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Fabrication of $SrCo_{0.5}FeO_x$ Oxygen Separation Membranes on Porous Supports

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Abstract

$SrCo_{0.5}FeO_x$ (SCF) is an attractive material for oxygen separation membranes and for use in catalytic membrane reactors. While tubes of this material have been prepared by extrusion, further improvements in oxygen transport performance may be gained by preparing thinner membranes on porous supports. In this paper, we will discuss the deposition of thick films by spray deposition and centrifugal casting, and thin films by pyrolysis of chemical precursors.

For the chemically derived thin films, porous MgO supports were used as membrane supports. Three types of precursor solutions were employed for dipcoating: a Pechini type solution, a nitrate-based solution, and a citrate-based solution. To prevent the infiltration of the precursor into the support, the support was backfilled with a material that decomposed at higher temperatures than the precursors. Cracking due to the volume changes during drying and pyrolysis of the precursors is discussed.

Thick films were prepared by spray coating and centrifugal casting. Spray deposition of thick film membranes was accomplished by air brushing SCF from a water-based suspension onto the surface of a porous MgO support. Films on the interior surface of the supports were prepared by centrifugal casting using a xylene/butanol-based SCF suspension. Unlike extruded tubes, thick films undergo constrained sintering due to the presence of the support, which greatly reduces the densification rate. For membranes prepared by both approaches, we will discuss the effects of heating schedules on membrane microstructure, densification behavior, and cracking.

Introduction

Oxygen separation membranes are of extreme interest for use in gas separation and petrochemical applications. For example, they may be used to provide oxygen for oxy-fuel firing in the steel and glass industries, resulting in reduced energy use and lower NO_x emissions. Another potential use is in petrochemical processes, where the membrane may be incorporated in the reactor

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design. In an oxidative hydrocarbon reforming process, such as conversion of methane to syngas (CO and H_2), ceramic membranes can separate pure oxygen from air in the reactor instead of using a cryogenic oxygen separation process, thus improving the energy efficiency of the process.

The typical oxygen permeating materials transport oxygen by either oxygen vacancy mobility or oxygen interstitials. Either of these mechanisms allows oxygen to permeate with infinite selectivity. The material selected for this study is $SrCo_{0.5}FeO_x$ (SCF). SCF is a mixed conductor that has an orthorhombic structure, and has an oxygen permeation that is two orders of magnitude higher at 800°C than other materials, such as stabilized zirconia or CeO_2. Further, its high ionic and electronic conductivities eliminate the need for external electrodes. In addition, SCF is very stable, even in reducing atmosphere. High flexural strength and fracture toughness are other advantages of this material.

SCF tubes have been extruded as membranes (Balachandran, 1995). The typical thickness of the extruded tubes is a few millimeters. Because the oxygen permeates via a diffusion mechanism, a thinner layer of SCF has the potential to increase the permeation rate, depending on the kinetics limits of the surface reaction. The design under investigation is illustrated in Figure 1.

The successful preparation of membranes on porous supports requires that the following conditions be met: dense and defect free membranes; chemical compatibility between the supports and the membranes; similar coefficients of thermal expansion; and mechanical integrity of the entire system. This paper addresses the fabrication of SCF membranes on porous support by two approaches: thin (~ 1 μm) film deposition by chemical methods, and thick film deposition (30-100 μm) by traditional ceramic processing techniques.

