



Electronic conductivity measurement of yttria-stabilized zirconia solid electrolytes by a transient technique



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HIGHLIGHTS

- A novel transient technique to measure electronic conductivity is proposed.
- Electronic conductivity of 8YSZ measured down to 550 °C.
- 8YSZ exhibits p-type electronic conduction in air.

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ABSTRACT

A new oxygen permeation technique is developed to measure the electronic conductivity of yttria-stabilized zirconia (YSZ). The permeation cell is a YSZ disc with an embedded Pt probe and a cavity at the center. Two porous platinum electrodes are applied on the disc surfaces. By applying a small DC bias (0.03 V) across one surface electrode and the embedded probe, oxygen is pumped into the YSZ disc and stored in the cavity. In steady state, a stable Nernst potential is developed between the cavity and the outer surfaces. The Nernst voltage is very close to the applied voltage since YSZ is essentially an ionic conductor. When the DC bias is removed, oxygen permeates out of the cavity leading to a decay of the Nernst potential. Electronic conductivity of YSZ corresponding to the ambient oxygen pressure (~0.21 atm) is determined by analyzing the time dependence of the decay of Nernst potential. The measured electronic conductivity is in good agreement with values reported in the literature.

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1. Introduction

Predominantly ionic conductors and mixed ionic and electronic conductors (MIEC) have numerous applications in gas permeable membranes, solid oxide fuel cells (SOFC), solid oxide electrolysis cells (SOEC) to name a few. Both ionic and electronic conductivities of MIEC are of interest.

The most commonly used technique to measure partial conductivity is the Hebb–Wagner polarization method [1–3]. In the original work by Hebb [1], electronic partial conductivity of Ag₂S was determined by measuring the electron electrochemical potential, $\bar{\mu}_e$, (the measurable electric potential being $\varphi = -\bar{\mu}_e/F$ where F is the Faraday constant) as a function of position and the net current in steady state. The derivative of the electric potential as a function of position, $\partial\varphi/\partial x$, allows for the estimation of the local

electronic partial conductivity, σ_{elec} . Wagner suggested a different but a more convenient method, especially useful for anion conductors such as YSZ, which involves the measurement of steady state current as a function of the applied potential [2]. The derivative of current with respect to the applied potential gives the partial conductivity at the blocking electrode. Wagner also expressed the electronic current as a function of the applied potential by considering both electron and hole transport. This expression since has been known as the Hebb–Wagner polarization equation. The application of the Hebb–Wagner method to materials such as YSZ involves fitting to the Hebb–Wagner equation [3] since in most studies the position-dependent electric potential cannot be easily measured. Many of the measurements are made under an applied voltage large enough so that parts of the sample exhibit n-type and p-type conduction as well as the intrinsic region in which the electronic conductivity is exceptionally low.

Another approach to measure the electronic conductivity of YSZ is the oxygen permeation method, which was discussed in detail by

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Heyne [4,5]. Oxygen permeation through a dense solid has been studied as early as the 1930s [6–8]. However, at the time the mechanism was not clear. Heyne explained oxygen permeation in terms of ambipolar transport. This method requires a permeation cell which consists of a gas-tight YSZ tubular cylinder and two YSZ discs. One disc is used to pump oxygen into the chamber; the other disc serves as the oxygen permeation path, although permeation can occur through all exposed YSZ surfaces. Heyne provided a detailed discussion on the steady state data analysis based on ambipolar transport [5]. Insofar as the non-steady state process is concerned, Fick's law of diffusion has been used to obtain diffusivity of electrons and holes in solid electrolytes [6]. Park and Blumenthal conducted both steady state and non-steady state measurements to investigate electronic transport in 8YSZ by using an oxygen permeation cell [9]. Over the past four decades, electronic conductivity of many oxygen ion conductors such as YSZ, rare earth oxide doped ceria, pyrochlores, etc. has been measured using Hebb–Wagner and permeation methods [10–17].

In the present work, we propose a new oxygen permeation technique using a YSZ disc with an embedded Pt probe and a cavity (volume $\sim 0.25 \text{ mm}^3$) at the center of the disc. The non-steady state (or transient process) is analyzed in terms of ambipolar transport.

2. Experimental details

Disc samples of 8YSZ with an embedded Pt probe without a cavity were made using the procedure described elsewhere [18]. A sample with an embedded Pt probe and a cavity at the center was made by pressing two powder pellets in each of which a removable metal disc was pressed in. After removing the metal discs the two powder pellets with surface recesses were pressed against each other (with the recesses facing each other), with a platinum wire placed in between, to create a YSZ disc with a cavity and an embedded Pt probe. The disc was then sintered at 1500°C for 5 h. Two porous platinum electrodes were symmetrically applied on the two circular surfaces of the disc and fired at 900°C for 2 h. All other exposed surfaces of the disc were coated with a glass and fired at 900°C for 2 h.

