



## Exploring mixed proton/electron conducting air electrode materials in protonic electrolysis cell



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### ABSTRACT

In this work, we investigate and compare the performance and cell polarization resistance of  $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_{3-\delta}$  (BLC) and double perovskite oxide  $\text{BaGd}_{0.8}\text{La}_{0.2}\text{Co}_2\text{O}_{6-\delta}$  (BGLC) anode on cathode supported protonic steam electrolysis cells using a  $20\ \mu\text{m}$   $\text{SrZr}_{0.5}\text{Ce}_{0.4}\text{Y}_{0.1}\text{O}_{3-\delta}$  electrolyte with Ni-SZCY541 composite as the cathode. The kinetics of protons through the bulk and across the gas electrolyte interfaces of both anode materials were also studied by direct measurement of their tracer diffusions using time-of-flight secondary ion mass spectrometry depth profiling (TOF-SIMS). Cell terminal voltages of 1.74 and 1.93 V, were observed at a current density of  $0.5\ \text{A cm}^{-2}$  for both BLC and BGLC whereas a hydrogen evolution rate of 121.85 and  $111.15\ \mu\text{mol cm}^{-2}$  every minute was also obtained at the same current density, translating to a current efficiency of 78 and 72% respectively. Hydrogen tracer diffusion studies confirm BGLC can incorporate protons into the bulk relative to BLC even though the present steam electrolysis results show a better performance for BLC at  $600\ ^\circ\text{C}$ .

### 1. Introduction

Ceramic proton conducting electrolytes (PCE) are a promising intermediate-temperature alternative to oxide ion conducting electrolytes (OCE) in solid oxide electrolysis (H-SOECs) and fuel (H-SOFCs) cells [1–6]. Interest in PCE stems from their high conductivity and low migration energy barriers which are usually within 0.3–0.5 eV, compared to typical values of 0.8–0.9 eV for OCE [7]. In addition almost pure hydrogen is produced at the hydrogen electrode whereas OCE produce wet hydrogen at the steam side when operated in electrolysis mode which thus requires an additional costly separation step [3,4–9]. Moreover the concept of reversible solid oxide fuel and electrolysis cells is more feasible with PCE rather OCE because the hydrogen electrode-supported electrolyte is the optimal configuration in both the fuel and electrolysis cells modes. In this way, the overall over potential is minimized, no matter which configuration is chosen [3,5,6].

Thus far strontium cerate and strontium zirconate-based compositions have emerged as strong candidate electrolytes for steam electrolysis due to their good chemical and mechanical stability respectively [1,3,4,6–13]. This class of materials has been intensively investigated since the discovery of proton conduction in perovskite type oxides by Iwahara et al. [10,11]. More recently research on solid solutions in the  $\text{Y}:\text{SrZrO}_3\text{-SrCeO}_3$  and  $\text{Y}:\text{BaZrO}_3\text{-BaCeO}_3$  systems has sparked widespread interest among researchers within the ceramic protonic

community, since they combine the better proton conduction of cerates with the greater chemical stability of zirconates [14–18].

Besides reaching sufficient electrolyte conductivity at intermediate-temperatures with most of these materials, a major concern and challenge with intermediate-temperature operation is the sluggish kinetics of the anode materials. The most frequently used materials like  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (SSC) [11],  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF) [12] and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  [5] unfortunately show either high polarization resistances particularly at high current densities or are not chemically stable under this operating conditions [19]. Also the steam dissociation reaction in most of these materials is strictly confined to the gas/electrode/electrolyte triple phase boundary (TPB) sites. Therefore anode materials combining high catalytic activity and proton conductivity exceeding  $10^{-5}\text{--}10^{-4}\ \text{S/cm}$  to initiate a bulk transport path are highly desirable. For this purpose,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$  (BSFZ) [19],  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$  [20] and double perovskite oxide  $\text{BaGd}_{0.8}\text{La}_{0.2}\text{Co}_2\text{O}_{6-\delta}$  (BGLC) [21] were proposed as possible mixed proton/electron conductors (P-MIECs) on account of their considerable protonation between 300 and  $400\ ^\circ\text{C}$ . Although some of these materials works effectively on proton conducting electrolytes very few studies have probe the specific ionic carriers responsible for transport within the bulk of such materials.

