**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 Ba0.5La0.5CoO3−δ (BLC) and double perovskite oxide BaGd0.8La0.2Co2O6−δ (BGLC) anode on cathode supported protonic steam electrolysis cells using a 20μm SrZr0.5Ce0.4Y0.1O3-δ 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 A cm−2 for both BLC and BGLC whereas a hydrogen evolution rate of 121.85 and 111.15 µmol 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 °C.

**Keywords**

Proton conductor; cell polarization resistance; hydrogen evolution; tracer diffusion;

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 Y:SrZrO3−SrCeO3 and Y:BaZrO3−BaCeO3 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 Sm0.5Sr0.5CoO3 (SSC) [11], Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF) [12] and La0.6Sr0.4Co0.2Fe0.8O3-δ [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 10-5–10-4 S/cm to initiate a bulk transport path are highly desirable.  For this purpose, Ba0.5Sr0.5Fe0.8Zn0.2O3-δ (BSFZ) [19], BaCo0.4Fe0.4Zr0.1Y0.1O3-δ [20]anddouble perovskite oxide BaGd0.8La0.2Co2O6−δ (BGLC) [21] were proposed as possible mixed proton/electron conductors (P-MIECs) on account of their considerable protonation between 300–400 °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 BGLC anode on cathode supported protonic electrolysis cells using a 20μm SZCY541 electrolyte with Ni-SZCY541 composite as the H2-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](javascript:popupOBO('CHEBI:24636','C2CP42278F','http://www.ebi.ac.uk/chebi/searchId.do?chebiId=24636')) and [oxide](javascript:popupOBO('CHEBI:25741','C2CP42278F','http://www.ebi.ac.uk/chebi/searchId.do?chebiId=25741')) ions conduction in both materials.

1. **Experimental**
   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-Kα radiations operating at 40 kV. Diffraction patterns were obtained in the 2θ range between 10o and 80o with a step size of 0.02o.

* 1. **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 °C for 5 h to obtain densified SZCY541 half cells. Fine BLC and BGLCpowders 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 °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 °C with humidified 1% O2 and 80% H2O fed in at the anode and 1%H2-99% Ar at the cathode as sweep gas, humidified by saturated water vapor at 17 °C (*P*H2O = 1.9 × 103 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.

* 1. **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 and 1250 °C respectively for 5h under a flow of dry oxygen. The pellets were then ground flat and thoroughly polished to a mirror finish (0.25 micron) 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 O2 and N2 (20/80%) at 300˚C. Following an initial drying step overnight, the mixture was humidified by bubbling in heavy water (Aldrich 99.9% deuterium oxide) at 46˚C. The samples were analysed by ToF-SIMS (IONTOF TOF.SIMS 5) before and after the exposure to D2O. 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 loadloack chamber (base pressure ~1x10-7 mbar) overnight before transferring into the analysis chamber (base pressure ~1x10-8 mbar). The ToF-SIMS analysis was conducted using a primary beam of 30 keV Bi+ ions operated in a bunched mode, and ions of negative polarity were collected. In order to maximise the mass resolution to resolve the 18O- / 16O2D- interference (required Δm/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 deuteron incorporation into the bulk, depth profiles were obtained using a sputtering beam of 2 keV Ar+.

1. **Results and discussions**
   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].



Fig. 1Room temperaturex-ray diffraction patterns of Ba0.5La0.5CoO3−δ, BaGd0.8La0.2Co2O6−δ (Prior to 16O annealing) and SrZr0.5Ce0.4Y0.1O3-δ specimens.

* 1. **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 ~10 Ω cm2 at 350 °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°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 μm in thickness, and adhere well to the 20 μm thick SZCY541 protonic electrolyte. A typical microstructure of the as fabricated device is shown in Fig. 2.

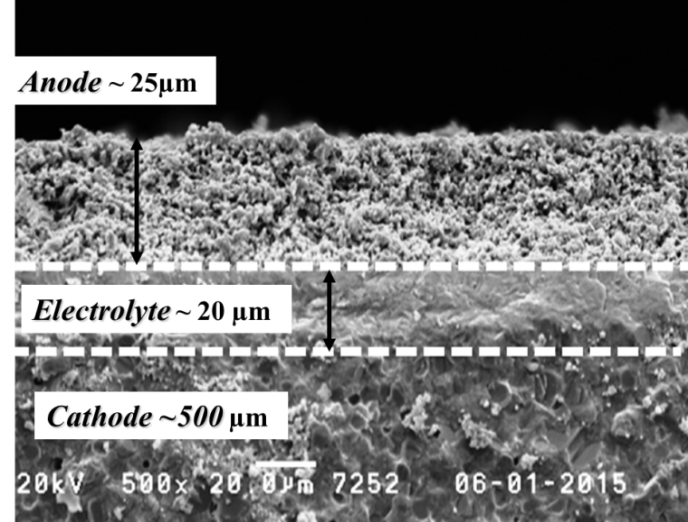


Fig. 2 Typical microstructures of as prepared steam electrolysis cell showing the respective three layers

