Methodology for the study of mixed transport properties of a Zn-doped $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ electrolyte under reducing conditions

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Abstract

The mixed ionic-electronic transport properties of the protonic ceramic electrolyser material $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$, with the addition of 4mol% ZnO as sintering additive, are analysed under reducing conditions. The study is performed by means of an active-load modification of the classical electromotive-force method to account for the non-negligible effect of the electrodes on the obtained electrical-transport numbers. The methodology is developed in detail in order to link the electrochemical criteria to simulated equivalent circuits. The observed electromotive force of the system is considerably affected by the introduction of the polarisation resistance of the electrodes in the corresponding analysis, resulting in a high deviation between the present results and those obtained by a classical analysis without attending to electrode effects. Under wet reducing conditions ($p_{\text{H}_2} \approx 0.05 \text{ atm}$, $p_{\text{H}_2\text{O}} \approx 3 \cdot 10^{-3} - 10^{-2} \text{ atm}$), the oxide-ionic transport number is negligible in the range of 600–900 °C, whereas pure protonic conductivity is observed for temperatures $\leq 700 \text{ °C}$ and $p_{\text{H}_2\text{O}} \geq 5.6 \times 10^{-3} \text{ atm}$. For higher temperatures and/or lower $p_{\text{H}_2\text{O}}$, mixed protonic-electronic conduction is exhibited. The electronic contribution under reducing conditions is consistent with n-type electronic behaviour.

Keywords: strontium zirconate; proton-conducting ceramic; modified electromotive force method; protonic transport number; reducing conditions; protonic ceramic electrolyser

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1. Introduction

In recent decades, much effort has been devoted to the development of new clean-energy systems due to widespread concern over global warming and dwindling fossil-fuel reserves ¹⁻⁵. Hydrogen as an energy vector is one of the most interesting alternatives to conventional conversion fuels as it is considered an ideal energy carrier ^{6,7}. In this context, proton-conducting ceramics (or high temperature proton conductors, HTPCs) have attracted the interest of many researchers due to their versatility in many electrochemical devices such as hydrogen-separation membranes, hydrogen sensors, protonic ceramic fuel cells and protonic ceramic electrolyser cells ^{3,8-11}. Most studied materials with protonic-transport properties at high temperature are perovskites (ABO_3), typically alkaline-earth-based cerates or zirconates ^{3,5}. SrZrO_3 -based perovskites are most interesting as protonic ceramic electrolyser candidates as they present good chemical and mechanical stability in comparison to other perovskite protonic conductors such as BaZrO_3 and SrCeO_3 ^{10,12,13}.

The introduction of lower valence dopants in the perovskite creates oxygen vacancies in the dry state, which allows proton incorporation by filling the vacancies on hydration via dissociative absorption of water ⁵. The protonic defects diffuse throughout

the solid by a hopping mechanism with low values of activation energy, leading to high conductivity at relatively low temperatures (350-600 °C) ⁵. Given that water absorption is exothermic ^{3,14,15}, oxygen vacancies are created as the temperature rises. As a consequence, the dominant conducting species typically change from protons at low temperature to oxide ions and/or electronic carriers as the temperature increases ¹⁶. The level of hydration is dependent on the equilibria between the defects under the corresponding conditions of water partial pressure and temperature, and determines the mixed transport properties of the material. The identification of the various conducting species under different working conditions is essential for targeting the potential of materials for application in electrochemical devices.

Ion-conducting oxides submitted to a gradient of active gases experience a temperature-dependent electromotive force (emf) ^{17,18}, which may lead to ambipolar diffusion in the case of mixed-conducting materials ^{8,19,20}. The electrochemical equilibria dictate that the chemical gradient is balanced by an electrical voltage, but also by an internal electrical current. As a consequence, the emf of the system is lower in comparison to a purely ionic conductor and the magnitude of the decrease is directly related to the mixed transport properties of the sample under the working conditions. This is the basis of the emf procedure for determination of the electrical transport numbers of mixed conducting oxides submitted to gradients of active gases. However, in the classical methodology, the electrochemical balance is developed without considering the effect of the polarisation of the electrodes under the internal current flux. Although this consideration has been widely taken into account for mixed oxide-ionic-electronic conductors ²¹⁻²⁵ through the use of modified methodologies, it has rarely been considered for mixed oxide ionic, protonic and electronic conductors ²⁶⁻²⁹.

In our previous work ²⁹, the modified methodology was thoroughly detailed for oxidising conditions and, in this paper, is extended to include reducing conditions where H₂ and H₂O are used as reacting gases. The electrochemical balance is directly linked to simulated equivalent circuits for the study of the mixed transport properties of SrZr_{0.9}Y_{0.1}O_{3-δ} with the addition of ZnO as a sintering additive.

2. Electrochemical potentials

2.1. Purely ionic conductor exposed to chemical potential gradients of active gases

When purely ion-conducting oxides, generically oxide-ionic or protonic conductors, with metallic electrodes at both surfaces, are exposed to a gradient of reacting gases of active species, such as O₂ and/or H₂, the following electrochemical equilibria take place at each interface between the electrode and the electrolyte ¹⁷⁻¹⁹

for an oxide ionic conductor, and

for a protonic conductor. These expressions relate the electrochemical potentials of electrons at the electrode (η_{e^-}) with the chemical potential of gaseous species (μ_{X_2} , where $\text{X}_2 = \text{O}_2$ or H_2) and the electrochemical potential of charge carriers at the electrolyte (η_{X^z} , $\text{X}^z = \text{O}^{2-}$ or H^+) according to ^{19,20,30}

$$\mu_{\text{X}_2} = 2\eta_{\text{X}^z} + 2z\eta_{\text{e}^-} \quad (3)$$

where z represents the charge of the carrier ($z = +1$ and -2 for protons and oxide ions, respectively). The electrochemical potential (η_{i}) of a given charged species “i” is related to the chemical potential (μ_{i}) and the internal electric potential (ϕ) by means of

$$\eta_{\text{i}} = \mu_{\text{i}} + z_{\text{i}}F\phi \quad (4)$$

where F is the Faraday constant.

