OXYGEN PERMEATION STUDIES OF DIFFUSION AND SURFACE EXCHANGE IN MIXED CONDUCTING OXIDE ELECTRODE MATERIALS
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ABSTRACT

Oxygen permeation measurements can be used to obtain both oxygen surface exchange and diffusion coefficients for cathode materials. Our previous analysis of results for planar membranes of SrCo$_{0.8}$Fe$_{0.2}$O$_{3-x}$ (SCFO) as a function of $pO_2$, temperature and thickness show that both the surface kinetics and the bulk diffusion determine the oxygen flux. The model has been extended to quantitatively predict the enhancement in oxygen flux observed experimentally when porous electrodes are added to one or both surfaces of the membrane. The permeation flux for a SCFO membrane has also been measured with a tubular geometry, thereby eliminating the need for edge effect corrections.

INTRODUCTION

The electrodes in solid oxide fuel cells contribute significantly to the overall cell resistance. In the cathode, resistance arises from several different processes including oxygen exchange between the gas phase and the solid, diffusion of oxygen ions through the electrode, transfer of oxygen from the electrode to the electrolyte and gas phase diffusion in the pores. A useful cathode material also requires appropriate mechanical and chemical stabilities and electronic conductivity. The interplay between various materials properties, including the bulk diffusion coefficient, the oxygen surface exchange coefficient and the electrode structure (total surface area, porosity, tortuosity) recently has been discussed and models have been developed that provide guidelines for the design of cathodes with improved performance (1-7). In general, the use of these approaches for a specific material requires a knowledge of the values of the diffusion and surface exchange coefficients in addition to a description of the electrode microstructure. A considerable amount of information is available from $O^{18}/O^{16}$ exchange measurements (8) and has been recently reviewed (9).

Measurements of oxygen permeation through dense membranes can also provide information about the bulk diffusion and surface exchange properties of mixed conducting oxide electrode materials (2, 3, 9, 10). Generally speaking, the permeation flux depends on the ambipolar oxygen ion-electron hole pair diffusion coefficient ($D_a$) and the surface exchange rate coefficient ($k_i$). For a specific material, the oxygen flux through the membrane can be increased by reducing the membrane thickness until $l < L_d$, where $L_d = D_a/k_i$. The length scale, $L_d$, determines the transition from diffusion limited to surface exchange limited transport. Any further increase in the permeation rate can then be achieved only by improving the surface exchange kinetics by coating the surfaces of the membrane with porous layers increasing the effective surface area, or by coating the membrane...
surfaces with materials of superior oxygen exchange properties. Measurements of the oxygen flux in the transition region or of the flux enhancements on surface modification can be used to determine $D_a$ and $k_j$.

Our previous studies of the oxygen permeation in disk membranes of $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_3.5$ (SCFO) demonstrated that surface exchange kinetics play an important role in determining the overall oxygen flux (10-13). In this paper we report further experimental results of oxygen permeation in SCFO. First, enhancements in the permeation flux through SCFO membranes modified by screen printing porous layer(s) of SCFO were used to determine the surface exchange rate and bulk diffusion coefficients. Secondly, the oxygen permeation flux and its pressure dependence were measured using a tubular membrane geometry.

EXPERIMENTAL

The details of the preparation and properties of SCFO powder, the fabrication of dense disk membranes, the measurement apparatus for disk membranes and the gas flow conditions have been described in the previous papers (10-15). The SCFO powder used in the present experiments was supplied by Praxair Specialty Ceramics.

The thickness and diameter of the membranes used for modification with porous layers were approximately 1.2 mm and 12.8 mm, respectively. To prepare the porous layers, SCFO powder was first calcined in air at 1060 °C for 10 h and then ball-milled in ethanol for 72 h. The dried powder was mixed with $\alpha$-terpineol (Aldrich) in which 10 wt.% of ethyl cellulose was dissolved. The suspension (30 wt. % solid) was screen printed onto the disk surfaces. Two disks were printed only on one surface. The screen printed disks were dried in air at 150 °C and then fired at 1000 °C for 2 h with 1°C heating and cooling rates. The thickness of the porous layers were shown by scanning electron microscopy to be approximately 20 μm with an average grain size of ~4 μm. The surface area of the calcined SCFO powder was determined by nitrogen adsorption using the BET method to be 0.065 m$^2$/g. The surface areas per unit volume of the porous layers were 1700 cm$^{-1}$ approximated from their weights and the powder surface area. The average inner and outer diameter of the gold O-rings used for sealing were 7.9 and 12.8 mm, leaving an effective permeation area ~0.5 cm$^2$.

