Ba0.5Gd0.8La0.7Co2O6 infiltrated BaZr0.8Y0.2O3- composite oxygen electrodes for protonic ceramic electrolysis cells

Wang, Q. J.; Ricote, S.; Hendriksen, P. V.; Wang, Y.; Wang, J. Q.; Chen, M.

Published in:
ECS Transactions

Link to article, DOI:
10.1149/10205.0003ecst

Publication date:
2021

Document Version
Early version, also known as pre-print

Citation (APA):
Wang, Q. J., Ricote, S., Hendriksen, P. V., Wang, Y., Wang, J. Q., & Chen, M. (2021). Ba0.5Gd0.8La0.7Co2O6 infiltrated BaZr0.8Y0.2O3- composite oxygen electrodes for protonic ceramic electrolysis cells. ECS Transactions, 102(5), 3-16. https://doi.org/10.1149/10205.0003ecst

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Ba$_{0.5}$Gd$_{0.8}$La$_{0.7}$Co$_2$O$_{6-\delta}$ Infiltrated BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ Composite Oxygen Electrodes for Protonic Ceramic Electrolysis Cells

Q. J. Wang$^a$, S. Ricote$^b$, P. V. Hendriksen$^a$, Y. Wang$^c$, J. Q. Wang$^c$, and M. Chen$^a$

$^a$ Department of Energy Conversion and Storage, Technical University of Denmark, Fysikvej, 2800 Kgs. Lyngby, Denmark
$^b$ Colorado School of Mines, 1500 Illinois Street, Golden, CO 80401, USA
$^c$ Key Laboratory of Interfacial Physics and Technology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China

In this study, a composite oxygen electrode is prepared by infiltrating a protonic-electronic conducting material, Ba$_{0.5}$Gd$_{0.8}$La$_{0.7}$Co$_2$O$_{6-\delta}$ (BGLC) into a proton-conducting BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ (BZY20) backbone. The composite oxygen electrode is studied in a symmetric cell configuration (BGLC-BZY20//BZY20//BGLC-BZY20). The electrochemical performance is characterized by varying the operating conditions, including temperature, oxygen, and steam partial pressures, with the purpose to identify and characterize the different electrochemical processes taking place in the oxygen electrode. Two electrode reaction processes are observed in the impedance spectra: one in the middle-frequency range (400 ~ 50 kHz) tentatively ascribed to the process of proton transfer from the electrode to the electrolyte, and the other in the low-frequency range (0.1 ~ 1 Hz) related to diffusion of O$^-$ species. The BGLC-BZY20 electrode developed in this work shows a low polarization resistance of 0.44, 1.17, and 2.87 $\Omega$ cm$^2$ in 3 % humidified synthetic air (21% O$_2$/79% N$_2$) at 600, 550, and 500 °C, respectively.

Introduction

Hydrogen is a promising link between the electricity, industry, and mobility sectors and appears as a unique energy carrier and energy storage solution (1)(2). Hydrogen can be produced via different routes; including thermal routes (natural gas reforming, biomass gasification and coal gasification), electrolytic routes (water splitting using input electricity from different sources), and photo-catalytic routes (splitting of water using sunlight through biological and electrochemical materials) (3)(4)(5). Industrially, today most hydrogen is produced from steam methane reforming. Among the different routes more green than steam methane reforming, protonic ceramic electrolysis cells (PCECs), which allow electrochemical conversion of surplus electricity into chemicals at intermediate or low temperatures, have attracted much attention due to the high efficiency, flexibility under diverse working conditions, and excellent performance. Unlike solid oxide electrolysis cells (SOECs), PCECs can produce directly dry
pressurized H\textsubscript{2} (electrochemical pressurization) at the fuel electrode without the multi-step gas separation (6).