According to Eq. (3), the difference in the electrochemical potential of electrons at both electrodes may be expressed as

$$\eta'_{e^-} - \eta''_{e^-} = -\frac{1}{z}(\eta'_{X_2} - \eta''_{X_2}) + \frac{1}{2z}(\mu'_{X_2} - \mu''_{X_2}) \quad (5)$$

In general, the gradient of the electrochemical potential of a charged species is related to the current density of the species according to ^{19,20}

$$j_i = -\frac{\sigma_i}{z_i F} \frac{d\eta_i}{dx} \quad (6)$$

If the system is under open-circuit conditions, the total current (ionic current) is equal to zero, and the electrochemical potential of the charge carriers (oxide ions or protons) is constant throughout the electrolyte. Hence, the difference of the electrochemical potential of the electrons at the electrodes may be expressed as a function of the chemical-potential difference of gaseous species in both compartments as follows:

$$\eta'_{e^-} - \eta''_{e^-} = \frac{1}{2z}(\mu'_{X_2} - \mu''_{X_2}) \quad (7)$$

The chemical potential of gaseous species X_2 may be expressed as ^{17,30}

$$\mu_{X_2} = \mu_{X_2}^0 + RT \ln pX_2 \quad (8)$$

where $\mu_{X_2}^0$ is the chemical potential of the species X_2 in standard conditions of temperature and pressure and pX_2 is the partial pressure of the gaseous species.

Recombination of Eqs. (7) and (8) leads to

$$\eta'_{e^-} - \eta''_{e^-} = \frac{RT}{2z} \ln \left(\frac{pX'_2}{pX''_2} \right) \quad (9)$$

where pX'_2 and pX''_2 are the partial pressures of the gaseous species in each compartment. On the other hand, if both electrodes are identical, the chemical potential of the electrons at the electrodes is also identical ³¹, and the difference in

electrochemical potential of the electrons at the electrodes is directly related to the electrical potential, Eq. (4), as follows:

$$\eta'_{e^-} - \eta''_{e^-} = -F(\phi' - \phi'') \quad (10)$$

Recombination of Eqs. (9) and (10) leads to the Nernst equation for determination of the measurable voltage between both electrodes as a function of partial pressures of the active gases in both compartments:

$$E' - E'' = -\frac{RT}{2zF} \ln \left(\frac{pX'_2}{pX''_2} \right) \quad (11)$$

2.2. Mixed conducting oxides submitted to chemical potential gradients of active gases.

2.2.1. Non-polarisable electrodes

The analysis for mixed-conducting oxides will focus on materials with generic charge carriers such as oxide ions, protons and electrons or holes. In this situation, the classical analysis is based on the study of the current density for each specific component according to Eq. (6), which may be rearranged to represent the work required for moving 1 mol of species i through the sample (from I to II) as follows:

$$\int_I^{II} d\eta_i = -\int_I^{II} (j_i z_i F \rho_i) dx \quad (12)$$

where $\rho = 1/\sigma_i$ is the resistivity of the species i . In the particular cases of oxide ions, protons and electrons, the relations may be expressed respectively as

$$\Delta\eta_{O^{2-}} = \int_I^{II} (2Fj_{O^{2-}}\rho_{O^{2-}}) dx \approx 2AFj_{O^{2-}}R_o \quad (13)$$

$$\Delta\eta_{H^+} = -\int_I^{II} (Fj_{H^+}\rho_{H^+}) dx \approx -FAj_{H^+}R_H \quad (14)$$

$$\Delta\eta_{e^-} = \int_I^{II} (Fj_{e^-}\rho_{e^-}) dx \approx AFj_{e^-}R_e \quad (15)$$

where R_O , R_H and R_e are the average values of the ohmic electrical resistance of oxide ions, protons and electronic carriers, respectively, under the specific chemical gradients; A is the area of the electrodes. Equations (3), (13) and (14) may be combined to give the change of electrochemical potentials of O^{2-} and H^+ as a function of both the changes of chemical potential of O_2 and H_2 and of the electrochemical potential change of electrons as follows:

$$2\Delta\eta_{e^-} + \frac{1}{2}\Delta\mu_{O_2} = 2AFj_{O^{2-}}R_O \quad (16)$$

$$-\Delta\eta_{e^-} + \frac{1}{2}\Delta\mu_{H_2} = -AFj_{H^+}R_H \quad (17)$$

Employing Eq. (8) to represent the chemical potentials of gaseous species as functions of the partial pressure of the gases and Eq. (10) to express the electrochemical potential change of the electrons as a function of the electrical voltage, the current densities of the different species may be determined. If no external current is flowing (open-circuit conditions), the total current density is

$$j_{e^-} + j_{O^{2-}} + j_{H^+} = 0 \quad (18)$$

and the measurable electrical voltage between the electrodes may be expressed as ^{26,32,33}

$$E_{th} = t_O \frac{RT}{4F} \ln \left(\frac{pO'_2}{pO''_2} \right) - t_H \frac{RT}{2F} \ln \left(\frac{pH'_2}{pH''_2} \right) \quad (19)$$

where t_O and t_H are the average values of oxide-ion and protonic transport numbers under the chemical gradients, respectively. The average value of the electrical transport number for each component is defined as

$$t_i = \frac{R_i^{-1}}{\sum_i^n R_i^{-1}} = R_T \cdot R_i^{-1} \quad (20)$$

where R_T and R_i are the total resistance of the sample and the ohmic electrical resistance of the species i , averaged under the specific chemical gradients.

