Proton-Conducting Dense Ceramic Membranes for Hydrogen Separation

Technical Progress Report

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DISCLAIMER

ABSTRACT

This project is aimed at preparation of thin membranes of a modified strontium ceramic material on porous substrates with improved hydrogen permeance. The research work conducted in this reporting period was focused on studying synthesis methods for preparation of thin thulium doped strontium cerate ($SrCe_{0.95}Tm_{0.05}O_3$, SCTm) membranes. The following two methods were studied in the past year: (1) polymeric-gel casting and (2) dry-pressing. The polymeric-gel casting method includes preparation of mixed metal oxide gel and coating of the gel on a macroporous alumina support. Micrometer thick SCTm films of the perovskite structure can be obtained by this method. However, the deposited films are not hermetic and it may require about 50 coatings in order to obtain gas-tight SCTm films by this method. Asymmetric SCTm membranes consisting of a thick macroporous SCTm support and a thin SCTm layer can be effectively prepared by the dry-pressing method. The membranes were prepared by pressing together a thick layer of coarse SCTm powder and a thin layer of finer SCTm powder, followed by calcination and sintering under proper conditions. The asymmetric SCTm membranes have desired phase structure and are hermetic. Hydrogen permeation flux through the SCT membranes is inversely proportional to the thickness of the dense layer of the asymmetric membranes. The results show a substantial improvement in hydrogen permeation flux by reducing the SCTm membrane thickness.

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INTRODUCTION

Dense proton-conducting ceramic membranes have recently received increasing interest since Iwahara and coworkers first discovered proton-conduction in $SrCeO_3$ based perovskite type ceramics in high temperatures (>500°C) in a hydrogen containing atmosphere [1]. The major problem with the $SrCeO_3$ based ceramic membranes is their low electronic conductivity, which leads to low hydrogen permeability. Therefore, the effective way to improve the electronic conductivity of this kind of membranes is to dope the strontium cerate with a metal having lower ionization potential. Results obtained in our laboratory show that thulium doped $SrCeO_3$ has much improved electronic conductivity and therefore a higher hydrogen permeability[2, 3]. For hydrogen permeation through proton-conducting ceramic membranes the bulk diffusion is more likely to be the rate-limiting step even for thin membranes because the surface charge transfer reaction for hydrogen requires lower energy as compared to oxygen. Therefore it is expected that reducing membrane thickness can be effective in increasing the hydrogen permeance for the proton conducting ceramic membranes. The objective of this project is to synthesize thin SCTm membranes and investigate hydrogen permeation properties of these membranes.

EXPERIMENTAL

Thin SCTm Membranes Prepared by Polymer-Gel Approach

Sr-Ce-Tm containing inorganic-organic polymeric sol was prepared from $Sr(NO_3)_2$, $Ce(NO_3)_2$ and Tm (NO_3) in stoichiometric proportions (100-**Sr, 95-Ce. 5-Tm)** (for 0.02 mole SCTm) in 20 ml distilled water, followed by mixing with 10 ml concentrated nitric acid, 40 ml ethylene glycol and 3 g glycine. The nitric acid and glycine was used to adjust and stabilize the pH value in the reacting solution. The solution was then heated to 93-96°C and stirred for 60 hrs at this temperature till the viscosity of the solution was in the range of 90~190 cP at room temperature. A highly viscous polymeric gel containing Sr, Ce and Tm in the desired proportion was obtained.

Submicron-pore α-alumina disks were dip-coated with the viscous polymeric gel (contact time 10-15 min), followed by drying at 40°C for 2 hr. The dip-coated polymer gels were calcined at 300°C in air for 3.5 hr, and the supported disks were dip-coated again with the polymer gel, followed by the same drying and calcination step, to obtain thicker SCTm layers. The final coated layers were sintered 1500°C for 13 hrs to convert the coated SCTm layers into the perovskite structure and to densify the coated layers. The membranes were characterized by XRD for phase structure and membrane thickness (confirmed by SEM), and helium permeation for gas tightness.

