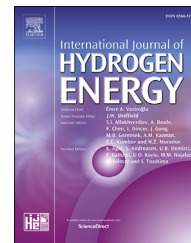


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# Nb-substituted $\text{PrBaCo}_2\text{O}_{5+\delta}$ as a cathode for solid oxide fuel cells: A systematic study of structural, electrical, and electrochemical properties

Mattia Saccoccio<sup>a</sup>, Chunli Jiang<sup>a</sup>, Yang Gao<sup>a</sup>, Dengjie Chen<sup>a,1</sup>,  
Francesco Ciucci<sup>a,b,\*</sup>

<sup>a</sup> Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Kowloon, Hong Kong, China

<sup>b</sup> Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Kowloon, Hong Kong, China

## ARTICLE INFO

### Article history:

Received 8 December 2016

Received in revised form  
29 March 2017

Accepted 7 June 2017

Available online 5 July 2017

### Keywords:

Solid oxide fuel cell (SOFC)

Cathode material

 $\text{PrBaCo}_2\text{O}_6$  (PBC)

Niobium (Nb) substitution

Layered double perovskite

## ABSTRACT

Double perovskite oxides, such as  $\text{PrBaCo}_2\text{O}_{5+\delta}$  (PBC), are among the most promising cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) thanks to their high catalytic activity and mixed ionic and electronic conductivity. Here, we investigate the impact of Nb substitution on the crystal structure, catalytic activity, and electrical conductivity of PBC. Several studies have outlined that doping high valence cations, such as  $\text{Nb}^{5+}$ , effectively stabilizes the perovskite structure, decreases the thermochemical expansion coefficient of the material, and can benefit the peak power density of the fuel cell.

The as-prepared  $\text{PrBaCo}_{2-x}\text{Nb}_x\text{O}_{5+\delta}$  with  $x = 0, 0.25, 0.50, 0.75,$  and  $1.00$  (PBCN) exhibit structural change from  $P4/mmm$  ( $x = 0$ ) to  $I4/mmm$  ( $x = 1$ ), whereas both phases are present for intermediate compositions. The analysis of electrochemical impedance spectroscopy (EIS) data shows that PBCN is characterized by relatively low polarization resistance. Between  $300$  and  $800$  °C, the electrical conductivity of PBCN, with  $x = 0.25, 0.50$ , lies above  $100 \text{ S cm}^{-1}$ . If  $x = 0.75$  or  $1.00$ , the conductivity drops below  $100 \text{ S cm}^{-1}$ . Our work suggests that the Nb-doped PBC exhibits excellent chemical compatibility with typical electrolyte material and good electrochemical performance, making it a promising cathode material for applications in IT-SOFCs.

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## Introduction

The world urgently needs sustainable energies to tackle the severe consequences of pollution and global warming on both

the environment and public health. Solid oxide fuel cells (SOFCs) are promising sustainable energy systems thanks to their high energy conversion efficiency and fuel flexibility [1]. The high operating temperature (above  $800$  °C) is one of the greatest obstacles faced in the large-scale deployment of this

\* Corresponding author. Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Kowloon, Hong Kong, China.

E-mail address: [francesco.ciucci@ust.hk](mailto:francesco.ciucci@ust.hk) (F. Ciucci).

<sup>1</sup> Present address: Department of Chemistry, Jinan University, Guangzhou, China.

<http://dx.doi.org/10.1016/j.ijhydene.2017.06.056>

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technology: it poses numerous challenges to the startup and shutdown of SOFCs, and it is linked to the fast degradation of various components such as sealant and electrodes. In addition, since thermal management is more challenging, the high operating temperature requires the selection of expensive materials for interconnects and seals [2]. However, lowering the temperatures to the intermediate range (~500–800 °C) causes a decrease in activity and an increase in the overall cell losses. The latter are known to be dominated by the sluggish oxygen reduction reaction (ORR) at the cathode side [3]. Hence, numerous researchers have searched for new high-performance cathode materials capable of working at a reduced temperature [3].

Perovskite oxides are a promising class of SOFC cathode materials [4–7]. Due to their compositional flexibility, they can be designed to have mixed ionic-electronic conductivity (MIEC) [8]. Among the perovskite compositions, double perovskites in particular have attracted significant attention [8]. A-site ordered double perovskites have the general formula  $AA'B_2O_{5+\delta}$  where A is a lanthanide, A' is an alkaline earth element, and B is a transition metal. Double perovskites are layered, and consist of a stacked sequence of  $AO_6|BO_2|A'O|BO_2$  layers along the c-axis [9]. Such structures enhance the oxygen transport in the ab plane, as observed by Taskin et al. [10,11] and previously studied by our group [12,13]. The latter property, together with their high activity, makes them particularly suitable for SOFCs.

Among the many possible A-site ordered double perovskite compositions, cobaltites with the general formula  $LnBaCo_2O_{5+\delta}$  (Ln: lanthanide element) are of interest thanks to their high oxygen diffusivity and catalytic activity towards ORR [14–17]. Some of the most investigated cobaltites are  $LaBaCo_2O_{5+\delta}$  [18],  $NdBaCo_2O_{5+\delta}$  [19,20],  $GdBaCo_2O_{5+\delta}$  [21–24], and  $PrBaCo_2O_{5+\delta}$  (PBC) [9,17,25–29]. PBC in particular is considered to be among the best cathode materials for SOFCs because it possesses a high electronic conductivity [9] and the highest oxygen mobility in the  $LnBaCo_2O_{5+\delta}$  series [30], resulting from a high concentration of oxygen vacancies.

