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Reversible operation of microtubular solid oxide cells using $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ oxygen electrodes

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HIGHLIGHTS

- Microtubular cells using LSCF electrodes and GDC barrier layers were fabricated.
- High current density (845 mA cm^{-2} at 800 °C and 1.3 V) was achieved in SOEC.
- No degradation under combined SOFC and SOEC operation for a period above 265 h.

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ABSTRACT

Yttria stabilized zirconia (YSZ) based microtubular solid oxide fuel cells (mT-SOFCs) using $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) and $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (GDC) as the oxygen electrode, along with a porous GDC electrolyte-electrode barrier layer, were fabricated and characterized in both fuel cell (SOFC) and electrolysis (SOEC) operation modes. The cells were anode-supported, the NiO-YSZ microtubular supports being made by Powder Extrusion Moulding (PEM). The cells showed power densities of 695 mW cm^{-2} at 800 °C and 0.7 V in SOFC mode, and of 845 mA cm^{-2} at 800 °C and 1.3 V in SOEC mode. AC impedance experiments performed under different potential loads demonstrated the reversibility of the cells. These results showed that these cells, prepared with a method suitable for using on an industrial scale, are highly reproducible and reliable, as well as very competitive as reversible SOFC-SOEC devices operating at intermediate temperatures.

1. Introduction

Fuel cells are devices that convert the chemical energy stored in a fuel into electricity through a chemical reaction of a fuel (hydrogen) with an oxidizing agent (air). They show high conversion efficiency and low emission of pollutants. The Solid Oxide Fuel Cells (SOFC), among the different types of cells, require high operating temperature (500–1000 °C), showing in return high fuel flexibility [1].

SOFCs can operate reversibly, producing hydrogen from steam in the Solid Oxide Electrolysis Cell mode (SOEC). The resulting hydrogen can be stored and subsequently used to generate electricity and heat in SOFC mode [2–4]. The use of reversible systems is of great interest in terms of reducing the costs. One single device can be used in electrolyser mode to produce hydrogen from intermittent renewable sources (e.g., wind or solar energy), and then to generate electricity, in fuel cell mode, when the demand increases. Moreover, SOEC can exploit waste heat from high temperature industrial processes (e.g. nuclear) to increase their nominal efficiency [5,6].

The ideal electrolyte material for both SOFC and SOEC has to be stable in a wide oxygen partial pressure (pO_2) range, with good oxygen ion conduction properties, and presenting no reactivity with other cell components at the preparation and operation temperatures. Conventional yttria stabilized zirconia (YSZ) fulfils most of these requirements. This compound typically presents an acceptable value of ionic conductivity in the range of the working temperature of SOFCs and SOECs, good sinterability and good thermal and mechanical properties. This is the main reason why YSZ still remains a very competitive electrolyte material in these devices [7–9].

The most commonly used fuel electrode material is the traditional Ni-YSZ cermet [10]. In turn, lanthanum strontium manganite (LSM) and YSZ-LSM composites are the most frequently used oxygen electrode materials for SOFC/SOEC applications at high temperatures ($>$ 800 °C). Current research aims to reduce the working temperature of electrochemical cells, especially in SOFC mode, between 500 and 750 °C,

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which prevents many of the inconveniences associated with operation at high temperatures. Inexpensive conventional metals for the stack components can be used, minimizing thermal degradation and the deleterious effects of chemical reactions between cell components [11,12], and also improving the durability. Alternative oxygen electrode materials for applications below 800 °C have been studied in detail, including lanthanum strontium ferrite (LSF) [13–15], lanthanum strontium cobaltite (LSCo) [14], lanthanum strontium copper ferrite (LSCuF) [13], lanthanum strontium cobalt ferrite (LSCF) [13,16] or nickelate based materials [17,18]. However, SOEC technology still presents some critical problems that hinder its application in the energy platform [5]. One of the major problems of SOEC devices is the delamination of the oxygen electrode. This is especially severe in the case of lanthanum strontium manganite LSM-YSZ composite electrodes, where delamination is caused by the accumulation of oxygen ions at the electrolyte-electrode interface under high current densities [19,20]. As a consequence, more efficient oxygen electrodes are required to achieve adequate oxygen evolution without overpressure at the electrolyte/electrode interface. In the present paper we propose the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF), that is a mixed electronic ionic conductor (MIEC), as the oxygen electrode. LSCF has been previously proposed by many different authors as the oxygen electrode for SOEC applications, but in planar configuration [2,13,16,21–25]. One of the most remarkable results is that of Schefold et al. [26], where they operate an electrolyte supported planar solid oxide cell in the steam-electrolysis mode for more than 23,000 h, with a current density of $j = -0.9\ \mathrm{A\,cm^{-2}}$. The cell consisted of a scandia/ceria doped zirconia electrolyte (6Sc1CeSZ), GDC diffusion-barrier/adhesion layers, LSCF as the oxygen electrode, and a Ni/GDC as the fuel electrode, obtaining a very low degradation rate (0.57%/1000 h). After dismantling, the cell showed no mechanical damage at the electrolyte and H_2/H_2O electrode. Furthermore, it is well known that the addition of an ionic conductor phase, such as YSZ or GDC, enhances the electrochemical performance of the oxygen electrode. Although LSCF is a MIEC presenting substantial ionic conductivity and the electrochemical reaction occurs at both the electrode surface and the bulk, the addition of an ionic conducting phase, such as GDC into LSCF, enhances the ionic conductivity and reduces the polarization resistance of pure LSCF cathodes, especially at low temperatures [27,28].

