

Infiltrated $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ in $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ scaffolds as cathode material for IT-SOFC

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ARTICLE INFO

Keywords:

Infiltration
Mixed ionic–electronic conductors
LBC cathode
LSGM electrolyte
SOFC

ABSTRACT

The electrochemical response of infiltrated $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ (LBC) in porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (LSGM) has been investigated. The thermal expansion coefficient (TEC) of the resulting electrode was measured, obtaining $\alpha = 12.5 \times 10^{-6} \text{ K}^{-1}$, a value similar to that of LSGM. The polarization resistance (R_p) and the processes involved in the oxygen reduction reaction (ORR) for the new electrode were studied and analyzed through complex impedance spectroscopy measurements as a function of temperature and oxygen partial pressure ($p\text{O}_2$), using a symmetrical cell. The value of R_p for the infiltrated LBC turned out to be lower than that measured for an electrode prepared with a composite LBC-LSGM (1:1 wt%) by an order of magnitude, for the temperature range $750^\circ\text{C} \leq T \leq 900^\circ\text{C}$, and about 5 times lower for the temperature range $450^\circ\text{C} \leq T \leq 650^\circ\text{C}$. At 600°C , the LBC infiltrated cathode exhibits a polarization resistance $R_p = 0.22 \Omega \text{ cm}^2$, in air. The complex impedance spectra show two processes, one identified as low frequency (LF), with a characteristic frequency of 10 Hz, and the other as intermediate frequency (IF), with a range between 0.05 and 2000 Hz. The LF process could be associated to the diffusion of oxygen in the gas phase through the pores of the electrode. Its resistance, $R_{LF} = 0.01 \Omega \text{ cm}^2$ was found to be independent of the temperature and half of that obtained for the LBC composite cathode. On the other hand, the IF process is related to charge transfer at the electrode surface and the electrode-electrolyte interface. The LBC cobaltite infiltrated in the LSGM scaffolds offers an adequate thermal expansion coefficient and good electrocatalytic activity for the ORR.

1. Introduction

Solid oxide fuel cells (SOFCs) are highly efficient electrochemical devices that convert chemical energy from fuel into electrical energy. They are mainly formed by the ensemble of three different oxides, the cathode, where the oxygen reduction reaction (ORR) takes place, the electrolyte and the anode, where fuel is oxidized [1]. Traditionally SOFCs operate at high temperatures, $800^\circ\text{C} \leq T \leq 1000^\circ\text{C}$, which allows the use of unreformed hydrocarbon as fuels. However, in order to become economically competitive, the operating temperature for SOFC devices should be lowered to an intermediate range, $500^\circ\text{C} \leq T \leq 800^\circ\text{C}$. This will reduce sealing and degradation problems, chemical reactions between cell components and will allow the use of cheaper materials, such as stainless steel, as interconnector material [2]. It will also improve the response in the on-off cycles between the ambient and the operating temperature. On the other hand, the polarization resistance of the cell components increases with decreasing temperature, deteriorating the cell performance, especially in the case

of the cathode [2,3].

Among cathode materials proposed for intermediate temperature, mixed conductors oxides (MIEC) with the ABO_3 perovskite structure, containing rare or alkaline earth in the A site and cobalt in the B site, have presented low polarization resistance (R_p) values [4–6]. In particular, the oxide with composition $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ (LBC) with cubic or double perovskite structure has low polarization resistance values, structural stability and good chemical compatibility with the electrolyte material [7–12]. When LBC oxide is used as cathode with $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (LSGM) as electrolyte, chemical compatibility up to 1100°C was observed and power density values greater than 500 mW/cm^2 were obtained for the system anode/LSGM/LBC [13]. On the other hand, as previously reported [7], the LBC oxide presents a thermal expansion coefficient (TEC) of $\alpha \approx 25 \times 10^{-6} \text{ K}^{-1}$, much larger than that of LSGM (which have a TEC value $\alpha \approx 12 \times 10^{-6} \text{ K}^{-1}$) or Gd doped ceria (GDC) usually proposed as electrolyte material in intermediate temperature SOFCs (IT-SOFCs). This TEC mismatch results in poor adhesion and degradation problems which grow worse with

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<https://doi.org/10.1016/j.ceramint.2018.06.121>

Received 22 March 2018; Received in revised form 28 May 2018; Accepted 14 June 2018
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temperature cycles. In order to reduce this difference, a mixture of the electrolyte and LBC materials can be used to form either composites [8,11] or compositionally graded cathodes [9]. In this last configuration, the electrode composition gradually changes from that of the electrolyte to the one corresponding to cathode material [7,9,14]. Another way of decreasing the difference in TEC values between cathode and electrolyte is to prepare an electrode by infiltrating the cathode material into a skeleton of the electrolyte material [15,16]. Several infiltration processes have been successfully developed and have shown to improve the performance and stability of the SOFC cell [17–20]. The utilization of an infiltrated electrode reduces the TEC mismatch, allows control of the particle size by selecting the calcination temperature [21], avoids reactivity between the electrode and the electrolyte if a low heat treatment temperature (400–1000 °C) is used [22], increases the electrode-electrolyte charge transfer surface compared to that corresponding to an electrode deposited on a flat electrolyte surface and, finally, thin dense electrolytes (< 50 µm) can be prepared by a simple technique, such as co-pressing, in which the skeleton is used as support [23].

