



## LaCoO<sub>3</sub>: Promising cathode material for protonic ceramic fuel cells based on a BaCe<sub>0.2</sub>Zr<sub>0.7</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> electrolyte

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### HIGHLIGHTS

- ▶ Successful infiltration of LaCoO<sub>3</sub> into a porous BCY27 after 6 infiltrations of 1 mol L<sup>-1</sup> solution.
- ▶ Single phased LaCoO<sub>3</sub> formed after 2 h at 600 °C in air.
- ▶ LaCoO<sub>3</sub> does not degrade nor react with BCZY27 at temperatures up to 600 °C.
- ▶ Cathode ASR of 0.39 and 0.11 Ω cm<sup>2</sup> in air, p<sub>H<sub>2</sub>O</sub> = 0.01 atm, at 500 and 600 °C respectively.
- ▶ Oxide ion conduction is not necessary in PCFC cathodes.

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### ABSTRACT

Symmetric cells (cathode/electrolyte/cathode) were prepared using BaCe<sub>0.2</sub>Zr<sub>0.7</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> (BCZY27) as proton conducting electrolyte and LaCoO<sub>3</sub> (LC) infiltrated into a porous BCZY27 backbone as cathode. Single phased LC was formed after annealing in air at 600 °C for 2 h. Scanning electron micrographs showed the presence of the infiltrated LC in the full cathode depth. Transmission electron micrographs revealed LC grains (60–80 nm) covering partly the BCZY27 grains (200 nm–1 μm). Impedance spectra were recorded at 500 °C and 600 °C, varying the oxygen partial pressure and the water vapour pressure. Two arcs correspond to the cathode contribution: a middle range frequency one (charge transfer) and a low frequency one (oxygen dissociation/adsorption). The area specific resistances (ASRs) of both contributions increase when decreasing the oxygen partial pressure. The low frequency arc is independent on the water vapour pressure while the charge transfer ASR values increase with higher p<sub>H<sub>2</sub>O</sub>. The cathode ASRs of 0.39 and 0.11 Ω cm<sup>2</sup> at 500 and 600 °C respectively, in air (p<sub>H<sub>2</sub>O</sub> = 0.01 atm) are the lowest reported to the authors' knowledge for PCFC cathodes. Furthermore, this work shows that the presence of oxide ion conduction in the cathode material is not necessary for good performance.

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### 1. Introduction

After more than two decades of research on the electrolyte materials for protonic ceramic fuel cells (PCFCs) [1–4] efforts are now focused on cathode development. Additional challenges compared to those of SOFCs include formation of water vapour at the cathode side and slower electrode kinetics due to the lower operating temperatures (400–600 °C). Because of the formation of water at the cathode of PCFCs, protonic conduction in the cathode is necessary in order to extend the reaction sites to the entire gas/cathode interface. If protonic conduction is absent, the water will be formed only at the electrolyte/cathode interface. Cercer made of the

electrolyte material (BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3-δ</sub>) and a mixed oxide ion and electron conductor MIEC (Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub> referred to as SSC or Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> referred to as BSCF) were used to impart protonic conduction to the cathode [5,6]. An optimal percentage of MIEC and proton conductor oxide exists for composite cathodes to get the lowest polarization resistance. In the case of SSC–BaCe<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>3-δ</sub>, this value was estimated to be circa 60 wt% of SSC [7]. However, due to the high temperature required for the cercer fabrication, cation interdiffusion was observed between the electrolyte material and MIEC. Infiltration of the MIEC into a porous backbone of proton conductor material was shown to be a good alternative, as this low temperature method prevents the cation interdiffusion [8]. Infiltration of electrode materials is commonly used for SOFC [9,10]: the particle size of the infiltrated MIEC is in

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the sub-100 nm range which creates a large surface area and can improve the surface-catalytic behaviour.