All tests were conducted in air over a range of temperatures from 550°C to 800°C by heating the sample in a tubular furnace. The disc sample was placed in a sample holder made of alumina. Each of the two porous Pt electrodes (II and III) was covered with Pt mesh, and Pt leads were connected to the two meshes and to the embedded Pt probe (I).

A DC voltage ($\sim 0.03 \text{ V}$) was applied across electrodes I and II using a constant voltage power source (National Instruments), and was monitored by a voltmeter (Keithley 2000). The positive of the voltage source was connected to the embedded electrode (I). The charging current from electrode I to electrode II and the Nernst potential between electrodes I and III were monitored both by a low speed multimeter (Keithley 2000) and a high speed multimeter (National Instrument PXI-4065).

3. Theoretical model

3.1. Charging stage

When a DC voltage is applied across electrodes I and II with the positive connected to electrode I (the embedded Pt electrode), oxygen ions migrate from electrode II to electrode I through the 8YSZ electrolyte as shown in Fig. 1(a). Electrons migrate from electrode I to electrode II through the external circuit. At electrode II neutral oxygen molecules (at triple phase boundaries) are reduced to oxygen ions. At electrode I oxygen ions are oxidized to neutral oxygen molecules and stored in the cavity. Fig. 1(c) shows

the equivalent circuit for the charging step. In the equivalent circuit, R_i denotes the ionic resistance of the YSZ disc between II and I, and R_e denotes the electronic resistance of the YSZ disc between II and I. Note that $R_e \gg R_i$. Thus, the charging current is dictated by the ionic resistance, R_i , between the surface electrode II and the embedded probe I. It is assumed that much of resistance is associated with the YSZ electrolyte and electrode polarizations are much smaller. This assumption was verified in an earlier study by the authors [18]. If the electrode polarization resistances cannot be neglected, the equivalent circuit will have three separate segments connected in series, as shown previously by one of the authors [19].

As the oxygen partial pressure in the cavity increases, the Nernst potential between the embedded Pt probe and the two porous Pt electrodes increases. The Nernst potential drives the dissipation current of oxygen ions from electrode I to electrode II and from electrode I to electrode III through the 8YSZ electrolyte. The balancing electron (hole) flow through the YSZ electrolyte occurs in the opposite direction – from II & III to I for electrons (in the same direction – from I to II & III for holes). The dissipation current eventually rises to the same value as the charging current so that the oxygen pressure in the cavity is maintained constant. The state in which the dissipation current equals the charging current is the steady state. Thus, during dissipation, the oxygen reduction reaction occurs at I and the oxygen evolution reaction occurs at II and III. A detailed analysis of the steady state was presented elsewhere [18].

3.2. Discharging stage

The DC voltage is removed after the establishment of steady state. Oxygen molecules that are stored in the cavity continue to migrate from electrode I through YSZ to electrodes II and III driven by the Nernst potential. This occurs as a coupled transport of oxygen ions and electrons (and holes) through YSZ. However, due to the absence of a DC bias there is no charging current any more. As a result, the amount of oxygen in the cavity decreases leading to a decrease in the Nernst potential. The dissipation current and the redox reactions are shown in Fig. 1(b).

As an essentially oxygen ion conductor, the ionic conductivity of 8YSZ is much larger than its electronic conductivity. Therefore, the measured potential between electrode I and electrode III during the dissipation stage nearly equals the Nernst potential given by

$$E_N(t) \cong -\frac{\Delta\tilde{\mu}_e(t)}{F} = \Delta\varphi(t) = \frac{\Delta\mu_{O_2}(t)}{4F} \quad (1)$$

where $\tilde{\mu}_e(t)$ is the electrochemical potential of electrons, $\mu_{O_2}(t)$ is the chemical potential of oxygen, F is the Faraday constant, $\Delta\tilde{\mu}_e(t)$ is the difference in electrochemical potentials of electrons between I & II and between I & III, and $\Delta\mu_{O_2}(t)$ is the difference in oxygen chemical potentials between I & II and between I & III. The electrochemical potential of electrons is given by

$$\tilde{\mu}_e = \mu_e - F\Phi \quad (2)$$

where μ_e is the Fermi level and Φ is the electrostatic potential. The measurable electric potential is

$$\varphi = -\frac{\tilde{\mu}_e}{F} = -\frac{\mu_e}{F} + \Phi \quad (3)$$

The Fermi level in YSZ is different (and is lower) than the Fermi level in Pt. Electron hole flux occurs down the gradient of φ (electron flow occurs up the gradient of φ). As a result, the Φ increases in YSZ from I to II and from I to III with abrupt changes occurring across all interfaces such that Φ is higher at I in YSZ than at II and III

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