Electrical properties of proton-conducting $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ and the effects of bromine addition

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Abstract

A detailed analysis of the electrical properties of the proton-conducting $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ phase (BCY20) and the effects of Br doping has been undertaken. Members of the system of nominal stoichiometry $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9-(x/2)\pm\delta}\text{Br}_x$ ($x = 0, 0.05, 0.1$ and 0.2) were synthesised by a citrate-nitrate process and high-temperature annealing up to 1500°C . X-ray diffraction revealed the formation of single-phase material with a monoclinically distorted perovskite structure (space group I2/m) with greater distortion for Br-synthesised phase. Significant contrasts in electrical behaviour and stability between BCY20 and Br-synthesised series members were also found. However, chemical analysis by total X-ray fluorescence spectroscopy indicated that only trace amounts of Br remain after synthesis, indicating that Br addition influences stoichiometry but not directly the physicochemical properties. Higher conductivity is observed for the Br-synthesised compositions in wet and dry oxidising conditions in the temperature range $300\text{--}900^\circ\text{C}$, reaching a value of $5.8\text{ S}\cdot\text{m}^{-1}$ at 800°C for the $x = 0.2$ member in wet O_2 ($\text{pH}_2\text{O} \sim 0.022$ atm). Determination of partial-conductivity components indicated that, in humid conditions and low temperature, conductivity of 20% Br-synthesised material is principally protonic ($t_{\text{H}} = 0.91$ at 600°C and $\text{pO}_2 = 0.2$ atm) and superior to that of BCY20. Mixed oxide-ionic-electronic conductivity dominates at high pO_2 (1 atm) and oxide-ionic conductivity at low pO_2 ($\sim 10^{-4}$ atm) in the temperature range $600\text{--}900^\circ\text{C}$ for both BCY and Br-doped samples. Stability was found to be poorer in CO_2 for the Br-synthesised phases as determined by thermogravimetry and prolonged conductivity measurements.

Keywords: yttrium-doped barium cerate (BCY); bromium-doped BCY; proton conducting electrolytes; partial conductivities; transport number

1. Introduction

The high proton conductivity of doped barium-cerate perovskites offers numerous possibilities for high-temperature electrochemical applications involving hydrogen. These include its conversion to electrical energy in protonic ceramic fuel cells [1,2], hydrogen production via electrolysis cells [3] and membrane reactors for the separation of hydrogen [4] coupled with useful reactions such as reduction of CO₂ [5], or the non-oxidative conversion of natural gas to aromatics [6]. The poor stability of BaCeO₃-based proton conductors [7], arising from the basic nature of the large cations, has led more recent research to focus on Zr-doped compositions such as BZCY72 [6,8,9]. The substitution of Ce with Zr enhances stability at the expense of sinterability [10] and also conductivity due, in part, to high grain-boundary resistances of BaZrO₃-based phases.

An alternative but, until recently, little explored strategy is to dope the oxide sublattice with halogen anions in order to lower the basicity of the anion network, thereby offering the possibility of enhanced stability in acidic gases such as CO₂ and high water-vapour partial pressures [11–13]. Although Cl and Br atoms are less electronegative (more basic) than elemental O, it may be expected that the lower charge of the monovalent halogen anions imparts less basic character in the O²⁻ anion network leading to improved stability of halogen-doped materials in acidic environments. Wang *et al.* [11] reported improved stability and higher proton conductivity in Cl-doped BaCe_{0.8}Sm_{0.2}O_{3-δ}, whereas Su and co-workers demonstrated a power density improvement of 20 % in a single cell PCFC with a F-doped BaCe_{0.8}Sm_{0.2}O_{3-δ} electrolyte compared to the halogen-free analogue with negligible degradation after 146 hours [14]. On employing F, Cl and Br as anion dopants in BaCe_{0.9}Gd_{0.1}O_{3-δ}, Zhou *et al.* reported that the halogens enter the lattice without structural changes while at the same time either lowering conductivity in air (F and Cl) or having a slightly positive effect on transport (Br) [12]. All these studies involve high-temperature annealing in the range 1375-1450 °C to sinter prepared powders into dense, gas-tight membranes.

Here, we report the synthesis of BaCe_{0.9}Y_{0.1}O_{3-δ} with a range of nominal concentrations of Br doping in the BaCe_{0.8}Y_{0.2}O_{2.9-(x/2)±δ}Br_x system (0 ≤ x ≤ 0.2), and assess the effects of Br as additive on phase composition, including the effects of high-

temperature firing. The differences in structure, stability and electrical conductivity of the parent BCY20 material and the phases prepared with Br are studied in detail.