In this work, we investigate and compare the performance and cell polarization resistances of BLC and P-MIEC double perovskite oxide

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BGLC anode on cathode supported protonic electrolysis cells using a 20  $\mu\text{m}$  SZCY541 electrolyte with Ni-SZCY541 composite as the  $\text{H}_2$ -electrode. Also we have studied the kinetics of protons through the bulk and across the gas electrolyte interfaces of both anode materials by measurement of their tracer diffusions using time-of-flight secondary ion mass spectrometry depth profiling (ToF-SIMS) as a means of broadening current knowledge on the availability of protons in BGLC and to clarify the relationship between protons and oxide ions conduction in both materials.

## 2. Experimental

### 2.1. Sample preparation and characterization

Powders of SZCY541, BLC and BGLC were prepared by the chemical solution approach as reported in ref. [14]. X-ray diffraction (XRD) analysis was performed to investigate the crystalline structure of the as prepared powders and pellets using Rigaku X-ray diffraction (XRD Ultima IV) with Cu-K $\alpha$  radiations operating at 40 kV. Diffraction patterns were obtained in the  $2\theta$  range between  $10^\circ$  and  $80^\circ$  with a step size of  $0.02^\circ$ .

### 2.2. Cell fabrication and testing

The cathode-supported Ni-SZCY541 composites (NiO, SZCY541, at a weight ratio of 60:40) were prepared by cold isostatic pressing (CIP), into disks of 20 mm in diameter and 1 mm in thickness at 300 MPa. The Electrolyte slurry composed of SZCY541 powder and 6 wt% of ethylcellulose in terpineol (wako) was carefully coated on top of the cathode-supported Ni-SZCY541 composite by screen-printing and subsequently sintered at  $1400^\circ\text{C}$  for 5 h to obtain densified SZCY541 half cells. Fine BLC and BGLC powders were then mixed thoroughly with a 6-wt% ethylcellulose–terpineol binder each to prepare the anode slurry which was then painted on SZCY541 electrolyte layer by screen-printing, and sintered at  $900^\circ\text{C}$  for 1 h in air to form single cells. A current pulse generator (Nikko-Keisoku, NCPG-101 Japan) was used as a DC power supply. Steam electrolysis was then evaluated at  $600^\circ\text{C}$  with humidified 1%  $\text{O}_2$  and 80%  $\text{H}_2\text{O}$  fed in at the anode and 1% $\text{H}_2$ -99% Ar at the cathode as sweep gas, humidified by saturated water vapor at  $17^\circ\text{C}$  ( $P_{\text{H}_2\text{O}} = 1.9 \times 10^3 \text{ Pa}$ ). Hydrogen evolution was determined by measuring the increase in hydrogen concentration in the cathode gas outlet by gas chromatography whereas the Ohmic loss and electrode polarization were measured by the current interruption method.

### 2.3. Isotope labelling experiments and ToF-SIMS measurements

Isotope labelling experiments combined with ToF-SIMS were used to study the proton uptake in the dense ceramic pellets. Dense and free from macroscopically visible crack pellets of BLC and BGLC were prepared by uniaxial pressing of the respective powders, followed by cold isostatic pressing at 300 MPa, and then sintering at  $1200^\circ\text{C}$  and  $1250^\circ\text{C}$  respectively for 5 h under a flow of dry oxygen. The pellets were then ground flat and thoroughly polished to a mirror finish ( $0.25 \mu\text{m}$ ) on one face using sequentially finer grades of SiC grinding paper and water based diamond suspensions.

For the isotope labelling experiments, the samples were exposed to a flowing mixture (50 mL/min) of  $\text{O}_2$  and  $\text{N}_2$  (20/80%) at  $300^\circ\text{C}$ . Following an initial drying step overnight, the mixture was humidified by bubbling in heavy water (Aldrich 99.9% deuterium oxide) at  $46^\circ\text{C}$ . The samples were analysed by ToF-SIMS (IONTOF TOF.SIMS 5) before and after the exposure to  $\text{D}_2\text{O}$ . In order to reduce the influence of loosely-bound hydrogen-bearing species at the surface on the subsequent analyses, samples were loaded the night before the analysis and left to pump down in the instrument's loadlock chamber (base pressure  $\sim 1 \times 10^{-7}$  mbar) overnight before transferring into the analysis chamber (base pressure  $\sim 1 \times 10^{-8}$  mbar). The ToF-SIMS analysis was

