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Characterization of electrical conduction and nature of charge carriers in mixed and ionic conductors

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HIGHLIGHTS

- The electronic transport of $La_{9.6}Si_6O_{26.4}$ oxyapatite is lower than 3×10^{-3}.
- $La_{9.6}Si_6O_{26.4}$ oxyapatite does not exhibit proton conduction under usual conditions.
- The measurement setup for the hydrogen semi-permeation is reported.

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ABSTRACT

The characterization of proton conduction leads to controversial data, often resulting from misinterpretation of the experimental measurements. All methods require the detection of minute variations in the hydrogen concentration in a flowing gas. Such analysis in a gas containing water vapor is a challenge. We propose a new setup allowing the measurement of $P(O_2)$, $P(H_2)$ and $P(H_2O)$. Two methods for determination of the transport numbers are used, i.e., the permeation and Faradaic efficiency methods. Two cases are considered in this study, i.e., a mixed conductor (mostly electronic conductor), i.e., palladium, and a purely ionic conductor, i.e., $La_{9.6}(SiO_4)_6O_{2.4}$ oxyapatite, which is an anionic conductor, though protonic conduction has been assumed in recent studies. This study clearly shows that $La_{9.6}(SiO_4)_6O_{2.4}$ oxyapatite is a pure anionic conductor, without contribution from protonic conduction, under usual conditions (1 atm., 475–615 °C).

1. Introduction

Recent developments in solid oxide fuel cells operating at low temperature (500–600 °C), electrolyzers, sensors, and membrane reactors are largely based on the use of proton conductors [1–9]. However, the mechanisms of proton incorporation and transport through the solid electrolyte are still not clearly understood due to the difficulty in quantifying and localizing protons in the electrolyte phase and in differentiating protonic conduction from the conductivity of "native" ions [10]. In an oxide, protonic conduction may arise from various equilibria:

$$- \text{hydration reaction in wet atmosphere}: \ H_2O + V_O^{\bullet\bullet} + O_O^{\times} \Leftrightarrow 2OH_O^{\bullet} \quad (1)$$

$$- \text{oxidation of hydrogen}: \ H_2 + 2O_O^{\times} \Leftrightarrow 2OH_O^{\bullet} + 2e' \quad (2)$$

The characterization of proton conduction is complex and leads to controversial data, resulting from the difficulty in carrying out experimental characterizations and from misinterpretation of the experimental measurements. Recent studies reported in the literature have suggested partial protonic conduction in some oxides, but the experimental approach was often not appropriate to give real evidence of proton conduction. As an example, $La_{9.75}(Ge_6O_{24})O_{2.62}$ oxyapatite is a well-known oxide ion conductor; however, a recent study based on impedance spectroscopy experiments suggested that this material presents partial protonic conduction [11]. In this study, electrical characterization has been performed under

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two different atmospheres (dry and wet synthetic air), and the authors assume that the variation in electrical conductivity of the apatite phase in both atmospheres can be linked to the variation in protonic conductivity. Nevertheless, the pellets used were not very dense (80–85% of the theoretical density), although the relative density of the material seems to be one of the key parameters of protonic conduction in numerous oxide materials [12]. Trace hydrated reagents as a secondary phase or absorbed water in the materials could also modify the protonic conductivity in the apatite phase or in other oxides, such as perovskite materials. In addition, impedance spectroscopy experiments do not allow the identification of charge carriers in materials, as explained in this work.

The goal of this study is, first, to briefly identify the advantages and limits of the different methods of characterization of proton conduction in oxides. We describe in further detail two methods allowing the determination of protonic conductivity in mixed or ionic oxide materials, i.e., the hydrogen semi-permeation and Faradaic efficiency methods. These two methods allow the clear identification of charge carriers, such as anionic oxygen or protons, with good accuracy for ionic conductivity measurements.

In all the developed methods, one of the most difficult experimental tasks is to measure small variations in the hydrogen partial pressure of a flowing gas containing water vapor. We propose an experimental method for the simultaneous measurement of $P(O_2)$, $P(H_2)$ and $P(H_2O)$ by using an oxygen zirconia pump, an oxygen zirconia sensor, and a chilled mirror hygrometer. In this work, we selected two materials, i.e., palladium as an example of a mixed electronic- and protonic-conductor and the oxyapatite phase, which is presently the subject of a controversial interpretation of its ionic transport mechanism.

