Temperature dependence of partial conductivities of the $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$ proton conductor

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Abstract

Partial conductivities are presented for $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$, an important proton conductor for protonic-ceramic fuel cells and membrane reactors. Atmospheric dependencies of impedance performed in humidified and dry O_2 , air, N_2 and $\text{H}_2(10\%)/\text{N}_2(90\%)$ in the temperature range 300-900 °C, supported by the modified emf method, confirm significant electron-hole and protonic contributions to transport. For very reducing and wet atmospheres, the conductivity is predominantly ionic, with a higher participation of protons with decreasing temperature and increasing water-vapour partial pressure ($p_{\text{H}_2\text{O}}$). From moderately reducing conditions of wet N_2 to wet O_2 , however, the conductivity is considerably influenced by electron holes as revealed by a significant dependence of total conductivity on oxygen partial pressure (p_{O_2}). With higher $p_{\text{H}_2\text{O}}$, proton transport increases, with a concomitant decrease of holes and oxygen vacancies. However, the effect of $p_{\text{H}_2\text{O}}$ is also influenced by temperature, with a greater protonic contribution at both lower temperature and p_{O_2} . Values of proton transport number $t_{\text{H}} \approx 0.63$ and electronic transport number $t_{\text{h}} \approx 0.37$ are obtained at 600 °C for $p_{\text{H}_2\text{O}} = 0.022$ atm and $p_{\text{O}_2} = 0.2$ atm, whereas $t_{\text{H}} \approx 0.95$ and $t_{\text{h}} \approx 0.05$ for $p_{\text{O}_2} = 10^{-5}$ atm. A hydration enthalpy of $-109 \text{ kJ}\cdot\text{mol}^{-1}$ is obtained in the range 600-900 °C.

Keywords: BZCY72, transport numbers, proton conductivity, defect chemistry, emf method

1. Introduction

Several ceramic membrane technologies requiring high-temperature transport of protons, co-ionic transport (protons and oxide ions) and mixed protonic-electronic conduction are based on perovskite systems (ABO_3) with large, basic cations [1,2].

Solid solutions of barium zirconate and cerate are of special interest due to the practical compromise of moderately high proton conductivity and good stability, respectively exhibited by the acceptor doped BaCeO_3 and BaZrO_3 end-members. The phase $\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZCY72, often referred to in the literature as BCZY27) is increasingly regarded as the optimised composition for a number of high-temperature electrochemical membranes. Recent publications have centred on this material as an electrolyte for a protonic ceramic fuel cell (PCFC) [3], and as a membrane reactor for ammonia synthesis [4] or conversion of methane to aromatics [5]. The process of non-oxidative methane dehydroaromatization (MDA) converts natural gas to transportable liquid fuels such as benzene. Critical to the performance of such membranes is the mixed-conducting properties. In the case of MDA, co-ionic transport is of primary importance since some oxide-ionic transport is required to inhibit excessive coke formation through the formation of steam [5]. Other applications such as fuel-cell cathodes and separation membranes benefit from mixed protonic-electronic conduction [6], whereas purely protonic transport is advantageous for PCFC electrolytes and protonic ceramic electrolyser cells [7].

Analysis of transport numbers is, accordingly, of considerable importance for evaluating the working conditions of an ion-conducting material in an electrochemical application. In the case of perovskite proton conductors, protons are incorporated on doping with a lower valence cation (acceptor doping) on the perovskite B site. A hydroxyl group from an ambient water molecule replaces the oxygen vacancy and a proton from the water molecule attaches itself to another lattice oxide ion (Kröger-Vink notation):

The hydration reaction corresponding to Eq. 1 is exothermic, thus in dry atmospheres and at high temperature, migration of oxide-ion vacancies is favoured. In oxidising atmospheres, the oxygen vacancies may instead be filled, leading to the formation of holes:

A variety of techniques may be employed for the determination of partial conductivities in mixed oxide-ionic-electronic conductors by dc techniques [8]. The further complication of proton transport has limited the determination of transport numbers principally to the electromotive force (emf) method, in which a membrane in a dual-chamber is subjected to gradients of controlled oxygen and water-vapour partial pressures [9]. An alternative methodology for measuring partial conductivities of mixed protonic, oxide-ionic and electronic conductors, described presently, was developed by means of the defect chemistry and exploiting the dependence of the partial conductivities on pO_2 and pH_2O [10,11].

In this paper, the transport numbers for protonic, oxide-ionic and electronic transport in the technologically relevant BZCY72 phase are determined in the temperature range 600 – 900 °C from the dependence of conductivity on the oxygen partial pressure under different wetting conditions. The results are complemented by those obtained by a modified emf method, in which polarisation resistance is corrected by an external load [12,13].

2. Determination of partial conductivities from the expected pO_2 - and pH_2O -dependencies of the charged species

The defect chemistry of mixed-conducting perovskites with protonic, oxide-ionic and electronic transport is widely discussed in the literature. The explicit solution for the concentrations of transport species as functions of oxygen and water-vapour partial pressures was derived by Frade [14] and supports the methodology subsequently developed for determination of different contributions to the electrical transport [10,11].

