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Manufacturing of anode-supported tubular solid oxide fuel cells by a new shaping technique using aqueous gel-casting

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ABSTRACT

A new gel-casting technique has been successfully developed to obtain tubular NiO–SDC anode-supported solid oxide fuel cells (SOFCs). Rheological parameters of the ceramic particle suspensions, directly influencing on casting and production, were investigated as a function of process parameters: solid loading, dispersant and agarose amounts. Afterwards, a SDC ($Sm_{0.2}Ce_{0.8}O_{1.9}$) electrolyte film was deposited on NiO–SDC tubular anode substrates by colloidal spray-coating technique and co-sintering at 1400 °C for 5 h. The shrinkage and microstructure of the sintered cell components were studied. SEM results revealed high porosities of anode (40%) and cathode ($La_{0.5}Sr_{0.5}CoO_3$, LSC), a dense SDC film electrolyte with a thickness of 30 μm and a good adhesion between the electrolyte, and the anode and cathode.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical energy conversion devices with high efficiency and low emissions of pollution [1]. However, high temperature SOFCs based on yttria-stabilised zirconia (YSZ) requires the use of expensive materials and leads to significant problems with seals and interconnects. The development of intermediate temperature SOFCs (IT-SOFCs) reduces manufacturing costs, because it can be used cheaper metallic components as interconnectors and sealants.

Among alternative electrolyte materials, gadolinium-doped ceria (GDC) and samarium-doped ceria (SDC) are some of the most promising [2]. Both electrolytes present higher ionic conductivities than yttria-stabilised zirconia (YSZ) at intermediate temperatures (500–700 °C). However, GDC and SDC exhibit lower mechanical and redox stability than YSZ [3,4]. The partial reduction of Ce^{4+} to Ce^{3+} under reducing conditions leads to a significant n-type electronic conductivity, thus causing a partial internal electronic short-circuit in the cell [5,6]. In comparison with the traditional Ni–YSZ cermet anode, the Ni–SDC has various advantages derived from the extraordinary properties of the SDC compositions. SDC is an ionic and electronic mixed conductor under reducing atmospheres, which can increase the length of triple phase boundary (TPB) within the anode, thus enhancing the anode performance [7]. Moreover, SDC also exhibits a good catalytic activity for the oxidation of hydrocarbon fuels [8]. So, Ni–SDC presents low carbon deposition, and as a result, the catalyst deactivation is diminished [9,10]. Therefore, Ni–SDC cermet is considered as a interesting candidate for IT-SOFC anode operated under hydrogen and hydrocarbon fuels [11,12]. On the other hand, the electrochemical performance of cathodes, based on strontium cobaltite-based (LSC) perovskites, can be enhanced by adding doped ceria, which results in the suppression of growth of cobaltite particles. Therefore, the porosity can be maintained and the length of triple phase boundaries increased [13,14]. For this reason, the cathode will be composed by LSC and SDC (70–30 wt.%).

Related to its design, SOFC systems can be classified into: planar and tubular. Tubular stacks have some advantages such as higher mechanical and thermal stability, and simpler seal requirements, as they are only required where the manifolds connect to the cells. This area can be kept outside of the active cell zone where temperatures remain lower. For this reason, seals can overcome any change in load or fuel feed, which could yield to a temperature increase [15]. Moreover, as was reported by Kendall et al. [16] and Yashiro et al. [17], micro-tubular SOFCs could endure strong thermal stresses caused by rapid heating up to operating temperature. Use of small-scale tubular SOFCs allows to design cell stacks with high volumetric power density as the electrolyte area per volume unit increases [18]. On the other hand, the ionic conductivity of an anode-supported fuel cell with a thin-film electrolyte at low temperature is higher than that of an electrolyte-supported one, due to the decrease of electrolyte resistance losses [19,20].

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Manufacturing is one of the major focuses of SOFC cost reduction. Among manufacturing techniques, gel-casting is a well-established colloidal processing method with a short forming time, high yields and low-cost equipment [21]. It can be used to prepare high-quality and complex-shaped from dense to porous ceramic modules. During gel-casting, the macromolecular gel network results from the *in situ* polymerisation of organic monomers added to the suspensions, holding the ceramic particles together. Then gel achieves enough strength to support its own weight and it can be handled without shape distortion [22]. Finally, this method can be used to shape the anode-supported tubular fuel cell both in laboratory and at industry scale [23,24].

In the present work, the aqueous gel-casting process has been successfully developed to obtain tubular NiO/SDC anode-supported SOFCs. The synthesis of the raw materials was performed by the polyacrylamide gel combustion method. Rheological behaviour of the ceramic particle suspension for gel-casting was investigated as a function of the process parameters. Afterwards, tubular anode was shaped by a new forming technique, which operates as a syringe. Thin-film SDC as an electrolyte was deposited by spraying method. Both anode and electrolyte were co-sintered at an optimized temperature and time from the obtained results of a design of experiments (DoE). The main objective of this method is to increase the productivity of the experimental process by lowering the number of experiments and increasing the accuracy of the results. It has been used in fuel cells field to optimize materials and components [25,26], and also to analyze and evaluate the performance of single cells and stacks [27]. As previously reported [28], we used the DoE method to optimize the anode microstructure of the fuel cell. After that, LSC–SDC (70–30 wt.%) as a cathode was deposited by spraying and sintered. Finally, microstructures of selected tubes were evaluated by SEM.