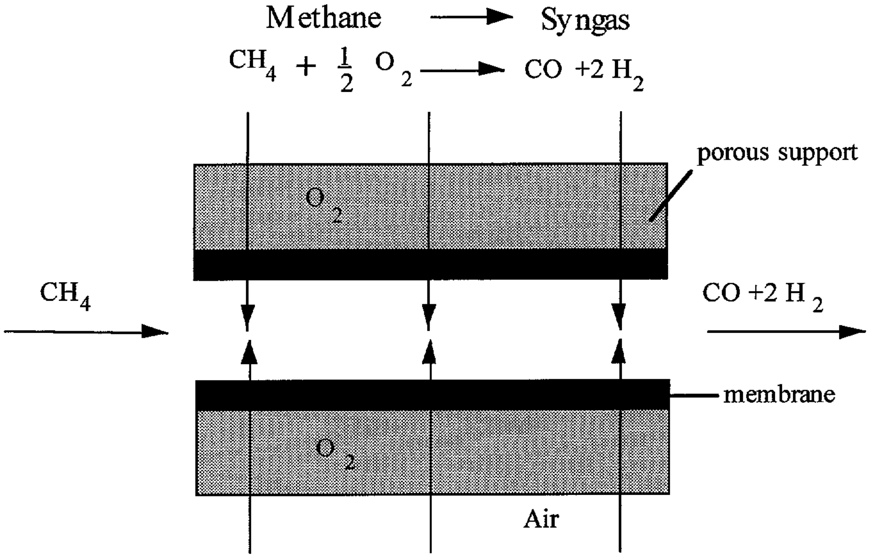

Figure 1. Schematic drawing of membrane reactor for syngas production.

Membrane Supports

For an application such as a membrane reactor, the issue of support materials and characteristics must first be addressed. Currently, porous tubes of alumina, magnesia, and alumina with an inner zirconia layer are commercially available. Alumina, however, has been found to react with Sr-Co-Fe-O compounds at temperatures as low as 800°C. To investigate zirconia and MgO as potential support materials, zirconia or MgO powders were mixed with SCF, pressed into pellets, and heated to 1000°C. After grinding, the pellets were characterized by powder X-ray diffraction (XRD) to determine if any reaction products were formed. For the zirconia/SCF mixture, $SrZrO_3$ was found to be a reaction product. MgO, however, was found to be inert with SCF up to 1000°C. Because the supported membrane is expected to function at high temperatures during normal operation, long term chemical stability was evaluated by heating an SCF film on MgO to 900°C for 400 hr. in an inert atmosphere. Again, no reaction products were detected by XRD.

In addition to chemical compatibility, another issue is the thermal expansion mismatch between the membrane and the support. Because of the potentially large number of thermal cycles that the membrane reactor may undergo, the thermal expansion coefficients of the membrane and the support must be very close to avoid cracking or delamination. To study the mechanical compatibility between SCF and MgO, dilatometry experiments were performed on SCF pellets and porous MgO tubes. Results of these studies indicate that the materials have very similar expansion coefficients ($\sim 14 \times 10^{-6}\ ^{\circ}C^{-1}$ up to 1100°C), and therefore, should possess good mechanical compatibility.

Four types of MgO tubes (Ozark Technical Ceramics, Webb City, MO) were used. Type I tubes were extruded and had a density of 60-65% and a very rough surface finish. The pore and particle size of the tube microstructure were 10-15 µm. Type II tubes were also extruded and had higher density and improved mechanical properties, but still had a rough surface finish. Type III tubes were green tubes, similar to the Type I, except that they were not sintered; sufficient binder, however, was present in the Type III tubes to provide adequate mechanical strength for handling. Type IV tubes were MgO dense supports formed by slip-casting. While they had the best surface finish, the surface roughness was still on the order of a few microns. Finally, although alumina tubes were known to react with SCF at high temperatures, some low temperature experiments were performed with tubes that had a pore size of 50 Å (US Filter, Warrendale, PA). These experiments were carried out to determine the influence of surface finish on the film processing.

Thin Supported Membranes

Oxygen transport is controlled by diffusion and surface reactivity. Because of the shorter diffusion path, thin membranes have the potential for higher oxygen permeation; however, the geometry of the support tubes makes it difficult for physical vapor deposition techniques to deposit a large, uniform film on the tubes. Therefore, one of the most promising techniques is pyrolysis of chemical precursors that are deposited by dipcoating from solution. The technical challenges we must overcome for successful chemical solution deposition include surface coverage, precursor infiltration into the supports, and cracking of the film due to high volume shrinkage.

Three types of chemical precursors were investigated in this study. They were: Pechini-type; citrates; and nitrates. Pechini-type precursors have been extensively used to produce powders of multicomponent ceramics (Falter, 1989). Citrate- and nitrate-based precursors have also been used to produce multicomponent ceramic thin films (Baythoun, 1982; Zhang, 1990; and Ng, 1994). In Pechini-type solutions, a polymer of citric acid and ethylene glycol bind the metal cations together. One advantage of the Pechini method is that the viscosity of the solution can be tailored to control the thickness of the deposited films. This processing variable can be used to reduce the infiltration of the precursors into the porous support. The Pechini approach also allows for precise control of stoichiometry and mixing at the molecular level.