In the BZCY72 composition under oxidising conditions, oxide-ion vacancies are created on aliovalent doping with Y^{3+} in the B position of the perovskite according to:

The constants for the external equilibria of the hydration and oxidation reactions (eqs.(1) and (2)) may be respectively expressed as

$$K_w \approx \frac{[OH_O^{\bullet}]^2}{[v_O^{\bullet\bullet}]pH_2O} \quad (4)$$

and

$$K_o \approx \frac{[h^\bullet]^2}{[v_o^{\bullet\bullet}]pO_2^{1/2}} \quad (5)$$

The charge neutrality condition may be simplified to

$$[Y'_B] \approx 2[v_o^{\bullet\bullet}] + [OH_o^\bullet] \quad (6)$$

assuming that the Schottky-Wagner defect equilibrium is negligible in heavily doped systems [15] and that the concentrations of electronic species are trivial compared to that of ionic species. Note that the existence of an appreciable ionic-conductivity contribution requires the concentration of the ionic carriers to be much higher than that of the electronic species since the mobility of the latter species are orders of magnitude higher than that of the former. Generic solutions for defect concentrations are thus derived on combining eqs. (4)-(6):

$$[OH_o^\bullet] \approx \frac{K_w pH_2O}{4} \left[\left(1 + \frac{8[Y'_B]}{K_w pH_2O} \right)^{1/2} - 1 \right] \quad (7)$$

$$[v_o^{\bullet\bullet}] \approx \frac{K_w pH_2O}{16} \left[\left(1 + \frac{8[Y'_B]}{K_w pH_2O} \right)^{1/2} - 1 \right]^2 \quad (8)$$

$$[h^\bullet] \approx \left(\frac{K_o K_w}{16} \right)^{1/2} \left[\left(1 + \frac{8[Y'_B]}{K_w pH_2O} \right)^{1/2} - 1 \right] pH_2O^{1/2} pO_2^{1/4} \quad (9)$$

The partial conductivity of the conducting species i is calculated from the concentration c_i , charge q_i and mobility μ_i :

$$\sigma_i = q_i c_i \mu_i \quad (10)$$

On assuming that mobilities are independent of oxygen and water-vapour partial pressures [10], generic formulae for conductivity may be expressed as:

$$\sigma_H = \sigma_H^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right] \frac{pH_2O}{(1 + \alpha)^{1/2} - 1} \quad (11)$$

$$\sigma_v = \sigma_v^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right]^2 \frac{pH_2O}{\alpha} \quad (12)$$

$$\sigma_h = \sigma_h^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right] \frac{pH_2O^{1/2}}{\alpha^{1/2}} pO_2^{1/4} \quad (13)$$

where the constant α is defined as

$$\alpha = \frac{8[Y'_B]}{K_w} \quad (14)$$

and σ_H^0 is the proton conductivity at $pH_2O = 1$ atm, σ_h^0 is the hole conductivity at $pO_2 = 1$ atm and $pH_2O = 0$ atm; σ_v^0 is the oxide-ion conductivity when $pH_2O = 0$ atm. These constants take the form:

$$\sigma_H^0 = \left[(1 + \alpha)^{1/2} - 1 \right] \frac{K_w q_H \mu_H}{4} \quad (15)$$

$$\sigma_v^0 = \frac{[Y'_B]}{2} q_v \mu_v \quad (16)$$

$$\sigma_h^0 = \left(K_o \frac{[Y'_B]}{2} \right)^{1/2} q_h \mu_h \quad (17)$$

The partial conductivities may be deduced from eqs. (11)-(13) under the imposed conditions of pO_2 and pH_2O on determining the constants α , σ_H^0 , σ_v^0 and σ_h^0 .

For a fixed condition of pH_2O , the protonic and oxide-ionic conductivities are essentially constant and the electronic conductivity presents a 1/4-power-law dependence on the oxygen partial pressure. Since

$$\sigma_{tot} = \sigma_H + \sigma_v + \sigma_h \quad (18)$$

the total conductivity may be expressed as a linear function of $pO_2^{1/4}$:

$$\sigma_{tot} = a + b pO_2^{1/4} \quad (19)$$

The intercept of Eq. 19, $a = \sigma_H + \sigma_v$, corresponds to

$$a = \sigma_H^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right] \frac{pH_2O}{(1 + \alpha)^{1/2} - 1} + \sigma_v^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right]^2 \frac{pH_2O}{\alpha} \quad (20)$$

and the slope, b , is expressed as

$$b = \sigma_h^0 \left[\left(1 + \frac{\alpha}{pH_2O} \right)^{1/2} - 1 \right] \frac{pH_2O^{1/2}}{\alpha^{1/2}} \quad (21)$$

According to eq. (21), the slope of the linear function represented by eq. (19) is only dependent on pH_2O , and the constants σ_{h}^0 and α may be determined from the combination of the slopes obtained at two different values of pH_2O [10]. The value of α provides that of K_{W} by means of eq. (14). On introducing the determined value of α in eq. (20), the constants σ_{H}^0 and σ_{V}^0 may be calculated from the combination of the intercepts obtained at two different values of pH_2O .