A tube was fabricated by cold isostatic pressing SCFO powder at 40000 psi using a custom-designed rubber mold with a stainless steel cylinder placed in the center. After pressing, the tube was cut and sintered at 1060 °C for 10 h. The heating and cooling rates were 1.5 °C/min. The outer and inner diameters and the length of the tube used for the measurements were 11.0, 6.0 and 9.3 mm, respectively. The permeation apparatus used for the tubular samples is a modified version of the previously reported apparatus (11). During the permeation measurements, the outer surface of the tube was exposed to various O$_2$-N$_2$ mixtures and the inner surface was exposed to a He sweep gas. Leakage through pin-holes or cracks was checked by monitoring the N$_2$ concentration in the He gas with a MTI 200M gas chromatograph (GC). The leakage was less than the detection limit of the GC (~5 ppm) during the entire series of measurements. Since no leakage was detectable a YSZ-based Ametek TM-1B oxygen sensor was used to monitor the oxygen permeate concentration in the He gas. In the permeation measurements, the pO$_2$ on the oxygen-rich
side ranged from 1 atm to 0.01 atm and the pO₂ in the oxygen-lean side ranged from $3 \times 10^{-2}$ to $2 \times 10^{-3}$ atm.

MODEL

For the case of a dense membrane with porous layers, the diffusion of oxygen molecules in the pores and of oxygen ion-electron hole pairs in the porous solid may be expressed by the molecule current, $I_g$ and the ion current $I_i$ (16):

$$ I_g = -\frac{\phi}{\tau} \frac{c_g D_g}{RT} \frac{d\mu}{dx} \quad [1] $$

$$ I_i = -\frac{1-\phi}{\tau_s} \frac{c_i D_a}{RT} \frac{d\mu}{dx} \quad [2] $$

where $\mu_g = RT \ln(p/p_0)$, is the chemical potential of the gas molecules, $p$ is the gas pressure, $\mu$ is the chemical potential of the oxygen ion-electron hole pairs, $D_g$ is the diffusion coefficient of the gas in the pores and $D_a$ is the ambipolar diffusion coefficient of the oxygen ion-electron hole pairs, $c_g$ and $c_i$ are the concentrations of the gas molecules in the pores and of the ions in the solid, $\phi$ is the porosity and $\tau$ the tortuosity of the pores, $\tau_s$ the tortuosity of the solid and the subscript 0 indicates that the quantity is determined at 1 atm pressure. Equation (2) applies in the dense layer with $\tau_s=1$ and $\phi=0$.

The chemical reaction at the pore wall-gas interfaces in the porous layer on the high pressure side of the membrane results in a decrease in $I_g$ and a corresponding increase in $I_i$ with increasing $x$, while in the porous layer on the low pressure side of the membrane $I_g$ increases and $I_i$ decreases with $x$. This is quantitatively described by the equations:

$$ \frac{dI_g}{dx} = -\frac{1}{2} Si \quad \text{and} \quad \frac{dI_i}{dx} = Si, \quad [3] $$

where $S$ is the pore surface area per unit volume and $i$ is the surface exchange current given by:

$$ i = c_i k_{i0} \left[ \exp(\mu_g / 2RT) - \exp(\mu / RT) \right] \quad [4] $$

where $k_{i0}$ is the surface exchange coefficient at oxygen partial pressure of 1 atm and $L_{d0} = D_a / k_{i0}$. With appropriate boundary conditions, equations (1-4) can be solved numerically for both modified and unmodified disk membranes. More details of the model and the numerical methods used for the solution are given elsewhere (2, 4, 13, 16). The enhancement factor $\eta$ obtained on the addition of porous layers is defined as the ratio of the
flux for modified and unmodified membranes. Analysis of the data from both modified and unmodified membranes can be used to obtain values for $D_a$ and $k_{i0}$.

For a dense tubular membrane and following the same approach used for disc membranes, the oxygen permeation rate, $F$ (mol/s) can be written as:

$$F = \frac{r_1}{c_i k_{i0} \pi w L} \ln \left( \frac{r_2}{r_1} \right) = \ln \sqrt{\frac{P_{rich}}{P_0} - \frac{F}{\pi r_1 w c_i k_{i0}}} - \frac{F}{\pi r_2 w c_i k_{i0}}$$

where $r_1$ and $r_2$ are the outer and inner radii of the tube, and $w$ is the length of the tube. Permeation rate is used instead of flux because of the different inside and outside areas.

RESULTS AND DISCUSSION

The variations of the permeation flux with temperature for the modified membranes are shown in Fig. 1. Above 760 °C where the membrane is single phase cubic perovskite, meaningful comparisons can be made with regard to the various modifications. The largest enhancement was found when both surfaces were coated with SCFO porous layers. When only one side was coated, a larger enhancement was observed when the oxygen-lean surface was modified. The experimental results for three temperatures, 870, 821 and 772 °C, are given in Table 1 in the form of enhancement factors.