The main advantage of the citrate route is that the precursors have smaller molecular structures than Pechini-type precursors, which results in have smaller total volume change during pyrolysis. The advantages of the nitrate route include simplicity in preparation, and even smaller molecular structures than the citrates, further reducing the total shrinkage the film undergoes.

The Pechini precursor was synthesized by first dissolving stoichiometric amounts of strontium, cobalt, and iron nitrate in water. Separately, a mixture of 4:1 ethylene glycol/citric acid was preheated to form a polymeric mixture. Three moles of citric acid were used per mole of metal. The nitrate solution was then added to the ethylene glycol/citric acid mixture, yielding a 0.1 M SCF solution. The solutions prepared with this approach have very long shelf life. However, if the nitrates, citric acid, ethylene glycol, and water were mixed and heated together, instead of having the ethylene glycol/citric acid prepared separately, precipitation was observed in the solutions within a few weeks.

To produce the citrate-based solution, stoichiometric amounts of metal nitrate were dissolved in water. Three moles of citric acid were added for each mole of metal nitrate. The solution was further diluted with methanol to approximately 0.2 M. To produce the nitrate-based solution, stoichiometric amounts of metal nitrate were added to water and mixed. Likewise, methanol was added for dilution to approximately 0.2 M.

In a separate set of experiments, to confirm that single phase SCF could be synthesized, all three precursor systems were dried and pyrolyzed in oxygen, and the resultant products were examined by XRD. All three precursors were able to produce phase-pure SCF (Figure 2). No secondary oxide or carbonate phases were observed.

To prepare thin supported membranes, the infiltration of the precursor solution into the porous supports must be minimized, which may be accomplished using a backfilling approach. In addition, for large grain size supports, the roughness of the support must be decreased to provide a suitable surface for deposition. This may be achieved by a planarization technique.

The two backfilling strategies evaluated were based on the use of: (i) a polymer of citric acid/ethylene glycol; and (ii) a solution of polymethylmethacrylate (PMMA) in acetone. Backfilling was accomplished by either submerging the support in the polymeric solutions for a short period of time, or by employing the standard dip-coating process used for membrane deposition. The polymer of citric acid/ethylene glycol was synthesized by the same method as used for the Pechini solution. The PMMA solution fill the porous supports, but none of the SCF precursor solutions effectively wets the PMMA modified support surface. The polymer of citric acid/ethylene glycol on the other hand allowed for wetting of the three SCF solutions, and effectively prevented infiltration of solutions into the pores. However, problems were still encountered with the porous support. Because the polymer was completely decomposed at high temperatures, the support roughness was not reduced, resulting in a low quality membrane.

Therefore, a backfilling/planarization approach using magnesium nitrate was developed. A molten nitrate bath, prepared by dissolving the nitrate in the water of hydration, was maintained at approximately 90-100°C. The as-received MgO support tubes were placed into the nitrate bath for 10 min. The tubes were then used for membrane dipcoating, either as-filled, or heated to 300, 350, or 900°C. Although the as-filled tubes were not porous and had a smooth surface finish, the infiltrated magnesium nitrate was susceptible to dissolution by the aqueous-based solution. The tubes treated at 300 or 350°C had the best backfilling characteristics. After 300-350°C pyrolysis, magnesium nitrate had undergone an irreversible change, and became insoluble in the solvents used. However, it still retained most of its volume, thus preventing the infiltration of the precursor into the support. Despite the improvement in the surface morphology, judging from SEM photomicroscopy, the surface finish still had approximate surface roughness of several hundred angstroms. After the 900°C pre-treatment, however, magnesium nitrate was completely decomposed, and did not prevent precursor infiltration.

The tubes were dip-coated onto the back-filled supports in a nitrogen dry box. The outer surface of the support tubes was wrapped with Teflon tape to confine the coating to the interior surface. The coated tubes prepared from the three precursors were then pyrolyzed in oxygen. Despite efforts to produce thinner films, due to the nature of the support surface, the pyrolyzed films had thicknesses approximately 2 to 6 μm on backfilled Type I and Type II tubes. Unfortunately, cracks, with a morphology consistent with drying cracks (Chen, 1995), were observed . Although slower heating rates were studied, even rates as low as 0.1 °C/min. did not totally eliminate all the cracks.