3. Experimental

$\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZCY72) was prepared by a citrate process based on the Pechini method. The water content of the nitrate precursors was firstly determined by thermogravimetry in air. The appropriate stoichiometric ratio of nitrates was added in the order $\text{Ba}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, and $\text{Y}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ to deionised water heated at $\sim 50^\circ\text{C}$ on a hotplate. On obtaining a transparent solution, citric acid and ethylene glycol (in the molar ratios of 10:1 and 40:1 with respect to the final product) were added and stirred for ~ 40 mins. At this point, the temperature was maintained in the range $60\text{--}80^\circ\text{C}$ for ~ 2 h then raised to $> 90^\circ\text{C}$ for 4–5 hours, and finally to above 100°C for over 12 h to obtain a dark-brown polymerized complex. The material was subsequently pyrolysed in an oven at 350°C for 4 h. The obtained polymeric precursor was then heated at 600°C for 4 h, milled and heat treated at 1100°C for a further 4 h to remove any remaining organic product, prior to attrition milling in a Teflon vial with YSZ balls and sieving ($100\ \mu\text{m}$). The powder was then fired at 1250°C for 24 hours with intermediate grinding in an agate mortar then ball-milled once more. Sintered samples were prepared from this powder by uniaxial pressing of cylindrical pellets and subsequent isostatic pressing at 190 MPa prior to firing at 1650°C for 4 hours; the relative density of samples was $> 95\%$.

The phase purity of lightly polished, crushed and milled pellets was confirmed by 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. Microstructure was analysed with a Hitachi TM-1000 tabletop scanning electron microscope.

Sintered pellet faces were coated with Pt electrodes for electrical measurements by painting with Pt paste (Heraeus CL11-5349) and heating at 950°C for 1 hour; four Pt wires were then attached to assure good electrical contacts and independent

measurement of the electrical current and voltage. Impedance spectroscopy was performed in potentiostatic mode in the temperature range 250-900 °C employing an Autolab PGStat302N instrument in the frequency range 0.1-10⁶ Hz with an applied voltage of 50 mV. The sample was housed in a single-chamber electrochemical cell equipped with an yttria-stabilised zirconia sensor placed close to the sample in order to monitor pO₂ and the system was submitted to wet and dry conditions of O₂, air, N₂ and H₂(10%)/N₂(90%) *via* electronic mass-flow controllers (Bronkhorst). The drying column contained a commercial moisture trap of aluminosilicate- and zeolite-based beads; humidification was achieved on bubbling the gases through KBr-saturated H₂O at room temperature (maximum water content, ~ 0.022 atm).

For determination of transport number employing the pO₂ and pH₂O dependence of the charge carriers, a range of oxygen and water-vapour partial pressures were attained on feeding mixtures of N₂/O₂ and N₂/H₂ through wet and dry columns in different ratios. The methodology consisted of studying the dependence of the total conductivity as a function of pO₂ for a fixed value of pH₂O. The experiment was independently conducted at pH₂O ≈ 2.2x10⁻² and 2.2x10⁻³ atm in the range 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 response into bulk, grain-boundary and electrode contributions, according to the corresponding specific capacitances of the processes [16].

Ionic and electronic transport numbers were also determined by the emf technique employing the method described in detail previously [12,13]. For this, a BZCY72 sample with attached Pt electrodes and four Pt wires was sealed to a YSZ tube using a glass-ceramic seal forming a dual-chamber electrochemical cell. The YSZ tube served as a pO₂ sensor by means of painting Pt electrodes to its inner and outer sides. The active-load methodology with a variable auxiliary parallel resistor was employed on direct application of a chemical potential gradient across the membrane, producing an electromotive force, which was monitored with an Agilent 34401A digital multimeter. The chemical potential gradients were attained by submitting each chamber to a different mixture of N₂/O₂/H₂O. The methodology is based on the effect produced by the variable auxiliary electrical resistance on the measured value of voltage drop through the sample. The emf measurements were repeated on reversing the gas flows between the dual-chamber compartments in order to eliminate the thermovoltage contribution.

4. Results and Discussion

4.1. Phase formation and microstructure

We recently reported a detailed structural characterisation of BZCY72 employing neutron and synchrotron X-ray diffraction data, indicating that symmetry is rhombohedral at room temperature (space group, $R\bar{3}c$) transforming to cubic $Pm\bar{3}m$ around 300° C [17].

Transversal views of a fresh fracture surface of a BZCY72 membrane (Fig. 1.) obtained by scanning electron microscopy revealed that the ceramic was free of cracks and open porosity, with a grain size in the micron range.

Fig. 1. Scanning electron micrograph of a transversal fracture surface of BZCY72.

