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## Lowering the Sintering Temperature of a SOFC by Morphology Control of the Electrolyte Powder

M. Machado<sup>a</sup>, L. P. R. Moraes<sup>a</sup>, L. N. Rodrigues<sup>a</sup>, T. S. Rodrigues<sup>a</sup>, and F. C. Fonseca<sup>a</sup>

<sup>a</sup>Nuclear and Energy Research Institute, IPEN-CNEN/SP, University of São Paulo, São Paulo, Brazil

Solid oxide fuel cells are fabricated by two-step sintering at low temperature by controlling the morphology of the gadolinium-doped cerium oxide (GDC) electrolyte powders. The GDC electrolyte was synthesized by a hydrothermal route to obtain highly reactive nanorods that can fully densify at temperatures around 1150 °C. The developed system consists of the GDC electrolyte support, lanthanum strontium cobalt ferrite (LSCF) cathode and Ni/GDC anode. The electrolyte support was prepared by uniaxial die pressing and sintered at 1150 °C, and fuel cells were obtained by co-sintering electrode layers at the same temperature. The performance of the cell was evaluated in hydrogen at intermediate temperatures (IT). The experimental results indicate that high-performance IT-SOFC can be obtained at low sintering temperatures by controlling the morphology of electrolyte powder.

### Introduction

Solid oxide fuel cells operating at intermediate temperature (IT-SOFCs) have been a crucial development for the widespread commercialization of SOFCs (1). Lowering the operating temperature allows the use of a wider range of materials as auxiliary components in the fuel cell. However, the decrease in temperature requires an electrolyte material with a high ionic conductivity in that temperature range and highly active electrodes. Doped cerium oxides are great candidates as electrolyte materials for IT-SOFC electrolyte as they exhibit higher ionic conductivity at temperature ranging from 500 °C to 700 °C than the standard electrolyte material yttria-stabilized zirconia (2,3). Ceria doped with aliovalent cations such as gadolinium creates extrinsic oxygen ion vacancies that are responsible for the ionic conduction. 10 mol% gadolinium doped cerium oxide (GDC) is one of the highest conductivity materials among doped ceria electrolytes.

One of the key challenges encountered with the processing of GDC electrolytes is the high sintering temperature, of around 1500 °C, usually required to obtain a high-density ceramic body, an essential property for the SOFC electrolyte (4-6). Such high sintering temperature also restricts the co-sintering of ceria and zirconia bi-electrolytes as undesirable reactions can happen at high temperatures (7). Several chemical techniques have been investigated to produce ultrafine GDC precursor powders with a homogeneous size distribution and a nanometric size aiming at a reduction of the sintering temperature (8,9). However, besides minimizing the particle size, the control of particle shape, can also be relevant in adjusting the densification process. Shapes that are not energetically favored,

such as nanorods (10), nanobelts, nanospheres (11), have a high surface energy and low crystallinity and therefore favor the densification process.

In this study, a solid oxide fuel cell sintered at a temperature of 1150 °C has been fabricated. For such low sintering temperature to be possible the electrolyte was made of GDC nanorods with a high surface energy that could densify at 1150 °C. The nanorods were synthesized through a facile hydrothermal route, the as-synthesized material was characterized and sintered at 1150 °C to obtain the dense electrolyte layer. An electrolyte supported solid oxide fuel cell was fabricated by painting the electrolyte with anode and cathode inks. The anode consisted of Ni/GDC and the cathode of high activity  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF). The electrochemical properties of the fuel cell were tested at temperatures between 500 °C – 700 °C.

## Experimental

A hydrothermal synthesis was used to obtain the nanorods of GDC (12). Cerium (III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ -99.9%, Sigma-Aldrich), gadolinium (III) nitrate hexahydrate ( $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ -99.9%, Sigma-Aldrich) and sodium hydroxide (NaOH-99%, Sigma-Aldrich) were used as reagents. An aqueous solution of NaOH was added to a Teflon lined stainless steel autoclave and aqueous solutions of the nitrates of cerium and gadolinium were gradually added. The autoclave was heated at 110 °C for 24 h. The product was washed in a centrifuge and dried in air.