A strategy commonly employed to adjust the properties of a material is doping: various groups have investigated the effect of cation substitutions into PBC at either the A-site [31,32], B-site [33–38], or both [39,40]. Among others, various Nb containing perovskite oxide have been investigated in the context of SOFCs, e.g., the  $Sr_2Fe_{1-x}Nb_xO_6$  [41–44],  $SrCo_{1-x}Nb_xO_{3-\delta}$  [45–47], and  $Ba_{1-x}Co_{0.9-y}Fe_yNb_{0.1}O_{3-\delta}$  [48–51] families. Furthermore, several studies have outlined that doping high valence cation, such as  $Nb^{5+}$ ,  $Ta^{5+}$ ,  $W^{6+}$ , and  $Mo^{6+}$  effectively stabilizes the perovskite structure. In turn, this can enhance the  $CO_2$  resistance [52–54]. Another potentially interesting effect of Nb substitution is the decrease of the thermochemical expansion coefficient [55,56], which improving the thermomechanical compatibility with solid electrolytes. While these improvements in stability are sometimes linked to lower electronic and ionic conductivities [55,56] and reduced oxygen permeability [54], this is not always the case. In fact, the structural stability, conductivity, and oxygen vacancy concentration of  $SrNb_xCo_{1-x}O_{3-\delta}$  benefit from the Nb doping [45,46,57,58]. Similarly, the peak power density of  $SrNb_xFe_{1-x}O_{3-\delta}$  ( $x = 0.05, 0.1, \text{ and } 0.2$ ) based fuel cells increases with Nb substitution [56].

Owing to the potentially interesting effects mentioned above, we systematically investigated the Nb substitution into PBC. We studied the structural, electrical, and electrochemical properties for  $PrBaCo_{2-x}Nb_xO_{5+\delta}$  (PBCN) with  $x = 0.25, 0.50, 0.75, \text{ and } 1.00$ , hereafter named PBCN025, PBCN050, PBCN075, and PBCN100, respectively.

## Experimental

### Fabrication

#### Sample preparation

We prepared  $PrBaCo_{2-x}Nb_xO_{5+\delta}$  powders with  $x = 0, 0.25, 0.50, 0.75, \text{ and } 1.00$  using the solid-state reaction method. Stoichiometric amounts of high purity  $Pr_6O_{11}$ ,  $BaCO_3$ ,  $Nb_2O_5$ , and  $Co_2O_3$  were first thoroughly mixed with ethanol by ball-milling (for 90 min, at 500 rpm in an Acron High Speed Ball Mill QM-3SPO4), and then dried. Next, we uniaxially cold pressed the resulting powders into disc shaped pellets, which we sintered for 12 h at 1100 °C, using a 10 °C/min heating rate. The same rate was used to cool the pellets down to 500 °C. Subsequently, the pellets were cooled naturally to the ambient temperature. We then reground the pellets (by hand grinding thus ball-milling), re-pelletized the powders, and calcined the pellets repeatedly (six times at least), to ensure the phase purity. The final calcination temperatures were 1200, 1250, 1250 and 1300 °C for  $x = 0.25, 0.50, 0.75, \text{ and } 1.00$ , respectively (the higher the Co contents, the lower the melting temperature of the material).

#### Fabrication of symmetrical cells

We fabricated symmetrical cells having PBCN| $Sm_{0.2}Ce_{0.8}O_{2-\delta}$  (SDC)|PBCN configuration. We prepared electrolyte pellets by first ball-milling the SDC powder in ethanol. After drying, the powder was cold pressed to obtain thin discs, which we then calcined at 1200 °C for 6 h. We prepared the PBCN electrode slurries for spray deposition by ball-milling (500 rpm for 30 min) the powder together with isopropanol, ethylene glycol, and glycerol. Then, we spray-painted the resulting slurry on both sides of the electrolyte disc, which was subsequently fired in air at 950 °C for 2 h. Lastly, we painted porous silver electrodes, and applied silver leads on both sides of the symmetrical cells using a Ag epoxy adhesive (DAD-87, Shanghai Research Institute of Synthetic Resins), cured for 30 min at 180 °C.

#### Fabrication of samples used for conductivity measurements

To measure the electrical conductivity, we prepared bar-shaped samples via uniaxial pressing. We then sintered the obtained bricks (measuring 1.8 mm × 5.6 mm × 4.7 mm) for 4 h at 1200, 1250, 1250, and 1300 °C for  $x = 0.25, 0.50, 0.75, \text{ and } 1.00$ , respectively to obtain dense samples. Heating and cooling ramp rates were kept low, 2 °C min<sup>-1</sup>, to avoid cracking of the sample. Next, four silver leads were attached using Ag epoxy adhesive to test the DC conductivity using the 4-probe method [59].

### Material characterization

#### Electrochemical performance

We carried out the impedance measurements on the symmetric cells described earlier using a BioLogic VSP impedance

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