4.2. Total conductivity

The temperature dependence of the electrical conductivity is shown in Fig. 2 for wet and dry conditions of O₂, air, N₂ and H₂ atmospheres. The presence of electron-hole carriers is clearly indicated from the higher conductivity obtained for atmospheres of greater oxidising character over the entire measured temperature range in dry conditions (Fig.2(a)), except H₂ at very low temperature. However, the same trend is only observed between 450-900 °C in wet atmospheres (Fig. 2(b)), suggesting a non-negligible presence of protons at lower temperatures, where the conductivity is very similar for N₂, air and O₂.

Fig. 2. Arrhenius dependence of the electrical conductivity under dry (a) and wet (b) conditions of O_2 , air, N_2 and H_2 .

This is more clearly appreciated in Fig. 2(c), which provides a comparison between the results in wet and dry atmospheres of the same gas. Higher conductivity is observed in humid conditions in the intermediate-low temperature range whereas the conductivity in dry and humidified atmospheres converges at high temperature. Such behaviour is typical of the presence of protonic species at low temperature, which are expelled from the material when the temperature is increased due to the exothermic character of the hydration reaction (eq. (1)). The confluence of the conductivity values in wet and dry atmospheres is displaced to lower temperatures as the oxidising character of the atmosphere is increased (Fig. 2(c)). This is a clear indication of the increasing role of the electron-hole contribution to transport with higher $p\text{O}_2$ for a fixed temperature, which serves to diminish the differences between wet and dry atmospheres. Indeed, perceptible differences between wet and dry O_2 are only observed at very low

temperature, where the concentration of electronic species may be considerably lower, due to the endothermic enthalpy associated with the creation of holes (eq. (2)).

4.3. Partial components of the electrical conductivity

Figure 3(a) shows the total electrical conductivity as a function of the oxygen partial pressure under a fixed, wet condition of $p_{\text{H}_2\text{O}} \approx 0.022$ atm. In isothermal conditions, the conductivity is essentially constant in the range of very reducing atmospheres (H_2/N_2), suggesting the predominance of ionic carriers in the electrical transport. On the other hand, from moderate reducing conditions (N_2) to oxidising conditions (O_2/N_2 atmospheres), the total conductivity increases sharply with p_{O_2} , as a result of the dominant electron-hole conductivity. The presence of electron holes is clearly reflected in the linear behaviour of σ vs $p_{\text{O}_2}^{1/4}$ (Fig. 3(b)), where the intercept corresponds to the value of the total ionic conductivity and the slope is associated with the electron-hole contribution (eqs. (18)-(19)). The decrease in slope with decreasing temperature reflects a lower electron-hole conductivity, mainly resulting from the poorer mobility at lower temperature.

Fig. 3. Dependence of the electrical conductivity as a function of p_{O_2} for a fixed value of $p_{\text{H}_2\text{O}} \approx 0.022$ atm at different temperatures: a) classical log-log representation and b) alternative representation according to eq. (19).

The effect of wetting on the electrical transport is shown in Fig. 4 at 600 °C and in Fig. S1 at 800 °C. In reducing conditions (Fig. 4(a)), the total conductivity increases

by a factor of ~ 2 when $p\text{H}_2\text{O}$ increases from 0.0022 to 0.022 atm, highlighting the significant role of protons to transport in the ionic region at this temperature.

Fig. 4. Effect of humidification on the $p\text{O}_2$ dependence of the electrical conductivity at 600 °C, for $p\text{H}_2\text{O} \approx 0.022$ and 0.0022 atm: a) classical log-log representation from very reducing to oxidising conditions; b) magnification of the log-log representation in the range of moderately reducing-oxidising conditions; c) representation of σ vs $p\text{O}_2^{1/4}$, according to Eq. (19).

Moreover, a similar but less pronounced effect is observed in the moderately reducing region (Fig. 4(b)). However, for higher values of pO_2 , the trend reverses, and electrical transport is greater in drier conditions. This transition is clearly illustrated in Fig. 4(c), where the higher slope of the drier conditions indicates a greater p-type electronic component. The lower intercept of the corresponding line is associated with lower ionic conductivity than that observed in the wetter atmosphere. The expected pO_2 dependence of $\log \sigma$ is displayed on linear fitting of the experimental data according to eq. (19), indicated with continuous lines in Figs. 3 and 4. The values of σ_h^0 and α may be obtained from the two experimental values of the slopes at $pH_2O \approx 0.022$ and 0.0022 atm, on consideration of eq. 21. These constants were, in turn, employed for determination of the electronic conductivity (eq. (13)) and the hydration equilibrium constant (eq. (14)). The latter values, listed in Table 1 at different temperatures, exhibit an Arrhenius-type dependence with the inverse of temperature (Fig. S2), suggesting a temperature-independent hydration enthalpy of $-109 \text{ kJ}\cdot\text{mol}^{-1}$. This value is within the range $-93 \text{ kJ}\cdot\text{mol}^{-1}$ to $-125 \text{ kJ}\cdot\text{mol}^{-1}$ previously reported for a similar system [18], and between the enthalpies of $-79.5 \text{ kJ}\cdot\text{mol}^{-1}$ and $-163.3 \text{ kJ}\cdot\text{mol}^{-1}$, respectively reported for the solid-solution end members $BaZr_{0.9}Y_{0.1}O_3$ and $BaCe_{0.9}Y_{0.1}O_{3-\delta}$. The more negative hydration enthalpy for compositions with higher cerium content has been reported previously [18,19], and has been rationalised on the basis of the more open structure and basicity with greater cerium content on the perovskite B site [20,21]. The determined value of α was substituted in eq. (20) for the calculation of σ_h^0 and σ_v^0 , employing the intercepts obtained for the two mentioned conditions of pH_2O . The process was independently repeated at each measured temperature in the range 600-900 °C.

