



Transport-number determination of a protonic ceramic electrolyte membrane via electrode-polarisation correction with the Gorelov method



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HIGHLIGHTS

- Transport numbers of $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ are measured in wet and dry oxidising atmospheres.
- The suitability of equivalent circuits to describe the system is analysed.
- Transport numbers are highly inaccurate if no polarisation correction is applied.
- Ionic conductivity is totally protonic for high $p\text{H}_2\text{O}$.
- Considerable electronic conductivity under dry and wet atmospheres is observed.

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ABSTRACT

Analysis of transport numbers is critical for assessing the suitability of an ion-conducting material for a given electrochemical application and the conditions for its employment. In this work, the proton, oxide-ion and electron transport numbers of the candidate protonic ceramic electrolyser and fuel cell material $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ (with the addition of 4 mol% ZnO as sintering aid) are measured in wet and dry oxidising atmospheres in the temperature range 700–850 °C. The determination of proton transport numbers is analysed in detail, encompassing the suitability of equivalent circuits in different conditions and the inclusion of an external parallel resistance for the correction of electrode-polarisation effects (Gorelov method). It is confirmed that transport numbers are highly inaccurate if no polarisation correction is applied. In dry oxidising conditions oxide-ion transport numbers, t_{O} , lie in the range 0.63–0.78. The conductivity in wet oxidising conditions is dominated by protons and an electronic component, with the proton transport number increasing from 0.79 to 0.88 with increasing $p\text{H}_2\text{O}$ in the range $1.1 \times 10^{-3} \leq p\text{H}_2\text{O} \leq 1.27 \times 10^{-2}$ atm at 700 °C.

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1. Introduction

One of the most important energy vectors of the future for motive power, stationary-energy needs and portable electronics is likely to be hydrogen [1–4]. Presently, many large and growing industrial processes also require this fuel as a reactant, which currently is mostly extracted from dwindling hydrocarbon sources. Alternative production methods, which are both sustainable and environmentally benign, are thus very necessary in the medium term.

Pure, dry hydrogen required for power in fuel cells and certain industrial applications may be produced efficiently in a high temperature range 600–900 °C through the electrolysis of steam employing a ceramic proton-conducting membrane [5,6]. Such protonic ceramic electrolyser cells (PCECs) conduct protons through a dense oxide, typically a stable perovskite membrane, evolving hydrogen at the cathode. In contrast to an oxide-ion-conducting membrane (SOEC, solid oxide electrolyser cell), the produced hydrogen does not need to be separated from reactant steam. The study of PCECs is still in its infancy, although SrZrO_3 -based phases have emerged as very strong candidates for this application due to their good chemical and mechanical stability in comparison to other perovskite proton conductors [5,7]. These advantages of SrZrO_3 suggest that, despite its more moderate conductivity than

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competitor perovskite proton conductors such as BaZrO₃- and BaCeO₃-based phases [8], it may also be employed as electrolyte in protonic ceramic fuel cells (PCFCs) in a thin-film configuration.

The determination of transport numbers of ion-conducting ceramics for electrolyzers, fuel cells and related electrochemical devices is of considerable interest for evaluating both their suitability for application and performance. In the case of PCECs, a high proton-transport number is required to maximize the current efficiency of steam electrolysis. Protons are incorporated in wet conditions as a result of acceptor doping on the B site of the perovskite, with a hydroxyl group and a proton from an ambient water molecule replacing an oxygen vacancy, V_O^{••}



In dry atmospheres and high temperatures water is desorbed, resulting in the formation and migration of oxygen vacancies. Alternatively, the oxygen vacancies may be compensated in oxidising atmospheres by the formation of electron holes.

The range of operation of an electrolyte material is limited by the electrolytic domain, whereas the joint diffusion of protonic defects and oxide-ion vacancies gives rise to the transport of water vapour in a chemical potential gradient of steam [9]. This is undesirable for the production of dry H₂ by electrolysis but could be favourable in a fuel-cell application where steam permeation from the cathode to the anode provides the water vapour for internal reforming of hydrocarbons [10]. Mapping of transport properties under a range of conditions is, therefore, most important for the further development of these promising materials in electrochemical applications.