2. Experimental

Samples with nominal stoichiometry $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9-(x/2)\pm\delta}\text{Br}_x$ ($x = 0, 0.05, 0.1$ and 0.2) were synthesised by a citrate-nitrate process based on the Pechini method using $\text{Ba}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, and $\text{BaBr}_2 \cdot x\text{H}_2\text{O}$ precursors. The water content of the nitrates was determined by thermogravimetry in air with an SDT Q600 instrument. The reactants were mixed in deionised water heated at $\sim 50^\circ\text{C}$ on a hotplate with continuous stirring. Citric acid and ethylene glycol were then added in molar ratios of 10:1 and 40:1 with respect to the final product and the solution held for 30 min before heating in the range $60\text{--}80^\circ\text{C}$ for ~ 2 h; the temperature was then raised to $\sim 100^\circ\text{C}$ and maintained for over 12 hours to obtain a dark-brown polymerized complex. The polymer was pyrolysed in an oven at 350°C for 4 h, milled in an agate mortar with acetone, heated at 600°C for a further 4 h then milled again. The obtained powders were then heat treated at 1100°C for 4 h in order to eliminate any remaining organic product, prior to attrition milling and sieving ($100\ \mu\text{m}$). Sintered samples were prepared from this powder by uniaxial pressing of cylindrical pellets and firing in the range $1300\text{--}1500^\circ\text{C}$ for 4h. Density was determined by careful measurement of the mass and geometrical volume; relative density was then calculated as a percentage of the theoretical X-ray unit-cell density.

Completeness of reaction and phase purity were determined by powder X-ray diffraction (XRD) on a Bruker D8 high-resolution diffractometer, using monochromatic $\text{Cu K}\alpha_1$ radiation ($\lambda=1.5406\ \text{\AA}$) obtained with a germanium monochromator. Material was prepared for XRD by removing the surface layer from sintered pellets before grinding to a fine powder. Rietveld refinement of crystal structures was performed with the Fullprof program [15] using powder XRD data collected over the range $15 \leq 2\theta \leq 100^\circ$ with a stepwidth of 0.02° (2θ) on the same instrument. The microstructures of fracture surfaces were analysed with a Hitachi S-4700 field emission scanning electron microscope.

Direct Solid Analysis (DSA) procedures proposed by Fernández-Ruiz *et al.* [16,17] were adopted for total-reflection X-ray fluorescence (TXRF) spectrometry to analyse the mass ratios of Ba, Ce, Y and Br. Measurements were performed with a benchtop S2 PicoFox spectrometer from Bruker Nano (Germany), equipped with a Mo X-ray source operating at 50 kV and 600 μA , a multilayer monochromator with 80 % of

reflectivity at 17.4 keV (Mo K α), a XFlash SDD detector with an effective area of 30 mm² and a resolution greater than 150 eV for 5.9 keV (Mn K α). The acquisition time was 500 seconds for all evaluated TXRF spectra. Suspensions for TXRF samples were prepared by initially grinding 25 mg of sample in an agate mortar for 5 min. An aliquot of 1 mL of water was then added to the mortar and then the sample was further ground during 15 min to obtain a homogeneous suspension. Subsequently, 200 μ L of Triton X-100 at 2% (v/v) was added to improve the suspension stability followed by the addition of 50 mL of Milli-Q water. Suspensions were sonicated and agitated by vortex to prevent possible particle agglomeration and local sedimentations prior to taking an aliquot of sample for deposition over the sample support. Solid suspensions (5 μ L) were then deposited over quartz reflectors and dried on a hot plate at 70° C in a class A-100 laminar flow chamber.

Thermogravimetric analysis (TGA) was performed with an initial heating-cooling cycle in air followed by heating in the range 40 – 900 °C in 10% CO₂: 90% Ar with a heating rate of 10 °C.min⁻¹ employing a Setaram Setsys Evolution 1700 system to check stability against carbonation.

Sintered and polished pellet faces were coated with Pt paste (Heraeus CL11-5349) and electrodes for electrical measurements prepared on heating at 950 °C for 1h. Impedance spectroscopy was performed in the temperature range 300-900 °C employing a signal amplitude of 50 mV in potentiostatic mode with an Autolab PGStat302N-FRA2 instrument operating over the frequency range $0.1 \leq f \leq 10^6$ Hz. Samples were measured on cooling in steps of 50 °C in wet and dry atmospheres of O₂ and N₂ via electronic mass-flow controllers (Bronkhorst). Dry gas was circulated through a drying column containing a commercial humidity trap of aluminosilicate- and zeolite-based beads (Supelco); humidification was achieved on bubbling the gases through KBr-saturated H₂O at room temperature (maximum water content ~ 0.022 atm).