Thin SCTm Membranes Prepared Dry-Pressing Approach

The citrate method was used to prepare the perovskite-type $SrCe_{0.95}Tm_{0.05}O_3$ powder. $Sr(NO_3)_2$, $Ce(NO_3)_3.6H_2O$ and $Tm(NO_3)_3.5H_2O$ in desired proportions were mixed with citric acid in distilled water to form a 0.2 M solution of total metal ions. The citric acid was 1.5 times

the total molar amount of metal ions. Then this solution was heated to 96°C –100°C, where polymerization reaction took place for 5 hrs with stirring in a refluxed-mode. Subsequently, the water was evaporated at 100°C and a condensation reaction happened. Finally, gel-like material was formed. After dried at 110^0C for 24 hours, the gel-like material became a sponge-like and brittle material, which was followed by self-ignition at 400°C for 30 min. The material after self-ignition was ground to powder with a mortar and pestle for about 10 min and calcinated at 600°C for 10 hrs to remove the residual organic compounds.

The SCTm particles of various sizes were obtained by the following procedure. The raw powder was labeled as P1. P1 was separated into two parts. After one part of P1 was carefully grounded by agate mortar for about 15 minutes, it was labeled as powder P2. Power P2 was separated into four parts. These four parts were pre-sintered at four different temperatures, 800°C, 1300°C, 1400°C and 1500°C respectively. They were labeled correspondingly in the above order as P3, P4, P5, P6. P2 was used to make the dense layer while P1, P3, P4, P5 and P6 were used to form the porous substrates. P1 (or P3, P4, P5, P6) was first put into a die of 25 mm in diameter and pressed under a hydraulic press apparatus of roughly 5 MPa. Then, the pressure was released and the die was taken out from the apparatus. A controlled amount of powder P2 was added uniformly on the surface of the roughly pressed membrane. The sample in the die was pressed again with a final pressure of 130MPa.

Table 1 SCTm symmetrical membranes prepared under various situations and their properties

Disk Sample No.	Ts[1]/time (°C/hr)	SubstrateTc[2]/ time (°C/hr)	Substrate	Gas Tight or Not	Appearance of Sintered Disks	Shrinkage Rate(%)	Good for H_2 Separation or Not
# 1	1495(24)	600(10)	P1	No	Slight green dark	19	No
# 2	1260(24)	600(10)	P2	No	Slight yellow	5	No
# 3	1495(24)	600(10)	P2	Yes	Green dark	22	Yes
# 4	1495(24)	800(10)	P3	Yes	Green dark	21	Yes
# 5	1495(24)	1300(10)	P4	No	Slight green dark	15	No
# 6	1495(24)	1400(10)	P5	No	Partially laminated	11	No
# 7	1495(24)	1500(10)	P6	No	Totally laminated	8	No

[1] Ts stands for the final sintering temperature, [2]Tc stands for powder calcination temperature

The total amount of powder for each membrane (or support) was 4.2g. The powder amount for top dense layer was changed from 0.2g to 2g. The green disks were sintered at 1300°C, 1495°C respectively for 24 hrs in a furnace with a ramp rate of 2°C/min during heating and cooling cycles. Finally, dense, asymmetrical SCTm membrane disks were obtained. These membrane disks were tested with respect to their structure and gas permeability. The gas

tightness of porous substrates and asymmetrical membranes was checked with an unsteady state helium permeation system at room temperature. The hydrogen permeation measurement system is shown elsewhere [3], The disk membrane with diameter of 21 mm was sealed by a ceramic-glass sealant [4].

RESULTS AND DISCUSSION

Membranes Prepared by Polymeric Gel Coating Method

The critical parameter for coating a continuous SCTm film on porous alumina substrates by this method is the viscosity of gel. It was found that the viscosity of 109 cp is optimum for dip-coating. Figure 1 shows the XRD patterns of the uncoated α-alumina support (0 dip-coating) and the same support coated with SCTm layer of different dip-coating numbers (after sintering at 1400°C). As shown, the coated SCTm layers have desired perovskite structure. Furthermore, the XRD peak intensity of the perovskite phase increases with increasing number of coating, consistent with the fact that multiple coating gives thicker SCTm layer. SCTm films up to 10 μm can be obtained through multiple coatings Each coating gives an SCTm layer of about 1 μm in thickness.