The performances of infiltrated electrodes, the processes involved during the ORR and the deterioration of the cathode performance over time are usually studied by complex impedance spectroscopy measurements in symmetrical cells. Wang et al. [24] observed that the polarization resistance due to charge transfer processes at gas/electrode surface and electrode/electrolyte interfaces in double perovskite $\text{PrBaCo}_2\text{O}_{3.8}$ (PBC) infiltrated in $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$ (SDC) was lower than that observed in a PBC + SDC composite electrode [25]. Han et al. [26] identified three limiting processes in a cathode prepared with $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (SBSC) infiltrated in a LSGM backbone: a) the charge transfer in the electrode-electrolyte interface, b) the charge transfer at the SBSC surface and c) the oxygen molecule diffusion in the gas phase, corresponding to the high, medium and low frequency ranges, respectively. In this case, the largest polarization resistance was obtained for the electronic charge transfer to adsorbed oxygen atoms on the electrode surface.

Previous studies of our group on LBC electrodes prepared as a composite with GDC [8] or as a graded cathode [9], have yielded a very low polarization resistance value, $R_p \sim 0.075 \Omega \text{ cm}^2$ at 600 °C, which is close to the lowest values reported in the literature [3]. Thus, based on these positive results and considering the advantages of the infiltration technique we prepared electrodes by infiltrating LBC in LSGM scaffolds in order to evaluate their electrochemical performances as cathodes for the ORR. The cathode response was evaluated by electrochemical impedance measurements on symmetrical cells as a function of temperature and oxygen partial pressure ($p\text{O}_2$). The limiting processes of the ORR were analyzed and identified. The performance of the infiltrated LBC electrode was compared with that corresponding to an electrode prepared with a composite of LBC + LSGM.

2. Experimental

LSGM powder was prepared by solid-state reaction using required amounts of La_2O_3 , previously dried overnight at 1000 °C, SrCO_3 , Ga_2O_3 and MgO . Raw materials were mixed using a jar mill with ethanol and 5 mm diameter ZrO_2 balls during 8 h and then calcined at 1000 °C for 12 h. The resulting powder was milled for 24 h and calcined at 1400 °C for 24 h in air. This procedure was performed twice. The cobaltite LBC was prepared by solid state reaction following the procedure previously reported [7]. The electrodes of the symmetrical cells for impedance spectroscopy measurements were prepared infiltrating the LBC precursor solution into the porous LSGM skeleton. The cell with the porous/dense/porous electrolyte configuration was fabricated using the co-pressing technique. The electrode skeletons were prepared mixing soluble starch as pore former with LSGM in a 40:60 wt% ratio in isopropyl alcohol using an agate mortar. The three electrolyte layers starch + LSGM/LSGM/starch + LSGM were pressed uniaxially at 100 MPa and

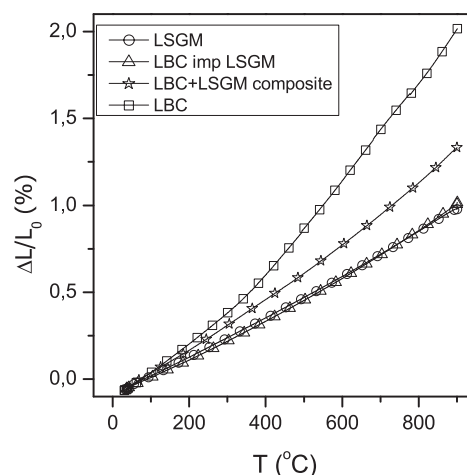


Fig. 1. Relative length change $\Delta L/L_0$ as a function of temperature for LBC, composite LBC + LSGM, infiltrated LBC in LSGM backbone and dense LSGM.

Table 1
TEC values.

	T (°C)		
	100–350	400–900	100–900
LBC	20.3	29.3	26.4
Composite	13.9	17.4	16.2
Infiltrated	10.6	13.7	12.5
LSGM	11.1	12.5	12.0

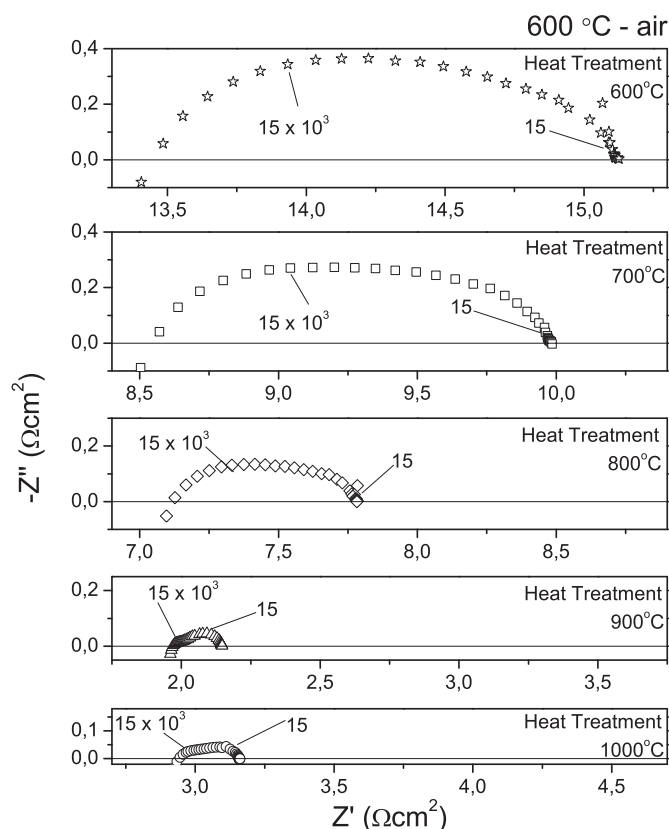


Fig. 2. Complex impedance spectra for infiltrated LBC electrodes. These impedance spectra were measured at $T = 600$ °C, in ambient air, after the electrode was heat treated at various temperatures between 600 and 1000 °C.

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