NEW MIEC MEMBRANES FOR HYDROGEN SEPARATION

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ABSTRACT

A new approach to separate hydrogen using dual phase composite MIEC membranes has been proposed and is being currently investigated. In this approach methane or reformate comprising CO and H₂ mixtures is fed to one side of the membrane, while water vapor is fed to the other side. Oxygen from the steam side of the membrane transports through coupled transport of oxygen ions and electrons across the membrane to the methane/reformate side resulting in a hydrogen rich product on the permeate side. Although single phase membranes such as strontium or calcium doped lanthanum cobalt iron oxides (LSCF and LCF) have very high mixed conductivity, they were found to be not stable for the process under investigation. New dual phase membranes consisting of doped ceria and doped strontium titanate have been developed with good stability and high ambipolar conductivity suitable for the permeation process.

INTRODUCTION

Mixed ionic and electronic conducting (MIEC) oxides are used as porous anode and cathode for fuel cell applications. The requirements for such electrodes include high ionic (oxygen ions in case solid oxide fuel cells (SOFCs)) and electronic conductivity and stability of the material in the atmosphere that will prevail on either cathode or anode side of the fuel cell. Dense MIEC membranes are recently receiving more attention due to their potential application as gas separation membranes. Oxygen separation from air using oxygen ion and electron conducting MIECs has recently been reported which illustrates the importance of these materials (1,2). Most of these applications involve relatively high oxygen partial pressure (1.0 to 10⁻⁴ atm) and under such conditions commonly known MIECs of the perovskite family La₁₋ₓSrₓCo₁₋₂ₓFeₓO₃₋₈ (LSCF) are quite stable. We have recently described a process that utilizes oxygen ion and electronic conducting MIECs for synthesizing and separating hydrogen (3) as shown in Figure 1.

This process involves reacting methane (or reformate) with steam in a membrane reactor to form syngas on one side of the membrane and yield a hydrogen-steam mixture rich in hydrogen on the other side of the membrane. In this process, the MIEC membrane will be subject to high water vapor content and moderately low oxygen partial pressure (pO₂ 10⁻⁷ to 10⁻¹¹ atm) on one side. The other side of the membrane will have very low partial pressure of oxygen (pO₂ 10⁻¹⁶ to 10⁻²⁰ atm). Membrane requirements for such process are (i) high ambipolar conductivity characterized by high chemical diffusion rates, (ii) stability under the prevailing conditions of low oxygen partial pressure and high water content and (iii) high surface reaction rates. Well known MIECs such as LSCF
perovskites have been investigated and our studies show that these materials do not possess the requisite chemical stability to function as membrane separators for use in this process. This paper reports the development of a novel dual-phase composite MIEC membrane system comprising of Gd-doped ceria (GDC) (ion conducting phase) and Y-doped strontium titanate (YSTA) (electronic conducting phase), both individually stable in the gas atmospheres prevailing on both sides of the membrane during the hydrogen separation process. The details of preparation, electrical and structural characterization of the single phase MIEC materials and the new dual phase composite material are reported and analyzed for suitability for the proposed hydrogen separation process.

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}^{2-} + 2e^- \]

**Figure 1. Schematic of the hydrogen separation process using MIEC membranes.**

**EXPERIMENTAL DETAILS**

**Powder Synthesis and Pellet Fabrication**

Single phase MIECs of the composition La$_{0.8}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ in the LSCF system and La$_{0.8}$Ca$_{0.2}$FeO$_{3-\delta}$ in the LCF system have been prepared using conventional powder processing method. Starting materials La$_2$(CO$_3$)$_3$-xH$_2$O, SrCO$_3$, Co$_2$O$_3$, Fe$_2$O$_3$, (or CaCO$_3$ for LCF system) were first mixed and ball-milled in methanol for 24 hours. The dried mixture was then calcined at 1300°C for 4 hours. Discs of the samples were prepared by pressing finely ground powders and sintering it at 1400°C for 4 hours.