The obtained powder was characterized using X-ray diffraction (XRD) Miniflex II diffractometer with  $\text{CuK}\alpha$  radiation source (0.15406 nm). Mean crystallite sizes were calculated using Scherrer's formula for peaks in the  $2\theta$  range from 20° to 80°. Cylindrical pellets were prepared by uniaxial pressing for dilatometry analysis using Setaram Labsys equipment. Dilatometry runs were carried out between room temperature and 1400 °C, with a heating rate of 10 °C/min under synthetic air flow.

A solid oxide fuel cell was prepared using GDC nanorod powder as the electrolyte. The as-synthesized powder was uniaxially pressed and sintered at 1150 °C for 2 h. Inks were prepared for the anode and cathode layers. The anode ink consisted of 60 wt% Ni/CGO powder obtained through a liquid mixture technique with ethanol (13,14), nickel(II) acetate tetrahydrate (99%, Sigma-Aldrich) and 10 mol% gadolinium-doped cerium oxide (99.9%, Praxair) calcined at 450 °C. The cathode was of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF, Fuel Cell Materials). The electrode inks were prepared by mixing the ceramic powders with PVP, ethylene glycol, PVB, terpineol and ethanol. The electrode layers were hand painted on the electrolyte support and the cell was sintered at 1150 °C for 2 h.

The microstructure of the cell was analysed using a scanning electron microscope MEV-FEG (JEOL, JSM-6010LA). The electrochemical properties of the cell were tested in the open flange test set-up from Fiaxell SOFC Technologies™. The current collection was carried out by gold wires connected to a gold mesh ( $\phi 37\text{mm}$ ) in the air outlet and by a nickel mesh on the fuel side. The measurements were carried out by a Zahner IM6 electrochemical workstation. I-V curves of the cell were measured in the temperature range of 500–700 °C with  $\text{H}_2$  as a fuel and air as the oxidant, both with flow rate of 200 mL/h.

The impedance under the open circuit conditions was measured in the frequency range of 1 MHz to 1 Hz with ac amplitude of 10 mV.

## Results and Discussion

Figure 1 shows the X-ray diffraction pattern and SEM morphology of as-synthesized GDC nanorods (NRs). The XRD pattern shows the peaks corresponding to the fluorite structure of the ceria material. The starting material shows broad diffraction peaks corresponding to an average crystallite size calculated by the Scherrer's equation of 7 nm. Scanning electron microscope image shows well defined nanorods of about 200 nm length and cross section of 20 nm, with a rather narrow size distribution.

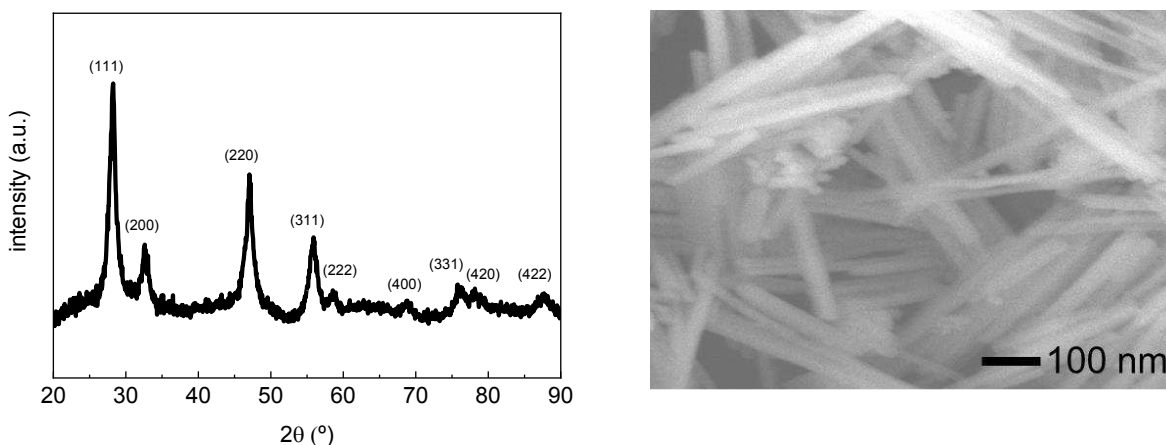


Figure 1. X-ray diffraction pattern (left) and scanning electron microscope image (right) of the as-synthesized GDC nanorods.