Table 2 SCTm asymmetrical membranes prepared under various situations and their properties

Disk Sample No.	Ts[1]/time (°C/hr)	SubstrateTc[2]/time (°C/hr)	Top layer	Substrate	Gas Tight or Not	Appearance of Sintered Disks	Shrinkage Rate(%)	Good for H_2 Separation or Not
# 8	1495(24)	600(10)	0.6g P2	3.6g P1	Yes	Top side is darker than substrate side	19	Yes
# 9	1495(24)	1300	0.6g P2	3.6g P4	No	Slight green dark	15	No

[1] Ts stands for the final sintering temperature, [2]Tc stands for powder calcination temperature

Figure 2 shows helium permeance through the uncoated α-alumina support and the same support coated with SCTm layers. A straight line, characteristic of the combined Knudsen and viscous flow transport mechanism, can correlate the helium permeance data. Helium permeance decreases with increasing number of coating due to increased resistance as a result of thicker SCTm layer. The reduction in helium permeance is not significant even after 10 cycles of dip-coating. These data suggest that it is very difficult to obtain a hermetic SCTm layer by this method. A rough estimate indicates that repeated coating of SCTm for about 50 times would result in a fairly hermetic SCTm membrane with SCTm thickness of about 50μm.

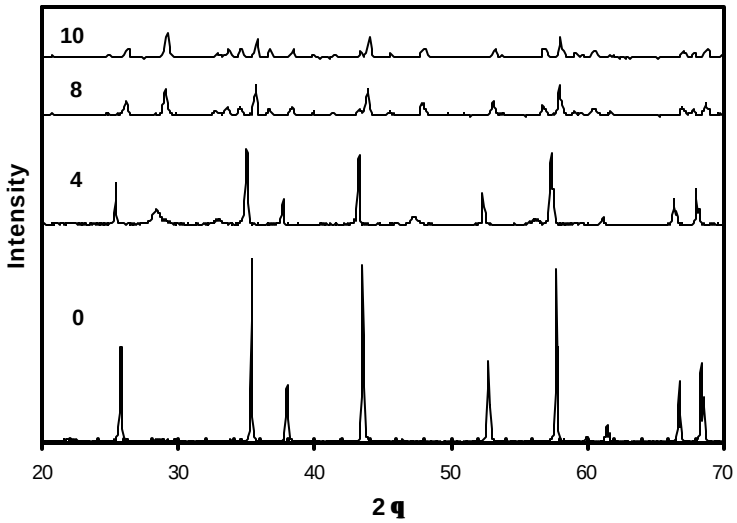

Figure 1 XRD Patterns of Alumina Supported SCTm Membranes Prepared by the Polymeric Gel Method with Different Number of Dip-Coating

Membrane Prepared by Dry-Pressing Method

The SEM analysis showed that the average particle sizes of Samples P1 to P6 are respectively 7µm, 0.2µm, 0.5µm, 20µm, 45µm, 70µm. Table 1 shows the SCTm symmetrical membranes prepared under various conditions and their properties. Among Sample # 1 to Sample # 7, Samples # 1 and #5 are potential candidates for the porous substrates. Results with Samples # 2 and # 3 show that the temperature is critical to the densification process. The final sintering temperature should be 1495°C in order to obtain a dense membrane. Both Sample # 3 and Sample # 4 are dense due to their smaller particle size compared to Sample # 1 and Sample # 4. Their appearance looks darker and their shrinkage rate is higher. From Sample # 3 to Sample # 7, one could see that with increasing particle size, the shrinkage rate of the membrane became smaller and the porosity became larger until it was laminated.

Table 2 shows the asymmetrical membranes based on two potential candidates of porous substrates. Sample # 8 was gas tight and suitable for use in hydrogen separation experiments. Sample # 9 was not hermetic due to a larger difference in the shrinkage rate between the top-layer and support. If the top layer was too thin, gas-tight top-layer could not be obtained as the thin layer could not stand interfacial resistant force caused by the difference in the shrinkage rate between the top-layer and support. The minimum thickness of dense film obtained by this method is 150µm. The thickness of dense layer can be accurately estimated from the amount of powder used for the top-layer and was also confirmed by the optical microscopy. Asymmetrical SCTm membranes with a large pore SCTm support and dense SCTm top-layer of various thickness (150-600 µm) were prepared by this method under optimized conditions. There asymmetric membranes are hermetic. XRD analysis shows that the dense SCTm top layers have desired perovskite type structure.

