as it presents a good compromise between conductivity, catalytic activity, thermal expansion coefficient (TEC) and reactivity with the electrolyte [20,25,26]. This composition is also attractive because high Fe-contents yield a lower TEC than Co-rich compositions, this being optimal for the mismatch of YSZ and doped-CeO_2 electrolytes. However, LSCF cathodes show a tendency to react with YSZ electrolytes, forming electronic and ionic resistant phases, such as $La_2Zr_2O_7$ and $SrZrO_3$, at the interface between the cathode and the electrolyte [13,27]. Therefore, when using LSCF as the cathode, we need to keep this contamination to the minimum level by using a barrier layer between the electrolyte and the cathode.

Gadolinium-doped ceria (GDC) is well known as a catalytic material and a mixed ionic–electronic conductor [28–30]. Therefore, the insertion of a thin layer of doped ceria between the porous cathode and the electrolyte can help to avoid electrode–electrolyte reactivity. Furthermore, it was reported from electrochemical impedance spectroscopy (EIS) studies that the presence of GDC in the cathode improves oxygen diffusion rates and charge transfers of oxygen ions at the cathode/electrolyte interface, thereby decreasing cathode polarization resistance [31]. Thus, the optimization of cathode composition and microstructure by adding GDC via ceramic processing routes could help to improve cell performance [32,33].

However, a critical problem of GDC arises from its poor sinterability. Ceria is highly refractory and exhibits a high melting point (2300 °C), which reduces densification kinetics even at temperatures as high as 1600 °C. As a result, most GDC layers presented in the literature are porous [34–39]. Usually, two alternatives are considered to improve densification. First of all, the use of nanopowders presents the difficulty of a higher tendency to grain agglomeration and hence to lower densities and sintering defects [37,38]. Secondly, the use of sintering aids, for example the use of a small amount of Co doping strongly promotes the grain boundary mobility of GDC and enhances the densification rate. However, the excess of cobalt in the GBs (grain boundaries) increases ohmic resistance, reducing the electrochemical performance of SOFCs [40,41]. Furthermore, although most efforts are focused on to deposit a dense layer of GDC, this results in an increase of the thickness of the electrolyte, and as a consequence of the ohmic resistance of the device. It is also important to keep in mind the stability problems of adhesion between the porous cathode and the electrolyte. Therefore, the study of the behavior of cells with a porous thin GDC barrier layer, minimizing chemical reactivity with both electrolyte and cathode, will be interesting.

Consequently, the aim of this work is to study the processing parameters to develop porous GDC electrolyte–cathode interlayers produced by conventional ceramic processes. For this purpose, we have to search for a balance between a high sintering of the GDC layer, and minimum cation diffusion from the cathode to the electrolyte. This will make it possible to achieve homogeneous, thin layers with controlled thickness and porosity. We will also investigate the effect of using LSCF–GDC composite cathodes compared with a single LSCF cathode layer. The manufacturing procedures used in this work are fully applicable at an industrial scale, as we are currently fabricating anode supports for mT-SOFC by the extrusion technique [4,12,42].

We have fabricated several anode-supported mT-SOFC cells with the following configurations: porous Ni–YSZ anode support, a thin dense YSZ electrolyte layer, a porous thin GDC barrier layer, and a porous LSCF or LSCF–GDC composite cathode. The cathode and the GDC barrier layer were deposited via dip-coating, whereas the electrolyte deposition was performed by wet powder spraying (WPS). Rheological studies have been also performed to determine the deposition conditions of each cell component. The sintering temperature of the GDC layer was varied between 1200 and 1450 °C. Microstructure studies on the cell components and energy dispersive X-ray spectroscopy (EDS) on barrier layer/electrolyte interface were carried out. Finally, the electrochemical characterization of the different cells performed at temperatures between 650 and 800 °C will also be discussed.

2. Experimental

Commercial NiO (Hart Materials, d_{50}=0.6 μm) and YSZ (TZ-8YS, Tosoh, d_{50}=0.5 μm) were employed for the anode; YSZ (TZ-8Y, Tosoh, d_{50}=0.2 μm) for the electrolyte; and $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (Fuel Cells Materials, d_{50}=1.0 μm) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (Fuel Cells Materials, d_{50}=0.3–0.6 μm) powders were employed for the cathode of the cell. The same GDC powders were used for the barrier layers. The impurity level is below the detection limit