The effect of oxygen partial pressure and water partial pressure on the electrical properties was simultaneously investigated by isothermal analysis of the pO₂-dependence of conductivity at various conditions of pH₂O [8,18,19] employing impedance spectroscopy with the same frequency range. The samples were submitted to different ratios of N₂/O₂, which were passed through wet and dry columns in suitable ratios to attain the desired value of pH₂O. The experimental study was focused in the approximate ranges $10^{-4} \leq pO_2 \leq 1$ atm and $2.2 \times 10^{-3} \leq pH_2O \leq 2.2 \times 10^{-2}$ atm, between 600-900 °C.

Analysis of impedance spectra was performed with the Zview 2.9c software (Scribner Associates) by fitting the data to appropriate equivalent circuits to resolve the impedance into bulk, grain-boundary and electrode contributions according to the respective capacitances of the processes [20]. Samples were also subjected to isothermal stability studies employing impedance measurements in O₂ and 10%CO₂:90%Ar for periods of up to 10 days with data collected every 4 hours.

3. Results and Discussion

3.1. Phase Analysis

The X-ray powder diffraction patterns for the BaCe_{0.8}Y_{0.2}O_{2.9-(x/2)±δ}Br_x series indicated the formation of perovskite material; structural features of the Br-doped samples were similar to BaCe_{0.8}Y_{0.2}O_{3-δ} (BCY20) but with a greater degree of peak splitting. No secondary phases were discernible in the XRD powder patterns. Density was determined to be ~ 92-97 % of the theoretical density for a sintering temperature of 1500 °C. Typical scanning electron micrographs of material sintered at 1500 °C are shown in Fig. 1 for the x = 0.2 composition (BCY20-20Br); the absence of cracks and open porosity is apparent, and the micrographs also support the monophasic character indicated by the XRD patterns.

Fig. 1. Scanning electron micrographs of a fracture surface of the x = 0.2 member of the series of nominal composition BaCe_{0.8}Y_{0.2}O_{2.9-(x/2)±δ}Br_x at two magnifications.

Phase composition was initially analysed by energy-dispersive X-ray spectroscopy; however, the presence of Br in measurable quantities was not detected for the Br-synthesised samples, despite the fact that the XRD patterns indicated a clear effect of the addition of Br on the structural parameters. Further analysis of the x = 0 and 0.2 samples performed by total X-ray fluorescence after the heat treatments at 1100 and 1500 °C suggested that the halogen dopant was only present in trace amounts (Table 1). The

results in Table 1 correspond to the average of three measurements per sample; reproducibility was assessed by measuring three different samples.

Table 1. Molar content of Br as determined by TXRF for members of the $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9-(x/2)\pm\delta}\text{Br}_x$ series.

Temperature (°C)	x=0.05	x=0.2
1100	0.0028	0.0047
1500	3.48×10^{-5}	3.89×10^{-5}

Fig. 2. Observed (circles), calculated (continuous line) and difference (continuous line at bottom) X-ray powder diffraction profiles of the $x = 0$ (a) and $x = 0.2$ (b) members of the series of nominal composition $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9-(x/2)\pm\delta}\text{Br}_x$; Vertical bars indicate the expected position of Bragg peaks on refinement in space group $I 2/m$

Tilting of the BO_6 octahedra in perovskites involving slight movements of the oxygen positions leads to a lowering of symmetry in many cases. Minor distortions may

be difficult to detect by XRD due to the low scattering length of oxygen on excitation by X-rays [21]. However, in the present series, the significant peak splitting in the Br-doped phases indicated considerable distortion of the perovskite lattice. The XRD powder diffraction data were employed for Rietveld refinement of the X-ray structure of the $x = 0.2$ composition in space group $I2/m$ in accordance with the monoclinic symmetry of the room-temperature structure of BCY20 [22]. Refinement in higher symmetry space groups $Imma$ and $Pnma$ led to poorer quality refinement criteria. In contrast, the BCY20 phase could be successfully refined with orthorhombic symmetry ($Pnma$ or $Imma$); however, we have provided the structural details of refinement of BCY20 in $I2/m$ to be consistent with the neutron refinement of Malavasi *et al.* [22]. The observed XRD patterns of $x = 0$ and 0.2 and the difference between observed and calculated patterns are shown in Fig. 2; selected structural parameters and agreement factors for the two phases are listed in Table 2. The thermal vibration factors were not refined in order to avoid correlation with background or other parameters [23].