2.2.2. Polarisable electrodes

The methodology presented above is based on the assumption that the electrodes are non-polarisable. However, in order to represent the true electrochemical balance, Eqs. (16) and (17) should be modified to include a factor related to electrochemical potential change at the electrodes when electrochemical reactions take place under an internal current load. As a consequence, the real situation leads to an alternative set of equations in which the electrochemical equilibria are expressed as

$$2\Delta\eta_{e^-} + \frac{1}{2}\Delta\mu_{O_2} = 2AF \cdot j_{O_2^-} (R_O + R_{\eta O}) \quad (21)$$

$$-\Delta\eta_{e^-} + \frac{1}{2}\Delta\mu_{H_2} = -AF j_{H^+} (R_H + R_{\eta H}) \quad (22)$$

where $R_{\eta O}$ and $R_{\eta H}$ are the polarisation resistances at the electrodes associated with the electrochemical reactions expressed in Eqs. (1) and (2). We note that Eqs. (21) and (22) are derived under the assumption of a nearly linear dependence of overpotential versus ionic current. This approximation may be considered appropriate for small values of leakage current³⁴. The electrical current of each component is

$$j_{O_2^-} = -\frac{\Delta\phi}{(R_O + R_{\eta O})A} + \frac{RT}{4AF(R_O + R_{\eta O})} \Delta \ln pO_2, \quad (23)$$

$$j_{H^+} = -\frac{\Delta\phi}{(R_H + R_{\eta H})A} - \frac{RT}{2AF(R_H + R_{\eta H})} \Delta \ln pH_2 \quad (24)$$

$$j_{e^-} = -\frac{\Delta\phi}{R_e A} \quad (25)$$

Following the procedure presented above, under open-circuit conditions, the total current of the system should be zero (Eq. (18)), which leads to the following relation for the measurable electromotive force ($E_{\text{obs}} \equiv \Delta\phi$):

$$E_{\text{obs}} = \frac{(R_{\text{O}} + R_{\eta\text{O}})^{-1} \cdot \frac{RT}{4F} \ln\left(\frac{p\text{O}'_2}{p\text{O}''_2}\right)}{(R_{\text{O}} + R_{\eta\text{O}})^{-1} + (R_{\text{H}} + R_{\eta\text{H}})^{-1} + R_{\text{e}}^{-1}} - \frac{(R_{\text{H}} + R_{\eta\text{H}})^{-1} \cdot \frac{RT}{2F} \ln\left(\frac{p\text{H}'_2}{p\text{H}''_2}\right)}{(R_{\text{O}} + R_{\eta\text{O}})^{-1} + (R_{\text{H}} + R_{\eta\text{H}})^{-1} + R_{\text{e}}^{-1}} \quad (26)$$

On comparing Eqs. (19) and (26), it is evident that the polarisation resistance at the electrodes considerably affects the observed electromotive force of the system. Moreover, the value of the measurable electromotive force is not easily related to the transport numbers because of the *a priori* unknown electrode-polarisation resistances.

2.3. Determination of transport numbers by emf methodology.

2.3.1. Classical analysis employing equivalent-circuit approach

In most literature reports of samples with conductive components consisting of protons, oxide ions and electronic carriers exposed to gradients of oxygen and/or hydrogen partial pressures, the electrochemical behaviour has been analysed according to Eq. (19)^{16,32,33,35–38}. This scenario may be represented as the equivalent circuit shown in Fig. 3, for which the voltages of the dc sources satisfy the Nernst equations for purely oxide-ionic and protonic conductors, respectively

$$E_{\text{O}_2} = \frac{RT}{4F} \ln\left(\frac{p\text{O}'_2}{p\text{O}''_2}\right) \quad (27)$$

$$E_{\text{H}_2} = \frac{RT}{2F} \ln\left(\frac{p\text{H}'_2}{p\text{H}''_2}\right) \quad (28)$$

It should be noted that the negative sign in Eq. (28), originating from Eq. (11), has been subtracted in the analysis of the equivalent circuits and should be taken into account on observing the correct location of the dc source, as shown in Fig. 3.

According to Eq. (19), the determination of t_o may be performed by the direct measurement of the emf of the system after setting a gradient of pO_2 in the absence of a pH_2 gradient. Similarly, t_H may be determined by setting a gradient of pH_2 without a pO_2 gradient. However, it is important to note that the situation represented by Eq. (19) and Fig. 3 is not suitable from a practical point of view because of the impossibility of simultaneously setting pO_2 and pH_2 by using oxygen and hydrogen as reacting gases due to the equilibrium between O_2 , H_2 and H_2O :

Given that under reducing conditions it is suitable to use H_2 and H_2O as reacting gases, advantage can be taken of the equilibrium represented by Eq. (29) to set desirable gradients of hydrogen partial pressure and water-vapour partial pressure under reducing atmospheres. In these conditions, the pO_2 gradient may be expressed as

$$\frac{1}{2} \ln \left(\frac{pO'_2}{pO''_2} \right) = \ln \left(\frac{pH_2O'}{pH_2O''} \right) - \ln \left(\frac{pH'_2}{pH''_2} \right) \quad (30)$$

The substitution of Eq. (30) into Eq. (19) leads to the following expression for the theoretical electromotive force of the mixed-conducting sample exposed to gradients of pH_2 and pH_2O :

$$E_{th} = t_o \frac{RT}{2F} \ln \left(\frac{pH_2O'}{pH_2O''} \right) - (t_H + t_o) \frac{RT}{2F} \ln \left(\frac{pH'_2}{pH''_2} \right) \quad (31)$$

Equation (31) provides the basis of the methodology for determination of transport numbers under reducing conditions. This expression is the solution of the equivalent circuit shown in Fig. 3(b), where the dc-source voltage E_{H_2O} takes the form

$$E_{H_2O} = \frac{RT}{2F} \ln \left(\frac{pH_2O'}{pH_2O''} \right) \quad (32)$$

An analogous equivalent circuit was previously developed by Frade²⁰ for oxidising conditions, and adapted here (Fig. 3(b)) for reducing conditions according to Eq. (31). Gradients of pH_2O with simultaneous fixed values of pH_2 in both compartments provide the average oxide-ionic transport number, whereas the application of gradients of pH_2 and the same value of pH_2O at both sides gives the average total ionic transport number. This methodology is consistent with the previously reported study of Yoo and Martin,³⁹ in which they concluded that retaining the chemical potential of one of the active gases as constant throughout the sample, while the other chemical potential gradient is applied, may be the only feasible method for determination of transport numbers for a compound with multiple mobile ionic species.

2.3.2. Modified methodology for the determination of transport numbers under reducing conditions.

From Eq. (26), it follows that the non-ideal electrochemical kinetics at the electrodes should be included in the equivalent circuit as electrical resistances located in series with the specific redox process (oxygen process or hydrogen process). Additionally, Eq. (26) may be expressed in terms of the gradients of pH_2 and pH_2O by means of Eq. (30), which results in the equivalent circuit shown in Fig. 4(a) for the expected electrochemical behaviour of the system, in which the polarisation resistances at the electrodes are non-negligible. The modified methodology presented here for the

determination of transport numbers focuses on the introduction of a parallel variable resistance and the study of its effect on the observed electromotive force, as has been widely performed for mixed electronic/oxide-ionic conducting materials^{23,24,25}.