The emf method for the determination of transport numbers in oxide-ion-conducting ceramics is fairly widely employed [11,12]. Electrode polarisation effects lead to a significant underestimation of the transport number of oxide-ion conductors by the emf method [13]. The Gorelov method of applying an external variable resistance in parallel with the cell, simulating the effect of enhanced electronic conductivity, provides a means of correcting for the polarisation resistance [13,14]. Very few works have applied the Gorelov method for the correction of proton transport numbers [15,16]. In this paper, we examine in more detail than these previous reports the emf technique for proton-transport determination and the application of the Gorelov (active-load) method for the correction of electrode polarisation in the candidate PCEC and PCFC material SrZr_{0.9}Y_{0.1}O_{3-δ} with the addition of ZnO (4 mol%) as sintering aid (SZY–Zn) [17] in wet oxidising conditions.

2. Theoretical

2.1. General aspects of the determination of transport numbers

In mixed-conducting oxides with several types of conducting species, it is practical to use the transport number of the corresponding species “*j*”, defined as:

$$t_j = \frac{\sigma_j}{\sigma_{\text{tot}}} = \frac{\sigma_j}{\sum_j \sigma_j} = \frac{1/R_j}{\sum_j 1/R_j} \quad (2)$$

where σ_j and σ_{tot} are the *j* carrier conductivity and total conductivity, respectively, and R_j is the resistance associated with the transport of the *j* carrier through the sample. It is apparent from Eq. (2) that

$$\sum_j^n t_j = 1 \quad (3)$$

When the charge carriers are protons, oxide ions and electrons (or holes), the electrical transport through the sample can be represented by the equivalent circuit shown in Fig. 1(a); Eqs. (2) and (3) then yield

$$t_{\text{H}} = \frac{R_{\text{H}}^{-1}}{R_{\text{H}}^{-1} + R_{\text{O}}^{-1} + R_{\text{e}}^{-1}} = 1 - (t_{\text{e}} + t_{\text{O}}) = 1 - R_{\text{T}} \left(\frac{1}{R_{\text{e}}} + \frac{1}{R_{\text{O}}} \right) \quad (4)$$

and

$$t_{\text{O}} = 1 - R_{\text{T}} \left(\frac{1}{R_{\text{e}}} + \frac{1}{R_{\text{H}}} \right) \quad (5)$$

where subscripts H, O and e represent protons, oxide ions and electronic carriers, respectively, and R_{T} is the overall resistance of the sample (bulk + grain boundary). Moreover, the total ionic transport number is given by

$$t_{\text{ion}} = t_{\text{H}} + t_{\text{O}} = 1 - t_{\text{e}} = 1 - R_{\text{T}} \frac{1}{R_{\text{e}}} \quad (6)$$

The application of an external electric field to the sample produces a combined charge-transport process with parallel flows of charged species. As a consequence, the main conducting contribution prevails and minor components may be masked. Thus,

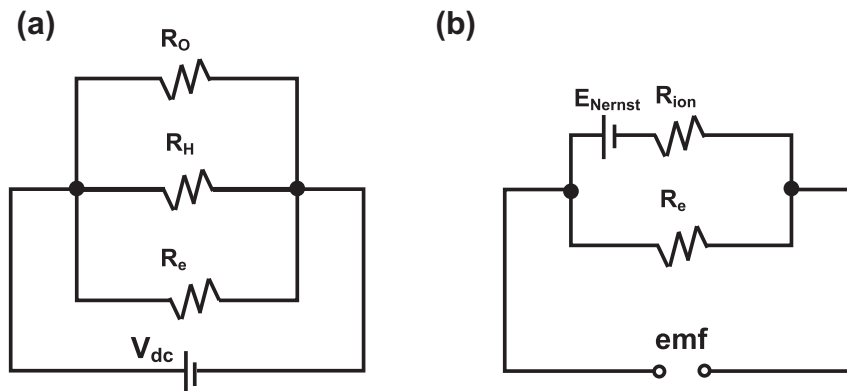


Fig. 1. (a) Parallel transport of oxide ions, protons and electronic carriers through the mixed conducting sample submitted to an electrical field. (b) Equivalent circuit of a mixed-conducting sample with generic ionic and electronic carriers submitted to a chemical potential gradient of the active species under the ideal assumption that there is no polarization at the electrodes.

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