Components of the dual phase composite membrane Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$ (GDC is an excellent oxygen ion conductor) (4) and Y$_{0.09}$Sr$_{0.91}$Ti$_{0.95}$Al$_{0.05}$O$_3$ (YSTA is an excellent electronic conductor) (5) powders were synthesized by conventional powder processing method as described above using Gd$_2$O$_3$ and CeO$_2$ for GDC, Y$_2$O$_3$, SrCO$_3$, TiO$_2$, and Al$_2$O$_3$ for YSTA as starting materials. The calcined products were then finely ground and the particle size distribution was estimated. The average particle sizes of the milled powders were around 2 and 4 microns for the GDC and YSTA phases respectively. These fine powders were then mixed in the volume ratio of 40% GDC and 60% YSTA and ball milled for 24 hours and dried. Pressed disks of the mixed powders were first sintered in air at 1500°C for 4 hours, and then were sintered in a reducing atmosphere with an oxygen partial pressure of around 10$^{-15}$ atm at 1400°C for 4 hours. Porous disks were prepared by using 50 volume% of amorphous carbon powder (5 μm) as pore former. The structure of the prepared powders and sintered disks were determined using X-ray diffraction (XRD) analysis using Cu Kα radiation. The surface morphology and elemental composition were analyzed using scanning electron microscopy (SEM) and wavelength dispersive spectrometry (WDS). The density of the sintered disks was measured by Archimedes method by using water as the medium.
Electrical Conductivity and Conductivity Relaxation

The electrical properties of the single phase and dual phase composite materials were measured by the standard four-probe dc method. Bar samples (30 mm x 3 mm x 3mm) were cut from pellets and polished for these studies. The ends of the bar sample were coated with platinum paste (Engelhard) and pure platinum wires were used as current and voltage leads. The sample was first allowed to equilibrate at a particular pO2 and temperature for a long time (≥ 5 hours). The stability of electrical conductivity and sample environment was continuously monitored by a low current galvanostatic scan and a pO2 sensor respectively. After equilibration the total conductivity of the sample was measured by obtaining I-V plots using a galvanodynamic scan.

The surface exchange coefficient \((K_{ex})\) and chemical diffusion coefficient \((\bar{D})\) of the membrane were obtained from a conductivity relaxation experiment. In a typical conductivity relaxation experiment, the sample was initially equilibrated in one atmosphere \((pO2 (I))\) and the atmosphere surrounding the sample was then abruptly changed to a new atmosphere \((pO2 (II))\). The change in electrical conductivity was continuously measured in a low current galvanostatic scan until a new equilibrium state is obtained. The difference in oxygen partial pressures \((pO2(I) - pO2(II))\) was kept as small as possible to obtain \(K_{ex}\) and \(\bar{D}\) continuously over the entire range of pO2’s of interest and also to avoid mechanical shock to the sample. The pO2 in the measurement chamber was continuously monitored by a YSZ sensor and a total gas flow of 200 to 300 cc/min was used. The pO2’s in the experiments were fixed by bubbling a variable mixture of argon and hydrogen gases through water. The re-equilibration process depends on the surface exchange coefficient \(K_{ex}\) and chemical diffusion coefficient \(\bar{D}\) of the MIEC membrane. For a rectangular bar sample with length \(2L\), widths \(2W_1\) and \(2W_2\), the fractional change in conductivity with time is given by:

\[
\frac{(\sigma_t - \sigma_e)}{(\sigma_i - \sigma_e)} = 1 - \sum_{n=1}^{m} \sum_{m=1}^{n} \frac{2L^2_e \exp(-\beta_m^2 \bar{D}t/W_2^2)}{2L^2_e \exp(-\beta_m^2 \bar{D}t/W_2^2)} \times \frac{\beta_m^2 (\beta_m^2 + L_1^2 + L_1)}{\beta_m^2 (\beta_m^2 + L_2^2 + L_2)}
\]

where \(\sigma_0\), \(\sigma_t\) and \(\sigma_e\) are the initial, time dependent and final electrical conductivities of the sample respectively, \(L_1 = W_1/L_e = \beta_n\tan \theta\) and \(L_2 = W_2/L_e = \beta_n\tan \theta\), \(L_e\) is the characteristic length given by \(L_e = \bar{D}/K_{ex}\), and \(\beta_i\) is the ‘i’th root of the equation \(L = \beta_i \tan \beta_i\). The details of diffusion equation and solution are available in literature (6).

The chemical diffusion coefficient \((\bar{D})\) and the surface exchange coefficient \((K_{ex})\) were obtained by fitting the conductivity relaxation data to equation [1]. A program was developed for the fitting procedure by the method of least squares and the summation was carried for the value of \(m = n = 10\).