2.3.2.1. Determination of oxide-ionic transport number (t_o).

Under the approach discussed above, a gradient of pH_2O is established between the two sides of the cell and the pH_2 is set to be equal in both compartments. From the equilibria between the three species, Eq. (29), it follows that

$$pH_2' \approx pH_2'' \quad (33)$$

$$\frac{pO_2'}{pO_2''} \approx \left(\frac{pH_2O'}{pH_2O''} \right)^2 \quad (34)$$

It is important to note that the presence of a pH_2O gradient under reducing conditions does not in itself produce an electromotive force in the absence of a pH_2 gradient. This would be the case, for example, of a mixed protonic-electronic conductor with no oxide-ionic conductivity, as is readily deduced from Eq. (31).

Under these working conditions, the resultant equivalent circuit modified with the parallel auxiliary resistance and including the electrode overpotential may be represented as shown in Fig. 4(b). Given that the pH_2 is set to be equal in both compartments, the dc source E_{H_2} and the overpotential contribution related to the hydrogen electrochemical reaction at the electrodes are removed from the equivalent circuit shown in Fig. 4(a), whereas the overpotential term associated with the oxidation-reduction of oxygen is present because the pH_2O gradient is directly related to the pO_2 gradient (Eq. 34). Solving the circuit it follows that

$$E_{obs} \left[\left(R_O + R_{\eta O} \right)^{-1} + R_e^{-1} + R_H^{-1} + R_{aux}^{-1} \right] = E_{H_2O} \left(R_O + R_{\eta O} \right)^{-1} \quad (35)$$

and

$$\frac{E_{H_2O}}{E_{obs}} - 1 = (R_O + R_{\eta O}) R_{aux}^{-1} + (R_O + R_{\eta O}) (R_e^{-1} + R_H^{-1}) \quad (36)$$

Equation (36) may be represented as a linear function, $y = A_1x + B_1$, where $y = (E_{H_2O} / E_{obs}) - 1$ and $x = R_{aux}^{-1}$. Variation of the external auxiliary resistance produces, therefore, the modification of the observed electromotive force of the system and t_O is directly obtained from the linear fitting of Eq. (36) from

$$t_O = 1 - (t_H + t_e) = 1 - R_T (R_e^{-1} + R_H^{-1}) = 1 - R_T (B_1 / A_1) \quad (37)$$

The total resistance of the sample R_T should be determined by an independent electrical measurement, such as impedance spectroscopy, under the same working conditions.

2.3.2.2. Determination of total ionic transport number ($t_{ion} = t_O + t_H$).

It should be mentioned that, in our approximation, the overall electrochemical behaviour of the sample is governed by the average conditions, which holds for small gradients of the active gases. Hence, the average conditions of pH_2 and pH_2O should be maintained at the same values as those adopted in subsection 2.3.2.1. A constant value of pH_2O equal to the average value of the gradient applied in the previous subsection is thus set in both compartments. Simultaneously, a gradient of pH_2 , with an average value equal to the constant pH_2 established in the previous subsection, is applied to the cell. The equilibrium between the species in the above conditions dictates that

$$pH_2O' \approx pH_2O'' \quad (38)$$

$$\frac{pO_2'}{pO_2''} \approx \left(\frac{pH_2''}{pH_2'} \right)^2 \quad (39)$$

In this context, the pH_2 gradient also produces a gradient in pO_2 , which implies that the electrode contributions assigned to redox reactions of both oxygen and hydrogen may be present. Figure 4(c) shows the resultant equivalent circuit which represents the

sample behaviour with the parallel auxiliary resistance under these conditions. Solution of this circuit leads to the following relation:

$$\begin{aligned} E_{\text{obs}} \left[\left(R_{\text{O}} + R_{\eta\text{O}} \right)^{-1} + \left(R_{\text{H}} + R_{\eta\text{H}} \right)^{-1} + R_{\text{e}}^{-1} + R_{\text{aux}}^{-1} \right] \\ = -E_{\text{H}_2} \left[\left(R_{\text{O}} + R_{\eta\text{O}} \right)^{-1} + \left(R_{\text{H}} + R_{\eta\text{H}} \right)^{-1} \right] \end{aligned} \quad (40)$$

Rearranging,

$$\begin{aligned} \frac{-E_{\text{H}_2}}{E_{\text{obs}}} - 1 = \left[\left(R_{\text{O}} + R_{\eta\text{O}} \right)^{-1} + \left(R_{\text{H}} + R_{\eta\text{H}} \right)^{-1} \right]^{-1} R_{\text{aux}}^{-1} \\ + \left[\left(R_{\text{O}} + R_{\eta\text{O}} \right)^{-1} + \left(R_{\text{H}} + R_{\eta\text{H}} \right)^{-1} \right]^{-1} R_{\text{e}}^{-1} \end{aligned} \quad (41)$$

The factor $(-E_{\text{H}_2} / E_{\text{obs}}) - 1$ may be represented as a linear function of R_{aux}^{-1} , $y = A_2x + B_2$, and the total ionic transport number ($t_{\text{ion}} = t_{\text{H}} + t_{\text{O}}$) is determined on observing the emf of the system for different values of auxiliary resistance according to

$$t_{\text{ion}} = t_{\text{H}} + t_{\text{O}} = 1 - t_{\text{e}} = 1 - R_{\text{T}} \cdot R_{\text{e}}^{-1} = 1 - R_{\text{T}}(B_2 / A_2) \quad (42)$$

The protonic and the electronic transport numbers are readily determined from the total ionic transport number and the previously obtained oxide-ionic transport number.

3. Experimental.

The composition $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ was prepared by solid-state reaction using the previously reported method²⁹. Stoichiometric amounts of SrCO_3 (99.9%, dried at 300 °C), ZrO_2 (99.7 % dried at 600 °C) and Y_2O_3 (dried at 950 °C) were attrition milled in teflon vials and heated at 1100 °C for 12 hours to improve homogenisation of the powders and eliminate organic matter. Subsequently, the mixture was heated at 1250 °C for 24 hours with intermediate milling in an agate mortar then ball-milled with the addition of 4 mol% $\text{Zn}(\text{NO}_3)_2$ as sintering agent, dried and sieved. Sintered samples were prepared from this powder by uniaxial pressing of cylindrical pellets of 15 mm in

diameter and subsequent isostatic pressing at 190 MPa prior to firing at 1500 °C for 6 hours.