Fig. [3](http://pubs.acs.org/doi/full/10.1021/am4020132#fig10)(a) corresponds to the *I*–*V* curves obtained at 600 °C with 80% H2O (0.8bar) and 1%O2-99% Ar fed in the anode for both cells. The open circuit voltages (OCV) of both devices reach approximately 0.79 and 0.77V 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°C, thus indicating the dense nature of the electrolyte. The current density in the two measurements increased with applied potential and reached a maximum of 0.5A cm−2 at 1.74 and 1.93 V, respectively. Also the values of the potential obtained at 0.1 A cm−2 (BLC 1.15 V, BGLC 1.27) are comparable to those reported previously by Matsumoto *et al* for cells using SZCY541 (22 μm) as the electrolyte [8]. It is important to note again that the microstructures of both cells were well-controlled to be similar and based on the I-V values it is apparent that BLC performs slightly better than BGLC at 600°C. Contrary to expectations that BGLC should, on account of its mixed proton/electron conducting nature. The total area specific resistances (area specific ohmic resistance + area specific polarization resistance,) of the devices were obtained using the following expression where is the electromotive force, is cell voltage at the current density [23] and are shown in Fig 3 (b). As observed, the ASR is higher for BGLC comparatively, especially at the early stages of the applied current density (0 – 0.25 A cm−2) and finally reaching a value of 2.3Ω cm2 at 0.5A cm−2.



Fig. 3 (a) Current–voltage curves of the steam electrolysis devices with anode based BLC and BGLC measured at 600°C with 80% H2O (0.8bar) and 1%O2-99% Ar (b) The area specific resistances (ASRs) extrapolated from the gradient of the I-V curves.

To further investigate the factors credited for the enhanced performance of the BLC cell, the electrode polarization resistance, for both anode materials, and ohmic losses IR, were adequately separated by current interruption measurement. Fig. [4](http://pubs.acs.org/doi/full/10.1021/am4020132#fig10) (a, b) corresponds to the electrode polarization *η*AC, and ohmic loss IR of the steam electrolysis cell using SZCY541 electrolyte with BLC and BGLC as anode respectively.

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Fig. 4The hydrogen evolution rate as a function of current density for (a) BLC, (b) BGLC together with the Ohmic loss IR, and electrode polarization *η*AC. Where ACrepresent the anode and cathode of the cell

It can be seen for both cells that the ohmic losses IR increase proportionally with current density in accordance with Ohm's law and are quite similar, reaching 0.64 and 0.68V at a current density of 0.5A cm−2 respectively. Area specific ohmic resistances of 1.3 and 1.4Ω cm2 were also deduced from the gradient of the IR curves as a function of current density respectively. Ohmic losses generally originate from the electrolyte and possibly the current collection arrangement, and thus dependent on geometric factors such as the cell component thickness and the contacts between the current collections on either electrodes and electrolytes [24]. It can thus be affirmed from the above results that, the SZCY541 electrolyte thickness and/or area specific ohmic resistance are quite comparable for both cells. Contrary we observe a difference in the electrode over-potentials for BGLC and BLC as shown in Fig 4(a, b) and thus confirming, the actual difference in performance may probably be emanating from the anode. It can be seen in Fig 4 (a) that the cell over-potentials for BLC increases gradually with current density and reach a value of 0.31 V at a current density of 0.5A cm−2 whereas the cell over-potentials for BGLC shows a remarkable increase, which is greater than the ohmic loss IR up to a current density of about 0.25A cm−2, thereafter stabilizes and reach a final value of 0.47V at 0.5A cm−2. These results suggest, the activation polarization, which is caused by electrochemical decomposition of steam and/or electrochemical generation of O2 on the BGLC anode is predominant in *η*AC, in the early current density region up to 0.25A cm−2 comparatively.