The densification and densification rate curves of the pressed pellet of NRs powder is shown in Figure 2, together with the microstructural (SEM) and structural (XRD) analyses of the pellet after sintering at 1400 °C. The NRs have a relative green density of ca. 40 % and the final density after the analysis is of ca. 95 %. The densification process starts at 500 °C and develops up to 1130 °C reaching a densification plateau for higher sintering temperatures. By analyzing the  $dp/dt$  two local maxima are observed at  $T = 800$  and 1050 °C. The rate of densification is more intense at 1050 °C indicating that there is a fast shrinkage at that temperature. SEM images of the pellet sintered at 1400 °C show a densified homogenous structure, with typical polyhedron shaped grain and well-defined grain boundaries. From the images there is no evidence of the previous nanorods morphology. Grain growth occurs in all of directions of the nanorods and they lose their shape to grow into a polyhedron grain shape. The XRD in Figure 2 of the sintered powder displays a highly crystalline structure and the calculated average crystallites size of 60 nm, which corresponds to almost 10-fold increase of the size of the as-synthesized material. SEM images of fractured cross-section show homogeneous microstructure and sub-micron grain size with average size roughly estimated at 300 nm.

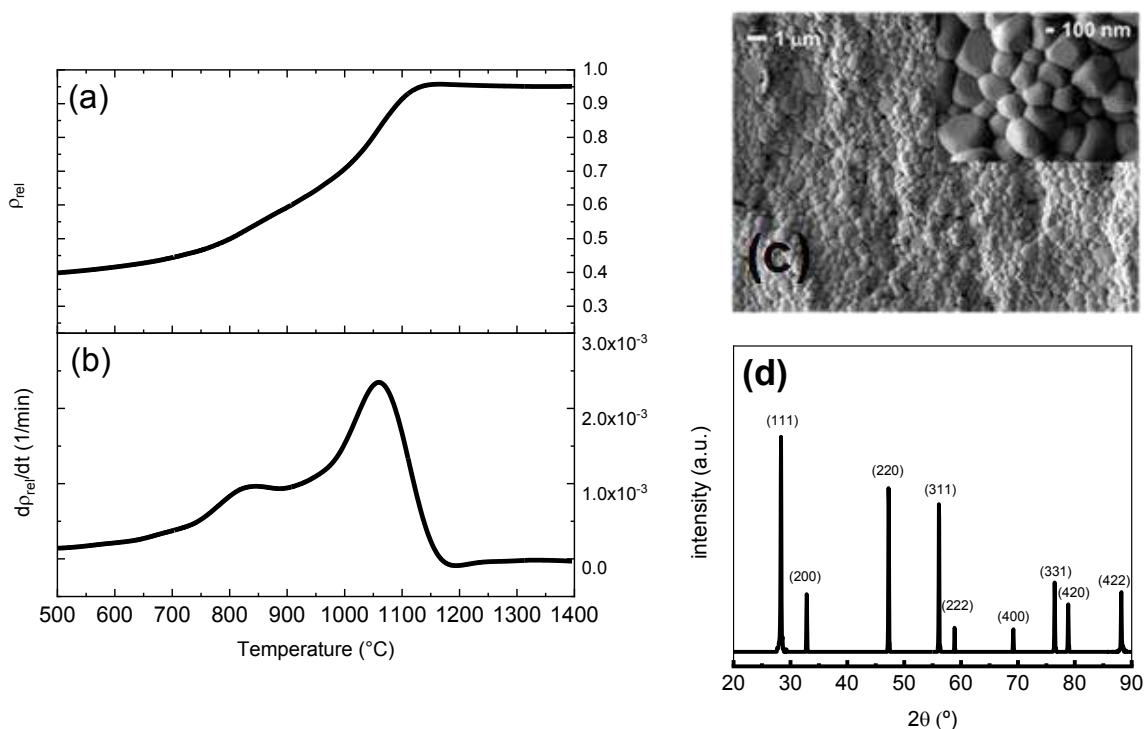


Figure 2. Densification (a) and densification rate (b) curves of GDC nanorods, and X-ray diffraction pattern (c) and scanning electron microscope (d) of GDC nanorods after sintering at 1400  $^{\circ}C$ .