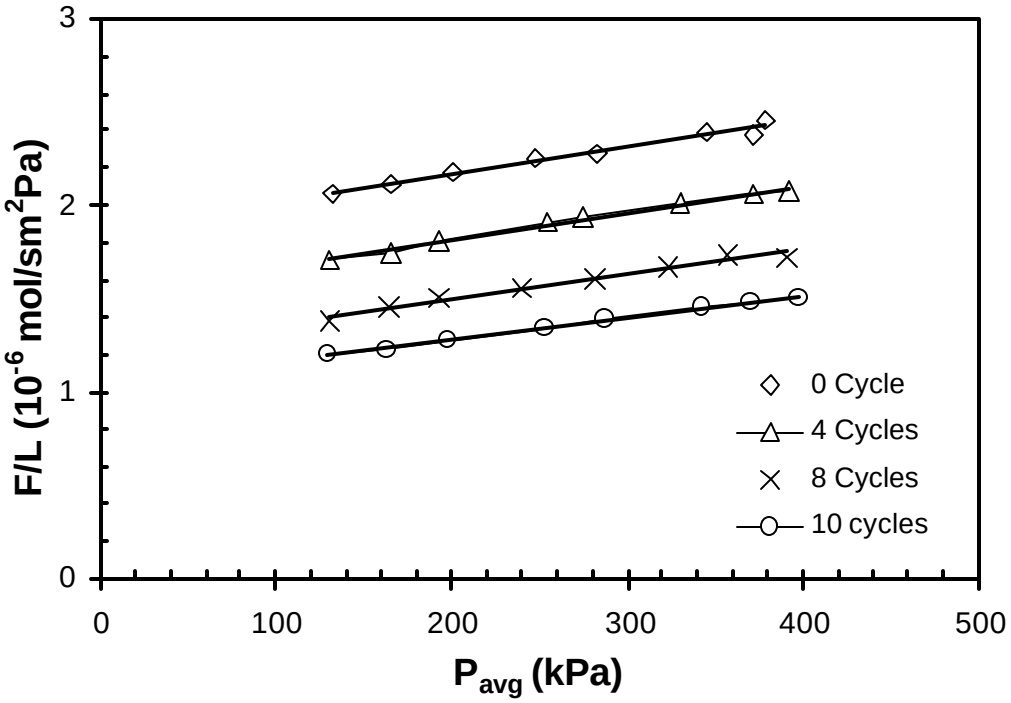

Figure 2 Helium Permeance versus Average Pressure across Membrane for of Alumina Supported SCTm Membranes Prepared by the Polymeric Gel Method with Different Number of Dip-Coating

Figure 3 shows hydrogen fluxes for several SCTm membranes with dense layers of various thicknesses under identical conditions while Figure 4 plots hydrogen flux versus the reciprocal of dense film thickness for samples presented in Figure 3. These two figures clearly show that hydrogen permeation flux is linearly proportional to the reciprocal of the membrane thickness in the studied thickness range (3 mm to 0.15 mm). This relationship confirms that the bulk diffusion step is rate-limiting step for hydrogen permeation through SCTm membrane with the thickness at least down to 0.15 mm. It should be noted that although all experimental conditions are identical for these membranes, the downstream hydrogen partial pressure increases with decreasing membrane thickness due to increasing hydrogen permeation flux. Thus, the driving force for hydrogen permeation through thinner membrane is smaller than the thicker ones, which might affect the linear relationship. However, further analysis reveals that this effect is negligible though it does exist [5]. In order to reach the level of commercial interests, the hydrogen permeation flux should be at least 7.4×10^{-7} mol/cm^2·s. Therefore, by extrapolation Figure 4, the membrane thickness should be at least reduced to 15 micron.