Although the refinement criteria are acceptable for both phases, the somewhat poorer refinement of the $x = 0.2$ composition may indicate further structural complexity, the detection of which is beyond the resolution of laboratory X-rays. For BCY20, Malavasi *et al.* [22] noted a secondary phase (7 %) with similar peak positions to the main perovskite phase by neutron diffraction. In our case, in accordance with the scanning electron micrographs, attempts to refine a second perovskite phase with the laboratory X-ray data proved to be unsuccessful for the $x = 0.2$ phase. We note that, as indicated on preliminary inspection of peak splitting, the monoclinic distortion of the $x = 0.2$ composition ($\beta = 91.23^\circ$) is greater than that of the pseudo-orthogonal BCY20 ($\beta = 90.06^\circ$), indicating that the introduction of Br in the reactant mixture has an important effect on structure. Moreover, the degree of structural distortion and, hence, symmetry in these perovskite phases are highly dependent on thermal history and, relatedly, minor compositional variations, which could explain the slight differences between our BCY20 refinement and that of Malavasi *et al.* [22]. In contrast, the thermal histories of the $x = 0$ and 0.2 compositions in the present study are analogous, suggesting that variations in stoichiometry arising from the effects of Ba evaporation or dopant partitioning [24] account for the greater monoclinic distortion of the $x = 0.2$ phase. The quality of data from the laboratory X-rays was not sufficient to accurately determine the source of these stoichiometric differences with any confidence.

Table 2. Structural parameters, interatomic distances and agreement factors for BaCe_{0.8}Y_{0.2}O_{2.9-(x/2)±δ}Br_x obtained from XRD data at RT.

	$x=0^a$	$x=0.2^b$
a (Å)	6.2086(2)	6.2309(4)
b (Å)	8.7435(2)	8.7227(6)
c (Å)	6.19156(2)	6.2458(4)
β (deg)	90.057(4)	91.233(4)
V (Å ³)	336.11(2)	339.39(4)
Ba	4i	4i
x	0.254(1)	0.262(2)
z	0.751(9)	0.741(2)
$U_{iso} \times 100$ (Å ²)	1.32(9)	0.7(2)
Ce/Y	4e	4e
$U_{iso} \times 100$ (Å ²)	1.7(1)	0.4(2)
O(1)	4i	4i
x	0.177(5)	0.300(9)
z	0.297(9)	0.172(9)
Occ	1.0	1.0
$U_{iso} \times 100$ (Å ²)	0.6	0.6
O(2)	4g	4g
y	0.298(6)	0.294(7)
Occ	0.91	0.91
$U_{iso} \times 100$ (Å ²)	0.6	0.6
O(3)	4h	4h
y	0.214(9)	0.217(4)
Occ	1.0	1.0
$U_{iso} \times 100$ (Å ²)	0.6	0.6

Space Group $I2/m$, (# 12): 4i (x,0,z), 4e (¼,¼,¼), 4g (0,y,0), 4h (½,y,0)

^a $\chi^2=1.97$, $R_{exp}=3.37\%$, $R_p=3.52\%$, $R_{wp}=4.73\%$, $R_B=4.13\%$, $\rho_{(cryst)}: 6.20 \text{ g/cm}^3$

^b $\chi^2=2.74$, $R_{exp}=3.64\%$, $R_p=4.32\%$, $R_{wp}=6.03\%$, $R_B=4.89\%$, $\rho_{(cryst)}: 6.14 \text{ g/cm}^3$

3.2. Electrical conductivity under wet and dry O₂ and N₂.

Figure 3(a) shows impedance plots of BCY20-20Br obtained under oxidizing and reducing conditions of dry and wet oxygen and nitrogen at 800 °C. Very similar spectra are obtained in both wet and dry oxygen at high temperature (Fig. 3(a)-inset), characterized by a principal arc in the intermediate-frequency range and a shift of the overall spectra from the origin of the real axis, corresponding to the total resistance of the

sample, accompanied by an inductive tail in the high-frequency range. The characteristic capacitance associated to the main arc is in the order of $\sim 10^{-6}$ F, attributable to the electrochemical processes at the electrode/sample interface [20].

Fig. 3. Impedance spectra obtained for BCY20-20Br under wet and dry conditions of O₂ and N₂ at 800 °C (a) and 400 °C (b); in (b) circles correspond to O₂, squares to N₂, closed symbols to wet and open symbols to dry atmospheres. Note that the data in the spectra are multiplied by the electrode area and divided by the sample thickness to obtain specific magnitudes.

The spectra present higher resistances both for the material and the electrode polarisation in wet and dry N₂ atmospheres, the latter of which is characterised by several contributions, compared with the apparently single electrode feature of the O₂ atmospheres. In contrast to the behaviour in oxygen, lower values of resistance are registered in wet N₂ than dry, which may be attributable to a higher contribution from protons in comparison to more oxidising atmospheres, as will be discussed later. On the other hand, at the lower temperature of 400 °C, a completely different behaviour is observed (Fig. 3(b)). A high-frequency arc corresponding to the grain-boundary process arises ($C \sim 10^{-8}$ F), concomitant with a displacement of the overall spectra from the origin corresponding to the bulk process. Similar spectra are obtained in dry O₂ compared to dry N₂, and also in wet O₂ compared to wet N₂, which suggests that the contribution from holes is minor in the lower temperature range. Moreover, the higher resistances in dry

atmospheres compared to wet indicate a considerable contribution from protons at this temperature.

