

Estimation of oxygen ionic conductivity in nickel-zirconia composite by oxygen permeation method

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Abstract The oxygen transport in the nickel-zirconia composite was investigated using the oxygen permeation method. A disk-shaped sample made of nickel (40 vol%) and yttria-stabilized zirconia (YSZ) was used to construct a permeation cell. By exposing one side of the sample to a CO₂ gas stream and the other side to a CO stream at elevated temperatures, oxide ions were extracted from CO₂ and transported to the other side to oxidize CO. The oxygen permeation flux through the composite was determined by analyzing the effluent from the permeation cell, and the oxygen ionic conductivity of the composite was derived from the permeation data and the oxygen partial pressures. It was shown that the oxygen ionic conductivity of the composite YSZ fraction was about one third of that for the single-phase zirconia ceramic, and the activation energy associated with the transport of oxide ions in the composite is somewhat greater than that of the single-phase zirconia.

Keywords SOFC anode · Oxygen ionic conductivity · Oxygen permeation · Zirconia · Nickel

Introduction

The nickel-zirconia composite has been used as the standard anode material for the solid oxide fuel cell

(SOFC) since it was proposed by Spacil nearly four decades ago [1–3]. The oxygen transport in the anode is considered to play an important role in determining the performance of the fuel cell [2]. However, the data on the oxygen ionic conductivity of the composite is scarce due to the lack of proper measurement methods. Since the dominant charge carrier in the composite is electron, rather than oxide ion, the conventional electrical conductivity measurement cannot be used for determination of the oxygen ionic conductivity. In principle, it can be done with a special electrode that allows oxide ions to pass through while block electrons, but this blocking electrode method has its own limitation [4].

In the study of mixed oxygen ionic and electronic conduction in single-phase perovskite oxide, the oxygen permeation method has been used in combination with the electrical conductivity measurement [5]. The oxygen permeation measurement gives the ambipolar conductivity σ_{ambi} which is defined as $\sigma_i\sigma_e/(\sigma_i + \sigma_e)$, while the electrical conductivity measurement provides the total conductivity σ_t which is the sum of oxygen ionic conductivity σ_i and electronic conductivity σ_e . This method is applicable to the Ni-zirconia composite provided that the oxidation of the nickel component of the composite is avoided during the permeation measurement. In the present study, the oxidation problem is avoided by performing the permeation measurement under reducing environment. The oxygen partial pressure difference required for oxygen permeation is established by exposing two sides of a disk-shaped composite membrane to various CO and CO₂ mixture stream. The rate of oxygen permeation through the composite is determined, and the total electrical conductivity is measured under the similar conditions, thus, the oxygen ionic conductivity of the composite is obtained.

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Experimental

The composite of yttria-stabilized zirconia (YSZ) and Ni with a volume ratio of 60:40 was prepared using a standard ceramic route. Appropriate amounts of 8 mol% Y_2O_3 -stabilized zirconia (YSZ, Tosoh, Japan) and nickel powders (>99.5%, Shanghai Chemical Agent Company, China) were mixed by ball-milling using zirconia balls for 30 h. The mixed powder was isostatically pressed into disks and bars at 300 MPa and sintered at 1,400°C for 10 h in flowing stream of nitrogen containing 8% hydrogen. The as-prepared disks had a density of 97% relative to the theoretical density.

The phase composition of the as-prepared composite was analyzed using X-ray diffraction (XRD) with $CuK\alpha$ radiation (Philips X'Pert Pro, Netherlands), and the microstructure was examined with optical microscopy (Olympus BX51M, Japan) and scanning electron microscopy (SEM; JEOL JSM-6700F, Japan). The oxygen permeation through the composite was measured using the experimental setup shown in Fig. 1. Disk-shaped samples were machined to the required thickness of 0.70, 1.52, and 2.82 mm and ultrasonically cleaned in ethanol, then sealed to the end of an alumina tube using a glass ring to form a permeation cell. To avoid permeation flux from the side face of the membrane, the side wall of the disk was coated with glass powder followed by in situ