PCECs are effectively protonic ceramic fuel cells (PCFCs) operated in reverse mode to convert electrical energy to chemical energy. The electrolyte and the hydrogen electrode of PCECs are similar to those for PCFCs; e.g. BaZr\textsubscript{x}Y\textsubscript{1-x}O\textsubscript{3-δ} (BZY) (7), BaCe\textsubscript{0.9-x}Zr\textsubscript{x}Y\textsubscript{0.1}O\textsubscript{3-δ} (BZCY) (8) or BaCe\textsubscript{0.7}Zr\textsubscript{0.1}Yb\textsubscript{0.2-x}Yb\textsubscript{x}O\textsubscript{3-δ} (BZCYYb) (9) for the electrolyte and mixtures of these with Ni for the hydrogen electrode. Additional research efforts for PCECs are needed on the oxygen electrode, where the electrode material should facilitate the oxygen evolution reaction (OER) in electrolysis mode, rather than the oxygen reduction reaction (ORR) in fuel cell mode. In PCECs, the oxygen electrode reactions involve water adsorption and splitting as well as oxygen release/proton transfer, leading to stringent requirements to the material composition and microstructure (10)(11)(12). Developing robust oxygen electrodes with high catalytic activity and chemical stability is imperative for the commercialization of intermediate temperature PCECs.

In developing high-performance oxygen electrodes, two strategies are often adopted; one is to look for new and superior materials, and the other one; to work with known materials but to optimize electrode microstructure with respect to active surface and interface area. The research and development of oxygen electrodes for protonic ceramic cells (PCCs) often follow strategies applied for the more mature case of oxygen electrodes for oxide-ion conducting solid oxide cells (O-SOCs). Many high-performance oxygen electrode materials originally developed for O-SOCs have also been tested for PCCs. Such examples include cubic-type perovskite oxides (ABO\textsubscript{3}) like La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} (LSM) (13) or La\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{1-y}Fe\textsubscript{y}O\textsubscript{3-δ} (LSCF) (14), Ruddlesden–Popper (RP) type oxides (A\textsubscript{n+1}B\textsubscript{n}O\textsubscript{3n+1}) including rare-earth nickelates La\textsubscript{2}NiO\textsubscript{4+δ} (LNO) (15) or Pr\textsubscript{2}NiO\textsubscript{4+δ} (PNO), and double-perovskite oxides (AA’B\textsubscript{2}O\textsubscript{6}) like Sr\textsubscript{2}Fe\textsubscript{1.5}Mo\textsubscript{0.5}O\textsubscript{6-δ} (SFMO) (16), BaLnCo\textsubscript{2}O\textsubscript{5+δ} (Ln = La, Pr, Nd, Sm a Gd), (BLnCO) compounds (17). Recently, Strandbakke et al. proposed a novel oxygen electrode materials, Ba\textsubscript{0.5}Gd\textsubscript{0.8}La\textsubscript{0.7}Co\textsubscript{2}O\textsubscript{6−δ} (BGLC) (18). The partial substitution of Ba with Gd and La results in material providing low apparent polarization resistance and high electronic conductivity (10)(19). Additionally, this material shows considerable proton conductivity in humidified atmosphere. To further maximize the active area of the electrode, efforts have been devoted to developing single-phase triple conducting (H\textsuperscript{+}/O\textsubscript{2−}/e\textsuperscript{−}) oxides, such as NdBa\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1.5}Fe\textsubscript{0.5}O\textsubscript{5-δ} (NBSCF) (20), PrBa\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{1.5}Fe\textsubscript{0.5}O\textsubscript{5+δ} (PBSDC) [20], LiNi\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{2} (LNO) (21), Ba\textsubscript{0.5}Sr\textsubscript{0.5}Fe\textsubscript{0.8}Zn\textsubscript{0.2}O\textsubscript{3-δ} (BSFZ) (22), BaCo\textsubscript{0.4}Fe\textsubscript{0.1}Zr\textsubscript{0.1}Y\textsubscript{0.1}O\textsubscript{3-δ} (BCFZY0.1) (23), BaCe\textsubscript{0.4}Fe\textsubscript{0.4}Co\textsubscript{0.2}O\textsubscript{3} (BCFC) (24) and Ba\textsubscript{0.9}La\textsubscript{0.05}Fe\textsubscript{0.8}Zn\textsubscript{0.2}O\textsubscript{3-δ} (BLSFZn5) (25). With regard to tailoring the electrode microstructure, previous studies have employed several different routes for deriving an optimal micro-morphology. This includes making composite electrodes by merely mixing two or more phases with different beneficial properties in an appropriate ratio (26), impregnating a protonic conducting “backbone” with suitable electro-catalysts (27), in-situ exsolation of nano-particles (28) to boost performance, incorporating 3D nanofibers (made by electrospinning), or finally depositing a tailored functional layer between the oxygen electrode and the electrolyte (29)(30).