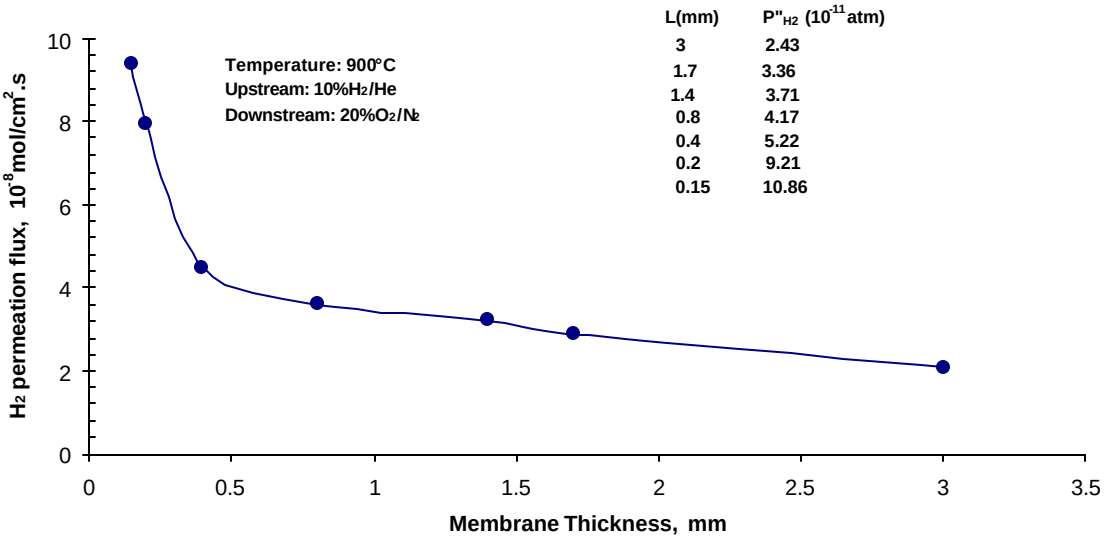

Figure 3 Hydrogen Permeation Flux for SCTm Membranes with Different Thickness

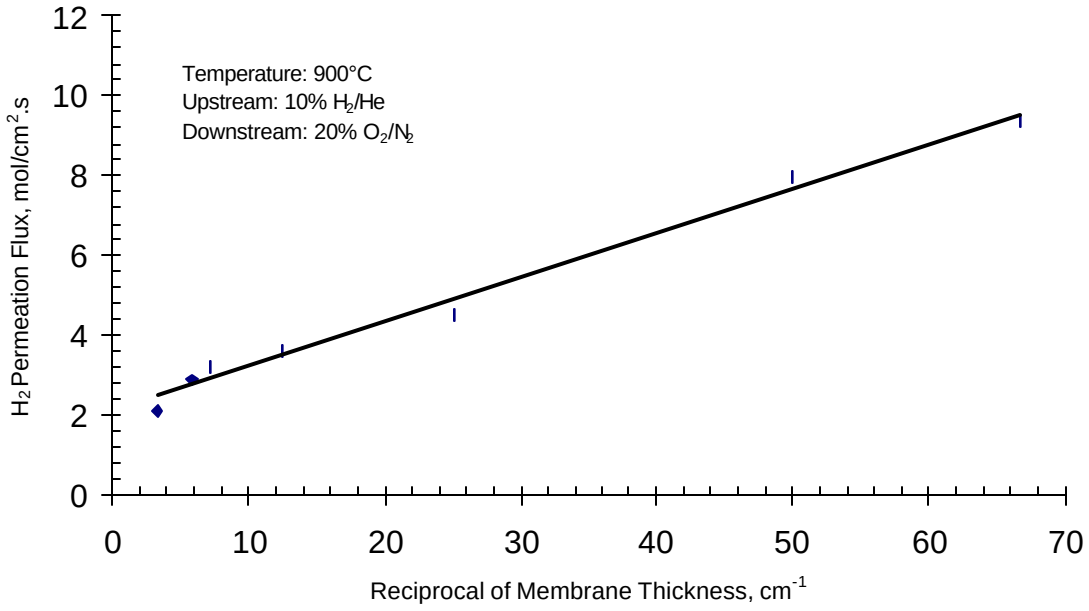

Figure 4 Hydrogen Permeation vs. Reciprocal of Dense Membrane Thickness

CONCLUSIONS

Micrometer thick SCTm films of the perovskite structure can be obtained by the polymer-gel coating method. However, the deposited films are not hermetic and it may require

about 50 coatings in order to obtain gas-tight SCTm films by this method. Dry pressing method proved to be effective for the preparation of SCTm perovskite asymmetrical membrane disks. Particle size was found to be the key factor in determining the porosity of layers in final membrane disks. The interfacial resistance force caused by the difference in shrinkage rate between the top layer and support affects the gas-tightness of top layer when the thickness reaches a certain limit. A compromise should be made between the particle size and difference in shrinkage rate in order to fabricate a good asymmetrical membrane. The thinnest dense layer obtained by the dry-pressing method is 150 μm. This thickness could be reduced when particle size is further optimized with respect to porosity and shrinkage rate between the top layer and support. A hydrogen permeation flux (J_{H2}) of 9.37×10^{-8} mol/cm^2· s was obtained at 900°C for the 150 μm thick SCTm membrane when 10% H_2/He and air were used as feed gas and sweeping gas respectively. Hydrogen permeation flux is inversely proportional to the thickness of the dense layer, confirming that the bulk diffusion in SCTm membrane is the rate-limiting step in the membrane thickness range studied.

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