heating. A gas stream of CO_2 was introduced to the down side of the cell at 50 mL min^{-1} , where a small amount of CO (approximately 100 ppm) was added to prevent the oxidation of the nickel phase of the composite. Then, a stream of CO balanced with N_2 (40 vol%) was led over the upper side of the membrane at a rate of 50 mL min^{-1} , where the N_2 also acted as an indicator for the gas tightness of the cell, for in the case of leakage, N_2 will be detected at the other side of the permeation cell. The composition of the effluent from the permeation cell was analyzed with an online gas chromatograph (Fuli GC9750, China). The total electrical conductivity of the composite under the reducing atmosphere was measured with a bar-shaped sample using the four-probe technique. The sample was placed in a tubular furnace and swept with a mixture of CO and CO_2 (30 vol%) at a rate of 50 mL min^{-1} , the corresponding oxygen partial pressure being 10^{-16} atm at 950°C and 10^{-15} atm at 1,000°C.

Results and discussion

Figure 2 shows the XRD pattern of the as-prepared composite. It can be seen that the composite consists of the Ni metal phase and the YSZ phase. Figure 3 presents the images of the sample by optical and SEM. In Fig. 3a, the white phase is YSZ and the dark is Ni, and in Fig. 3b, the dark gray particles with irregular shape are Ni grains, and the white gray matrix is YSZ. The composite exhibits a dense microstructure with the Ni grains embedded in the YSZ matrix.

Figure 4 shows the oxygen permeation rate as a function of temperature for the composite membranes with various thicknesses. As shown in Fig. 4, the permeation rate of all samples increases with temperature as expected. It can also be seen that the permeation flux increases with reducing the membrane thickness. At 1,000°C, the typical operation temperature for SOFC with YSZ as the electrolyte, an oxygen flux of 1.7×10^{-7} was attained for the 2.82-mm thick membrane and $3.2 \times 10^{-7}\text{ mol cm}^{-2}\text{ s}^{-1}$ for the 1.52-mm thick sample, showing an inverse proportionality between the flux and the thickness. However, decreasing the membrane thickness from 1.52 to 0.70 mm did not yield proportional increase of the permeation flux ($4.1 \times 10^{-7}\text{ mol cm}^{-2}\text{ s}^{-1}$).

The oxygen permeation process consists of the reaction $CO + 1/2O_2 \rightleftharpoons CO_2$ occurring at the surfaces of the composite (forward at the CO-rich side and backward at the CO_2 -rich side) and transport of oxide ions along the YSZ phase and electrons along the Ni phase in the bulk of the membrane. If the surface reaction proceeds much faster than the bulk transport step, i.e., the latter is the rate-limiting step for the overall oxygen permeation process, then the permeation flux should be inversely proportional to the membrane thickness. This is the case for the membranes