Figure 5 provides examples of the partial conductivities of the different species as functions of pH_2O for two fixed conditions of pO_2 (0.2 and 10^{-5} atm) at 600 and 800 °C. Under oxidising conditions of $pO_2 = 0.2$ atm, Fig. 5(a), the total conductivity at 800 °C is mainly governed by the electronic component, even for relatively high values of humidification ($pH_2O \leq 0.1$ atm). The dominance of electronic transport arises due to both the high concentration of holes and the negative enthalpy of the hydration reaction, which results in a low concentration of protonic carriers at high temperature. On the other hand, the contribution ascribed to oxide-ionic carriers remains below that attributable to protons for $pH_2O \geq 0.002$ atm, which indicates that the presence of the

latter species is non-negligible at temperatures as high as 800 °C. Although the protonic conductivity increases with $p_{\text{H}_2\text{O}}$, it remains below the electronic conductivity for at least a $p_{\text{H}_2\text{O}}$ of ≈ 0.4 atm. On reducing p_{O_2} to $\sim 10^{-5}$ atm (a value similar to that of a N_2 atmosphere), the electron-hole conductivity decreases by more than one order of magnitude, which modifies the mixed-conducting character of the material considerably (Fig. 5(b)). Interestingly, the partial conductivities remain within the same order of magnitude for $p_{\text{H}_2\text{O}} \sim 0.001$ -0.01 atm, whereas the total conductivity becomes mainly dominated by the protonic contribution for $p_{\text{H}_2\text{O}} > 0.06$ atm.

Fig. 5. Representation of the partial conductivities of oxide ions, protons and electron holes as a function of $p_{\text{H}_2\text{O}}$ at 800 °C, ((a) and (b)) and 600 °C ((c) and (d)); $p_{\text{O}_2}=0.2$ atm for (a) and (c), and $p_{\text{O}_2}=10^{-5}$ atm for (b) and (d).

On decreasing temperature, the mobilities of all species are expected to decrease as a consequence of their thermally activated character, lowering conductivity, as is observed for σ_h and σ_v . However, the proton concentration increases at lower temperature, as expected from the higher equilibrium constant of the hydration reaction (Table 1). This has the effect of producing only moderate changes in the protonic conductivity in the interval 600-800 °C (Fig. 5). Consequently, proton transport is the main transport component at 600 °C for $p_{H_2O} \geq 0.01$ atm, under oxidising conditions of $p_{O_2} = 0.2$ atm (Fig. 5(c)). Moreover, at the same temperature, the total conductivity is completely dominated by the protonic contribution under moderately reducing conditions ($p_{O_2} \approx 10^{-5}$ atm) even for very low values of humidification ($p_{H_2O} \sim 0.001$ atm, Fig. 5(d)). Note that the very low oxide-ionic conductivity obtained at 600 °C is affected by considerable experimental uncertainty, and for this reason is not represented in Figs. 5(c)-(d).

The Arrhenius representations of the different components of conductivity for a humidification of $p_{H_2O} = 0.022$ atm under conditions of $p_{O_2} = 0.2$ and 10^{-5} atm are shown in Figs. 6 (a) and (b), respectively. The plots confirm the mixed protonic-electronic conducting character at $p_{O_2} = 0.2$ atm for temperatures below 700 °C (Fig. 6(a)), whereas a majority protonic contribution is observed at $p_{O_2} = 10^{-5}$ atm below 750 °C (Fig. 6(b)). The protonic conductivity remains practically constant in the range 600-800 °C at both levels of oxidation, whereas the oxide-ionic component is only relevant to the total transport for temperatures of at least 800 °C under reducing atmospheres (Fig. 6(b)).

4.4. Electrical transport numbers

The role of the various components to transport is clearly illustrated on analysis of the electrical-transport numbers, which may be obtained from the methodology presented above. As mentioned, this technique is based on the defect chemistry of the system under the corresponding working conditions. In order to check the accuracy of the results, assessment of the transport numbers by a direct procedure developed previously based on a modified emf method was employed at 750 °C [12,22]. The sample was located in parallel with a variable auxiliary resistor and submitted to a gradient of p_{O_2} at a fixed condition of p_{H_2O} for determination of the electronic transport number and the total ionic transport number. The observed electromotive force