The temperature dependence of total conductivity of the series in dry O_2 is shown in Fig. 4 (a), with comparisons between compositions without Br addition and 20% Br addition in the two atmospheres provided in Figs. 4 (b) and (c).

Fig. 4. Arrhenius representation of the electrical conductivity of the $BaCe_{0.8}Y_{0.2}O_{2.9-(x/2)\pm\delta}Br_x$ series for dry oxygen (a) and comparison between the results in wet and dry oxygen for $x = 0$ (b) and that with $x = 0.2$ (c).

The composition $x = 0.2$ with the highest nominal Br content exhibits higher conductivity than the other series members (Fig. 4(a)). The higher conductivity in wet compared to dry

O₂ in the low-temperature range provides an initial indication that protons contribute significantly to transport (Figs. 4(b) and (c)). The conductivity in wet and dry O₂ converge at high temperature, as is typical for proton-conducting oxide systems [8,25], due to decreasing proton content with increasing temperature attributable to the exothermic hydration reaction:

The conductivity obtained in dry conditions of O₂ and N₂ is compared for selected samples in Fig. 5 (a) and (b).

Fig. 5. Comparison between the conductivity results in dry conditions of oxygen and nitrogen ((a) and (b)), and wet and dry nitrogen ((c) and (d)) for the BaCe_{0.8}Y_{0.2}O_{2.9-(x/2)±δ}Br_x series with nominal Br contents of x = 0 ((a) and (c)) and x = 0.2 ((b) and (d)).

In all compositions, conductivity is higher in O₂ than N₂ suggesting a greater contribution from electron holes for the more oxidising conditions according to:

However, these differences become increasingly smaller as temperature is lowered, which indicates that the respective contributions of electronic and ionic species change with

temperature and that the electronic contribution decreases at lower temperature. The conductivity difference in the lower temperature regime is greater in wet N₂ with respect to dry N₂, Fig. 5 (c) and (d), in comparison to the difference observed between wet and dry O₂ (Figs. 4(b) and (c)). Moreover, the conductivities in wet and dry N₂ converge at a higher temperature in comparison to the case of the O₂-containing atmospheres. Both behaviours are attributable to a lower electron-hole conductivity as pO₂ decreases (Eq. (2) goes to the left), which may yield a higher protonic contribution to the total electrical transport. A more detailed analysis of the partial components of electrical conductivity is presented below.

3.3. Partial components of electrical conductivity

The electrical components of conduction in BCY and Br-synthesised systems were determined following previously developed methodology [8,18,19,26]. Briefly, the procedure involves linear fitting the experimental dependence of conductivity as a function of $pO_2^{1/4}$ for a fixed condition of pH₂O, according to:

$$\sigma = a + b \cdot pO_2^{1/4} \quad (3)$$

where a and b correspond, respectively, to the intercept and the slope of the line; moreover, $\sigma_o + \sigma_h = a$ and $\sigma_h = b \cdot pO_2^{1/4}$.

Determination of the linear-fitting parameters of conductivity versus $pO_2^{1/4}$ for two different conditions of pH₂O allows the partial components of conductivity to be obtained as functions of pO₂ and pH₂O according to:

$$\sigma_H = \sigma_H^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right] \frac{pH_2O}{(1+\alpha)^{1/2}-1} \quad (4)$$

$$\sigma_O = \sigma_O^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right] \frac{pH_2O}{\alpha} \quad (5)$$

$$\sigma_h = \sigma_h^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right] \frac{pH_2O^{1/2}}{\alpha^{1/2}} pO_2^{1/4} \quad (6)$$

where

$$\alpha = \frac{8[Y_B']}{K_w} \quad (7)$$

and σ_H^0 , σ_O^0 and σ_h^0 correspond to the proton conductivity at $p_{H_2O} = 1$ atm, the oxide ionic conductivity at $p_{H_2O} = 0$ atm and the hole conductivity at $p_{O_2} = 1$ atm and $p_{H_2O} = 0$ atm, respectively. The constants σ_H^0 , σ_O^0 , σ_h^0 and α are determined by means of linear fitting of the σ vs $p_{O_2}^{1/4}$ plots for two different conditions of p_{H_2O} . Further details can be found in previous reports [8,27].

Fig. 6. Logarithmic dependence of conductivity on p_{O_2} for $p_{H_2O} = 2.2 \times 10^{-2}$ atm for the samples BCY20 (a) and BCY20-20Br (b) in the range 600-900 °C. Solid lines are derived from the linear fitting of Eq. 3.