In this work, we report on a composite oxygen electrode developed by infiltrating a mixed protonic-electronic conducting oxide; Ba\textsubscript{0.5}Gd\textsubscript{0.8}La\textsubscript{0.7}Co\textsubscript{2}O\textsubscript{6−δ} (BGLC), in the
following referred to as a “MPEC-material”, into a proton-conducting BaZr$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ (BZY20) backbone. In a composite oxygen electrode made of a proton-conducting phase and a conventional mixed (oxygen ion) ionic and electronic conducting (MIEC) phase (Figure 1a), the triple-phase boundaries (TPB) are limited to the electrode-electrolyte interface. By replacing the MIEC with a MPEC, the TPB sites for water splitting reactions (WSR) are extended to the whole surface of the MPEC phase (shown in Figure 1b). In the composite electrode based on a MPEC two potential pathways for proton transport to electrolyte exist: surface pathway and bulk pathway, which simultaneously influence electrochemical activities. The BGLC catalysts is introduced into the electrode structure by infiltration. This ensures: (1) Particle size of the infiltrated catalyst in the sub-100 nm range, which creates a large surface area and improves the surface-catalytic behavior; (2) Improved compatibility between the electrode and the electrolyte; and, finally (3) the low-temperature calcination that prevents cation inter-diffusion. The manufactured electrodes are characterized by electrochemical impedance spectroscopy under various conditions to elucidate which processes that limit performance.

![Figure 1](image)

**Figure 1.** Potential reaction paths at the composite oxygen electrode for PCEC, containing a proton-conducting phase and (a) a mixed O$_2^-$/e$^-$ conducting phase or (b) a mixed H$^+$/e$^-$ conducting phase.

### Experimental

**Sample Preparation**

The symmetrical cells consist of a dense BZY20 electrolyte and two identical BGLC-BZY20 electrodes. The BZY20 precursor powder for the electrode backbone was prepared by solid-state reaction using stoichiometric amounts of barium carbonate (Alfa Aesar, 99.8%), zirconium oxide (Alfa Aesar, 99+ %), and yttrium oxide (Alfa Aesar, REacton ® 99.9% (REO)). The mixture of the precursors was calcined at 1400 °C for 24 h. The BZY20 electrolyte pellets were prepared by solid-state reactive sintering, as described in previous work (31). Shortly, the mixture of precursors (similar to solid-state reaction) was mixed with 1 wt. % of NiO. This mixture was pelleted by uniaxially pressed at 2500 lbs for 10s, and the samples were subsequently sintered at 1550 °C for 6 h on a bed of BZY20 powder. After sintering, the pellets were polished down to a thickness of ~ 800 µm.
The electrode backbone slurry was prepared by mixing the BZY20 pre-synthesized powder with 4 wt.% NiO and 3 wt.% ethylcellulose in alpha terpineol. Subsequently, the slurry was painted on both sides of the BZY20 electrolyte pellets and fired at 1350 °C in air for 3 h to form a porous BZY20 backbone structure. Electrolyte-supported porous BZY20 // dense BZY20 // porous BZY20 symmetrical cells with a geometrical electrode area of 0.65 cm² per side were obtained.

The BGLC infiltration solution with a concentration of 0.3 mol L⁻¹ was prepared as follows: (1) First, stoichiometric amounts of BaCO₃ with purity of 99.8% (wt.%), Gd(NO₃)₃·6H₂O (99.9%), La(NO₃)₃·6H₂O (99.9%), and Co(NO₃)₂·6H₂O (98%) were dissolved in deionized water. (2) The complexation agent of ethylenediaminetetraacetic acid (EDTA, 99%) and citric acid (99.5%) were added according to a molar ratio of EDTA/citric acid/metal ions = 1:2:1. (3) After the pH value was adjusted to 7 by adding appropriate amounts of ammonia water, the solution was stirred continuously for 2 h during heating (80 °C) to form a precursor solution. A surfactant; Pluronic® P123 (1.7 wt %) was added to improve wetting/penetration properties of the solution. Afterward, the BZY20 backbones were infiltrated with the BGLC solution. The solution was observed to spread over the entire surface and was sucked into the pores of the backbone by capillary forces, followed by calcination at 300 °C in air for 15 min. The infiltration processes were repeated seven times to ensure that the pores of the backbone were completely filled. Finally, the symmetrical cells were calcined at 700 °C in air for 2h.