(E_{obs}) varies with the magnitude of the auxiliary resistance (R_{aux}) as a consequence of the modification of the electronic current leakage, as follows [12,22]:

$$\left(E_{\text{O}_2} \cdot E_{\text{obs}}^{-1}\right) - 1 = C \cdot R_{\text{aux}}^{-1} + C \cdot R_e^{-1} \quad (22)$$

where C is a constant dependent of the protonic, oxide-ionic and electrode-polarisation resistances, R_e is the electronic resistance and E_{O_2} is the Nernst voltage created by the $p\text{O}_2$ gradient, according to:

$$E_{\text{O}_2} = \frac{RT}{4F} \ln \left(\frac{p\text{O}_2'}{p\text{O}_2''} \right) \quad (23)$$

Fig. 6. Arrhenius representation of partial conductivities for $p\text{O}_2 = 0.2 \text{ atm}$, at $p\text{H}_2\text{O} = 0.022 \text{ atm}$ (a) and $p\text{H}_2\text{O} = 10^{-5} \text{ atm}$ (b).

Representation of eq. (22) as a linear function of the inverse of the variable auxiliary resistance allows the electronic component of the resistance to be obtained from fitted values of the slope over the intercept. Figure S3 shows an example of the effect of the modification of the variable external resistance on the observed electromotive force at 750 °C, where a very good fit between the experimental results and expected linear behaviour (eq.(22)) is obtained. The electronic- and ionic-transport numbers were then determined from the electronic and total resistances, employing in-situ impedance spectroscopy under the same working conditions.

The protonic transport number was subsequently determined under a pH_2O gradient, with an average value corresponding to the fixed pH_2O of the first experiment, at a fixed condition of pO_2 (corresponding to the average pO_2 gradient of the first approach). The effect of the variable resistance on the electromotive force of the system may be represented as follows [12,22]:

$$\left(E_{\text{H}_2\text{O}} \cdot E_{\text{obs}}^{-1}\right) - 1 = D \cdot R_{\text{aux}}^{-1} + D \cdot (R_{\text{e}}^{-1} + R_{\text{O}}^{-1}) \quad (24)$$

where D is a constant associated to the contributions of protonic and electrode polarisation resistances and R_{O} is the oxide-ionic resistance of the sample. $E_{\text{H}_2\text{O}}$ is the Nernst voltage associated to the pH_2O gradient:

$$E_{\text{H}_2\text{O}} = -\frac{RT}{2F} \ln \left(\frac{\text{pH}_2\text{O}'}{\text{pH}_2\text{O}''} \right) \quad (25)$$

The protonic transport number was calculated from the fitted parameters of the linear representation of eq.(24) and the total resistance was determined by impedance spectroscopy [12]. The procedure was repeated for different conditions of pH_2O to determine the effect of the degree of humidification on the electronic, protonic and oxide-ionic transport.

The modified emf technique accounts for the voltage loss associated with the electrochemical reactions at the electrodes, considerably improving the accuracy of the determined transport numbers for systems with high electrode-polarisation resistance or with appreciable mixed ionic-electronic transport and high permeation currents [12].

The electrical transport numbers determined from the modified emf method, together with those determined on the basis of the defect-chemistry method, are shown in Fig. 7. Although the two methodologies were applied at different temperatures, there is a good agreement between the results obtained independently from both procedures,

supporting the validity of the defect-chemistry strategy. The oxide-ionic transport numbers determined by the emf method were lower than 0.05 but the uncertainty may be considerable, taking into account the very low oxide-ionic conductivity of the present material under the measured conditions.

Fig. 7. Protonic (a) and electronic (b) transport numbers as a function of p_{H_2O} determined by the defect-chemistry model (closed symbols) and by direct measurement employing the modified emf methodology (open symbols).

Under the oxidising conditions of $p_{O_2} = 0.2$ atm, BZCY72 exhibits mixed-conducting character with an increase of the protonic transport number and decrease of the p-type-electronic transport number for higher values of p_{H_2O} , a trend which is especially apparent at lower temperature (Fig. 7). The p-type electronic transport number is higher than 0.67 for temperatures ≥ 700 °C and $p_{H_2O} < 0.02$ atm. However, this value rapidly decreases to ≈ 0.37 at 600 °C at a water-vapour partial pressure of $p_{H_2O} \approx 0.02$ atm, with a corresponding protonic transport number of ≈ 0.63 under

similar conditions. Levels of humidification of $p\text{H}_2\text{O} \approx 0.1$ atm are required to obtain a value of $t_{\text{H}} \approx 0.8$ at $p\text{O}_2 = 0.2$ atm and $T = 600$ °C. Interestingly, Ricote et al. [23] reported values of t_{H} in the range 0.64-1.00 for the same composition using an isotopic effect of between 1.4 and 1.8 at 600 °C under wet oxidising conditions. Although these values were estimated employing the electrochemical analysis of D_2O - and H_2O -exchanged states, the results determined directly in the present set of experiments fall within this wide range of values. In contrast, emf measurements for BZCY72 with the presence of small amounts of Ni in the perovskite structure or in the grain boundary gave values of total ionic transport numbers in the range 0.25-0.28 at 600 °C under wet oxidising conditions, indicating an enhancement of the p-type electronic component due to the presence of Ni [19]. Nevertheless, in this case, the ionic transport numbers may be underestimated due to the effects of electrode polarisation [12].