The p_{O_2} dependence of conductivity of BCY20 and BCY20-20Br for $p_{H_2O} \approx 0.022$ atm is shown in Fig. 6, with an alternative representation for two different conditions of p_{H_2O} for both samples following the linear relationship of eq. (3) plotted in Fig.7. The good agreement between theory and experimental results is revealed by the linear fitting shown in Fig. 7 and the corresponding solid lines in Fig. 6. The slope of the lines in Fig. 7 increases with increasing temperature and lower levels of humidification due to greater electron-hole conductivity. Moreover, a comparison of the intercepts registered at the two levels of p_{H_2O} , corresponding to the total ionic conductivity at each condition, reveals that both oxide ions and protonic species contribute to ionic transport. This, in turn, suggests that temperature determines which ionic species is most prevalent in electrical conduction. Although analogous behaviours are obtained for BCY20 and BCY20-20Br,

the linear curves are displaced to higher values of conductivity for the Br-synthesised sample. The influence of each species in this enhancement is analysed below.

Fig. 7. Alternative representation of conductivity as function of $p\text{O}_2^{1/4}$ for $p\text{H}_2\text{O} = 2.2 \times 10^{-2}$ atm (open symbols) and $p\text{H}_2\text{O} = 2.2 \times 10^{-3}$ atm (closed symbols) at different temperatures, for the samples BCY20 (a) and BCY20-20Br (b).

Examples of the partial components of electrical conductivity as a function of $p\text{H}_2\text{O}$, determined by means of the values of α , σ_H^0 , σ_O^0 and σ_h^0 , for the sample BCY20-20Br are shown in Fig. 8. As expected, the various profiles associated with the different charge carriers are highly dependent on temperature and $p\text{O}_2$. Generally speaking, similar dependencies on temperature, $p\text{O}_2$ and $p\text{H}_2\text{O}$ are obtained for the BCY20 sample without Br addition, whose differences with respect to the Br-synthesised samples are analysed later. At 800 °C and $p\text{O}_2 = 1$ atm (Fig. 8(a)), the total conductivity in the dry region ($p\text{H}_2\text{O} < 10^{-5}$ atm) is principally determined by the contributions from electron holes and oxide ions, which diminish only slightly with increasing water content up to $p\text{H}_2\text{O} \sim 10^{-3}$ atm. In the lower $p\text{H}_2\text{O}$ region, the proton conductivity increases with a $1/2$ -power law as $p\text{H}_2\text{O}$ increases, as expected from the defect-chemistry equilibria when protons are the minor charge carriers [27]. Proton transport becomes significant for higher values of humidification ($p\text{H}_2\text{O} > 5 \cdot 10^{-3}$ atm), with concomitant decreases of the oxide-ionic and electron-hole contributions. The overall effect of increasing the water-vapour partial pressure at 800 °C with $p\text{O}_2 = 1$ atm is to decrease slightly the total conductivity, in good agreement with the results presented in Fig. 3(a)-inset for dry and wet conditions of oxygen. On the other hand, the principal effect of decreasing $p\text{O}_2$ from 1 to 10^{-4} atm (close

to that typical of an N₂ atmosphere) at this temperature is to reduce the electron-hole component by an order of magnitude, Fig. 8(b). This has a direct impact on lowering the total electrical conductivity in both dry and wet conditions. Moreover, the total transport in both situations is essentially ionic, which is reflected in a larger electrode-polarisation process, as observed in Fig. 3(a). On decreasing the temperature to 600 °C (Figs. 8(c) and (d)), the lower charge-carrier mobility decreases the conductivity of the different species; however, much less of a decrease is observed for protons due to their greater concentration at lower temperature (Eq. (1)).

Fig. 8. Partial components of electrical conduction for BCY20-20Br as a function of pH₂O at 800 °C ((a) and (b)) and 600 °C ((c) and (d)). The pO₂ conditions correspond to 1 atm ((a) and (c)) and 10⁻⁴ atm ((b) and (d)).

Consequently, total conductivity is essentially protonic for $p\text{H}_2\text{O} \geq 10^{-2}$ atm in both oxidising and reducing conditions. However, at $p\text{O}_2 = 1\text{ atm}$ (Fig. 8(c)), the total conductivity is only slightly higher under typical wet ($p\text{H}_2\text{O} \sim 0.022$ atm) in comparison to dry ($p\text{H}_2\text{O} < 10^{-5}$ atm) conditions due to the combination of the electrical profiles of the three species, which agrees well with the results of total conductivity presented in Fig. 4(c) at this temperature. On the other hand, at lower $p\text{O}_2$ (Fig. 8(d)), the ionic species dominate, due to the lower electron-hole conductivity, leading to a greater increase of total conductivity for higher $p\text{H}_2\text{O}$, which is also supported by the results shown in Fig. 5(d) at 600 °C.