**Electrochemical Characterization**

The electrochemical performance and durability of the symmetrical cells were tested in an in-house built one-atmosphere testing rig, as described in previous work (32)(33). To perform electrochemical measurements, Pt paste was used as the current collector on both electrodes. The cells were heated in dry synthetic air (21% O₂/79% N₂) to 600 °C with a heating rate of 1 °C min⁻¹. The electrochemical performance of the cells under various oxygen and steam partial pressures was evaluated in the temperature range between 500 and 600 °C. In order to make sure that the samples were at equilibrium when collecting spectra, a dwell time of 2 h was employed after each change in conditions. The partial pressure of O₂ was controlled by adjusting the flow rate ratios of N₂/O₂. The total gas flow to the setup was kept at 100 mL min⁻¹. The steam was produced by passing the feed gas flow through a water bubbler, and the steam content was varied by adjusting the water temperature. The electrochemical performance of the cells was characterized by electrochemical impedance spectroscopy (EIS) using a Solartron 1260 frequency response analyzer at frequencies from 96485 to 0.06 Hz with an amplitude of 0.33 V. The in-house developed Python-based software Ravdad was used for plotting and analyzing the EIS data (34).

**Structure Characterization**

The prepared materials were analyzed after each synthesis step by the X-ray diffraction (XRD, Rigaku Minflex 600) with a scanning range from 20-80°, a scanning speed rate of 5° min⁻¹. The microstructure and morphology of the BGLC-BZY20 composite electrodes were further investigated using a field emission scanning electron microscope (FE-SEM, Zeiss Ultra) with an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS)
characterizations were carried out using a Tecani-G2 T20 and F20 operated at an acceleration voltage of 200 kV. The samples for TEM measurements were prepared based on the standard lift-out procedure using a Zeiss Crossbeam 540 dual-beam system equipped with an Oxford OmniProbe 400 micromanipulator.

Results and Discussion

Structure Analysis

Figure 2 presents the XRD patterns of the as-synthesized BGLC powder, the BZY20 backbone, and the BGLC-BZY20 composite electrode. The BGLC powder was synthesized by calcining the infiltration catalyst solution at 700 °C in air for 2 h and phase-pure BGLC was obtained as confirmed by Figure 2a. The diffractogram in Figure 2b was collected on a BZY20//BZY20//BZY20 symmetrical cell (prior to infiltration), where only the BZY20 phase is observed. Figure 2c shows the X-ray diffraction pattern of the BGLC infiltrated BZY20 composite electrode calcined at 700 °C in air for 2 h. Peaks corresponding to pure phases of BZY20 and BGLC are identified, and no distinct reaction product between BGLC and BZY20 could be observed.

Figure 2. XRD patterns of (a) BGLC powder synthesized from the infiltration solution (700 °C in air for 2 h); (b) the BZY20 electrode backbone; (c) the BGLC infiltrated BZY20.
Figure 3 presents SEM images on the fractured cross-sections of symmetrical cells without and with infiltration. As illustrated in Figure 3a, dense BZY20 electrolyte without noticeable pores or cracks is obtained, and the adhesion between the BZY20 backbone electrode appears good. Figure 3b shows a high magnification SEM image of the porous backbone which reveals a fairly uniform microstructure suitable for catalyst infiltration and gas diffusion. Figures 3c and 3d display the BGLC-BZY20/BZY20 interface and a high magnification of the BGLC-BZY20 composite electrode, respectively.

The BGLC-BZY20 oxygen electrode appears well attached to the BZY20 electrolyte (Figure 3c). BGLC nano-particles (50 ~ 100 nm) are well deposited on the internal surfaces of the porous BZY20 backbone (Figure 3d) providing a continuous porous film with a thickness in the range of 0.1 µm. Distinct particles/grains can be observed in the film and the catalyst coating increases the overall surface area available for the electrode reaction as targeted.

![SEM images](image_url)

**Figure 3.** SEM images on the fractured cross-sections of symmetrical cells without and with infiltration showing (a) the interface between BZY20 backbone and BZY20 electrolyte; (b) BZY20 oxygen electrode backbone; (c) the interface between the BGLC infiltrated BZY20 composite oxygen electrode and the BZY20 electrolyte; (d) BGLC infiltrated BZY20 composite oxygen electrode.