The dilatometry analysis shows that densification occurs up to the temperature of 1130  $^{\circ}C$ . Thus, to prepare the electrolyte support a uniaxial pressed pellet was sintered at 1150  $^{\circ}C$ . The calculated relative apparent density of the GDC support was 93 %. This support was used for electrodes deposition and co-sintered at 1150  $^{\circ}C$ . The SEM images of both electrodes of the electrolyte supported SOFC is shown in Figure 3. The electrolyte is a dense support with a thickness of ca. 1 mm and the electrodes are porous layers with  $\sim 2 \mu m$  thickness. The image shows that the 1150  $^{\circ}C$  co-sintering steps exhibits the desirable microstructural features of a SOFC.

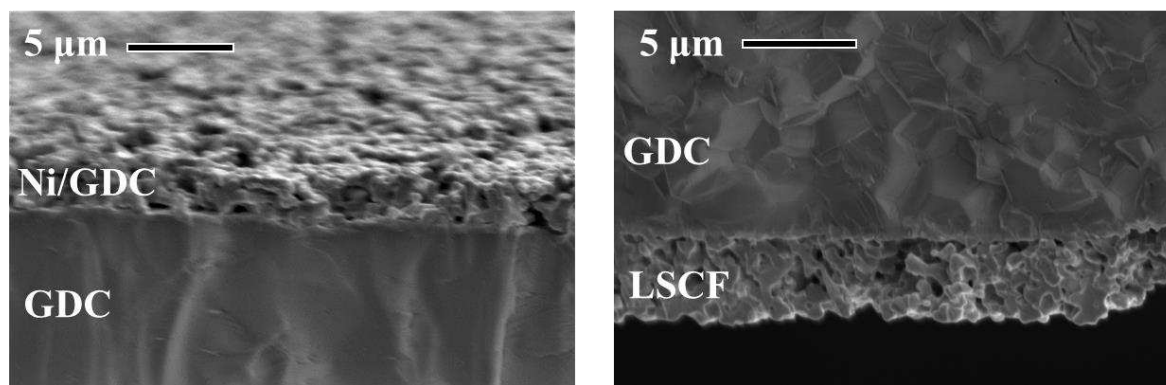


Figure 3. Scanning electron microscope image of anode (left) and cathode (right) layers after co-sintering at 1150  $^{\circ}C$ .

The electrochemical properties were accessed by the I-V curves of the GDC-based SOFC single cell in the 500 – 700 °C temperature range, as shown in Figure 4. The open-circuit voltage (OCV) was observed to decrease with increasing temperature from 0.98 V at 500 °C to 0.79 V at 700 °C. Such a result indicate good gas tightness of the electrolyte and it is in accordance with the properties of GDC electrolytes, which are known to exhibit electronic defects with increasing temperature (> 500 °C) that cause a reduction of cell's OCV. Despite the decreasing OCV, maximum power densities increase with increasing measuring temperature. The highest maximum power density of 104 mW/cm<sup>2</sup> was obtained at 700 °C. Nevertheless, I-V curves are rather linear indicating that ohmic losses are dominating over the performance of the fuel cell. Such ohmic resistance is possibly due to the rather thick (1 mm) electrolyte used and suggests that improved performance can be readily obtained by reducing electrolyte thickness.