Fig. 9. Comparison between partial components of conductivity for BCY20 (open symbols) and BCY20-20Br (closed symbols) as a function of $p\text{H}_2\text{O}$ for $p\text{O}_2 = 0.2$ atm at 800 °C (a) and 600 °C (b); squares, triangles and diamonds correspond respectively to protonic, oxide-ionic and p-type electronic conductivities.

Although similar profiles were also obtained illustrating the effect of $p\text{O}_2$, $p\text{H}_2\text{O}$ and temperature on the electrical transport properties of BCY20, some noteworthy differences were observed for the partial components of conductivity in comparison to the Br-added samples, as reflected in Fig. 9. Under dry conditions (Fig. 4(a)), the enhancement of conductivity observed for the Br-synthesised sample in comparison to BCY20 is related to an improvement in oxide ionic conductivity; the impact of electron holes is only minor, given that both samples have very similar profiles (Fig. 9). On the other hand, the

improvement observed in wet conditions for the Br-synthesised composition (Figs. 4(b) and 4(c)) is a direct consequence of its greater protonic conductivity (Fig. 9). The behaviour in both atmospheres is consistent with a greater concentration of positive defects, mainly oxygen vacancies and protonic species, in Br-synthesised BCY20 in comparison to BCY20. Although the reasons for this enhancement are not readily apparent, we suggest that evaporation of some Ba may occur along with that of Br in the synthesis procedure, which would promote the creation of negative species such as Ba vacancies. Regarding this, a higher level of Ba nonstoichiometry in BCY20-20Br in comparison to BCY20-10Br is expected, given that the Ba deficiency may be introduced on synthesizing with the corresponding amounts of BaBr₂, which would lead to the higher conductivity observed in Fig. 4(a).

Fig. 10. Electrical transport numbers of BCY20 ((a) and (c)) and BCY20-20Br ((b) and (d)) as a function of p_{H_2O} at 800 °C ((a)-(b)) and 600 °C ((c)-(d)), determined for p_{O_2} values of 0.2 atm; squares, triangles and diamonds correspond respectively to protonic, oxide-ionic and p-type electronic transport numbers.

It has been shown that the effects of Ba substoichiometry may have important effects on improving electrical properties [28,29]. Nevertheless, such compositional differences are likely to be small and neither the Rietveld refinement nor TXRF results were of sufficient resolution to provide conclusive evidence of Ba site vacancies.

Selected electrical transport numbers for BCY20 and BCY20-20Br at $pO_2 = 0.2$ atm, under different conditions of pH_2O and temperature are shown in Fig. 10. Whereas BCY20 presents values of oxide-ionic and electron-hole transport numbers of ~ 0.52 and ~ 0.48 , respectively, at 800°C under dry conditions (Fig. 10(a)), BCY20-20Br shows respective values of $t_o \sim 0.68$ and $t_p \sim 0.32$ under identical conditions (Fig. 10(b)). However, the oxide ionic component decreases to a greater extent than the electronic contribution as pH_2O increases, notably above $\sim 10^{-4}$ atm, accompanied with increasing protonic transport number, leading to values of $t_H \sim 0.36$ and ~ 0.63 for BCY20 and BCY20-20Br, respectively, at $pH_2O \approx 0.022$ atm.

Table 3. Electrical transport numbers of BCY20 and BCY20-20Br at 700°C compared with similar compositions previously reported in the literature.

Composition	t_H	t_o	t_p	Reference
BCY20 ($pH_2O=0.022$ atm)				this work
$pO_2=1$ atm	0.64	0.10	0.26	
$pO_2=0.2$ atm	0.70	0.11	0.19	
$pO_2=10^{-4}$ atm	0.83	0.13	0.03	
BCY20-20Br ($pH_2O=0.022$ atm)				this work
$pO_2=1$ atm	0.84	0.05	0.11	
$pO_2=0.2$ atm	0.86	0.05	0.09	
$pO_2=10^{-4}$ atm	0.93	0.06	0.01	
BaCe _{0.9} Y _{0.1} O _{3-δ} $pH_2O \approx 0.025$ atm; air	0.35	0.45	0.2	[31]
BaCe _{0.9} Y _{0.1} O _{3-δ} $pH_2O \approx 0.023$ atm; $pO_2=0.2$ atm	0.46	0.22	0.32	[32]
BaCe _{0.9} Y _{0.1} O _{3-δ} $pH_2O \approx 0.03$ atm; He	0.74	0.26		[33]
BaCe _{0.95} Y _{0.05} O _{3-δ} 8% O ₂ +2.81% H ₂ O /sample/ 100% O ₂ +2.81% H ₂ O	0.12	0.4	0.48	[34]
BaCe _{0.9} Yb _{0.1} O _{3-δ} H ₂ /sample/air	0.80	0.20		[35]