Completeness of reaction and phase purity were determined by powder X-ray diffraction (XRD) with a Bruker D8 diffractometer equipped with a solid-state LynxEye detector, using monochromatic $\text{CuK}\alpha_1$ radiation. The microstructure of a polished, thermally-etched transversal membrane surface was examined by field-emission scanning electron microscopy (FE-SEM) with a Hitachi S-4700 instrument. Density was determined by careful measurement of the mass and geometrical volume.

The ionic and electronic transport numbers were determined by the emf methodology following the criteria presented above, employing a previously described dual-chamber electrochemical cell ²⁹. For this purpose, the sintered pellet faces were coated with Pt electrodes by painting with Pt paste (Heraeus) and heating at 950 °C for 1 hour; Pt wires were then attached to assure good electrical contacts. The sample was subsequently sealed to an yttria-stabilised zirconia (YSZ) tube using a glass-ceramic seal ⁴⁰. The electrochemical cell was designed to include a pO_2 sensor by means of painting Pt electrodes to the inner and outer sides of the YSZ tube, which were connected to a multimeter (Agilent 34401A) by Pt wires. The pO_2 sensor is located close to the sample with the purpose of determining the pO_2 gradient across the sample. The chemical-potential gradients of the active species at both sides of the sample were controlled by means of a set of mass-flow controllers following the scheme we reported previously ²⁹, which is similar to that described by Sutija *et al.* ³³. Dry and wet mixtures of N_2 and $\text{N}_2(90\%)/\text{H}_2(10\%)$ were applied to the cell chambers, employing the appropriate fluxes to produce the desired conditions of pH_2 , pH_2O and pO_2 (reducing conditions); Tables 1-3 provide a summary of the gas compositions. The active-load methodology was applied in the temperature range 600-900 °C by the use of a variable

auxiliary parallel resistor and the observed emf of the system was monitored by an Agilent 34401A digit multimeter. In the practical implementation of the procedure, the emf measurement was firstly performed by the direct application of the gases and, secondly, by reversing the gas flows between both compartments in order to eliminate the thermovoltage contribution, as was reported earlier^{27,29,33}. The total resistance of the sample in the set experimental conditions was determined by impedance spectroscopy in the frequency range 0.1-10⁶ Hz with an applied voltage of 250 mV using an Autolab PGStat302N instrument.

4. Results

4.1. Structural and microstructural characterisation

The X-ray powder diffraction pattern of SrZr_{0.9}Y_{0.1}O_{3-δ}-4 mol% ZnO was consistent with the formation of an orthorhombically distorted perovskite structure (space group, *Pnma*) with the presence of ~ 3wt% of SrY₂O₄ as second phase, as determined by Rietveld refinement (Fig. 1). Further details of structural parameters and the effects of the addition of Zn on phase composition and transport properties will be published elsewhere.

A scanning electron micrograph of a polished transversal pellet surface reveals a grain size in the micron range, and that the membrane is free of cracks and open porosity (Fig. 2). Relative density was determined to be ~97 %, above the limit required for gas tightness. The membrane maintained mechanical integrity throughout exposure to the sequence of experimental reducing atmospheres.

4.2. Electrical transport numbers under reducing conditions

Study of the oxide-ionic transport number was performed by setting the same value of p_{H_2} in both cell compartments and applying several different gradients of p_{H_2O} . For this purpose, p_{H_2} was set to 0.05 atm in both chambers by mixing 25 ml·min⁻¹ of N₂ with 25 ml·min⁻¹ of N₂(90%)/H₂(10%). Wetting of the gases was performed by bubbling at room temperature in a KBr-saturated water solution to achieve ~ 83.5% humidification⁴¹, and thereby prevent subsequent condensation in the gas lines. Gradients of p_{H_2O} were created across the membrane by mixing different flow rates of dry and wet gases for each compartment. Under the studied reducing conditions, with no p_{H_2} gradient, the emf is approximately the same in the direct and reverse modes, which suggests that it is mainly associated with the thermovoltage. This magnitude, created by the existence of a real temperature gradient between both surfaces, is highly dependent on the thermoelectrical properties of the sample, and ranges from 6-8 mV at 600 °C to 80-90 mV at 900 °C. In the absence of a p_{H_2} gradient, a minor residual value of emf is usually observed after subtraction of the thermovoltage. Figure 5 represents the effect of the auxiliary resistance on the residual value of the observed emf of the sample, according to Eq. (36), for a fixed condition of $p_{H_2} \approx 0.05$ atm in both compartments and a p_{H_2O} gradient of $p_{H_2O'}/p_{H_2O''} \approx 0.0208/0.0014$ (atm/atm) (Table 1). It is observed that the residual value of the voltage does not follow the linear behaviour of Eq. (36), which indicates that the oxide-ionic transport number should be very close to $t_O \approx 0$, as was inferred by the very low residual value of E_{obs} compared to the expected E_{H_2O} . Similar behaviour was observed in the entire studied range of water-vapour partial pressure and temperature, suggesting that oxide-ionic conduction is essentially absent under the studied range of reducing conditions.

For determination of the total ionic-transport number, a gradient of p_{H_2} was set across the membrane with the same value of p_{H_2O} established in both chambers. The

experiment was performed for several gradients of pH_2 and values of pH_2O (Tables 2 and 3), in which the average conditions were restrained to be identical to those fixed for determination of t_0 . Figure 6 shows an example of the experimental results obtained according to Eq. (41) for a pH_2 gradient of $pH'_2/pH''_2 \approx 0.07/0.03$ (atm/atm) with a fixed value of $pH_2O \approx 0.005$ atm at 600 °C. The measurements were restricted to values of auxiliary resistance in the range 10-100 k Ω in order to prevent any local modification of the concentration of the species in the chambers arising from high currents, and associated deviation of the linear dependence of the overpotential. The very good fit of the experimental data to a linear dependency should be highlighted, which supports the use of Eqs. (41) and (42) for determination of the total ionic transport number. Considering that the oxide-ionic transport number is negligible in the whole range of studied reducing conditions, the total ionic transport is equivalent to the protonic transport number.

