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The Thickness Dependence of Oxygen Permeability in Sol-Gel Derived Ce0.8Gd0.2O2-δ-CoFe2O4 Thin Films on Porous Ceramic Substrates: A Sputtered "Blocking Layer" for Thickness Control.

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The Thickness Dependence of Oxygen Permeability in Sol-Gel Derived $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$CoFe_2O_4$ Thin Films on Porous Ceramic Substrates: A Sputtered "Blocking" Layer for Thickness Control

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ABSTRACT

Mixed conductive oxides are a topic of interest for applications in oxygen separation membranes as well as use in producing hydrogen fuel through the partial oxidation of methane. The oxygen flux through the membrane is governed both by the oxygen ionic conductivity as well as the material's electronic conductivity; composite membranes like $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO)-$CoFe_2O_4$ (CFO) use gadolinium doped ceria oxides as the ionic conducting material combined with cobalt iron spinel which serves as the electronic conductor. In this study we employ ~ 50 nm sputtered CeO_2 layers on the surface of porous CGO ceramic substrates which serve as solution "blocking" layers during the thin film fabrication process facilitating the control of film thickness. Films with thickness of ~ 2 and 4 microns were prepared by depositing 40 and 95 separate sol-gel layers respectively. Oxygen flux measurements indicated that the permeation increased with decreasing membrane thickness; thin film membrane with thickness on the micron level showed flux values an order of magnitude greater (0.03 μmol/cm^2 s) at 800°C as compared to 1mm thick bulk ceramic membranes (0.003 μmol/cm^2).

INTRODUCTION

The use of mixed conductive oxides in thin film form has led to a resurgence of interest into the utilization of these materials for a variety of applications including membrane separations and catalysis [1, 2]. The production of high purity oxygen is one potentially exciting application for these mixed conducting oxides [3]. One of the major drawbacks to the industrial use of is the limited oxygen permeation rates in bulk mixed conducting ceramics and ceramic/metal composite membranes. Recently, mixed ionic and electronic conducting (MIEC) thin film on porous ceramic substrates were prepared exhibiting order of magnitude greater oxygen flux as compared to conventional bulk ceramic membranes [4, 5]. However, thickness control of the thin films was problematic and the relation between thickness and oxygen flux were not evidenced in these sol-gel films on porous ceramic substrates. A greater understanding of the relationship between thickness dependence and nanocrystalline grain size on the oxygen permeation characteristics of MIEC materials are required in order

to determine the optimum processing conditions required to fabricate separation membranes and provide additional input to material synthesis community for improved membrane material design. This work is focused on filling the knowledge gap regarding the impact of thickness and grain size of sol-gel derived MIEC thin films on porous ceramic substrates for enhanced oxygen permeation.

EXPERIMENT

The porous $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ gadolium doped cerium oxide substrates were prepared by ball milling cerium oxide and gadolium oxide with 7 weight% carbon powder in ethanol for 24 hours. After drying and sieving, ceramics were mixed with a binder and uniaxially pressed into pellets of 16 mm diameter with a force of 20 kN and sintered at 1500°C for 6 hours in air. Sintered ceramic samples had relative densities of 70% (30% porous) with pore size of 1 to 3 micron and a physical flux greater than 2 μmol/cm^{2}s. A "barrier layer" was deposited by sputtering a layer of cerium oxide onto the polished porous substrate surface in order to inhibit sol-gel solution leakage during film processing. Sputtering was performed on JEOL (JEC-SP360M) system at 200 W and 0.5 Pa of Ar gas at room temperature using a cerium oxide target resulting in nominal 50 nm thickness of dense cerium oxide blocking layer. The final step in sample preparation was the chemical solution deposition of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$CoFe_2O_4$ (CGO 85 mol %, CFO 15 mol%) sols onto the porous substrate and blocking layer by a spin coating technique. Solutions with concentration of 0.5 M of 85%CGO 15%CFO were prepared from nitrate precursors in a 2-Methoxyethanol solvent [4, 5] were spin coated and pyrolyzed at 400°C for 3 minutes in 4 layer sequences followed by intermediate firing at 700°C for 30 minutes in air. Ceramic membranes were prepared from sol-gel solutions by drying, ball milling and calcined at 1100oC before sintering at 1380°C for 5 hours. Oxygen flux measurements were performed by placing the sample between two quartz tubes using a glass ring (melting point 620°C) for gas sealing, and a metal spacer with a diameter of 5 mm to control the area of gas flux. The sealing was done on the film surface with air at 1 atm was supplied to the bottom of the porous substrate (feed side) while flowing He (20 sccm) was supplied to the permeate side (film surface). The gas concentration of O_2 and N_2 was measured on the permeate side using a gas chromatograph (GC323; GL Sciences Co., Ltd).