The evolution of hydrogen gas at the cathode on passing a direct current through the cell was confirmed by gas chromatography for both BGLC and BLC. Fig. 4 (a, b) also summarizes the hydrogen evolution rate at 600 ºC. The hydrogen production rate showed a deviation from the theoretical one calculated from Faraday's law in both cells. These deviations also confirm, besides the ionic currents, some amount of electronic current probably go through the electrolyte during the electrolysis process. Generally, ceramic protonic oxides show partial electron hole conduction in oxidative atmospheres [3, 7, 8]. These hole conduction are probably responsible for the partial electronic current leakages in this materials. A hydrogen evolution rate of 121.85 and 111.15 µmol cm-2 every minute was obtained for BLC and BGLC at 0.5A cm−2, translating to a current efficiency of 78 and 72 % respectively.

* 1. **Isotope labelling and Mass spectrum**

Figure 5 shows mass spectra for dense ceramic pellets of BGLC after drying the samples by annealing in dry oxygen (of natural isotopic abundance), and after subsequent exposure to a steam of artificial air humidified by bubbling through D2O at 46 ºC. The spectra were obtained whilst sputtering the sample with a low energy Ar+ beam to remove surface material, and hence the analysis is integrated over a depth of around 3 microns. The signals have been normalized to the intensity of the 18O- peak (the oxygen activity of the two annealing environments are the same, so the overall oxygen content is not expected to change) [25, 26]. The spectrum for the exposed sample clearly shows a peak for 2D16O- (*m/z* ~18.01) and D- (*m/z* ~2.014), indicating deuterium is incorporated into the sample. The fact that the deuterium signal persists even with sputtering away from the surface layers suggests that the deuteration of the sample is not merely due to surface adsorption or reaction with a segregated surface layer, but that deuterons are indeed incorporated into the bulk material [25, 26 ].



Fig. 5 Mass spectra of dried and D2O exposed BaGd0.8La0.2Co2O6−δ specimens (bulk analysis over ~3 microns)

Fig. 6 shows comparable data for a BLC ceramic subjected to the same drying and D2O exposure protocol.



Fig.6 Mass spectra of dried and D2O exposed Ba0.5La0.5CoO3−δ specimens obtained using a 2 keV Ar+ beam (bulk analysis over ~3 microns)

Again, whilst the drying anneal does effectively remove deuterons from the material bulk, they are incorporated with subsequent D2O exposure. The 2D16O- / 18O- ratio is lower in the BLC sample than for the BGLC sample as shown in Fig 5. Since the compositions are comparable, and Gd3+ is isovalent to La3+, it is not likely that the lower ratio is due to increased oxygen content; nor is it likely that the useful ion yield of oxygen will be very different for these similar materials. Thus, these data reflect a difference in the deuterium concentration, suggesting that the gadolinium-substituted composition is more readily protonated than the BLC. Our results also show an initial drop in the 16O2D- / 18O- signal ratio for both BGLC and BLC over the first ~300 nm. The initial high intensity is, possibly due to deuterium-containing species simply adsorbed on the surface. On the other hand, it is likely that the heat treatment has induced some segregation of barium [27], which may have reacted with the atmosphere to form hygroscopic phases such as BaCO3 and BaSO4 which are then deuterated by exposure to D2O. The present results also corroborate well with previous experimental data reported by Strandbakke *et. al* that BGLC can hydrate significantly higher than similar perovskites. However it seems that the incorporation of some protonic mobility in BGLC does not have a mark effect on the performance at 600 ºC, suggesting that, the oxygen ion mobility might probably be the most important factor at this temperature. Also the amount of protons (concentration) incorporated in BGLC and whether it can initiate a bulk transport path, is still under investigation. High ionic conductivity (>0.001S/cm) at intermediate-temperatures should in principle expand the active interphase in a H+-SOEC with BGLC and thus better performance. These results are just a snapshot of the performance at 600°C and it would be interesting to also look at the performances at much lower temperatures of 500 to 300 °C. While P-MIEC are quite desirable for H+-SOEC application a deeper understanding of all parameters determining device performance is required for further improvement.

1. **Conclusion**

Steam electrolysis was carried out at 600°C using a ~20μm SZCY541 electrolyte with Ni-SZCY541 composite as the H2-electrode and BLC,BGLC as the steam electrodes. Cell terminal voltages of 1.74 and 1.93 V, were observed at 0.5 A cm−2 for both BLC and BGLC corresponding to an area specific resistance of 1.9 and 2.3 Ω cm2 respectively. Hydrogen tracer diffusion studies using time-of-flight secondary ion mass spectrometry depth profiling confirm protons are incorporated into the bulk of BGLC relative to BLC however the present steam electrolysis results show a better performance for BLC at 600°C.

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