The cathode mechanism of PCFCs, being more complex than that of an SOFC cathode, is still not fully understood. First, Uchida et al. [11] proposed the elementary steps of a PCFC cathode by considering the addition of the formation and evolution of water to the dissociative adsorption and diffusion of oxygen species. Later on, He et al. [12] further developed these steps based on the transfer and reaction of protons. For each of these steps (i), the cathode polarization resistance ( $R_p$ ) depends on the water vapour and/or the oxygen partial pressures and can be written as follow:

$$R_{p_i} \propto (p_{O_2})^{-m_i} \cdot (p_{H_2O})^{-n_i} \quad (1)$$

where  $n_i$  and  $m_i$  correspond the reaction orders. The different steps and expected dependences of the polarization resistance with the water vapour and oxygen partial pressures are listed in Table 1.

As mentioned above, protonic conduction is necessary in the cathode of a PCFC, in addition to the electronic conduction. But it is not known for certain whether oxide ion conduction is mandatory, as long as the cathode material exhibits good catalytic properties for oxygen dissociation. To address this question, we have chosen to study  $LaCoO_3$  as PCFC cathode material because  $LaCoO_3$  does not form oxygen vacancies at temperatures below 600 °C and is therefore a pure electronic conductor in the expected operating temperature range of a PCFC [13]. Indeed, the cobalt cations are not easily reduced when six-fold coordinated. Moreover  $LaCoO_3$  was shown to be stable: no phase changes were observed after 350 h stability tests at 600 °C in air as well as at 400 °C in humidified air with  $p_{H_2O} = 0.2$  atm [13]. In addition to its stability in air and wet atmosphere,  $LaCoO_3$  does not react with solid solutions of barium cerate–zirconate at temperatures below 1100 °C [14]. However a secondary phase ( $YBaCo_2O_{5+\delta}$ ) was detected by XRD after heat treatment at 1270 °C [13].  $LaCoO_3$  has also been studied as SOFC cathode material, exhibiting a very low area specific resistance:  $0.079 \Omega \text{ cm}^2$  at 600 °C [15].

In this work, the performance of infiltrated  $LaCoO_3$  cathodes was studied in a symmetric cell configuration:  $LaCoO_3$  infiltrated in porous BCZY27/dense BCZY27 electrolyte/ $LaCoO_3$  infiltrated in porous BCZY27. Microscopy and Energy Dispersive Spectroscopy (EDS) analysis were performed on the symmetric cells after testing.

## 2. Experimental

### 2.1. Preparation of symmetric cells

Dense samples of BCZY27 ( $BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ ) were prepared by solid state reactive sintering as described in Ref. [16]. Bars (8 mm·8 mm·35 mm) were made by uniaxial pressing and were

**Table 1**  
Cathode reaction steps for a PCFC cathode [11,12].  $m$  and  $n$  are respectively the reaction orders with respect to the oxygen partial pressure and water vapour pressure.

Step	Process	Elementary reaction	$m$	$n$
1	Adsorption of oxygen gas	$O_2(g) \rightarrow 2 O_{ad}$	1	0
2	Reduction of the adsorbed oxygen	$O_{ad} + e^- \rightarrow O^-_{ad}$	3/8	0
3	Diffusion of the oxygen from the surface to the TPB	$O^-_{ad} \rightarrow O^-_{TPB}$	1/4	0
4	Charge transfer of the oxygen	$O^-_{TPB} + e^- \rightarrow O^{2-}_{TPB}$	0	0
5	Diffusion of the proton from the electrolyte to the TPB	$H^+_{electrolyte} \rightarrow H^+_{TPB}$	0	1/2
6	Reaction proton/oxygen to form hydroxide at TPB	$H^+_{TPB} + O^{2-}_{TPB} \rightarrow OH^-_{TPB}$	0	1/2
7	Reaction proton/hydroxide to form water at TPB	$H^+_{TPB} + OH^-_{TPB} \rightarrow H_2O_{TPB}$	0	1
8	Desorption of water	$H_2O_{TPB} \rightarrow H_2O(g)$	0	1

sintered in air at 1500 °C for 4 h. The resulting black coloured bars were cut into 700  $\mu\text{m}$  thick square slices. The surface of these substrates was manually polished with a 500 grade SiC paper.

