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Processing of graded anode-supported micro-tubular SOFCs based on samaria-doped ceria via gel-casting and spray-coating

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Abstract

A simple gel-casting method was successfully combined with the spray-coating technique to manufacture graded anode-supported micro-tubular solid oxide fuel cells (MT-SOFCs) based on samaria-doped ceria (SDC) as an electrolyte. Micro-tubular anodes were shaped by a gel-casting method based on a new and simple forming technique that operates as a syringe. The aqueous slurry formulation of the NiO–SDC substrate using agarose as a gelling agent, and the effect of spray-coating parameters used to deposit the anode functional layers (AFLs) and electrolyte were investigated. Furthermore, pre-sintering temperature of anode substrates was systematically studied to avoid the anode–electrolyte delamination and obtain a dense electrolyte without cracks, after co-sintering process at 1450 °C. Despite the high shrinkage of substrate (∼70%), an anode porosity of ∼37% was achieved. MT-SOFCs with ∼2.5 mm of outer diameter, 370 μm thick substrate, 20 μm thick AFLs and 15 μm thick electrolyte were successfully obtained. The use of AFLs with 30:70 and 50:50 wt% NiO–SDC allowed to obtain a continuous gradation of composition and porosity in the anode–electrolyte interface.

Keywords: SOFC; Micro-tubular SOFC; Graded anode; Doped ceria; Gel-casting; Spray-coating

1. Introduction

Last decade, a great interest in the development of SOFCs for portable devices has been generated [1–4]. In order to achieve this goal, new configuration designs, materials and processing methods have been developed [5]. Among alternatives, micro-tubular SOFCs (MT-SOFCs) present several advantages in comparison with planar configuration: a rapid start-up and shut-down operation [6], high long term structural stability, high thermal-shock resistance [7], and high volumetric output power density [8,9]. In addition, the research in the field of micro-tubular SOFCs has followed the same patterns pursued to reduce the operating temperature in large-scale and planar SOFCs [10–12]. For this purpose, there are two main strategies: to decrease the electrolyte thickness in order to reduce its ohmic resistance losses, using anode-supported thin-film electrolytes in micro-tubular configuration [13,14]; and/or to use an electrolyte material with high ionic conductivity at intermediate temperatures (500–700 °C), such as gadolinium (GDC) or samarium doped ceria (SDC) [15–17].

In terms of manufacturing, the most common technique for MT-SOFCs processing is the traditional extrusion method, but it presents several difficulties such as a relatively high investment in equipment, and long time for the adjustment of processing parameters [18,19]. Aqueous gel-casting is a well-known colloidal processing method that presents several advantages with respect to conventional shaping processes, for instance extrusion or isostatic pressing [13,19,20]. First of all, it can be used to prepare ceramic modules from dense to porous with high quality and complex shaped [21]. Secondly, green body has enough strength being handled without shaping distortion [22]. Moreover, gel-casting processing exhibits a short forming time, high yields and low-cost equipment [23]. So, it can be used to shape the tubular fuel cell both in laboratory and at industry scale [24,25]. In the early gel-casting developed systems, acrylic monomers were used as gelling agents in organic solvents [26]. Owing to the toxicity of these

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systems, various alternatives based on aqueous monomers have been proposed [27]. Natural polysaccharides, such as agar and agarose, have been used as gelling agents, which form a gel on cooling, thus exhibiting large similarities to the principles of injection moulding [23].

On the other hand, another effective way to enhance the cell performance and prevent the quick cell degradation can be the use of an anode functional layer (AFL) between the anode substrate and electrolyte. The AFL should have a gradient in particle size and Ni content, thus obtaining a gradient of porosity, electrical conductivity and thermal expansion coefficient (TEC) [28]. It can be achieved by using a compositional graded functional layer with several sub-layers [29]. According to different previous works [28,30,31], an AFL thickness of 10–40 μm seems to be appropriately selected to enhance the cell performance. Among the deposition methods of composite layers [32,33], spray-coating technique is one approach for low-cost production with high potential to control the quality and thickness of cell layers [34]. In the simplest way, this method is performed with no handling, thus presenting a highly reproducible process. However, some efforts on timing and nozzle stabilization optimization are needed to acquire control over consistent deposition thickness with good results. A normal setup requires the adjustment of several spray parameters such as the spray nozzle to be placed over a substrate, and the rotational speed of substrate.

