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Transport number measurements and fuel cell testing of undoped and Mo-substituted lanthanum tungstate

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HIGHLIGHTS

- Partial conductivities have been extracted for LWO and Mo-LWO.
- Lanthanum tungstate is suitable as electrolyte for PC-SOFCs.
- Mo-substituted LWO is more suited as membrane material for H_2 gas separation.

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ABSTRACT

The partial protonic, oxide ion and electronic conductivities of lanthanum tungstate ($La_{28-x}W_{4+x}O_{54+\delta}$ with $x = 1$, LWO54) and 30% molybdenum substituted lanthanum tungstate (Mo-LWO54) have been extracted using the EMF method. LWO54 is a relatively pure ionic conductor up to ~800 °C; above that temperature electrons start to contribute significantly (under reducing conditions). The maximum protonic conductivity is $\sim 2-3 \times 10^{-3}$ S cm^{-1}, and protonic conductivity dominates the ionic regime under wet conditions below ~700 °C. Above this temperature, oxide ion conductivity dominates the ionic contribution. The protonic and oxide ion conductivities for Mo-substituted LWO54 are quite similar to the Mo-free material, while the electronic conductivity is almost one order of magnitude higher for the former in wet 5% H_2/Ar. From this report is clear that nominally undoped lanthanum tungstate is most suited for applications as electrolyte in proton conducting SOFCs, while Mo-LWO54 presents improved mixed proton-electron conductivity for use as dense membrane for hydrogen separation.

1. Introduction

Lanthanum tungstate with the newly proposed stoichiometry $La_{28-x}W_{4+x}O_{54+\delta}v_{2-\delta}$ (earlier on referred as La_6WO_{12}) [1] belongs to a family of materials with very interesting properties for technological applications [2–6]. The nominally undoped material ($0.78 \geq x \geq 1.08$) [6] has inherently vacant oxygen sites (v) that can be hydrated in a similar manner as an acceptor-doped material [7–9]. Lanthanum tungstate (LWO) is a relatively pure proton conducting oxide at low and intermediate temperatures and can therefore be used as electrolyte in proton conducting solid oxide fuel cells (PC-SOFCs) [10,11]. At higher temperatures, the material exhibits additional p-type and n-type electronic conductivity under oxidizing and reducing conditions, respectively. The material can, under reducing conditions, be used as a dense membrane for hydrogen separation *via* ambipolar transport of protons and electrons [12–14]. It has been reported that hydrogen permeation is limited by electrons at all measured temperatures (up to 1000 °C) [12].

It has recently been shown that partial replacement of tungsten by molybdenum in lanthanum tungstate enhances electronic conductivity due to the higher reducibility of Mo compared to W. It was anticipated that the increase in electronic conductivity did not affect the ionic (and protonic) conductivity significantly, so that ambipolar transport would be higher with Mo substitution [15]. Mo-LWO is therefore an improved composition for hydrogen permeation applications compared to LWO.

The transport properties and the defects contributing in lanthanum tungstate and Mo-substituted LWO are relatively well established and understood, but quantification of the partial conductivities of each charge carrier (protons, oxide ions and holes under oxidizing conditions; protons, oxide ions and electrons under reducing conditions) still need to be established. The present contribution will thus focus on the determination of the partial conductivities of each defect using the electromotive force (EMF)

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generated over a concentration cell [16,17]. The study will be complemented by testing of the performance of electrolyte-supported specimens under fuel cell mode.

2. Experimental section

2.1. Description of the tested samples

Nanometric powders of nominally undoped LWO54 ($La_{27}W_5O_{55.5}$) and 30% Mo-substituted LWO54 (Mo-LWO54; i.e. $La_{27}(W_{0.7}Mo_{0.3})_5O_{55.5}$) were purchased from Cerpotech AS (Trondheim, Norway). The powders were pressed at 100 MPa by uniaxial pressing and the specimens were sintered at 1500 °C for 10 h. The density of the pellets was 98 and 99% of the theoretical for LWO54 and Mo-LWO54, respectively. The samples were single phase materials by X-ray diffraction (Bruker D8, 3-circle diffractometer), in accordance with earlier reports [5,15]. Pt electrodes (Pt ink 6926 from Metalor) were painted on each side of the specimens and fired at 1000 °C for 30 min. The final geometrical factors were the following: area $= 0.95$ cm^2 and thickness $= 0.19$ cm (LWO54); area $= 0.79$ cm^2 and thickness $= 0.21$ cm (Mo-LWO54).