RESULTS AND DISCUSSION

Figure 1 displays the results of this process improvement comparing the surface of thin films on porous substrates with and without the buffer layer. It is seen that after 10 layers of sol-gel depositions the thin films deposited on the buffer layer are of a more continuous nature as the solution leakage into the substrate was inhibited. A fine grain size ~100 nm of the CGO-CFO thin films similar to that observed via directly depositing onto CGO ceramic substrate suggesting that the CeO_2 buffer layer does not significantly affect the nucleation of the CGO-CFO thin films[4, 5].

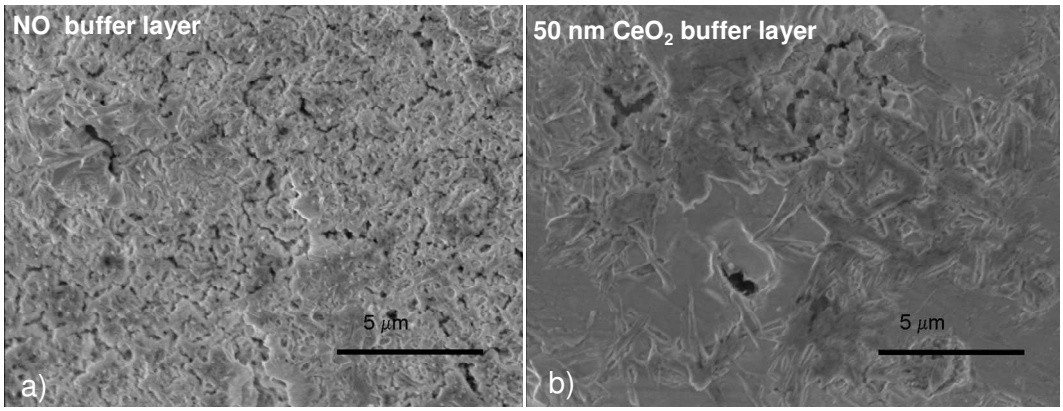

Figure 1. SEM image of 500 nm CGO-CFO thin film on a porous CGO substrate with (b) and without (a) 50nm sputtered CeO_2 buffer layer

A cross section image of a two micron thick CGO-CFO thin film on buffer layer coated porous substrate in shown in figure 2. The porous nature of the substrate as compared to the dense thin films are clearly seen in Figure 2 a), while 2b) provides a close up view of the thin film, buffer layer and ceramic substrate interface. The cross section shows that the thin film is dominated by homogeneous nucleation in the bulk of the film.

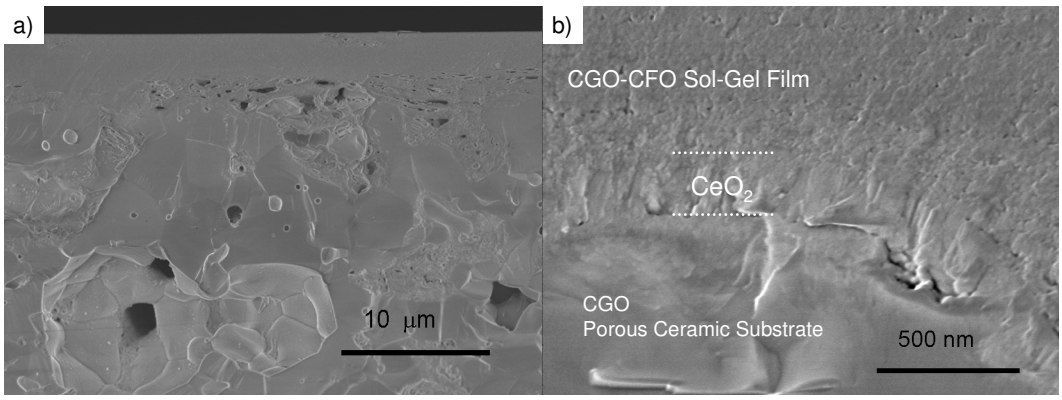

Figure 2. SEM image of 4 micron (95 sol-gel layers) CGO-CFO on buffer layer coated CGO porous substrate (a) 10 micron scale view of the porous substrate, and thin film (b) close up view of the substrate/buffer layer/thin film interface.

The microstructure as seen from plain view SEM is shown in figure 3 for a) thin films and b) ceramics sintered at 1380°C for 5 hours from sol-gel derived powders. The nanocrystalline grain size of the thin films is clearly seen as compared to the micron sized grains in the conventionally sintered ceramic membrane.