Equation [1] is well-behaved when the dimensionless parameter \(L_1\) and \(L_2\) are around 0.03 to 30 (7). The composite membranes are expected to have more complex surface reaction mechanisms than single phase MIEC materials and may have situations where \(L_1, L_2 \leq 0.03\) or \(L_1, L_2 \geq 30\). Thus, in order to obtain \(K_{ex}\) independently we performed conductivity relaxation experiments using porous samples (8) and used these \(K_{ex}\) values in equation [1] to obtain \(\bar{D}\). In the case of porous sample, the diffusion distances are

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much reduced to the dimension of the average grain size of the material which is of the order of few microns. Thus, the conductivity relaxation is rate-controlled by the surface exchange coefficient process. If \( l \) is the average grain size of the porous specimen then equation [1] in the case where diffusion is not rate-controlling reduces to,

\[
\frac{(\sigma_l - \sigma_o)}{(\sigma_l - \sigma_o)} = 1 - \exp \left[ -\frac{K_{ex} t}{l} \right]
\]  

[2]

If \( \sigma_p \) is the conductivity of the sample with a surface porosity of \( p \) then it is related to the conductivity of the dense sample \( \sigma \) as,

\[
\sigma_p = \sigma (1 - p)
\]

[3]

Equation [2] has a single time constant and the quicker relaxation process allows us to extract \( K_{ex} \) independently and use them in equation [1] to obtain \( D \) from dense samples.

RESULTS AND DISCUSSION

Single Phase MIECs (LSCF and LCF)

Figure 2 shows the XRD traces of the as prepared LSCF and LCF samples and the corresponding traces after 11 days exposure to reducing conditions at \( pO_2 = 10^{-17} \) atm and 900°C. The LSCF sample exposed to reducing conditions shows new peaks characteristic of \( Sr_2FeO_4 \) and / or \( La_2CoO_4 \). This clearly shows that the LSCF decomposed to strontium ferrite or lanthanum cobaltite phases. The total electrical conductivities of the LSCF and LCF samples under reducing conditions (\( pO_2 = 10^{-17} \)) are only about 0.6 and 0.3 S/cm respectively and are expected to be predominantly electronic conducting even at these conditions. In addition the conductivity at a \( pO_2 \) of \( 10^{-17} \) atm is also found to decrease with time as shown in Figure 3. Hence both LSCF and LCF have

![Figure 2. XRD traces of (a) LSCF and (b) LCF samples before and after exposure to reducing atmospheres.](image)

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low conductivity and are unstable under reducing conditions and are not suitable for application in the hydrogen separation process described here.

![Figure 3. Conductivity as a function of time for LCF at $pO_2 = 10^{-17}$ atm.](image)

**Dual Phase Composite (GDC+YSTA)**

XRD traces obtained from the composite sample and its components are shown in Figure 4. Analysis of the XRD traces reveals that no third phase is present in the composite pellet which was sintered and reduced. The absence of new phases in the XRD pattern suggests that GDC and YSTA are chemically inert towards each other and thus the GDC-YSTA composites may be suitable for the intended application. Further, YSTA is an excellent n-type semiconductor whose conductivity increases with decreasing $pO_2$ and is thus ideally suited for the intended application where relatively reducing conditions are expected to prevail on both sides of the membrane. SEM images of the fracture surface of the dense and porous composite membrane sintered in air at 1500°C for 4 hours, and subsequently reduced at 1400°C for 4 hours at an oxygen partial pressure of less than $10^{-18}$ atm are shown in Figure 5. The grain sizes are in the range of 3-6 μm. The two phases are contiguous and well-percolated, which is very important from the standpoint of achieving high ambipolar conductivity. The porous sample has well-connected pores and the porosity is estimated to be 20%.

![Figure 4. X-ray diffractogram of the GDC, YSTA powders and their composite.](image)
Elemental analysis of the dark and light phases indicated that the phases were essentially GDC and YSTA perovskite confirming the XRD analysis. However, the doping levels of the species of were different from the starting composition due to the interdiffusion of elements across the two-phase grain boundaries. We observed some interdiffusion of the rare-earth elements Y and Gd between the perovskite and fluorite phases. However, this interdiffusion is not expected to cause a major change in the defect chemistry of the individual phases since Gd and Y are both rare-earth and trivalent.