To investigate the effect of surface roughness on membrane quality, we also fabricated membranes on smoother (roughness ~ 2-3 μm), dense Type III supports. For films pyrolyzed under the same conditions, films prepared on these supports displayed less extensive cracking than those prepared on backfilled/planarized supports. The films deposited on these supports were also thinner, with an average thickness of ~1 μm. Citrate-based solutions produced films that consisted of loosely packed particles, while Pechini-type and nitrate-based precursors produced films that were dense, but still cracked. The extent of cracking in the films derived from nitrate-based precursors was less than the films derived from the Pechini precursors, consistent with the lower weight loss in this system.

Unfortunately, even these dense MgO supports have substantial surface roughness. To determine if crack-free, chemically derived SCF membranes could be deposited onto a suitable surface, alumina tubes with inner layer of 50Å pores were used for dipcoating. Due to the small pore size, the extent of precursor infiltration during the dipcoating process was minimal, even without backfilling. In this evaluation, the pyrolysis temperatures were limited to 500°C to avoid a reaction between the membrane and support. The products at this processing stage were a mixture of cobalt oxide, iron oxide, and strontium carbonate. Electron microscopy was used to compare the microstructure of this film to an analogous film deposited on Type I MgO tubes. SEM investigations revealed that membranes deposited on porous alumina supports were crack-free, while membranes on MgO were highly cracked. This shows that crack-free, solution deposited thin membranes can be fabricated, provided that a suitable smooth (surface finish ~50 Å) support is used. Unfortunately, for the fabrication of SCF membranes, MgO tubes with such a high quality finish are not commercially available.

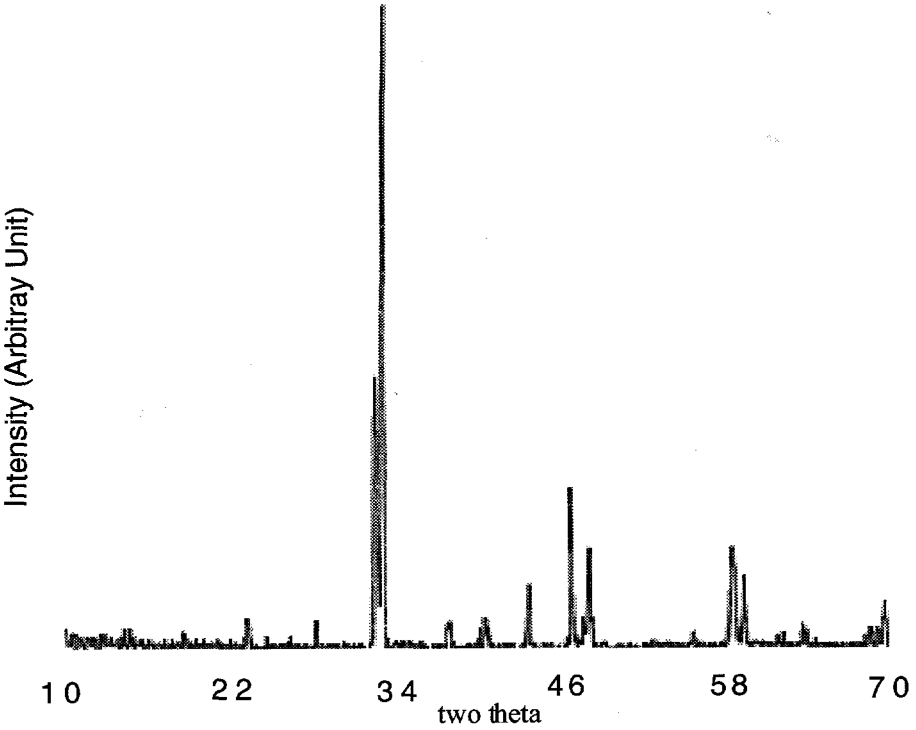

Figure 2. XRD pattern of SCF derived from Pechini solution.

Thick Supported Membranes

Because of the difficulties in obtaining a suitable support for chemically derived thin films, thick films fabricated by traditional ceramic processing techniques may provide an attractive alternative. In traditional ceramic processing, membranes of SCF derived from powder precursors are first deposited, then subsequently densified by sintering at high temperatures.