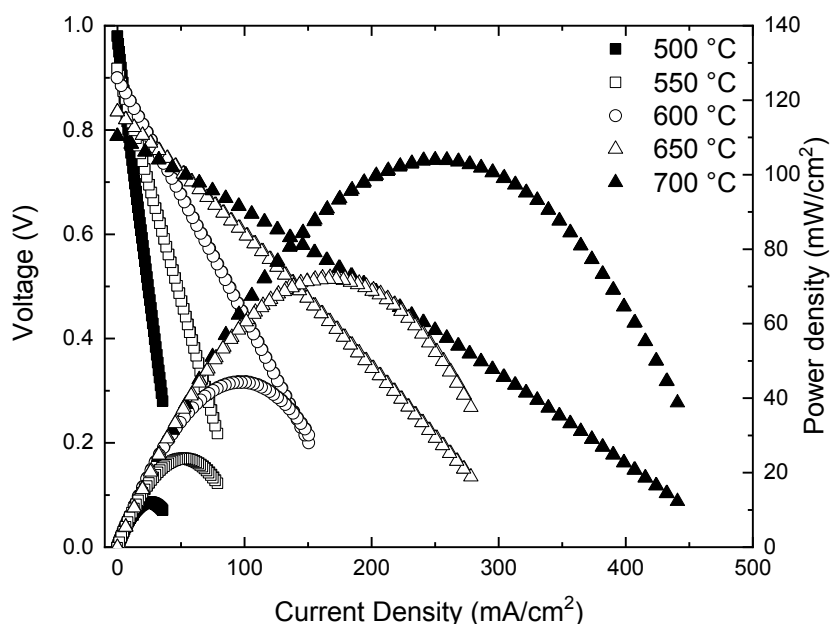


Figure 4. Current-voltage (I-V) and current-power density (I-P) curves of the GDC IT-SOFC measured at temperatures between 500 °C and 700 °C.

The high-frequency ohmic resistance ( $R_{\Omega}$ ) was extracted from the impedance diagrams taken at OCV at different measuring temperatures. Figure 5 shows the Arrhenius diagram of the ohmic conductivity of the IT-SOFC along with data corresponding to the total conductivity of commercial (Praxair) GDC pellets sintered at 1400 °C. The experimental data of both bulk CGO and the  $R_{\Omega}$  of the IT-SOFC are in excellent agreement. The electrical conductivity of the GDC electrolyte is  $1.8 \times 10^{-2}$  S/cm at 600 °C and has an activation energy of 0.9 eV. Such results are consistent with previously reported values (15,16) and confirm that the main loss component of the IT-SOFC is the ohmic resistance due to the thick electrolyte.

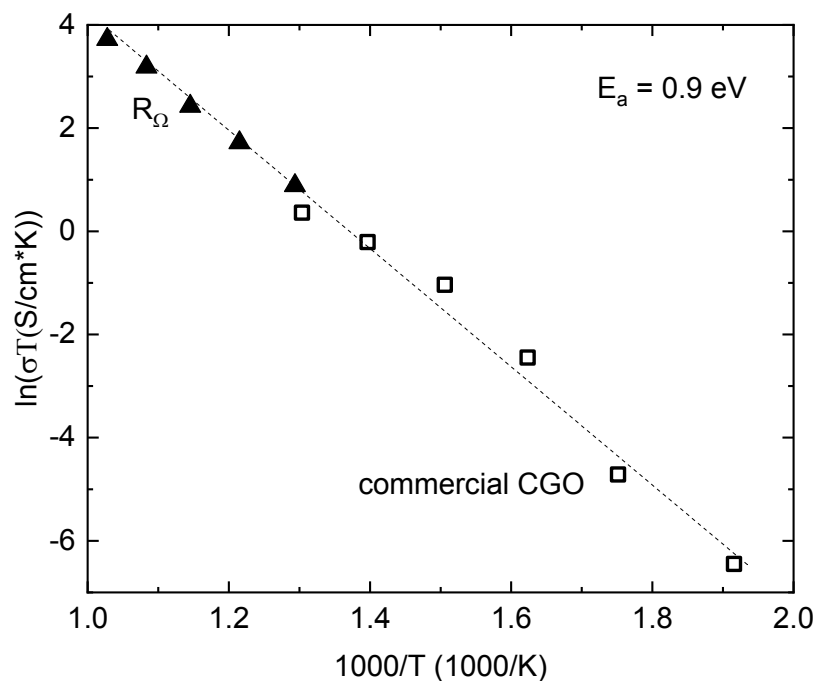


Figure 5. Arrhenius plot of the ohmic conductivity ( $R_{\Omega}$ ) extracted from impedance data of the fuel cell sintered at 1150 °C and total conductivity (grain+grain boundary) of commercial CGO.

### Conclusion

A ceria-based electrolyte supported solid oxide fuel cell was successfully fabricated at a sintering temperature of 1150 °C. The morphology of gadolinium-doped ceria nanorods was essential in promoting densification of the GDC electrolyte at mild temperatures. The as-synthesized GDC material exhibits a large sintering driving force, enabling the material to reach high relative density at temperature as low as 1150 °C. The I-V curves indicate that sintering at 1150 °C resulted in IT-SOFC with good gas tightness, low electrode polarization, and power output limited by the electrolyte thickness. The experimental results evidenced that shape control synthesis of doped ceria is a promising route to promote significant cost reduction and increased fabrication flexibility to ceria-based solid oxide fuel cells.

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