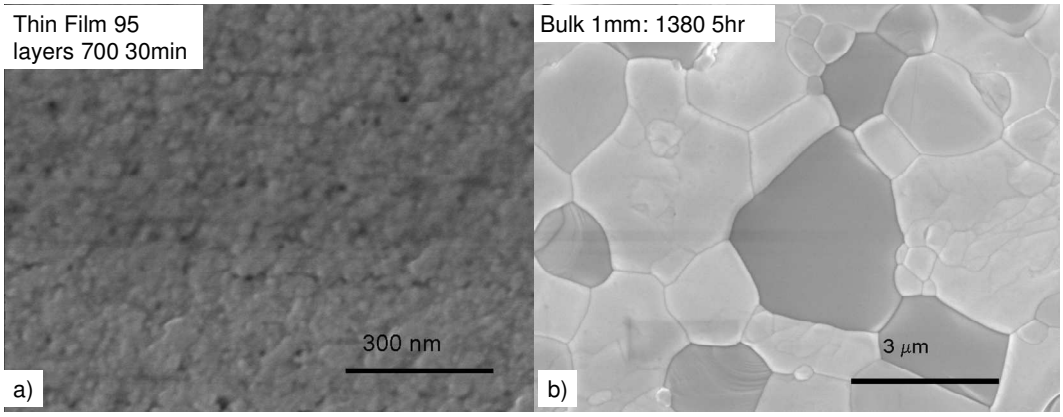

Figure 3. Top surface SEM image of a) CGO-CFO thin film on a porous CGO substrate and b) ceramic prepared from sol-gel solutions sintered at 1380°C for 5 hours.

The oxygen flux characteristics are presented in figure 3 where the time average value over the 40 minute measurement time of 0.027 (μmol/cm^2 s) for 2 micron and 0.017 (μmol/cm^2 s) for 4 micron thick films compared with literature values of values of 0.015 (μmol/cm^2 s) at 800°C previously reported in this system with thin films directly deposited onto porous substrates using 70 layer deposition process with various solution concentrations from 0.2 to 2M with estimated thickness ranging from 200 nm to 1 micron[4, 5]. In this study the use of sputtered cerium oxide blocking layers allowed films of up to four microns to be fabricated from a single solution concentration allowing the impact of thickness in the micron range on the oxygen permeation to be investigated.

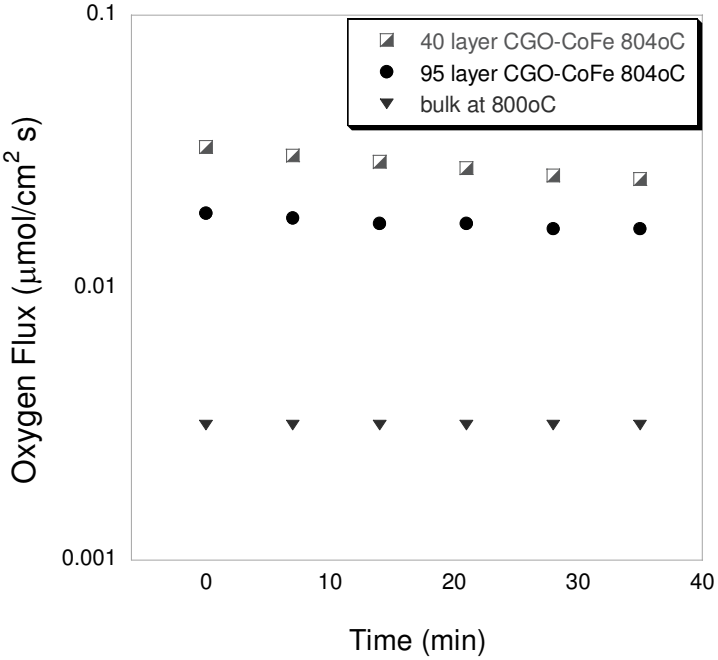

Figure 4. Oxygen flux (μmol/cm^2 s) versus measurement time at 800°C for 2 micron (40 sol-gel layers), 4 micron (95 layers) and 1mm thick ceramic sintered from sol-gel derived powders.

The oxygen flux of the thin films membranes is seen to decrease with time over the 40 minute measurement period at 800°C. This behavior has been seen in nanocrystalline CGO films and is believed to originate from grain coarsening. The ceramic membrane showed constant oxygen flux with a value of 0.003 (μmol/cm^2 s), nearly an order of magnitude less than the flux of the 2 micron thin films of 0.027(μmol/cm^2 s). Figure 5 shows the a) oxygen flux correlation with the inverse of sample thickness and b) the natural logarithm of oxygen flux versus natural log of sample thickness. It is seen that there is a linear relation between the flux and thickness pointing to the dominant role of bulk diffusion in oxygen permeation at this temperature and oxygen flux gradient from air to He at thickness on the 2 micron level. This is contrasted with the case of surface limited flux represented by the hypothetical dashed line in figure 5a). The slope of the line in figure 5b) showing a value of -1 further reinforces the importance of bulk permeation; a value of 0 would represent surface kinetic limited permeation and values between 0 and -1 would suggest both bulk and surface diffusion[6].