![Figure 5. SEM micrograph of surfaces of the (a) dense and (b) porous composite material, sintered in air at 1500°C for 4 hours, was and subsequently reduced at 1400 °C for 4 hours. The dark phase is GDC, and the light phase is YSTA.](image)

**Defect chemistry of the phases.** In Y-doped SrTiO$_3$, incorporation of Y dopant on the Sr sublattice occurs according to the following reaction

\[
\text{Donor doping of Sr-site: } Y_2O_3 + 2TiO_2 \xrightarrow{2\text{SrTiO}_3} 2Y^{\text{Sr}}_r + 6O^{\text{Sr}}_r + 2Ti^{\text{r}}_r + \frac{1}{2}O_2(g) \quad [4]
\]

Further, at low oxygen partial pressures, oxygen vacancy formation reaction can occur through:

\[
2Ti^{\text{r}}_r + O^{\text{r}}_r \leftrightarrow V^{\text{r}}_r + 2Ti^{\text{r}}_r + \frac{1}{2}O_2(g) \quad [5]
\]

The mass action law for the redox defect reaction [5] and the electroneutrality condition can be written as,

\[
K_{\text{red}} = \sqrt{P_{O_2}} n^3 \quad [6]
\]

\[
2\delta + [Y^{\text{Sr}}_r] = n \quad [7]
\]

Solving equations [6] and [7] simultaneously gives,

\[
n^3P_{O_2}^{1/2} - n^2[Y^{\text{Sr}}_r]P_{O_2}^{1/2} - 2K_{\text{red}} = 0 \quad [8]
\]
In an intermediate oxygen partial pressure regime the oxygen vacancy concentration is insignificant, \( n = [V'_o] \) and the electronic charge carrier concentration is constant with respect to \( p_{O_2} \). At very low oxygen partial pressures, where oxygen vacancies are numerous, the electroneutrality condition can be simplified to \( n = 2\delta \). Under these conditions, the electronic charge carrier concentration can be simplified to,

\[
    n = (2K_{\text{red}})^{1/2} p_{O_2}^{-1/6}
\]

Thus, under reducing conditions the electronic conductivity is expected to initially remain constant as a function of decreasing oxygen partial pressure. Upon further decrease in oxygen partial pressure, the electronic conductivity is expected to increase as \( p_{O_2}^{-1/6} \).

For Gd-doped CeO\(_2\) (Gd\(_y\)Ce\(_{1-y}\)O\(_{2-y/2}\)), the Gd dopant incorporation occurs through,

\[
    \text{Gd}_2\text{O}_3 + 2\text{CeO}_2 \rightarrow 2\text{Gd}^{4+} + 3\text{O}_2 + V''_o + \text{Ce}^{4+}
\]

In an intermediate oxygen partial pressure regime, the electrical conductivity is expected to be almost entirely ionic and constant since the oxygen vacancies are charge compensated by the Gd dopant, i.e. \([\text{Gd}_{\text{Ce}}] = 2[V'_o]\). Under very reducing conditions, intrinsic oxygen vacancy formation reaction can take place according to the following defect reaction,

\[
    \text{O}_2 + 2\text{Ce}_{\text{Ce}}^{4+} \Leftrightarrow \frac{1}{2} \text{O}_2(g) + V''_o + 2\text{Ce}^{4+}_{\text{Ce}}
\]

Wang et al. (4) demonstrated that under these conditions, GDC behaves as a mixed electronic and oxygen ionic conductor. The concentrations of \( V''_o \) and electrons are,

\[
    [V''_o] = [\text{Gd}_{\text{Ce}}]/2 + kp_{O_2}^{-1/4}
\]

\[
    n = kp_{O_2}^{-1/4}
\]

where \( k \) is a temperature dependent constant. Thus, from equation [12], under these very reducing conditions, the oxygen ionic conductivity is related to the Gd dopant concentration and \( p_{O_2}^{-1/4} \). The ionic conductivity of GDC is expected to remain high over a wide range of oxygen partial pressures since it is principally determined by the Gd dopant concentration. From equation [13], at very low oxygen partial pressures GDC develops some electronic conductivity; however, it is not expected to be detrimental to the gas separation process.

**Total electrical conductivity.** YSTA is an n-type semiconductor whose conductivity in air is very low. When annealed in a reducing atmosphere, oxygen vacancies and electron formation will occur as discussed in the previous section and its conductivity increases significantly. Dense YSTA sample has a total electrical conductivity of about 22 S/cm.