To analyze the data, we used $x_s = 1.16$ and $T_g = 2 (2.4) \phi = 0.3$. For $D_g$ we use the relation $D_g = \frac{1}{2} v_{th} \lambda$, where $v_{th}$ is the thermal velocity of the molecules and $\lambda$ is the molecular mean free path in the pores. The dependence of $c_i$ and $D_a$ on chemical potential is neglected. To fit the experimental data we used $c_i = 0.069$ mol/ cm$^3$, and the estimates for the membrane surface area and microstructural parameters discussed above. The remaining free parameters, $L_{d0}$ and $k_{i0}$ were used as adjustable parameters to fit simultaneously the oxygen flux in the dense membrane with no porous layers and that of the membrane with porous layers on both sides of the membrane. The values obtained are given in Table 2. We then used the same best fit values of $L_{d0}$ and $k_{i0}$ to calculate the oxygen flux for the membranes with only one porous layer either on the oxygen rich or oxygen lean sides of the membrane. As can be seen from the results summarized in Table 1, the model predicts correctly the asymmetric behavior and the magnitude of the enhancement.

The steady state permeation rate plotted against $P_{rich}^{0.5} - P_{lean}^{0.5}$ for the unmodified tubular sample for three different temperatures is shown in Fig. 2. Linear variation with $P_{rich}^{0.5} - P_{lean}^{0.5}$ is expected in the surface limited regime, the observed deviation from linear behavior is a consequence of the fact that transport in this sample is limited by both bulk diffusion and surface exchange. The calculated values of the permeation rate from Eq.(5) using $L_{d0}$ and $k_{i0}$ as adjustable parameters (Table 3) agree well with the experimental values. We note that while the values of $L_{d0}$ agree with those determined from the enhancement measurements the values of $k_{i0}$ are about a factor 2-3 lower. This discrepancy could in part be due to the fact that the enhancement measurements were made on disc shaped samples and in the modeling we did not take into account leakage effects from the edge of the discs.
For the predominantly electronic conductor SCFO, the ambipolar diffusion coefficient $D_a$ is expected to be close in value to the ionic diffusion coefficient $D_i$ (17). Indeed we find that the values of the diffusion coefficients reported in Table 1 agree well with those determined from electrical conductivity ($\sigma$) measurements using the relation $D_i = \sigma RT/\epsilon z^2 F^2$. We note however that values of $k_{10}$ and $D_a$ are appreciably higher than those determined from isotope exchange experiments for other oxide materials at similar temperatures (7 - 9). A comparison of our values of $k_{10}$ and $D_a$ with those determined on the same material by other techniques is required in order to validate the model that we have used to describe the permeation data.

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Table 1. Comparison of experimental and theoretical enhancement factors of the membranes modified with porous layer(s).

| T, °C | $\eta_{\text{exp}}$ | $\eta_{\text{cal}}$ | $\eta_{\text{exp}}$ | $\eta_{\text{cal}}$ | $\eta_{\text{exp}}$ | $\eta_{\text{cal}}$ |
|-------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 772   | 2.35                | 2.34                | 1.68                | 1.57                | 1.24                | 1.30                |
| 821   | 1.87                | 1.87                | 1.51                | 1.45                | 1.41                | 1.40                |
| 870   | 1.74                | 1.72                | 1.41                | 1.40                | 1.10                | 1.17                |

Table 2. Kinetic parameters used to calculate the enhancement factors given in Table 1.

| T, °C | $D_0$, cm$^2$ s$^{-1}$ | $k_{ij0}$, cm s$^{-1}$ | $L_{ij0}$, cm |
|-------|-----------------------|------------------------|--------------|
| 772   | $3.5 \times 10^{-6}$  | $7.5 \times 10^{-5}$   | 0.047        |
| 821   | $4.0 \times 10^{-6}$  | $1.6 \times 10^{-4}$   | 0.025        |
| 870   | $5.0 \times 10^{-6}$  | $2.5 \times 10^{-4}$   | 0.020        |

Table 3. Kinetic parameters derived from the flow data for the tubular membrane.

| T, °C | $D_0$, cm$^2$ s$^{-1}$ | $k_{ij0}$, cm s$^{-1}$ | $L_{ij0}$, cm |
|-------|-----------------------|------------------------|--------------|
| 797   | $3.1 \times 10^{-6}$  | $3.5 \times 10^{-5}$   | 0.087        |
| 840   | $3.2 \times 10^{-6}$  | $7.0 \times 10^{-5}$   | 0.046        |
| 890   | $3.8 \times 10^{-6}$  | $1.0 \times 10^{-4}$   | 0.038        |
Fig. 1. Permeation flux through modified SCFO membranes. Solid circles: both side modified (membrane thickness 1.20mm); solid triangles: oxygen-lean side modified (1.19mm); open triangles: oxygen-rich side modified (1.14mm); and open circles: non-modified membrane (1.14mm).

Fig. 2 Pressure dependence of the oxygen permeation flow for a tubular SCFO membrane. The experimental values are given by the open squares, the calculated values (+), were obtained from Eq. (5) using the parameters in Table 3.