Two deposition procedures were used to prepare membranes on the interior and exterior surfaces of the supports. The outer surface of the MgO tubes was coated using a spray deposition technique. An aqueous-based slurry was made by mixing SCF powder (Seattle Specialty Ceramics, Seattle, WA), citric acid, polyvinylalcohol, and polyethylene glycol. The powder was submicron in size but was agglomerated. To improve particle dispersion, the slurry was ultrasonicated prior to spraying. The slurry was sprayed on using an air brush. The support tube was spun at 200-300 rpm during deposition to achieve a uniform coating. After drying, the samples underwent binder burnout and sintering.

Membranes were deposited on the inside of the support tube by centrifugal casting. Two advantages of centrifugal casting over spraying are higher packing density, due the acceleration force, and coating uniformity. The slurry for centrifugal casting was prepared by adding Menhaden fish oil and polyvinylbutyral to a powder suspension in a xylene/1-butanol solvent. The support was first attached to a silicon wafer using crystal-bond and then centrifugal casting was accomplished by first filling the support tube with slurry, capping the open end, and spinning the tube along its own axis. Following spinning, the excess slurry was pipetted out of the tube. After drying, the layer was subjected to binder removal and sintering.

Binder removal was carried out in an oxygen atmosphere to facilitate the removal of carbon. The typical sintering schedule was 1200°C for 24 hr. Oxygen, nitrogen, and 2% oxygen (balance nitrogen) atmospheres were employed for sintering. Membranes sintered in a nitrogen atmosphere displayed higher densities, and the resultant microstructures were dense with a few isolated pores. Membranes tended to break up into islands of dense regions separately by macro-cracks when heated directly to 1200°C. However, a short hold at intermediate temperatures, such as 2 hr. at 850°C, eliminated the macrocracking. This result is similar to the observations of constrained sintering in other ceramic materials (Garino, 1987).

One problem that has plagued the sintering of the supported membranes is the constraint due to the support tube. Because the membrane is bonded to the support surface, shrinkage is restricted to the direction perpendicular to the surface. As a result, densification was difficult to achieve. The best result we have obtained to date is shown in Figure 3. Efforts to "fill in" the pores of the original layer by depositing subsequent layers were ineffective in the preparation of leak-tight membrane.

To compare the densification of the membranes under constrained versus unconstrained sintering, a free-standing film was formed and sintered as a control sample. The free-standing film was prepared by centrifugal casting onto the inside surface of a 0.05 μm pore size zirconia coated alumina tube. After burnout, the film was detached from the inside surface and was sintered for 24 h at 1200°C in a nitrogen atmosphere. Observations of the microstructure of the free-standing film (Fig. 4) show that under unconstrained conditions, the SCF materials can be sintered to essentially theoretical density.

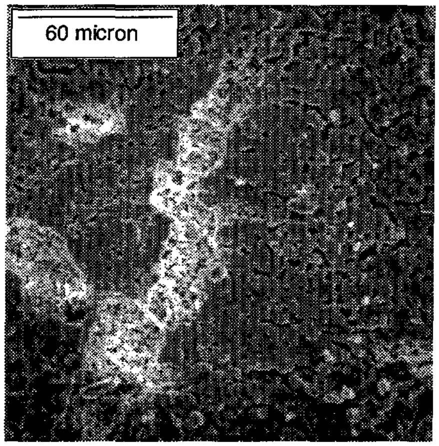

Figure 3. SEM micrograph of a supported SCF that has undergone constrained sintering.

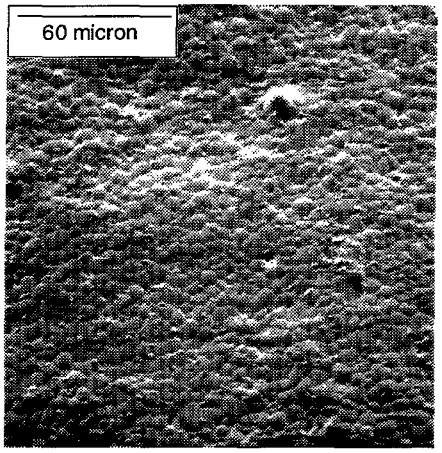

Figure 4. SEM micrograph of a free standing SCF film that has undergone unconstrained sintering

One approach to overcome the problem of support constraint is to select a support that will undergo shrinkage at the same temperature/rate as the membrane. Type IV (green) MgO tubes were used in this approach, because these tubes had not been sintered and should partially sinter at the high temperatures used for membrane densification. In the present study, however, the resultant SCF films did not show an improvement in densification, presumably due to the limited sintering of MgO at 1200°C.