At the lower temperature of 600°C (Fig. 10(c)-(d)), the onset of protonic transport is displaced to lower pH_2O , reaching values as high as 0.91 at $pH_2O \approx 0.022$ atm for both compositions. It is also apparent that under dry atmospheres, the BCY20 sample possesses a marked mixed conducting behaviour (oxide ions and holes) whereas oxide ions predominate in the BCY20-20Br sample. Table 3 shows values of the electrical

transport numbers obtained in the current work for Br-added and Br-free BCY20 compositions compared to results previously reported in the literature for similar systems under various conditions. There is a rather wide discrepancy among the results reported in the literature, which may be ascribed to slightly different compositions and inherent uncertainties associated to the employed methodologies. In the current work, the transport numbers are directly derived from the experimental results by means of the defect chemistry.

Stability

A preliminary examination of the stability of the series was performed in O₂ and 10% CO₂:90% Ar employing prolonged isothermal conductivity measurements at 700 °C, Fig. 11.

Fig. 11. Conductivity as a function of exposure time in dry oxygen (a) and dry 10% CO₂:90% Ar (b) for BCY20 and BCY20-10Br. The results are normalised to the initial values of conductivity.

The conductivity decreased slightly over a period of 10 days in O₂ for both Br-free (~ 11%) and Br-synthesised BCY material (~ 4%). However, both materials degraded considerably in the CO₂-containing atmosphere, with the greatest drop in conductivity observed for the Br-synthesised sample. The poorer stability of the Br-synthesised material in CO₂ was confirmed by TGA (Fig. 12). Whereas the BCY20 phase shows only

a moderate increase in weight on heating in CO₂, the $x = 0.2$ composition undergoes significant weight increase as a result of reaction with CO₂ and decomposition. As the effect of synthesis with Br is to increase distortion of the perovskite structure, this may lower phase stability [30]. Moreover, the possible presence of minor amounts of Ba segregated at the grain boundaries would also favour reaction with CO₂. In this sense, given that Ba is introduced stoichiometrically during the synthesis, it may be the case that the excess Ba which is not incorporated in the structure, leading to Ba vacancies in the bulk, is not completely evaporated and is, therefore, in higher concentrations in the grain boundaries, which has the effect of lowering stability in comparison to samples without Br addition. In contrast, other authors report that Br-doped barium cerate material enhances stability in comparison to the undoped phase [12]. Discrepancies between different studies may be related to uncontrolled, variable halogen content on high-temperature sintering.

Fig. 12. TGA plots for the $x = 0$ and 0.2 members of the $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{2.9-(x/2)\pm\delta}\text{Br}_x$ series in 10% CO₂:90% Ar with a heating rate of 5 °C.min⁻¹.

4. Conclusions

A detailed analysis of partial conductivities in $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ synthesised with and without the addition of bromine has been undertaken by a defect-chemistry method under different conditions of $p\text{H}_2\text{O}$ and $p\text{O}_2$ in the temperature range 600-900 °C, revealing the influence of oxide-ionic, protonic and electronic charge carriers on electrical transport.

High-temperature sintering leads to evaporation of Br on its incorporation as dopant in the synthesis of $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$, as confirmed by analysis of ion content by total X-ray fluorescence spectroscopy. Nevertheless, significant differences are found between $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ synthesised with and without Br in the starting reactants, involving effects on structure, stability and electrical conductivity. Dense $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ material was obtained for Br-synthesised compositions on sintering at 1500 °C with a monoclinic distortion of the perovskite structure greater than that observed for BCY20 synthesised free of Br. The Br-synthesised samples exhibited greater conductivity in both dry and wet ($p\text{H}_2\text{O} \sim 0.022$ atm) oxidising and reducing (N_2) conditions in comparison to the Br-free phase. In dry oxidizing conditions, mixed oxide-ion-electron-hole conductivity predominates; however, in wet atmospheres, (~ 0.022 atm) conduction is principally protonic at lower temperature (600 °C), with a greater influence of holes and oxide ions as temperature rises. The enhancement of total conductivity observed for Br-synthesised compositions is mainly related to the greater contribution of oxide-ionic and protonic components in dry and wet conditions, respectively, which may be associated to some Ba deficiency generated during the evaporation of Br. Long-term stability measurements in O_2 and CO_2 and thermogravimetry in CO_2 revealed poorer stability of the Br-synthesised material, in contrast to previous reports.

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