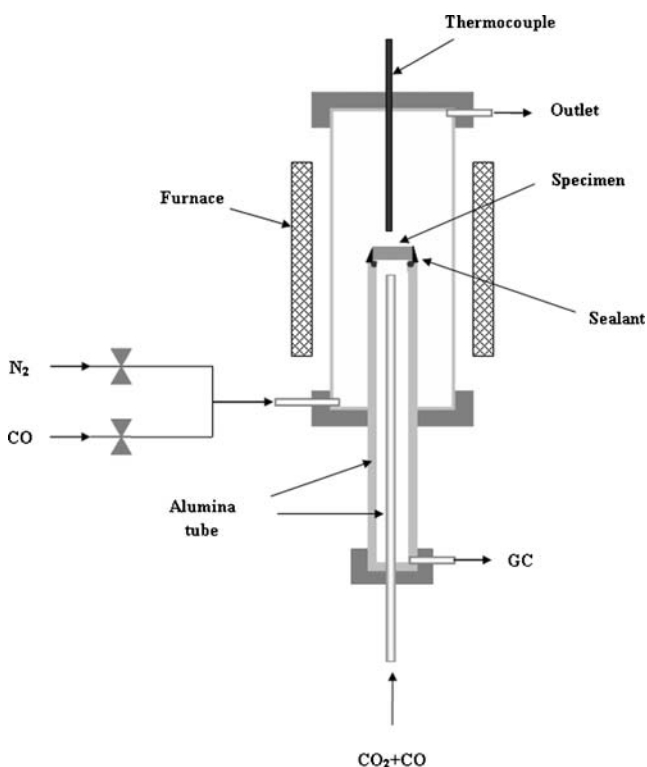


Fig. 1 Schematic diagram of the oxygen permeation setup

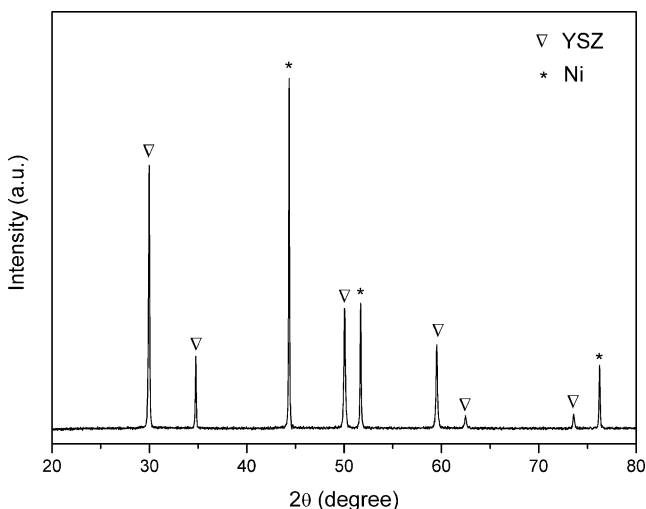


Fig. 2 X-ray diffraction pattern of the Ni/yttria-stabilized zirconia composite

of thickness 2.82 and 1.52 mm. For membrane in the bulk-controlled region, it follows that [6]

$$J_{O_2} = \frac{RT\sigma_{ambi}}{(4F)^2L} \ln \frac{P'_{O_2}}{P''_{O_2}} \quad (1)$$

In the present study, the oxygen partial pressure value was calculated with

$$P_{O_2} = \left(\frac{P_{CO_2}}{P_{CO} \times K} \right)^2, \quad (2)$$

where K is the equilibrium constant for the reaction $CO + 1/2O_2 \rightleftharpoons CO_2$, and its value is derived from the thermodynamic data [7, 8]. The partial pressures of CO_2 and CO were determined from their concentrations, for the permeation cell was set to operate at a total pressure of 1 atm, thus, the partial pressure of each component was equivalent to the concentration in molar fraction. For the CO_2 -rich side, the concentrations of CO and N_2 were determined by the gas chromatography, and the CO_2 concentration was then calculated from $C_{CO_2} = 1 - C_{CO} - C_{N_2}$. Note that the appearance of N_2 at the CO_2 -rich side was due to the leakage from the CO-rich side, but its concentration was negligible (200 ppm in the worst case of leakage) for calculation of the C_{CO_2} value. As to the other side of the permeation cell (CO-rich side), the CO_2 concentration was determined according to the reaction stoichiometry. The amount of CO_2 generated at the CO-rich side (less than 0.6 vol%) was equal to that of CO generated at the CO_2 -rich side, and due to the small degree of the reactions, the CO concentration at the CO-rich side departed slightly from the initial value (60 vol%). After knowing the CO and CO_2 concentrations and thus their partial pressures, the oxygen partial pressures were calculated using Eq. 2. The results are listed in Table 1. It is clear

from Table 1 that the oxygen partial pressure is very low, which is comparable to the one experienced by the SOFC anode under operation conditions.

With the as-calculated oxygen partial pressure and the measured oxygen permeation rate, the ambipolar conductivity σ_{ambi} is estimated from the permeation data of the 2.82-mm thick sample using Eq. 1. At the same time, the total electrical conductivity σ_t has been determined by using the four-probe technique. After obtaining the values of σ_{ambi} and σ_t , the electronic conductivity σ_e and oxygen ionic conductivity σ_i are deduced readily [5], and the results are presented in Fig. 5. It shows that σ_e is about three orders of magnitude larger than σ_i . For instance, σ_e took a value of 61 S cm^{-1} at $1,000^\circ\text{C}$ and 62 S cm^{-1} at 950°C , while σ_i was 0.032 S cm^{-1} at $1,000^\circ\text{C}$ and 0.023 S cm^{-1} at 950°C . Obviously, the Ni phase dispersed in the YSZ matrix has formed a percolative network, allowing electrons to transport