Up to date, most of the MT-SOFC works have been focused on the manufacture of anode-supported cells using yttria-stabilized zirconia (YSZ) as an electrolyte. However, only some researchers have processed small-scale tubular SOFCs based on doped ceria [13,35]. Most of these MT-SOFCs were shaped by isostatic pressing or traditional extrusion methods [13,18]. In this work, we present the processing of anode-supported MT-SOFCs with a SDC electrolyte using the gel-casting and spray-coating techniques. Although it has been reported by some researchers, the effect of multiple processing parameters on the substrate and coating characteristics has rarely been reported in detail. Therefore, the purpose of this study was to investigate the influence of the gel-casting and spray-coating parameters on the characteristics of both substrate and coatings for MT-SOFCs based on SDC electrolyte. First, a useful formulation based on aqueous suspension of agarose for gel-casting was obtained. Afterwards, micro-tubular anodes were shaped by gel-casting method based on a new, simple and low-cost forming technique, which operates as a syringe. Secondly, thin-films of NiO–SDC as a graded AFL, SDC as an electrolyte and cobaltite–SDC as a cathode were deposited by spray-coating method. A suitable spray setting was determined to control the thickness and quality of every layer. Before electrolyte deposition, anode substrates with AFLs were pre-sintered to avoid the delamination of the anode–electrolyte interface, and obtain a dense electrolyte without cracks after co-sintering process. Thus, the effect of pre-sintering temperature on anode support shrinkage was systematically studied. The microstructures of the different components of the MT-SOFCs were evaluated by scanning electron microscopy (SEM).

2. Experimental procedure

2.1. Synthesis and characterization of the materials

Samarium-doped ceria, nickel oxide-samarium doped ceria (60:40, 50:50, and 30:70 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 [36–38]. 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 [36], and further milled. All these powders were characterized by BET specific surface and XRD.

2.2. Preparation and characterization of the suspensions

Porous anode tubes were prepared by aqueous gel-casting method. Ceramic suspensions with anode powder and distilled water were prepared by adding a commercial dispersant (DOLAPIX Zschimmer & Schwarz España, S.A.). Suspension 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 was maintained above 60 °C until casting in order to avoid a premature gelation. Furthermore, the suspension viscosity was determined within temperature range of 40–60 °C using a viscosimeter (HAAKE Viscotester 6R plus). In this step, the optimization of several process parameters such as solid loading (22–30 wt%), dispersant concentration (0.5–2.0 wt%) and agarose amount (0.5–2 wt%) was investigated.

2.3. Cell manufacturing

The experimental procedure to prepare the MT-SOFCs is shown in Fig. 1. First of all, the NiO–SDC tubes were extruded from the gel-casting using a steel punch (Ø 3 mm) with an in-house-designed aluminium die (Ø 6 mm and length = 20 cm), which is exhibited in Fig. 2. It presents two different sections: the reservoir and the syringe. The reservoir, which contains the slurry, is closed and made of silicone to avoid temperature gradients and a premature gelation of slurry; it is also conical to allow a free flow of the slurry towards the syringe. The plunger can be moved by hand, pulling or pushing along the tube, thus allowing to take in, gelify and expel the body through the open end of the tube. The resulting green tubes were dried in air for 24 h. They were then cut to a length of 6 cm. After finishing the process, the total (open and closed) porosity of anode substrate was determined from the difference between the theoretical and real densities, and using a helium gas absorption pycnometer (Micromeritics) to determine the apparent density.

After shaping the tubular anodes, two anode functional layers (AFL I and II) with the compositions of 30:70 and