Fig. 8. Protonic, oxide ionic and electronic transport numbers as a function of temperature at $p\text{O}_2 = 0.2$ atm (a) and $p\text{O}_2 = 10^{-5}$ atm (b) for a wetting condition of $p\text{H}_2\text{O} = 0.022$ atm

The effect of temperature and oxygen partial pressure on the electrical transport numbers is observed in Fig. 8. Under pO_2 conditions close to air (0.2 atm) and for a typical wetting condition of $pH_2O = 0.022$ atm (Fig. 8(a)), there is an inversion of the principal transport species at ~ 650 °C: p-type electronic transport dominates for temperatures ≥ 700 °C whereas protonic transport does so for temperatures ≤ 600 °C. The protonic transport number increases substantially on decreasing pO_2 under wet conditions. For $pH_2O = 0.022$ atm and $pO_2 = 10^{-5}$ atm, close to typical conditions obtained under N_2 saturated with water at RT, the monotonous decrease of the electron-hole conductivity with lower pO_2 , followed by a negligible change of the protonic and oxide-ionic conductivities (Fig. 6), results in a drop of the electronic transport number with a concomitant enhancement of the transport numbers associated to ionic species (Fig. 8(b)). The transport number associated to protonic species attains a value of about 0.95 at 600 °C and decreases progressively as temperature increases. However, it remains greater than that of the other transport carriers up to 900 °C. Note that the oxide-ionic transport number under oxidising conditions of $pO_2 = 0.2$ atm (Fig. 8(a)) remains below ~ 0.04 for temperatures < 900 °C, but increases considerably to ≈ 0.14 and ≈ 0.17 at 800 and 900 °C, respectively, under moderately reducing conditions ($pO_2 = 10^{-5}$ atm). Figure S4 provides further information of the changing electrical properties with varying conditions employing a 3D configuration of the transport numbers plotted as a function of pO_2 , pH_2O and temperature in the range 600-900 °C.

5. Conclusions

Mapping of the mixed proton and electron-hole transport of the perovskite $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ (BZCY72) is important for the development of this promising material in a number of high-temperature electrochemical applications such as protonic ceramic fuel cells, protonic ceramic electrolyser cells and membrane reactors. In this study, a dense, ceramic membrane of BZCY72 was prepared on synthesis by a modified Pechini method followed by sintering at 1650 °C for 4 hours. Electrical characterisation under different conditions of pH_2O and pO_2 revealed the influence of the different transport species, in accordance with the expected defect chemistry. More oxidising atmospheres increase the total conductivity in dry conditions due to a greater

contribution from electron holes. Under wet conditions, protonic transport predominates at low temperature, with the effect that similar values of conductivity are obtained in O₂, air and N₂ for temperatures lower than 450 °C. The partial components of electrical conductivity, determined in the range 600-900 °C, are considerably affected by pO₂, pH₂O and temperature. Under oxidising conditions (pO₂ ≈ 0.2 atm), the electron-hole component dominates the electrical conduction in dry and humidified (pH₂O ≈ 0.022 atm) atmospheres for temperatures higher than 700 °C. For lower temperatures, in comparable conditions of pO₂ and pH₂O, the principal transport species are protons, with the mixed-conducting character decreasing with temperature. Under wet, moderately reducing atmospheres (pO₂ ≤ 10⁻⁵, pH₂O ≈ 0.022 atm) at temperatures lower than 700 °C, transport is primarily attributable to protons. An apparent contribution from oxygen vacancies occurs only at temperatures ≥ 800 °C, where holes, protons and oxide ions all contribute to conductivity.