2. Experimental methods proposed for transport characterization in protonic conductors

The three main objectives of the following studies are the determination of additional electronic conductivity (n- or p-type), the determination of ionic conductivity as a function of temperature and composition, and the determination of the nature of the ionic carriers. In oxide ion conductors, the mobile carriers are generally oxide ions and electrons or electron holes (the electronic defects are generally localized small polarons and not conduction- or valence-band electrons). Moreover, the gas composition can be determined accurately using specific oxygen sensors. With hydrogen, the situation is much more complicated for two main reasons: no adequate hydrogen sensors are available and the materials are often conducting through anionic, cationic and electronic defects, according to the gas composition and temperature. Consequently, for the development of these promising protonic materials in electrochemical applications, mapping of the transport properties under a range of experimental conditions is essential.

The usual methods reported in the literature to determine transport numbers in protonic conductors are measurement of the bulk conductivity [10,13–15], electromotive force (emf) measurements [10,16–21], and the Faradaic efficiency technique [22,23]. Even if it is a widely used method of characterization of transport properties in oxide ion conductors, to our knowledge, permeation measurements on protonic oxides have not yet been carried out. It should be noted that these methods require careful signal treatment in order to account for all the sources of error. Moreover, these methods allow the determination of ionic and electronic transport numbers. However, in the case of two or more ionic carriers, the identification of the charge carrier and its corresponding transport number is not easy and not always possible.

Thus, this work suggests a rational approach with different methods for transport measurement to identify the transport number or ionic conductivity in relation to the nature of the charge carrier. For example, for palladium (predominant electronic conductor) and oxyapatite materials (predominant ionic conductor), the general approach is given in Fig. 1.

The various techniques available for conductivity measurement and/or transport number determination are described in the next Sections 2.1–2.4.

2.1. Conductivity measurement

This method consists of the measurement of the total electrical conductivity by using impedance spectroscopy or the 4 points ("van der Pauw") method. The usual approach using these two methods is based on the determination of the "electrolytic domain" corresponding to an ionic transport number higher than 0.99 by plotting the total conductivity as functions of $P(O_2)$ (or $P(H_2)$) ("Patterson diagram"), as shown in Fig. 2. If a plateau is obtained (see Fig. 2a and c), the additional conductivity, either p-type conductivity (in the high oxygen pressure domain) or n-type electronic conductivity (in the low oxygen pressure range) can be easily estimated. In other cases (see Fig. 2b), a plateau is not obtained, and an additional technique, coupled with a thermodynamic model of the point defects, has to be used.

The studied material is in equilibrium with the gas phase, and no polarization phenomena have to be taken into account, as with

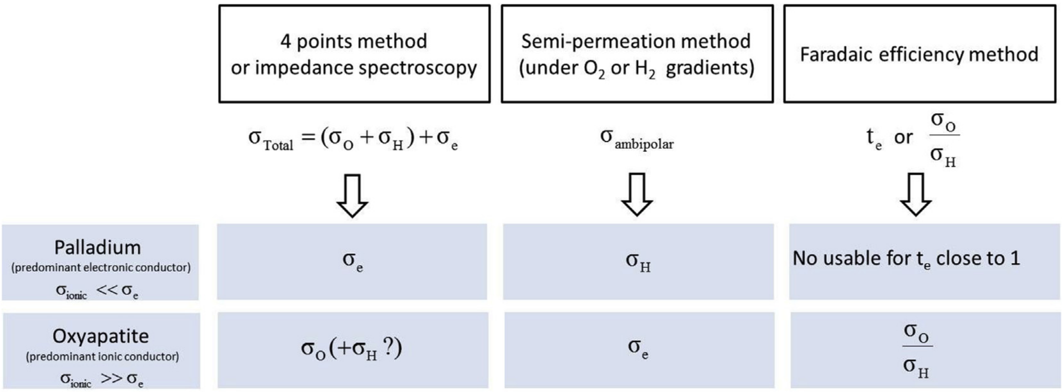

Fig. 1. The general approach suggested in this work with different methods used for conductivity measurements: σ_e electronic conductivity, σ_O oxygen anionic conductivity, σ_H protonic conductivity (with $\sigma_{ambipolar}$ ambipolar conductivity and σ_{Total} total conductivity).