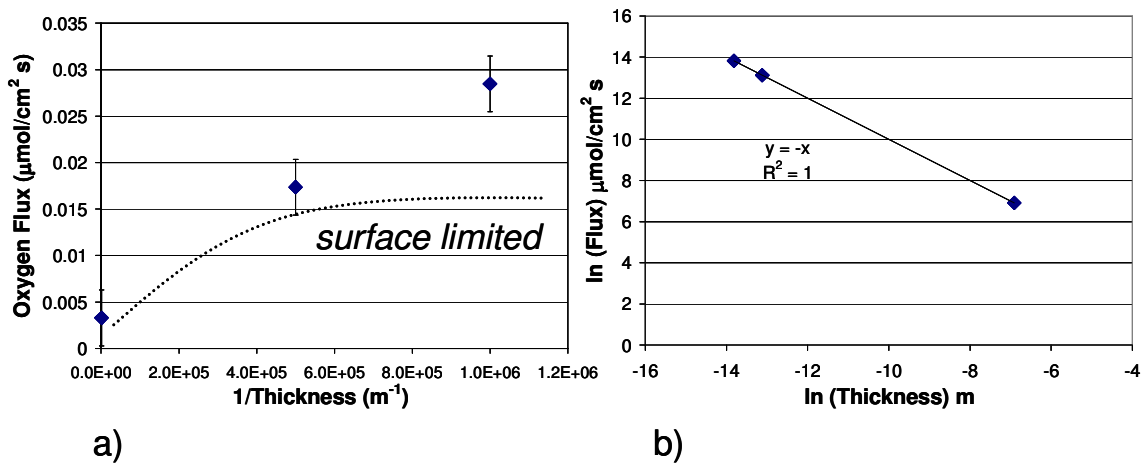

Figure 5 . a) Oxygen flux (μmol/cm^2 s) versus reciprocal thickness (m-1) and b) natural log of oxygen flux versus natural log of sample thickness showing a slope of -1 indicating bulk limited permeation. The dashed line in a) indicated hypothetical surface limited behavior.

The description above is formally described by considering the Wagner description of oxygen flux[7]:

$$JO_2 = \gamma \frac{RT}{16F^2 L} \int_{\ln PO_2'}^{\ln PO_2''} \frac{\sigma_e \sigma_i}{\sigma_e + \sigma_i} d \ln PO_2 \qquad (1)$$

Where JO_2 is the permeation flux of gas (O_2 in this case) mol/m^2 s, F is the Faraday constant, R is the gas constant, σ_e and σ_i are the electronic and ionic conductivities and PO_2' and PO_2'' are the gas partial pressure on the oxygen rich and oxygen lean sides of the membrane respectively. The factor γ is derived from the introduction of a "characteristic length, L_c" below which the flux does not increase with sample thickness reduction.

$$\gamma = \frac{1}{1 + 2(Lc / L)} \qquad (2)$$

Characteristic thicknesses of single phase mixed conducting ceramic such as $La_{0.3}Sr_{0.7}CoO_{3-\delta}$ sintered by conventional methods resulting in micron grain size showed characteristic length (L_c) on the order of 80 microns under an oxygen flux gradient of air to helium similar to that used in the present manuscript [8]. The characteristic length of conventionally sintered dual phase $Ce_{0.8}Gd_{0.2}$ (CGO)-$MnFe_2O_4$ (MFO) in the molar ratio 85:15 prepared via a chemical solution process under at oxygen permeation gradient from to air Argon/5%H_2 was determined to be approximately 500 microns [9, 10]. Due to the larger oxygen permeation gradient due to the hydrogen sweep gas in this study it is expected that surface exchange reactions would be more important than under the less dramatic air to Helium oxygen gradient used in the current study. Nevertheless, the dramatic decrease of the characteristic length over 2 orders of magnitude, from 500 microns [9] to less than 2 microns in the current work points to impact of the nanocrystalline state on the oxygen permeation properties of mixed electronic and ionic conducting membrane systems.

CONCLUSIONS

Blocking Layers ~50 nm thick of sputtered CeO_2 layers on the surface of porous CGO ceramic substrates were employed during the thin film fabrication process facilitating the control of film thickness. Films with thickness of ~ 2 and 4 microns were prepared by depositing 40 and 95 separate sol-gel layers respectively. Oxygen flux measurements indicated that the permeation increased with decreasing membrane thickness; thin film membrane with thickness on the micron level showed flux values an order of magnitude greater (0.03 $\mu mol/cm^2$ s) at 800^oC as compared to 1mm thick bulk ceramic membranes (0.003 $\mu mol/cm^2$). The oxygen permeation in nanocrystalline thin films was shown to be bulk limited even at film thicknesses as small as 2 microns.

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