Electrochemical Performance Under Different Temperatures
EIS measurements were performed on the infiltrated cells under open-circuit (OCV) condition in 3% humidified synthetic air (21% O\textsubscript{2}/79% N\textsubscript{2}) in the 600-500 °C range. Nyquist plots of the measured EIS are reproduced in Figure 4a. To deconvolute the overall impedance into different reaction processes, an equivalent circuit model consisting of a resistance and an inductance element (L-R\textsubscript{S}) in series with three series connected RCPE elements (RCPE: a resistor (R) in parallel connection with a constant phase element (CPE)) was used to fit the EIS data: \(LR\textsubscript{S}(R\textsubscript{1}CPE\textsubscript{1})(R\textsubscript{2}CPE\textsubscript{2})(R\textsubscript{3}CPE\textsubscript{3})\). The different arcs were tentatively assigned to the different reaction steps according to the associated pseudo-capacitance values (C). The first and second arcs (\(R\textsubscript{1}, R\textsubscript{2}\)), with pseudo-capacitances \(C\textsubscript{MF}\) of \(10^{-4} \sim 10^{-6}\) F cm\textsuperscript{-2} and summit frequency between 400 to 50 kHz, are referred to as \(R\textsubscript{M}\) (middle-frequency contribution). The third arc (\(R\textsubscript{3} = R\textsubscript{L}\)) with \(C\textsubscript{LF}\) of \(10^{0} \sim 10^{1}\) F cm\textsuperscript{-2} and frequency between 0.1 and 1 Hz is referred to as the low-frequency resistance. The sum of \(R\textsubscript{M}\) and \(R\textsubscript{L}\) corresponds to the total polarization resistance (\(R\textsubscript{P}\)). As shown in Figure 4a, the \(R\textsubscript{P}\) for the infiltrated BGLC-BZY20 backbone electrodes are 0.44, 1.17, and 2.87 Ω cm\textsuperscript{2} in 3% humidified synthetic air (21% O\textsubscript{2}/79% N\textsubscript{2}) at 600, 550, and 500 °C, respectively. The activation energy of \(R\textsubscript{S}\), the pure ohmic part of the impedance, is 0.54 eV, which is within the range of activation energies reported for typical proton conducting oxides (0.3-0.6 eV) (35)(36). Figure 4b presents the Arrhenius plot for the polarization resistance, as well as for \(R\textsubscript{M}\) and \(R\textsubscript{L}\). Both \(R\textsubscript{M}\) and \(R\textsubscript{L}\) are strongly thermally activated processes. Hence, it can be concluded that these are not associated with mass transport processes in the gas phase as this would be virtually temperature-independent (37).

Previous studies have attempted to describe the overall oxygen electrode reaction mechanism and the rate-limiting step(s) (ORR in PCFC mode, OER, WSR in PCEC mode, respectively) for various electrode materials, such as Sm\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3-δ} (SSC) (38)(39), La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3-δ} (LSCF) (40) and BaCo\textsubscript{0.4}Zr\textsubscript{0.1}Fe\textsubscript{0.4}Y\textsubscript{0.1}O\textsubscript{3-δ} (BCZFY) (41) and relate to electrode compositions, but without coming to a simple consensus. Table 1 summarizes the possible elementary reaction steps at the oxygen electrode for PCC as reported in the literature (42)(43)(38), and it shows totally reversed reaction steps in PCFC and PCEC modes. It is worth mentioning that all the measurements in this work were conducted under OCV. Hence, only ORR and water adsorption and dissociation reactions can happen on the BGLC-BZY20 oxygen electrode surface. The \(R\textsubscript{M}\) and \(R\textsubscript{L}\) can be associated with one of the steps or a convoluted process listed in Table 1. The capacitance value is a strong indicator of the process involved in the oxygen electrode reaction kinetics, and it can give a fingerprint for interface, surface or bulk reaction mechanisms (44). Based on the above-observed capacitance values in middle- and low-frequency range, \(R\textsubscript{M}\) (\(R\textsubscript{1} + R\textsubscript{2}\)) may represent the interfacial process, for example, the charge or ion transfer through the electrode/electrolyte interface (i.e. proton transfer from the electrode to the electrolyte). \(R\textsubscript{L}\) (\(R\textsubscript{3}\)) may be ascribed to oxygen surface exchange reactions, such as oxygen adsorption on the electrode surface, oxygen dissociation into two oxygen atoms or oxygen ion diffusion on the electrode surface (8)(45)(46)(26)(15). However, it cannot be excluded that one of the contributions observed in the impedance spectra could be associated with other oxygen electrode reaction processes or a convoluted process.
Figure 4. (a) Impedance spectra of the symmetric cells measured in humidified (3% H$_2$O) synthetic air from 600-500 °C under OCV together with fitted spectra using a three-arc equivalent circuit model and (b) Temperature dependence of the resistances ($R_S$, $R_M$, and $R_L$) derived from the EIS and the calculated activation energy.