At this point, it is important to state that the accuracy of the determined values of transport numbers are highly influenced by the true gradient of pH_2 and/or pH_2O , which will have an incidence on E_{H_2} and E_{H_2O} , according to Eqs. 28 and 32. In this respect, Eq. 30 can be expressed as

$$E_{H_2} = E_{H_2O} - E_{O_2} \quad (43)$$

Hence, $E_{H_2O} \approx E_{O_2}$ when the system is submitted to a gradient of pH_2O without any pH_2 gradient and $E_{H_2} \approx -E_{O_2}$ under the presence of a pH_2 gradient with no pH_2O gradient. As a consequence, the emf observed by the auxiliary YSZ pO_2 sensor submitted to the same conditions as those of the sample could be used for determination of the expected voltages of the virtual dc sources used in the corresponding equivalent circuits (Figs. 4(b) and 4(c)). In this regard, we found non-negligible discrepancies for E_{H_2} and E_{H_2O}

determined from readings of the mass-flow controllers and those determined by the pO_2 sensor, mainly at very low values of applied pH_2O . Such differences may arise from the uncertainty of the mass flow controllers, but also from some discrepancies between the partial pressure of the species at equilibrium in comparison to the starting gradient. For this reason, the study at very low applied pH_2O has been discounted in the analysis. This issue is the subject of further study and will be reported elsewhere. Hence, the presence of the YSZ sensor is essential for an accurate determination of the pH_2 and pH_2O gradients and the study of the electrical transport numbers.

The protonic transport number as a function of the water-vapour partial pressure for an average condition of $pH_2 \approx 0.05$ atm ($\log pH_2$ (atm) ≈ -1.30) determined by both modified and classical methodologies is shown in Fig. 7. It should be noted that a large discrepancy between the results obtained by the two methods is observed. The electrode overpotential has, therefore, a very considerable effect on the observed emf, as we reported for oxidising conditions²⁹ and previously concluded by Bentzer *et al.*²⁶. This is especially the case for the lower values of protonic transport number due to the higher rate of hydrogen permeability. This is confirmed by impedance spectroscopy, Fig. 8, where the presence of a very large electrode contribution is observed. It is worth noting that the low-frequency intercept is not observable in the studied frequency range, which was also reported for similar systems under different working conditions⁴². The determination of the transport number without recourse to determination of the electrode polarisation is thus an advantage of our methodology in comparison to other procedures for the correction of the electrode polarisation effect in emf measurements⁴³. The protonic transport number is higher at lower temperature and is almost unity at 600 °C for an average condition of $\log pH_2O$ (atm) ≈ -2 , but decreases monotonously to $t_H \approx 0.9$ as the pH_2O decreases to $\log pH_2O$ (atm) ≈ -2.5 .

The effect of temperature on the protonic transport number is readily observed in Fig. 9(a), which shows that t_H is approximately constant between 600 and 700 °C, and then decreases considerably as the temperature increases to 800 and 900 °C. This behaviour is observed for different conditions of water-vapour partial pressure, with lower values of t_H as p_{H_2O} decreases. Given that oxide-ion transport is negligible under the studied wet reducing conditions, the protonic transport number is balanced only by the electronic transport number (Eq. (20)), which is represented as a function of temperature for different values of wet conditions in Fig. 9 (b). It follows that the electronic transport number remains practically constant at 600-700 °C and then increases monotonously as temperature increases to 800 and 900 °C. The behaviour of the material thus changes from purely proton conducting at 600-700 °C for the higher values of humidification ($\log (p_{H_2O}^{av}/\text{atm})$ between ≈ -2 and -2.25) to protonic-electronic mixed conducting for higher temperatures and/or lower values of p_{H_2O} (Fig. 6).

4.3. Protonic and electronic conductivities

Figure 10 shows the temperature dependence of the protonic conductivity for an average value of $p_{H_2}^{av} \approx 0.05$ atm for different values of $p_{H_2O}^{av}$, obtained from combining the determined proton transport number with the total resistance of the system measured by impedance spectroscopy under the same working conditions. As is expected, the conductivity increases at higher temperatures due to the increasing mobility of the carriers. Moreover, a typical bending at high temperature is apparent under different conditions of p_{H_2O} , attributable to the loss of protonic charge carriers at higher temperature according to the exothermic character of the hydration reaction^{3,14,15,44}.

In accordance with Fig. 9, a high level of hydration proportional to pH_2O is retained until 700 °C; however, at higher temperatures, the sample starts to dehydrate. It is notable that, although some oxide-ionic transport may be expected from Eq. (44), the decrease of the concentration of protonic defects is not sufficient to produce measurable values of oxide-ionic conductivity, given that, even at higher temperature, it is shown that $t_{\text{ion}} \approx t_{\text{H}}$.

Figure 11 shows the representation of different components of conduction as functions of $\text{pH}_2\text{O}^{\text{av}}$ for a fixed condition of $\text{pH}_2^{\text{av}} \approx 0.05$ atm. It is observed that both the total conductivity and the protonic conductivity decrease monotonously as pH_2O decreases. For the higher value of pH_2O ($\log(\text{pH}_2\text{O}^{\text{av}}/\text{atm}) \approx -2$), total conductivity is mainly protonic as is apparent from the high values of protonic transport number, even at high temperature ($t_{\text{H}} \geq 0.91$). However, as pH_2O decreases, the difference between the total conductivity and the protonic conductivity increases, due to the increasing role of electronic charge carriers on the total transport; the greater influence of electronic transport with decreasing pH_2O is more evident at higher temperature as the sample is less hydrated. This suggests that electronic carriers are generated under reducing conditions according to the following equilibrium^{5,45,46}:

The decrease of the concentration of protonic defects is thus countered by an increase of the concentration of electrons for a given condition of pH_2 and T . This can be understood on consideration of the equilibrium of Eq. (29), where a fixed condition of pH_2 directly relates the decrease of pH_2O with a decrease of pO_2 leading to an increase of the electronic conductivity, in good agreement with the expected n-type electronic contribution for reducing conditions:

Note that Eq. (45) is a combination of Eqs. (29), (44) and (46). We note that the very low values of electronic transport number (mainly at lower temperature and higher pH_2O) are susceptible to a high amount of uncertainty which is reflected in the calculation of the electronic conductivity.