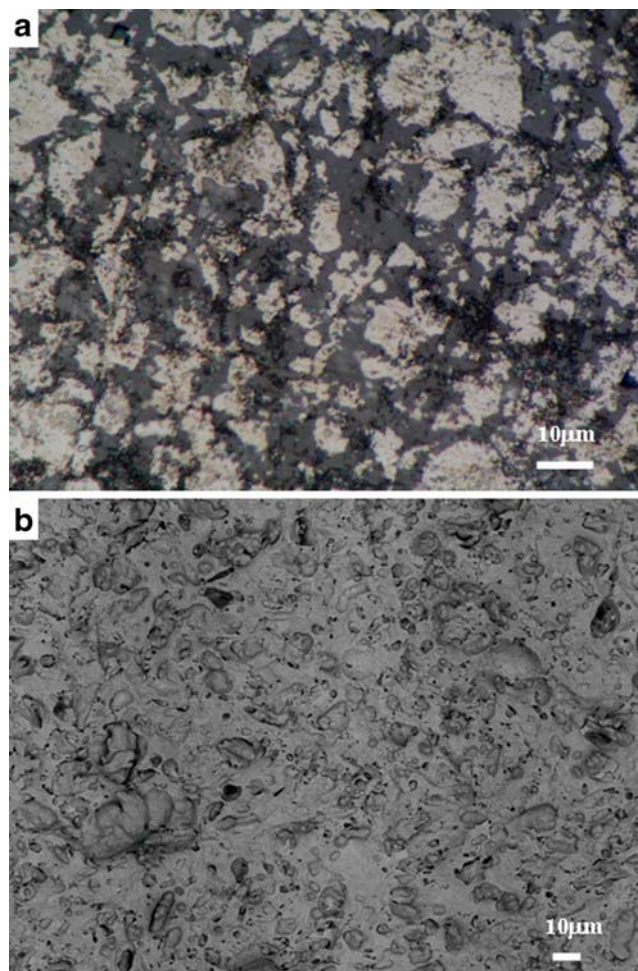


Fig. 3 Images of the Ni/yttria-stabilized zirconia composite by optical and scanning electron microscopy. **a** Reverse-contrast optical micrograph. **b** Scanning electron microscopy image of the cross-section of the composite

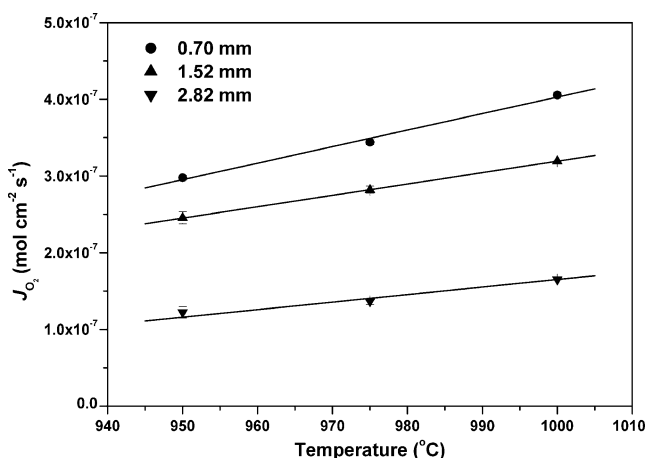


Fig. 4 Temperature dependence of the oxygen permeation flux through the Ni/yttria-stabilized zirconia composite membrane with the thickness of (circle) 0.70, (triangle) 1.52, and (inverted triangle) 2.82 mm. Solid lines are guide to the eye

through it with ease. From the Arrhenius plot of the oxygen ionic conductivity (Fig. 5), the associate activation energy for oxygen transport was calculated to be $97 \pm 1 \text{ kJ mol}^{-1}$. This value is somewhat greater than the one reported for the single-phase YSZ (82 kJ mol^{-1}) [9, 10].