TABLE 1. Possible elementary oxygen electrode reaction steps in PCCs modified after literature (38)(43).

<table>
<thead>
<tr>
<th>PCEC</th>
<th>$H_2O(g) \rightarrow H_2O(ad)$</th>
<th>Water adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2O(ad) \rightarrow OH^{+}(ad) + H^{+}(ad)$</td>
<td>Water dissociation</td>
</tr>
<tr>
<td></td>
<td>$OH^{+}(ad) \rightarrow O^{2+}(ad) + H^{+}(ad)$</td>
<td>Water dissociation</td>
</tr>
<tr>
<td></td>
<td>$O^{2+} - e^- \rightarrow O$(ad)</td>
<td>Oxygen oxidation</td>
</tr>
<tr>
<td></td>
<td>$O$(ad) $- e^- \rightarrow O$(ad)</td>
<td>Oxygen oxidation</td>
</tr>
<tr>
<td></td>
<td>$O_2(ad) \rightarrow O_2$</td>
<td>Oxygen formation</td>
</tr>
<tr>
<td></td>
<td>$H^+$(ad) $\rightarrow H^+$(TPB)</td>
<td>Oxygen desorption</td>
</tr>
<tr>
<td></td>
<td>$H^+$(TPB) $\rightarrow H^+$(electrolyte)</td>
<td>Proton transfer</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PCFC</th>
<th>$O_2(g) \rightarrow 2O_{ad}$</th>
<th>Oxygen adsorption and splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$O_{ad} + e^- \rightarrow O_{ad}^-$</td>
<td>Oxygen reduction</td>
</tr>
<tr>
<td></td>
<td>$O_{ad}^- \rightarrow O_{TPB}$</td>
<td>Oxygen surface diffusion toward the reaction site</td>
</tr>
<tr>
<td></td>
<td>$O_{TPB} + e^- \rightarrow O_{TPB}^-$</td>
<td>Oxygen reduction</td>
</tr>
<tr>
<td></td>
<td>$H^+$(electrolyte) $\rightarrow H^+$(TPB)</td>
<td>Proton migration toward the reaction site</td>
</tr>
<tr>
<td></td>
<td>$H^+$(TPB) + $O_{TPB}^-$ $\rightarrow OH^+$(TPB)</td>
<td>Hydroxide formation</td>
</tr>
<tr>
<td></td>
<td>$OH^+$(TPB) + $H^+$(TPB) $\rightarrow H_2O$(TPB)</td>
<td>Water formation</td>
</tr>
<tr>
<td></td>
<td>$H_2O$(TPB) $\rightarrow H_2O(g)$</td>
<td>Water desorption</td>
</tr>
</tbody>
</table>

Electrochemical Performance Under Different P(O$_2$)