2. Materials and experimental procedure

Samarium-doped ceria, nickel oxide-samarium doped ceria (60:40 wt.%) and lanthanum strontium cobaltite powders, with a nominal composition of $Sm_{0.2}Ce_{0.8}O_{1.9}$, NiO–$Sm_{0.2}Ce_{0.8}O_{1.9}$ (NiO–SDC) and $La_{0.6}Sr_{0.4}CoO_3$ (LSC) respectively, were synthesized by polyacrylamide gel combustion as described elsewhere [29]. The materials were prepared from Sm_2O_3 (Strem Chemical 99.9%), CeO_2 (Strem Chemical 99.9%), La_2O_3 (Alfa Aesar 99.9%), $Sr(CH_3COO)_2$ (Pro-BVS 99%), $Ni(CH_3COO)_2$ (Alfa Aesar 99%) and $Co(CH_3COO)_2$ (PANREAC 99%). After combustion, the materials were calcined at 500 °C for 2 h to assure the total organic removal [29]. All these powders were characterized by BET specific surface and XRD. Morphological analysis of the powders was performed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Afterwards, porous anode tubes were prepared by aqueous gel-casting technique. The experimental procedure used to shape NiO–SDC tubes is shown in Fig. 1. Ceramic suspensions with anode powder and distilled water were prepared by adding a commercial dispersant (DOLAPIX Zschimmer & Schwarz Spain, S.A.) Homogenization was performed by an ultrasonic finger (Sonics Vibracell VCX-130). Agarose solution was prepared by adding an industrial agar (Conda Lab.) and then activated by heating above 80 °C. The agarose solution must be maintained above a determined temperature until casting in order to avoid a premature gelation. To determine the gelation temperature of the paste, the system viscosity was studied with the temperature using a viscosimeter (HAAKE Viscotester 6R plus). In this step, the optimization of several process parameters such as solid loading (20–30 wt.%), dispersant concentration (0.2–3 wt.%) and agarose amount (0.25–2 wt.%) were investigated. The tubes were extruded from the gel-casting using a punch (∅ = 6 mm) with an in-house-designed die (∅ = 10 mm).

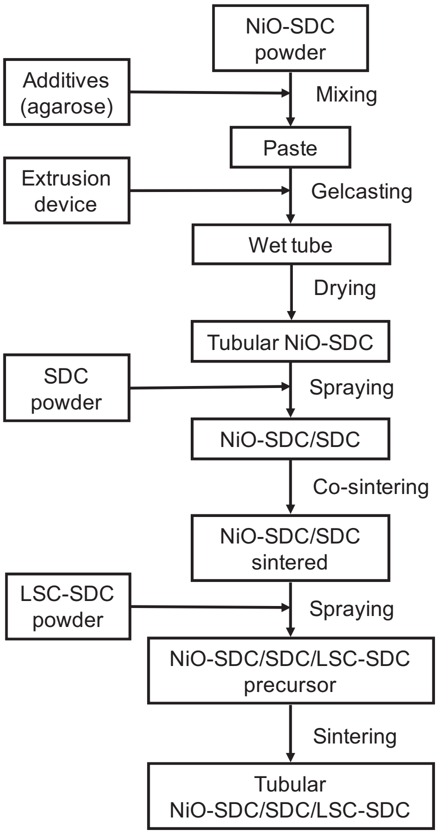

Fig. 1. Diagram of the process to obtain NiO–SDC tubes.

After drying the tubes in air, they were cut to length. Previously to the colloidal spraying deposition of the electrolyte, SDC powder was ball-milled in ethanol media for 6 h using a zirconia jar and yttria balls (5 mm diameter) to decrease and homogenize the particle diameter. A rotational speed of 300 rpm was used during ball milling. The colloidal suspension for spray-coating was made by mixing the corresponding powder with terpineol (1:2 wt.%). The final suspension was ultrasonically mixed. An air pressure-assisted spray was used to deposit the SDC colloidal suspension onto the rotating tubular anode substrate. The spray conditions such as nozzle distance, the rotational speed of substrate, nozzle speed, and air pressure were studied. After that, the film electrolyte of the tubular half-cell was dried in air. The tubes were vertically hung on a sample holder to remain straight during sintering.

Finally, both anode and electrolyte were co-sintered. In order to optimize the anode porosity at different process parameters, DoE was performed by using factorial experiments instead of the classical one-factor-at-a-time method. It allowed to determine the interactions between the studied parameters. A type of response surface design known as Box-Behnken design was used (Fig. 2). It allows to exclude the cube corners, because all variables are simultaneously determined at the maximum levels. This experiment matrix consisted of three factors with three levels for each one. So, the slope rate of heating (2, 5 and 10 °C min^{-1}), temperature (1300, 1350 and 1400 °C), and time (2, 3.5 and 5 h) were studied. The DoE results were analyzed by Statgraphics Plus Software. The total (open and close) anode porosity was then determined from the difference between the theoretical and real density, and using a helium gas absorption pycnometer (Micromeritics) to determine the apparent density.

After co-sintering treatment, the anode tubes with electrolyte were spray-coated with a LSC–SDC (70–30 wt.%) cathode suspension. Cathode powders were firstly ring-milled for 60 s in a WC ring