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under reducing conditions ($pO_2 = 10^{-17}$ atm) at 900 °C. GDC has a total electrical conductivity of about 0.2 S/cm in air and its conductivity increases to about 1 S/cm when reduced ($pO_2 < 10^{-17}$) at 900°C. The 40% GDC + 60% YSTA composite has a total conductivity of 4 S/cm at 900°C at $pO_2 = 10^{-17}$ atm. The temperature dependence of total conductivity in forming gas (95% Ar + 5% H$_2$) is shown in Figure 6. As shown the conductivity remains high over a wide temperature range.

![Figure 6. The conductivity measurement of the composite material in reducing environment with 95% Ar-5% H$_2$ bubbled through water ($pO_2 < 10^{-16}$ atm).](image)

**Electrical conductivity relaxation.** A typical relaxation transient for the composite material is shown in Figure 7, where the symbols represent experimentally measured conductivity data, while the dotted line is a curve fit using equation [1]. This transient was measured by abruptly changing $pO_2$ from $5 \times 10^{-17}$ atm to $1 \times 10^{-18}$ atm at 700 °C. The step-change in oxygen partial pressure for these experiments is usually kept below one order of magnitude for reasons discussed earlier. A plot of $D$ values obtained from fitting the data is shown in Figure 7.

![Figure 7. (a) Relaxation transient for the composite material, circles are experimental data and the curve is the fit to equation [1]. (b) Chemical diffusion coefficient $D$ as a function of temperatures for the composite material.](image)
Surface exchange coefficient and porous sample. The surface exchange coefficient of the dense GDC+YSTA composite at low oxygen partial pressures (pO₂ < 10⁻¹⁵ atm) is shown in Figure 8. These values are obtained by fitting the relaxation transients to equation [1]. The completion of the relaxation process in dense samples took more than 2 hours. With porous sample as described earlier, it was dramatically reduced to about 200 to 300 seconds. The surface exchange coefficient estimated using equation [2] for a porous sample is shown in Figure 8(b). At the gas permeation temperature which is typically ~ 900 °C, D and Kex have the values around 10⁻⁵ cm²/s and 10⁻⁴ cm/s respectively. The Kex values obtained from dense and porous samples are comparable. The diffusion distances in the porous samples are equal to the grain size of the sample and hence the conductivity relaxation is rate controlled by the oxygen surface exchange process. Therefore, Kex values obtained from porous samples are used for further studies.

Figure 8. Surface exchange coefficients of the GDC+YSTA composite at different temperatures at very low oxygen partial pressures (a) dense sample and (b) porous sample.

Figure 9. (a) Partial pressure dependence of conductivity at different temperatures and (b) temperature dependence of ‘1/N’ obtained from the slopes.

Partial pressure dependence of total conductivity. The quick re-equilibration of the porous GDC-YSTA composite samples enabled us to conduct partial pressure dependence studies of the total conductivity at various temperatures and these results are
shown in Figure 9(a). The exponents ‘1/N’ obtained from the slope of the log σ vs log pO₂ plots are shown in figure 9(b). A systematic decrease in slope or the increase in the exponent ‘N’ from 6 to 10 with increasing temperature is observed. The expected values of the exponent for YSTA and GDC phases from equation [9] and [13] are 6 and 4 respectively. The experimentally observed values are greater than 6 and indicate that the changes in conductivity with oxygen partial pressure can be ascribed to the YSTA phase. At the same time the sample is expected to have very high oxygen ion conductivity due to the presence of the percolating GDC phase. The total conductivity of the porous sample is found to be very stable with time and is very suitable for permeation applications to split hydrogen from water. Hydrogen separation studies as illustrated in Figure 1 are being performed and the results will be reported in a future publication.

CONCLUSIONS

Single phase MIEC membranes such as LSCF and LCF do not possess sufficient chemical or electrical stability under reducing conditions (pO₂ < 10⁻¹⁵ atm) and hence are not suitable for the proposed hydrogen separation process. A new composite MIEC membrane consisting of GDC and YSTA has been developed. Characterization studies indicate that these membranes have good phase stability and electrical conductivity in the atmosphere that will prevail in the hydrogen separation process described here. Detailed experimental studies of this process using this composite material are underway.

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