To further investigate the nature of different resistance contributions, the electrodes were characterized under different P(O$_2$) at 500 °C. The spectra were fitted as previously with an $LR_S(R_1CPE_1)(R_2CPE_2)(R_3CPE_3)$ equivalent circuit model. Figure 5a shows the impedance spectra of the symmetrical cells at 500 °C under varying the O$_2$/N$_2$ ratio from 100/0 to 1/99. Both $R_S$ and $R_P$ increase with decreasing P(O$_2$). It is speculated that the oxidation state of Co in the BGLC phase may affect the ORR/OER. In general, the oxygen exchange reaction rate on oxide electrodes increases with increasing P(O$_2$). The P(O$_2$) may also affect the reaction rate via its effect on the hole concentration in the
electrode which increases with increasing \( P(O_2) \) \((18)\). Figure 5b represents the isothermal analysis of \( R_P \), \( R_M \), and \( R_L \) resistance contributions as a function of \( P(O_2) \) at constant \( P(H_2O) \) \((\sim 3\%)\). The dependence of \( R_M \) and \( R_L \) on \( P(O_2) \) is fitted using a power law, \( R_i \alpha (P(O_2))^m \), where \( m \) is the apparent reaction order of \( R_i \) with respect to \( P(O_2) \). With increasing \( P(O_2) \), both contributions \((R_M, R_L)\) decrease, and consequently, so does \( R_P \). The strongest dependence is observed for \( R_L \) with a linear correlation of \((P(O_2))^{-0.203}\). He et al.[40] reported a \( Sm_{0.5}Sr_{0.5}CoO_3–δ–BaCe_{0.8}Sm_{0.2}O_3–δ \) (SSC-BSC) composite cathode with a reaction order of \( m = 0.25 \), slightly higher than the value reported in the current work \((0.203)\). They linked the process to the diffusion of \( O^- \) species along the SSC surface to triple surface boundaries \( (TPBs) \). \( R_M \) shows a weaker oxygen partial pressure dependence of \( 0.116 \), consistent with the small value of chemical capacitance. \( R_M \) is likely associated with the ion transfer through the electrode/electrolyte interface since the charge transfer step and proton transport across the BGLC and BZY20 phases are independent of \( P(O_2) \) \((37) \) \((40)\).

![Figure 5](image_url)

**Figure 5.** (a) Impedance spectra of the symmetric cells measured at 500 °C under different oxygen particle pressures \( P(O_2) \), always with 3% \( H_2O \), together with the fitted curves. (b) Dependence of \( R_P \), \( R_M \), \( R_L \) as a function of \( P(O_2) \) at 500 °C.

**Electrochemical Performance Under Different \( P(H_2O) \)**

In this work, impedance spectra were also recorded with three different degrees of humidification: 3%, 5%, and 10%, under OCV at 500 °C in synthetic air. A low temperature of 500 °C was chosen to ensure that the proton conduction plays a dominant role in the ionic conduction. The experimental and fitted impedance spectra are presented in Figure 6a. The results clearly show that the presence of steam has a negative influence on the oxygen electrode performance. The increase in electrode polarization resistance with \( P(H_2O) \) could be related to the presence of steam at the \( TPBs \): the surface sites may be occupied by adsorbed steam, hindering the low-frequency ORR steps of surface oxygen adsorption, dissociation, and diffusion. Similar to the results under different \( P(O_2) \), under varying \( P(H_2O) \), the same two electrode reaction processes \( R_M \) and \( R_L \) are
identified. The dependence of $R_M$ and $R_L$ on $P(H_2O)$ is illustrated in Figure 6b. A fairly linear dependency between Log($R$) and Log($P(H_2O)$) is observed, for $R_M$, $R_L$, and $R_P$. The increase of the steam concentration from 3% to 10% leads to an increase in $R_M$, which was tentatively ascribed to proton transfer from the electrode to the electrolyte. He et al. reported a negative dependence of the electrode resistance on $P(H_2O)$ for SSC-BSC oxygen electrode (38). The different behavior for BGLC-BZY20 and SSC-BSC could be due to the difference in the ionic transport pathways and localization of the active sites for electrode reactions.

![Figure 6](image)

Figure 6. (a) Impedance spectra of the symmetrical cells measured at 500 °C in synthetic air with different $P(H_2O)$, together with fitted curves; (b) Dependence of $R_P$, $R_M$, $R_L$ on $P(H_2O)$ at 500 °C.

**Durability**

The durability of the oxygen electrodes was further examined under humidified (10% H$_2$O) synthetic air at 600 °C. The symmetrical cell was characterized via electrochemical impedance spectroscopy at open circuit voltage (OCV). Figure 7a, b present the measured impedance spectra and the deduced $R_S$, $R_P$ values of the symmetrical cell as a function of testing time. The BGLC-BZY20//BZY20//BGLC-BZY20 cell displays initially good stability without obvious degradation within the first 350 h. There is very little change in the impedance spectra and hence the deduced $R_S$ and $R_P$ values for the periods up to 350 h. The cell, however, starts degrading afterwards. Fractured cross-sections of the tested symmetrical cell were subjected to SEM analysis to clarify the mechanisms behind the observed impedance degradation. As shown in Figure 7c, no layer delamination or formation of cracks is observed in the tested cell. On the other hand, exposure to steam seems to cause some decomposition of the electrode materials and formation of the secondary phase with a sheet-like morphology (flakes) all over the electrode surface (Figure 7d). The formation of these new phase flakes on the surface of the BGLC phase could be one of the reasons accounting for the degradation of the BGLC-BZY20 oxygen electrode.
Figure 7. (a) Time evolution of the symmetrical cell EIS measured at 600 °C in humidified (10% H₂O) synthetic air; (b) Rs, Rp as a function of testing time deduced from the measured EIS; (c) SEM image on the fractured cross-section of the symmetrical cell after stability testing; (d) High magnification SEM image of the BGLC-BZY20 oxygen electrode.