Regarding the nature of the electronic behaviour, the effect of ZnO as sintering additive on the mixed transport properties of SZY will be analysed elsewhere. However, reports on the electrical properties of ZnO ^{47,48} revealed that hydrogen could act as a donor, increasing the n-type electronic conductivity.

Figure 12 shows the protonic conductivity as a function of the water-vapour partial pressure for reducing conditions compared with our results obtained under oxidising conditions ²⁹. It is observed that the sample presents similar values of protonic conductivity in both wet hydrogen and oxygen. This interesting result suggests that the concentration of protonic defects in our sample is mainly governed by the equilibrium of Eq. (44) for both reducing and oxidising atmospheres. An independent study of the protonic conductivity as a function of hydrogen partial pressure for a fixed value of $\text{pH}_2\text{O} \approx 10^{-2}$ atm, presented in the inset of Fig. 12, confirms that the protonic conductivity is practically constant over a wide range of pH_2 . This indicates that the concentration of protonic defects is mainly dependent on pH_2O , most likely because the oxygen-vacancy concentration of the sample is not considerably affected by pO_2 and/or pH_2 for the fixed condition of pH_2O . The conductivity results were compared with the expected values calculated from defect equilibria. Hence, for further analysis, the concentration of protonic and electronic defects were expressed as a function of the oxygen vacancy concentration by means of Eqs. (44) and (46):

$$[\text{OH}_\text{O}^\bullet] \approx K_\text{H}^{1/2} p\text{H}_2\text{O}^{1/2} [\text{V}_\text{O}^{\bullet\bullet}]^{1/2} \quad (47)$$

$$[\text{e}'] \approx K_\text{r}^{1/2} p\text{O}_2^{-1/4} [\text{V}_\text{O}^{\bullet\bullet}]^{-1/2} \quad (48)$$

where K_H and K_r represent the equilibrium constants associated with Eqs. 44 and 46, respectively. On the other hand, the concentration of the different species is related by means of the electroneutrality conditions as follows:

$$[\text{OH}_\text{O}^\bullet] + 2[\text{V}_\text{O}^{\bullet\bullet}] \approx [\text{e}'] + [\text{Y}'_\text{Zr}] \quad (49)$$

Equations 47-49 may be recombined and expressed as a polynomial equation, which is solved by means of the Newton-Raphson numerical method⁴⁹, using values of equilibrium constants for Eqs. (44) and (46) consistent to those previously reported in the literature for similar systems^{49,50,51,52} (Table 4). An estimation of the concentration of various defects as a function of water partial pressure is represented in Fig. 13. These results agree with the defect profiles of the generic mixed-conducting perovskite system $\text{AB}_{1-y}\text{M}_y\text{O}_{3-y/2\pm\delta}$ (where A and B are divalent and tetravalent cations and M is a trivalent cation) reported by Bonanos et al.⁴⁹ for different conditions of $p\text{O}_2$ and $p\text{H}_2\text{O}$, where the protonic species show the same increase with increasing $p\text{H}_2\text{O}$ under both reducing and oxidising conditions at constant values of $p\text{O}_2$. We note that our results are obtained with a H_2 flux ($p\text{H}_2 \approx \text{constant}$), which means that $p\text{O}_2$ is not constant but increases with increasing $p\text{H}_2\text{O}$. However, this should not affect the expected concentration of protonic defects and oxygen vacancies, which are mainly independent of $p\text{O}_2$ in the range $10^{-20} - 1$ atm for a fixed $p\text{H}_2\text{O}$ of $10^{-3} - 10^{-1}$ atm, in good agreement with the results shown in Fig. 12. The defect profiles were adjusted to the conductivity data assuming reasonable relations among the mobility of the different carriers (Table 4). The experimental conductivity results for the different carriers fit reasonably well to the expected behaviour according to the defect chemistry for $p\text{H}_2\text{O} > 10^{-3}$ atm (Fig. 14). It is apparent that the total conductivity is mainly influenced by protonic conductivity; however, n-

type electronic carriers affect the overall behaviour for lower values of $p\text{H}_2\text{O}$. It is worth noting that the oxide-ionic-conductivity profile was obtained considering that the mobilities of oxide ions and protons follow $\mu_{\text{H}} \approx 50 \mu_{\text{O}}$, a comparable ratio to that previously assumed⁵⁰. Although the profile is very estimative, the obtained values of oxide-ionic transport number (Fig. 14(b)) remain below 0.05, in good agreement with our findings of negligible oxide-ionic conduction. In conclusion, the mixed transport properties of the title compound determined by the modified emf methodology follow the behaviour expected on the basis of the defect chemistry and mobility values reported in the literature.

5. Conclusions

The mixed transport properties of $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ under wet reducing conditions have been analysed by an active-load modification of the electromotive force methodology to correct for electrode polarisation in the measurement of transport numbers. The modified procedure was specifically developed in detail in this work for reducing atmospheres, relating the expected electrochemical behaviour in controlled working conditions of $p\text{H}_2$, $p\text{O}_2$ and $p\text{H}_2\text{O}$ to different equivalent circuits. It was shown experimentally that the classical analysis of transport-number determination by the emf method leads to considerable deviations of the measured transport properties if the samples exhibits mixed conduction and the electrode polarisation is non-negligible.

The results confirmed that $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ with the addition of 4 mol % ZnO is a purely protonic conductor for conditions of high humidification ($\log [p\text{H}_2\text{O} (\text{atm})] \geq -2.25$) in the range 600-700 °C. For higher temperatures and/or lower values of humidification, the sample is an electronic-protonic mixed conductor. The protonic conductivity was highly dependent on $p\text{H}_2\text{O}$ for a fixed condition of $p\text{H}_2$, decreasing

considerably with decreasing $p\text{H}_2\text{O}$. In contrast, the electronic conductivity increased with lower levels of humidification, consistent with the prevalence of n-type electronic charge carriers under a hydrogen flux. In this context, for fixed conditions of $p\text{H}_2\text{O}$, the protonic conductivity was practically independent of $p\text{H}_2$ and $p\text{O}_2$ over the approximate range $10^{-20} \leq p\text{O}_2 \leq 10^{-1}$ atm.