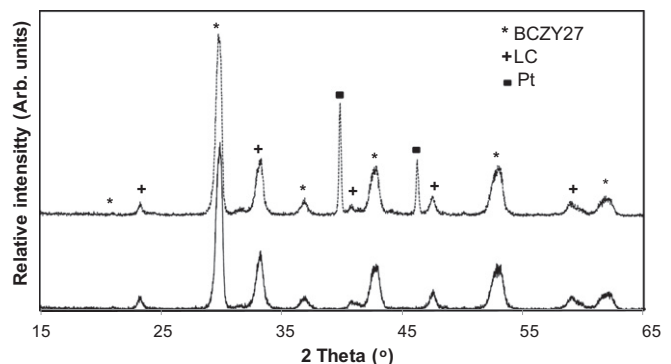
BCZY27 powder was prepared by conventional solid state reaction at 1400 °C for 30 h in air. A slurry was prepared using this BCZY27 powder, Solspere 20 wt% in Terpeneol, dibutylphthalat as plasticizer and 5 wt% ethylcellulose in Terpeneol as binder. A layer was screen printed on each side of the dense BCZY27 substrate with a Polyester 92 mesh using a blade speed of  $60 \text{ mm s}^{-1}$ . The samples were dried at 90 °C in a rolling furnace and were then fired at 1300 °C for 2 h in air. The resulting BCZY27 porous backbone is beige/light brown. The La and Co nitrate solution ( $1 \text{ mol L}^{-1}$ ) was prepared in a similar way as described elsewhere [15]. A drop of solution was deposited on one side and the sample was dried at 70 °C on a heating plate, followed by the same procedure on the second side. Between each infiltration, the samples were calcined at 350 °C for 30 min in air. After the last infiltration, the calcination time at 350 °C was extended to 2 h. The samples were infiltrated 6 times on both sides and finally annealed in air at 600 °C for 2 h.

### 2.2. Characterization of the samples

Crystallographic phases were determined at room temperature with a Stoe X-ray diffractometer, in the  $\theta/2\theta$  mode, using the  $K_{\alpha}1\text{Cu}$  radiation.

Micrographs of polished and unpolished cross sections were recorded using field-emission gun scanning electron microscopes (SEM): JEOL JSM-6700F and Nova NanoLab 600 FIB/SEM. Deposition of a thin carbon layer was necessary because of the insulating properties of the samples. The porosity of the cathodes was determined from the polished cross section micrographs by estimating the area occupied by pores (low intensity) divided by the total image area. The uncertainty of this determination arises from the difficulty of fixing the intensity threshold separating pores from material. An electron transparent specimen was prepared by focus ion beam (FIB) *in-situ* lift out technique [17,18] using an FEI Nova NanoLab 600 FIB/SEM and investigated in a JEOL 3000F transmission electron microscope (TEM). Scanning transmission electron microscopy (STEM) was used to record micrographs with a high angle annular dark field (HAADF) detector and energy dispersive spectroscopy (EDS) maps using an Oxford Instruments INCA X-Max silicon drift detector. Si, which could come from the polishing, was not detected in the analyses.

For AC electrical measurements, Pt current collectors (Ferro) were painted on the samples and heated *in-situ* to 600 °C in air. Impedance spectra were recorded at 600 and 500 °C in five different oxygen partial pressures (mixing of air or oxygen with



**Fig. 1.** XRD pattern before (solid line) and after (dotted line) electrochemical testing on the  $LaCoO_3$  (LC) infiltrated cells. The diffractograms are shifted vertically for clarity.

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