XRD and TEM analyses on the tested BGLC-BZY20 electrode were further carried out to investigate the observed structural/phase changes. Figure 8a presents the XRD plot of the oxygen electrode after testing. Pt peaks are present because Pt paste was applied as current collector for the symmetrical cell testing. In addition to the BZY20 and BGLC peaks, minor peaks corresponding to BaCoO₃ and BaCO₃ were also identified. The existence of these secondary phases was further confirmed by high-resolution transmission electron microscopy (HRTEM) images, as shown in Figure 8b-e. The HRTEM analysis on the region with the flake morphology revealed a lattice spacing of 0.28 nm (Figure 8c), consistent with the reported lattice distance of (020) planes of monoclinic BaCoO₃ determined from XRD analysis (0.281 nm). Additionally, a lattice spacing of 0.50 nm is also found (shown in Figure 8d), very close to the lattice spacing of 0.496 nm between the two (110) planes of the monoclinic BaCoO₃ (47). Note that BaCoO₃ has been demonstrated to have some electrochemical activity when applied as catalyst for oxygen electrodes. Its flake-like morphology structure can further extend the reaction sites (48). Hence, the BaCoO₃ secondary phase formed in the BGLC-BZY20 electrode may not necessarily be detrimental to the electrode performance. The EDS mapping shown in Figure 8e also suggests the formation of carbonate, most likely BaCO₃, as also detected by XRD. From this post-mortem analysis, we conclude that the surface of the BGLC phase is covered by BaCoO₃ and BaCO₃. While BaCoO₃ is not detrimental
to the electrode performance, BaCO$_3$ probably inhibits the proton transfer process which could contribute to the observed electrode performance degradation. When Ba is lost from the compound (to form Ba-carbonate and Ba-cobaltite) the defect concentrations in the modified BGLC phase change, which could impede the electrode process.

Figure 8 (a) XRD pattern of the BGLC-BZY20 oxygen electrode after long-term testing at 600 °C in humidified (10% H$_2$O) synthetic air; (b) High-resolution transmission electron microscopy (HRTEM) images of the BGLC-BZY20 oxygen electrode; (c) and (d) the sheet-like morphology (flakes) taken from various spots; (e) Energy-dispersive X-ray spectroscopy (EDS) maps of Ba, C, O.

**Conclusion**

In this work, a composite oxygen electrode for PCECs was successfully prepared by infiltrating mixed protonic-electronic conducting Ba$_{0.5}$Gd$_{0.8}$La$_{0.7}$Co$_2$O$_{6-\delta}$ into proton-conducting BZY20 backbone. The electrochemical performance of the BGLC-BZY20 composite electrode was investigated at different temperatures, $P$(O$_2$) and $P$(H$_2$O). Decent electrochemical performance was obtained with the BGLC-BZY20 oxygen electrode, showing an electrode polarization resistance of 0.44, 1.17, and 2.87 Ω cm$^2$ in 3 % humidified synthetic air at 600, 550, and 500 °C, respectively. Based on the chemical capacitance values and frequency ranges, two distinct electrode reaction processes were observed, one possibly representing the proton transfer from the electrode to the electrolyte, whereas the other is speculated to be related to diffusion of O$^-$ species. The symmetrical cells were also exposed to a 480 h durability test at 600 °C in 10 % humidified synthetic air. The cell showed no degradation in the first 350 hours but
degraded afterwards. XRD and TEM analyses of the tested electrode indicate that the degradation could be caused by the formation of BaCO₃ on the electrode surface.

Acknowledgments

Qingjie Wang acknowledges financial support from the China Scholarship Council (CSC201807040049) and from DTU Energy. The authors would like to thank H. Henriksen for technical assistance with cell testing.

References

34. C. R. Graves, **4**, 1 (2011).