Clearly, the YSZ phase in the composite is responsible for the conduction of oxide ions. To have a fair comparison with the single-phase YSZ, the value of the oxygen ionic conductivity for the composite is corrected for the YSZ volume fraction (0.6). After correction, the oxygen ionic conductivity of the composite YSZ fraction was 0.053 and 0.038 S cm^{-1} , respectively. It is shown that the oxygen ionic conductivity of the YSZ fraction in the composite is about one third of that for the single-phase YSZ sample [9, 11, 12]. The decrease in the oxygen ionic conductivity has also been observed for YSZ in composite with other materials. For instance, the ionic conductivity of YSZ in composite with 27 vol% of alumina was found to be about half of that of the single-phase zirconia [13]. This can be explained as follows. Due to the presence of the second phase, the transport path for oxide ions becomes tortuous, and a large portion of zirconia is situated on the ‘dead ends’, both leading to a decrease in oxygen ionic conductivity. The decrease in the ionic conductivity also arises from the constriction of the

Table 1 Oxygen partial pressures at the CO_2 and CO side of the permeation cell

Temperature ($^{\circ}\text{C}$)	$\text{Log}_{10}K$	P'_{O_2} (10^{-10} atm)	P'_{O_2} (10^{-19} atm)
1,000	7.02	1.3~4.4	4.2~16
975	7.26	0.62~2.0	1.1~3.9
950	7.50	0.27~1.0	0.22~0.96

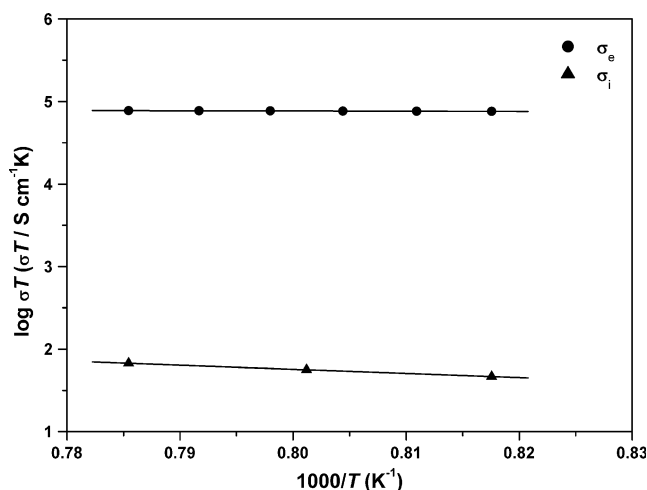


Fig. 5 Arrhenius plots of conductivities for the Ni/yttria-stabilized zirconia composite. (Circle) electronic conductivity, (triangle) oxygen ionic conductivity. Solid lines are guide to the eye

ionic current lines in the vicinity of three-phase boundary (TPB) of YSZ/nickel/gas phase [14]. It is known that the charge transfer takes place in the TPB area, and the distortion and inhomogeneous distribution of the current lines gives rise to larger resistances of the ionic conductive phase (zirconia) and electronic conductive phase (Ni) [15].

The determination of the oxygen ionic conductivity is difficult for materials with dominant electronic conduction, especially under the anodic (reducing) environment. Thus, the oxygen ionic conductivity data is scarce for the anode materials. In principle, the oxygen permeation method developed in this work can be applied to other materials with potential applications as SOFC anodes.

Conclusions

The oxygen ionic conductivity of the Ni/YSZ composite under near operation conditions of SOFC has been estimated by using an oxygen permeation method. By exposing the composite to a CO_2/CO gradient at elevated temperatures, oxygen ions are extracted from CO_2 at one side of the composite and transported to the other side where they oxidize CO to CO_2 . From the measured oxygen permeation flux and the calculated oxygen partial pressures, the oxygen ionic conductivity can be derived. The oxygen ionic conductivity of the composite YSZ fraction (after correction for the YSZ volume fraction) is only about one third of the single-phase zirconia, which is attributed to the blocking effect of the Ni phase to transport of the oxygen ions, and the activation energy of the oxygen ionic conductivity of the composite YSZ is somewhat greater than that of the single-phase YSZ. The method described in

this work in principle can be applied to other potential SOFC anode materials.

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