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References

- [1] H. Iwahara, Solid State Ionics 168 (2004) 299.
- [2] T. Norby, Y. Larring, Solid State Ionics 137 (2000) 139.
- [3] S. Robinson, a. Manerbino, W. Grover Coors, N.P. Sullivan, Fuel Cells 13 (2013) 584.
- [4] E. Vasileiou, V. Kyriakou, I. Garagounis, a. Vourros, M. Stoukides, Solid State Ionics 275 (2015) 110.
- [5] S.H. Morejudo, R. Zanon, S. Escolastico, I. Yuste-Tirados, H. Malerod-Fjeld, P.K. Vestre, W.G. Coors, A. Martinez, T. Norby, J.M. Serra, C. Kjolseth, Science 353 (2016) 563.
- [6] E. Fabbri, L. Bi, D. Pergolesi, E. Traversa, Energy Environ. Sci. 4 (2011) 4984.
- [7] K. Xie, Y. Zhang, G. Meng, J.T.S. Irvine, J. Mater. Chem. 21 (2011) 195.
- [8] R.M.C. Marques, F.M.B. Marques, J.R. Frade, Solid State Ionics 73 (1994) 15.
- [9] D. Sutija, T. Norby, P. Björnbohm, Solid State Ionics 2738 (1995) 167.
- [10] H.-D. Baek, Solid State Ionics 110 (1998) 255.
- [11] D.-K. Lim, C.-J. Park, M.-B. Choi, C.-N. Park, S.-J. Song, Int. J. Hydrogen Energy 35 (2010) 10624.
- [12] D. Pérez-Coll, G. Heras-Juaristi, D.P. Fagg, G.C. Mather, J. Power Sources 245 (2014) 445.
- [13] D. Pérez-Coll, G. Heras-Juaristi, D.P. Fagg, G.C. Mather, J. Mater. Chem. A 3 (2015) 11098.
- [14] J.R. Frade, Solid State Ionics 78 (1995) 87.
- [15] N. Bonanos, F.W. Poulsen, J. Mater. Chem. 9 (1999) 431.
- [16] J.T.S. Irvine, D.C. Sinclair, A.R. West, Adv. Mater. 2 (1990) 132.
- [17] G.C. Mather, G. Heras-Juaristi, C. Ritter, R.O. Fuentes, A.L. Chinelatto, D. Pérez-Coll, U. Amador, Chem. Mater. 28 (2016) 4292.
- [18] S. Ricote, N. Bonanos, G. Caboche, Solid State Ionics 180 (2009) 990.
- [19] S. Ricote, N. Bonanos, H.J. Wang, R. Haugsrud, Solid State Ionics 185 (2011) 11.
- [20] T. Norby, M. Widerøe, R. Glöckner, Y. Larring, Dalt. Trans. (2004) 3012.
- [21] K.D. Kreuer, Annu. Rev. Mater. Res. 33 (2003) 333.
- [22] D. Pérez-Coll, J.C. Pérez-Flores, N. Nasani, P.R. Slater, D.P. Fagg, J. Mater. Chem. A 4 (2016) 11069.
- [23] S. Ricote, N. Bonanos, M.C. Marco de Lucas, G. Caboche, J. Power Sources 193 (2009) 189.

Table 1. Equilibrium constant values of the hydration reaction, according to Eqs. 1 and 4, at different temperatures.

Temperature (°C)	K_w (atm ⁻¹ ·cm ³)
900	0.61
800	2.83
700	5.88
600	36.31

Table captions

Table 1. Equilibrium constant values of the hydration reaction, according to Eqs. 1 and 4, at different temperatures.

Figure captions

Fig. 1. Scanning electron micrograph of a transversal fracture surface of BZCY72.

Fig. 2. Arrhenius dependence of the electrical conductivity under dry (a) and wet (b) conditions of O₂, air, N₂ and H₂.

Fig. 3. Dependence of the electrical conductivity as a function of pO₂ for a fixed value of pH₂O $\approx$ 0.022 atm at different temperatures: a) classical log-log representation and b) alternative representation according to eq. (19).

Fig. 4. Effect of humidification on the pO₂ dependence of the electrical conductivity at 600 °C, for pH₂O $\approx$ 0.022 and 0.0022 atm: a) classical log-log representation from very reducing to oxidising conditions; b) magnification of the log-log representation in the range of moderately reducing-oxidising conditions; c) representation of σ vs pO₂^{1/4}, according to Eq. (19).

Fig. 5. Representation of the partial conductivities of oxide ions, protons and electron holes as a function of pH₂O at 800 °C, ((a) and (b)) and 600 °C ((c) and (d)); pO₂=0.2 atm for (a) and (c), and pO₂=10⁻⁵ atm for (b) and (d).

Fig. 6. Arrhenius representation of partial conductivities for pO₂ = 0.2 atm, at pH₂O = 0.022 atm (a) and pH₂O = 10⁻⁵ atm (b).

Fig. 7. Protonic (a) and electronic (b) transport numbers as a function of pH₂O determined by the defect-chemistry model (closed symbols) and by direct measurement employing the modified emf methodology (open symbols).

Fig. 8. Protonic, oxide ionic and electronic transport numbers as a function of temperature at pO₂=0.2 atm (a) and pO₂=10⁻⁵ atm (b) for a wetting condition of pH₂O=0.022 atm.

Supplementary Material

Temperature dependence of partial conductivities of the

BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-δ} proton conductor

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Fig. S1. Effect of oxygen partial pressure on the electrical conductivity at 800 °C. The results were obtained at two different values of humidification, $p_{\text{H}_2\text{O}} \approx 0.022$ atm and $p_{\text{H}_2\text{O}} \approx 0.0022$ atm. a) classical log-log representation from very reducing to oxidising conditions; b) magnification of the log-log representation in the range of moderately reducing-oxidising conditions; c) representation of σ vs $p\text{O}_2^{1/4}$, according to Eq. (19).

Fig. S2. Temperature dependence of the hydration-equilibrium constant.

Fig. S3. Effect of an auxiliary parallel variable resistance on the observed electromotive force of the BZCY72 sample subjected to a pO_2 gradient of 0.3/0.1 atm/atm at a fixed condition of $pH_2O = 0.012$ atm, at 750 °C.

Fig. S4. Protonic (a-d), oxide-ionic (e-h) and electron-hole (i-l) transport numbers as functions of pO_2 and pH_2O in the range 600-900 °C.