Because of the ineffectiveness of standard sintering approaches in preparing dense SCF membranes, a melting and recrystallization approach was evaluated. The melting temperature of SCF was determined to be approximately 1250°C in air, and slightly higher in nitrogen. For melting and recrystallization, it was found that still higher processing temperatures were preferred, in order to decrease the viscosity of the molten oxide just enough to facilitate densification without having the molten oxide permeate the pores. XRD patterns of the recrystallized films show that the SCF remains phase pure. Figure 5 shows the microstructure of a film that was heated to 1500°C for 0.5 h in air followed by cooling to room temperature. The microstructure shows that a high density material has been obtained; however, extensive cracking was also observed. The cracks were transgranular, indicating that they were formed after crystallization. It therefore seems likely that the cracking is due to either the thermal shock during cooling, or the volume change associated with crystallization. The latter explanation is supported by the observation that membranes which contain some porosity were typically uncracked, even when cooled at a much faster rate.

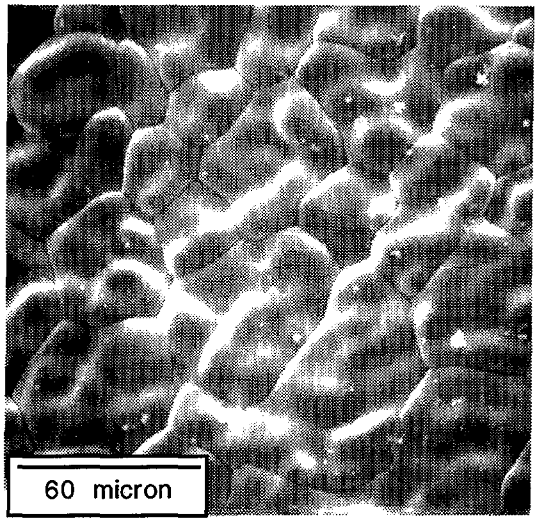

Figure 5. SEM micrograph of a supported SCF membrane after melting and recrystallization.

Conclusions

We have attempted to produce thin film SCF membranes on porous supports by chemical solution deposition routes. All three techniques (Pechini-type, nitrate-based, and citrate-based) are capable of generating single phase SCF upon pyrolysis. In the present application, nitrate-based precursors appear to have the best potential for producing dense membranes. However, the lack of a suitable commercially available support hinders progress in this area. We are therefore presently developing a planarization approach to improve the surface roughness of the MgO supports. This should improve our ability to prepare SCF membranes.

Thick films were produced by centrifugal casting or by spray deposition. Centrifugal casting results in higher density green film, which leads to a higher final densities. Nevertheless, due to the constraint of the support, the films could not be completely densified as in the case of the free-standing film.

The most promising technique to date for fabricating SCF membranes on porous supports is by melting/recrystallization of the thick film coating. High density films are produced by this method, however, cracking of the film after melting and recrystallization is still an issue which must be overcome.

Future Work

Although SCF has some of the most desirable oxygen transport, the lack of high quality MgO support tubes makes the fabrication of membrane very difficult. Therefore, the fabrication of membrane from other materials that are chemically compatible with the commercially available high quality alumina tubes may be more feasible. Recent experimental results suggest that calcium-doped lanthanum chromite may have higher oxygen permeation than previously thought (Kawada, 1995). Therefore, we have begun to investigate the feasibility of preparing lanthanum chromite membranes.

Precursor solutions of $La_{0.7}Ca_{0.3}CrO_3$ were synthesized by mixing stoichiometric amounts of lanthanum, calcium, and chromium nitrates in methanol to make a solution with a chromium concentration of 0.5 M to 1.0 M. To aid the wetting of the solution on the support, 1 ml of Triton X-100 was added to 50 ml of the 0.5 M precursor solution. Porous alumina support tubes were again used, and the films were deposited by dipcoating. Again, an aliquot of the precursor solution was dried and pyrolyzed to 900°C. The product was determined to be single phase perovskite by XRD, and the surface morphology was observed to be crack-free. Even for these initial investigations, it was possible to prepare membranes with low leak rates (< 7 cc/min. at a pressure of 10 psi). This results emphasize the importance of support quality on the ability to prepare thin film supported membrane.

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