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Tables

Table 1. Composition of gases applied to each chamber for determination of the oxide ionic transport number in the range 600-900 °C.

t_o	Gas A N ₂ (ml/min)	Gas B H ₂ (10%)/N ₂ (90%) (ml/min)	Dry gas (ml/min)	Wet gas (ml/min)
Chamber I	25	25	48	2
Chamber II	25	25	49	1
Chamber I	25	25	0	50
Chamber II	25	25	49	1

Table 2. Gas composition at each compartment employed for determination of the total ionic transport number at each temperature. The study was performed as a function of pH₂O in the range 600-900 °C. The values of open-circuit voltage of the sample obtained at 700 °C are also shown.

t_{ion}	Gas A N ₂ (ml/min)	Gas B H ₂ (10%)/N ₂ (90%) (ml/min)	Dry gas (ml/min)	Wet gas (ml/min)	E _{obs-OCV} (mV)
Chamber I	15	35	33.25	6.75	17.1
Chamber II	35	15	33.25	6.75	
Chamber I	15	35	37	13	18.1
Chamber II	35	15	37	13	
Chamber I	15	35	24.5	25.5	17.6
Chamber II	35	15	24.5	25.5	

Table 3. Gas composition at each chamber for the study of the total ionic transport number as a function of pH₂. The observed values of open-circuit voltage of the sample at 800 °C are also presented.

t_{ion}	Gas A N ₂ (ml/min)	Gas B H ₂ (10%)/N ₂ (90%) (ml/min)	Dry gas (ml/min)	Wet gas (ml/min)	E _{obs-OCV} (mV)
Chamber I	35	15	24.5	25.5	15.2
Chamber II	45	5	24.5	25.5	
Chamber I	30	20	24.5	25.5	10.5
Chamber II	40	10	24.5	25.5	
Chamber I	25	25	24.5	25.5	8.5
Chamber II	35	15	24.5	25.5	
Chamber I	5	45	24.5	25.5	21.9
Chamber II	35	15	24.5	25.5	

Table 4. Values of equilibrium constant and relation between mobilities of different charge carriers employed for determination of the defect profiles and conductivities. Some results previously reported in the literature are shown for comparison.

Reference	Compound	K_H (atm^{-1})	K_r ($\text{atm}^{1/2}$)	μ_H/μ_O	μ_e/μ_H
This work, 900 °C	$\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$	1.3	2×10^{-20}	50	105
Bonanos and Poulsen ⁴⁹ , 800 °C	$\text{AB}_{1-y}\text{M}_y\text{O}_{3-y/2 \pm \delta}$	20	10^{-17}		
T. Schober et al. ^{50,51} , 900 °C	$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$	0.8		20	100
H. Uchida et al. ⁵² , 900 °C	$\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$	1.1			

Figures

Fig. 1. Observed (circles), calculated (continuous line) and difference (continuous line at bottom) X-ray powder diffraction profiles of $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$. Upper and lower vertical bars indicate the expected position of $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ and SrY_2O_4 Bragg peaks, respectively

Fig. 2. Scanning electron micrograph of a polished, thermally-etched, transversal surface of $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ with 4 mol% ZnO

Fig. 3. (a) Equivalent-circuit model representing the electrochemical behaviour of a mixed-conducting oxide with protons, oxide ions and electronic species as charge carriers, exposed to gradients of pO_2 and pH_2 ; (b) modification of the equivalent circuit, representing the expected behaviour under reducing conditions with simultaneous control of pH_2 and pH_2O gradients. The effect of the electrodes is not taken into account in either representation.

Fig. 4. (a) Equivalent-circuit model representing the real electrochemical behaviour of a mixed-conducting sample exposed to gradients of pH_2 and pH_2O ; (b) equivalent- circuit model representing the electrochemical behaviour of the sample exposed to a gradient of pH_2O with fixed values of pH_2 in both electrochemical-cell compartments and a parallel external resistance; (c) equivalent-circuit model of the sample submitted to a gradient of pH_2 without gradient of pH_2O in parallel with an external resistance.

Fig. 5. Representation of experimental data obtained employing the modified methodology for determination of the oxide-ionic transport number according to Eq. (36).

Fig. 6. Representation of the experimental data obtained by the modified emf methodology for different values of auxiliary resistance registered at 600 °C under a pH_2 gradient of 0.07/0.03 atm/atm with $pH_2O \approx 0.005$ atm in both cell compartments.

Fig. 7. Protonic transport number under reducing conditions as a function of the water-vapour partial pressure at 600 and 900 °C. Open and closed symbols correspond to the values calculated according to the classical (Eq. (31)) and modified (Eq. (41)-(42)) methodologies, respectively.

Fig. 8. Typical impedance spectrum obtained under a hydrogen chemical potential gradient without water-vapour gradient.

Fig. 9. Temperature dependence of protonic (a) and electronic (b) transport numbers for different values of water-vapour partial pressure at a given condition of hydrogen partial pressure.

Fig. 10. Temperature dependence of the protonic conductivity for an average value of $p\text{H}_2 \approx 0.05 \text{ atm}$ and selected humidity conditions.

Fig. 11. Representation of protonic conductivity (closed squares), electronic conductivity (circles) and total conductivity (open squares) as a function of the water-vapour partial pressure under reducing conditions ($p\text{H}_2^{\text{av}} \approx 0.05$ atm).

Fig. 12. Comparison of protonic conductivity as a function of the water-vapour partial pressure for reducing ($\text{pH}_2 \approx 0.05 \text{ atm}$) and oxidising ($\text{pO}_2 \approx 0.2 \text{ atm}$) conditions. The inset represents the protonic conductivity as a function of pH_2 for a fixed value of $\text{pH}_2\text{O} \approx 0.01 \text{ atm}$.

Fig. 13. Estimation of defect-concentration profiles for different carriers as function of $p\text{H}_2\text{O}$ obtained by solving the defect-chemistry equilibria employing the equilibrium constants presented in Table 4.

Fig. 14. Experimental results of conductivity (a) and transport numbers (b) compared to the values calculated from the defect-chemistry equilibria employing the values of equilibrium constants and mobility ratios from Table 4. Experimental data are represented as symbols and calculated results as lines.