2.2. Dependency of the conductivity with oxygen and water partial pressure

The conductivity was measured using an Alpha A impedance spectrometer + POTGAL interface (Novocontrol technologies) in a ProboStat™ measurement cell (NorECs, Norway) by the 2-point 4-wire method. Impedance spectra were recorded in the 1 MHz to 0.1 Hz frequency range with an oscillation voltage of 50 mV. The dependence of the conductivity with oxygen partial pressure was measured from O_2 to H_2 at constant pH_2O (~2.5% H_2O). Typical flow rates are 20–50 ml min^{-1}. The variation of conductivity with water vapor partial pressure was performed in O_2 (oxidizing conditions were chosen in order to minimize the contribution from n-type conductivity for Mo-LWO54). The conductivity was monitored *vs.* time at each new set of conditions to ensure that equilibrium was achieved before taking a measurement.

2.3. Transport number measurements

EMF measurements were performed from 500 to 1000 °C to extract transport numbers using the setup and procedure described in Refs. [16,17]. A thick gold gasket was placed between the specimen and the support tube for sealing, which was accomplished by annealing at ~1060 °C. The open-circuit voltage (OCV) resulting from differences in the gas composition and chemical potentials across the specimen were measured with an Agilent/HP 34401A multimeter. Impedance measurements were conducted under the same gradient in order to correct the transport number (t_i) by electrode polarization, following the suggestion by Liu and Hu [18]:

$$t_i = 1 - \frac{R_b}{R_{tot}}\left(1 - \frac{V_{OC}}{E_N}\right) \quad (1)$$

where R_b and R_{tot} are the material and total resistance deconvoluted from the impedance measurement, and the V_{OC} and E_N are the measured and the Nernst voltage, respectively. The measurements were conducted in both oxidizing (air) and reducing (5% H_2/Ar) conditions to test the consistency of the measurements.

2.4. Fuel cell performance

After the transport numbers were completed, fuel cell performance was recorded using the same setup. The gases were changed to wet air and wet 5% H_2/Ar on either side of the specimens, and the OCV was followed until equilibrium was reached. Then, the cell performance was measured using an Alpha A + POTGAL interface (Novocontrol technologies) on the sealed cell from 500 to 1000 °C. The current–voltage response was collected during 5 s in intervals of 0.1 s under potentiostatic mode from OCV to ~0.1 V in steps of 0.05–0.1 V.

3. Results and discussion

3.1. Measurement of the transport number in mixed ionic-electronic conductors using the EMF method

The total electrical conductivity of a substance is the sum of the partial conductivities of the different charge carriers, and the transport number is the share of conductivity that is due to a species *i*, where the sum of all transport numbers equals unity. In our case, the expression reads:

$$\sum_i t_i = t_{O^{2-}} + t_{H^+} + t_{electronic} = 1 \quad (2)$$

Carl Wagner [19] was the first to combine chemical and electrical potentials and potential gradients to describe the oxidation of metals, and the Wagner-type theory forms the basis for the treatment of all mass transport processes involving charged species in ionic solids. Sutija et al. [20] and Norby [16] derived the expressions for transport number determination by the concentration-cell/open-circuit voltage method for oxides with mixed electronic, ionic and protonic conductivity. When measuring the voltage under a gradient in partial pressure of O_2 (pH_2O must be kept constant), the voltage under the assumptions and simplifications described in Refs [16,17] can be described as:

$$E_{II-I} = t_{ion}\frac{RT}{4F}\ln\left(\frac{P^{II}_{O_2}}{P^{I}_{O_2}}\right) \quad (3)$$

where t_{ion} denotes the sum of transport number for ionic species (protons and oxide ions in this case) and E_{II-I} refers to the measured voltage under the given gradient I and II. Other entities have their usual meanings. When the voltage is measured under a gradient of partial pressure of H_2O (pO_2 must be kept constant), the corresponding Nernst equation may be derived in terms of the oxygen and water partial pressures:

$$E_{II-I} = t_{H^+}\cdot\frac{RT}{2F}\ln\left(\frac{P^{II}_{O_2}}{P^{I}_{O_2}}\right) - t_{H^+}\cdot\frac{RT}{2F}\ln\left(\frac{P^{II}_{H_2O}}{P^{I}_{H_2O}}\right) \quad (4)$$

When t_{ion} and t_{H^+} are determined, $t_{O^{2-}}$ and $t_{electronic}$ can be easily calculated using $t_{ion} = t_{O^{2-}} + t_{H^+}$ and equation (2). It is worth to mention that, in the present contribution, several OCVs have been measured per each set of conditions (temperature and either pH_2O or pO_2) and the given t_i is the transport number extrapolated to zero gradient as reported in Refs. [21], in order to satisfy one of the assumptions of equations (3) and (4). A representative example is given in Fig. 1. Typical gas conditions under oxidizing and reducing conditions are displayed in Table 1.

3.2. Transport number measurements of LWO54 and Mo-LWO54

Fig. 2 displays the variation of the conductivity with the oxygen partial pressure (pO_2) and shows the behavior of a mixed ionic-electronic conductor. The conductivity is independent of the pO_2 at intermediate pressures, indicating dominating ionic conductivity. At high temperatures and high pO_2, the conductivity increases with increasing the pO_2, indicating the presence of p-type