However, the main drawback of the LSCF-YSZ electrode-electrolyte pair is the reactivity of YSZ with the oxygen electrode material, for example developing insulating phases such as $La_2Zr_2O_7$ and $SrZrO_3$ [29]. Barrier layers between the electrolyte and the oxygen electrode, such as GDC, are used to avoid this reactivity [30–33].

Within the different configurations of SOFC (planar, tubular and micro-tubular), the microtubular geometry is characterized by a low thermal mass that allows devices with a rapid start-up and shutdown, high volumetric power densities, better mechanical strength and thermal shock resistance [34–36]. Cell composition and microstructure play a primary role in SOFC electrochemical performance, and the processing path usually determines those parameters. In this sense, fabrication methods have to be reproducible and scalable, powder extrusion moulding (PEM) being one of the most promising methods for massive microtubular substrate production because of its low-cost, well-established methodology and good standardization of the final product [37]. As a consequence, microtubular SOFCs (mT-SOFC) with supports fabricated by PEM, are excellent candidates for portable applications and they can also be used for high temperature steam electrolysis in the sector of low power devices [38,39]. In addition mT-SOFC's are excellent for the laboratory testing of SOFC devices because they are cheap and simple to handle. Most of the technological problems can be easily and accurately studied in mT-SOFC's.

Although the use of reversible SOFC/SOEC systems presents a wide range of potential applications, they are still under development because high temperature stable electrodes are required in both operation modes [40–42]. This work presents a detailed SOFC–SOEC analysis of anode-supported mT-SOFC cells, with porous Ni-YSZ fuel electrode supports fabricated by PEM, a thin dense YSZ electrolyte layer, a porous thin GDC barrier layer and a porous LSCF-GDC/LSCF double oxygen electrode. It aims to provide detailed information about the behaviour of LSCF oxygen electrodes in microtubular cells operated in reversible SOFC and SOEC mode. Special attention will be paid to the electrolysis operation mode.

2. Material and methods

2.1. Fabrication of microtubular cells

Anode-supported tubes were prepared by powder extrusion moulding (PEM) following the procedure described by Arias-Serrano et al. [43] and Monzón et al. [31]. For this purpose, the final composition of the anodic support is 25% nickel and 25% YSZ (TZ-8YS Tosoh, $d_{50} = 0.9\ \mu m$) in volume, after reducing NiO (Hart Materials, Grade F, $d_{50} = 0.7\ \mu m$) to Ni. The anode porosity was adjusted to 50% using corn starch as pore former. The morphology of starch powders used in this work has been recently published [43]. They present irregular prismatic shapes with a relatively narrow particle size distribution, $d_{50} = 10\ \mu m$, as measured by laser diffraction in Mastersizer 2000 equipment. Subsequently, YSZ electrolyte suspensions were deposited on the mT supports by dip-coating. These suspensions were prepared using TZ-8YS (Tosoh, $d_{50} = 0.9\ \mu m$) powders in an isopropanol–ethanol azeotropic mixture, with PVB (polyvinyl butyral) as binder and Beycostat (phosphate ester) as dispersant agent. The rheology of suspensions was controlled to achieve optimum processing conditions. In particular, the composition of the colloids was adjusted to get the adequate viscosity for proper filling of mould without entrapping air bubbles. The half-cells were dried at room temperature and co-sintered at 1500 °C for 2 h in air. GDC, LSCF-GDC and LSCF suspensions were prepared using GDC ($Ce_{0.9}Gd_{0.1}O_{2-d}$, Fuel Cell Materials, $d_{50} = 0.1–0.4\ \mu m$) and LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, Fuel Cells Materials, $d_{50} = 0.7–1.1\ \mu m$) powders with an appropriate amount of solvent (ethanol), binder (PVB) and dispersant (Beycostat), following the same preparation described elsewhere [33]. GDC barrier layer suspensions were also deposited by dip-coating, dried at RT and sintered at 1400 °C for 2 h in air. Then, LSCF-GDC and LSCF oxygen electrode suspensions were also deposited by dip-coating, dried at RT and sintered at 1150 °C for 2 h in air, each independently. The oxygen electrode active area was limited to 1 cm^2.

2.2. Microstructural and electrochemical characterization

Microstructural characterization was performed in polished transverse cross-sections using a field-emission scanning electron microscopy (model Merlin from Carl Zeiss, Germany) equipped with an energy dispersive analytical system (EDS) for characteristic X-ray analysis (INCA450, Oxford Instruments, UK). Open and connected porosity of the anode supports was measured by means of an Hg porosimeter (Poremaster, Quantachrome; maximum pressure 30,000 psi). Total porosity of the anode supports was determined by gravimetric density measurement. Electrochemical characterization was carried out in both SOFC and SOEC modes using the experimental setup described elsewhere [4,44,45]. The cells were heated up to 800 °C under nitrogen atmosphere and then switched to humidified hydrogen for a period of 24 h, in order to assure full accommodation of the nickel particles after NiO reduction [46,47]. The fuel composition used was of 3% H_2O – 97% H_2 for operation in the fuel cell mode, and 50% H_2O – 50% H_2 in reversible SOFC-SOEC experiments. Electrical contacts were made using silver and gold wires. For the inner contact (fuel electrode), Ag wires were coiled and mechanically attached into featured holes (visible in Fig. 1 b) on both ends of the Ni-YSZ microtubes. For the outer contact (oxygen electrode), Au wire was coiled around the surface of the electrode ($\sim 1\ cm^2$), adding Au paste to improve electrical contact and current collection, as shown in Fig. 1 (b). The cells were