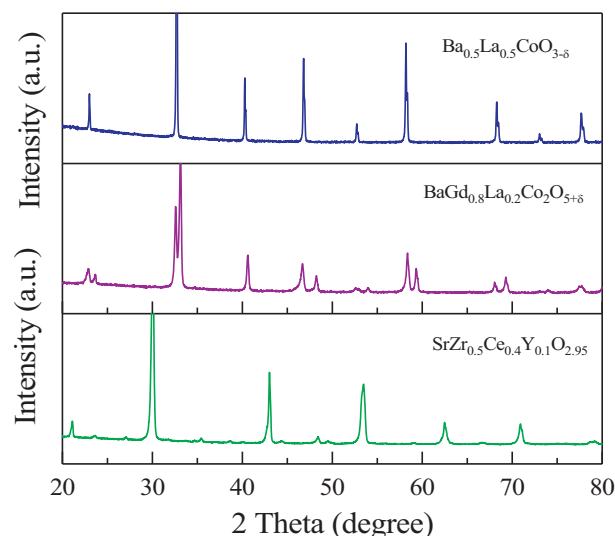


Fig. 1. Room temperature X-ray diffraction patterns of  $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_{3-\delta}$ ,  $\text{BaGd}_{0.8}\text{La}_{0.2}\text{Co}_2\text{O}_{5+\delta}$  (Prior to  $^{16}\text{O}$  annealing) and  $\text{SrZr}_{0.5}\text{Ce}_{0.4}\text{Y}_{0.1}\text{O}_{2.95}$  specimens.

conducted using a primary beam of 30 keV  $\text{Bi}^+$  ions operated in a bunched mode, and ions of negative polarity were collected. In order to maximise the mass resolution to resolve the  $^{18}\text{O}^-/^{16}\text{O}^{2-}\text{D}^-$  interference (required  $\Delta m/M = 1838$ ), the energy of the ions in the analyser drift tube was reduced from the typical value of 2 keV, to 1 keV, resulting in longer flight times and hence better separation of the relevant peaks. In order to distinguish between deuteration of the surface of the samples (e.g. adsorbates, or hygroscopic segregated layers) versus deuterium incorporation into the bulk, depth profiles were obtained using a sputtering beam of 2 keV  $\text{Ar}^+$ .

## 3. Results and discussions

### 3.1. Characterization of samples

The XRD patterns of BLC, BGLC and SZCY pellets are shown in Fig. 1. Single phase compounds were obtained for all the samples synthesized. BLC could be indexed to a simple cubic perovskite with space group Pm3m [22]. BGLC diffraction peaks, points to a tetragonal system with a  $p4/mmm$  space group [21,22] quite similar to other double perovskites whereas SZCY541 exhibits an orthorhombic perovskite structure in good agreement with the XRD patterns of previous reports [14].

### 3.2. Steam electrolysis

Double perovskite BGLC has recently been reported by R. Strandbakke et al. [21] as a promising steam electrode material with an apparent polarization resistance of  $\sim 10 \Omega \text{ cm}^2$  at  $350^\circ\text{C}$ , and a high ability to hydrate. To understand its electrochemical performance as a typical P-MIEC, we exemplify its application in a typical steam electrolysis cell at  $600^\circ\text{C}$ , using SZCY541 electrolyte with Ni-SZCY541 composite as cathode and compare it to cubic cation disordered perovskite BLC a good oxygen ion conductor [22]. Both porous anode layers are approximately  $25 \mu\text{m}$  in thickness, and adhere well to the  $20 \mu\text{m}$  thick SZCY541 protonic electrolyte. A typical microstructure of the as fabricated device is shown in Fig. 2.

Fig. 3(a) corresponds to the  $I$ - $V$  curves obtained at  $600^\circ\text{C}$  with 80%  $\text{H}_2\text{O}$  (0.8 bar) and 1% $\text{O}_2$ -99% Ar fed in the anode for both cells. The open circuit voltages (OCV) of both devices reach approximately 0.79 and 0.77 V for BLC and BGLC respectively. These values are somewhat close to the theoretical electromotive force (EMF) values calculated from the Nernst equation for these atmospheres at  $600^\circ\text{C}$ , thus

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