Supported Dense Ceramic Membranes for Oxygen Separation

Annual Report

Period Starting: June 25, 1999
Period Ending: June 24, 2000

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June 2000

DOE Award No.: DE-AC26-98FT40120

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DISCLAIMER

ABSTRACT

Mixed-conducting membranes have the ability to conduct oxygen with perfect selectivity at elevated temperatures, which makes them an extremely attractive alternative for oxygen separation and membrane reactor applications. The ability to reliably fabricate these membranes in thin or thick films would enable solid-state diffusional limitations to be minimized, thus providing higher oxygen flux. Based on that motivation, the overall objective for this project is to develop and demonstrate a strategy for the fabrication of supported thick film ceramic mixed conducting membranes, and improve the understanding of the fundamental issues associated with reliable fabrication of these membranes. The project has focused on the mixed-conducting ceramic composition $SrCo_{0.5}FeO_x$ because of its superior permeability and stability in reducing atmospheres. The fabrication strategy employed involves the deposition of $SrCo_{0.5}FeO_x$ thick films onto porous supports of the same composition. In the second year of this project, we completed characterization of the sintering and phase behavior of the porous $SrCo_{0.5}FeO_x$ supports, leading to a standard support fabrication methodology. Using a doctor blade method, pastes made from aerosol-derived $SrCo_{0.5}FeO_x$ powder dispersed with polyethylene glycol were applied to the supports, and the sintering behavior of the thick film membranes was examined in air and nitrogen atmospheres. It has been demonstrated that the desired crystalline phase content can be produced in the membranes, and that the material in the membrane layer can be highly densified without densifying the underlying support. However, considerable cracking and opening of the film occurred when films densified to a high extent. The addition of MgO into the $SrCo_{0.5}FeO_x$ supports was shown to inhibit support sintering so that temperatures up to 1300 °C, where significant liquid formation occurs, could be used for film sintering. This successfully reduced cracking, however the films retained open porosity. The investigation of this concept will be continued in the final year of the project. Investigation of a metal organic chemical vapor deposition (MOCVD) method for defect mending in dense membranes was also initiated. An appropriate metal organic precursor (iron tetramethylheptanedionate) was identified whose deposition can be controlled by access to oxygen at temperatures in the 280-300 °C range. Initial experiments have deposited iron oxide, but only on the membrane surface; thus refinement of this method will continue.

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EXECUTIVE SUMMARY

Ceramic mixed-conducting membranes separate oxygen with perfect selectivity via ionic oxygen transport by vacancy or interstitial diffusion through the crystalline material.[1-11] The potential impact of such membranes for high-temperature applications such as partial oxidation reactors and oxidative reformers is well recognized.[1-4] The performance of several compositions of this type of membrane has been demonstrated using thick-walled ceramic membranes (wall thickness of 0.5 - 1.0 mm).[4-10] There is a drive to develop reliable methods to fabricate thin or thick film membranes so that solid-state diffusional resistance can be minimized, and oxygen flux thus maximized. Reliable fabrication of dense ceramic membrane films on porous supports has been a challenging task that has still not been solved, though there have been some instances of reported success. These issues constitute the motivation for this project.

The overall objective of this project is to explore important fundamental and practical issues confronting the successful development of thick-film dense ceramic membrane technology for oxygen separation. More specifically, the project goals are to: utilize aerosol pyrolysis[12,13] to produce ultrafine powders for fabrication of thick film Sr-Co-Fe-O (SCFO) membranes, explore strategies for fabrication of defect-free thick-film membranes on porous supports using those powders, develop an improved understanding of the fundamental issues impacting successful thick film membrane fabrication (such as particle deposition and infiltration into porous supports, film and support sintering behavior, crystalline phase evolution, and membrane stability), and explore and demonstrate the use of a novel metal organic chemical vapor deposition technique to mend membrane defects.

The fabrication strategy in this project is to deposit thin or thick films of ultrafine powders produced by aerosol pyrolysis[12,13] onto (or into) partially sintered porous supports, followed by co-sintering of the film and support, with the objective of densifying the film while retaining open porosity in the support. The supports are being made using commercially-produced $SrCo_{0.5}FeO_x$ powder (Prax-Air), and the same overall composition is being used for the dense membrane layer. The $SrCo_{0.5}FeO_x$ composition has been reported to have a high oxygen permeability, while also possessing good phase stability in reducing environments that are typical of important applications involving synthesis gas (CO/H_2).[4,9-11]

In the first (previous) project year, substantial progress was made on fabrication of the porous supports, and methods of thick film deposition were screened, leading to adoption of a doctor blading process for subsequent membrane deposition and sintering studies. The sintering behavior of the supports was studied in different atmospheres, ultimately leading to a standard support fabrication procedure that was detailed in a previous annual report. In addition, much was learned about the microstructure and crystalline phase development that complemented the study of the membrane processing in the past year. For fabrication of the membrane layer, submicron $SrCo_{0.5}FeO_x$ powder was fabricated using the aerosol pyrolysis technique, as detailed in the previous annual report. This synthesis led to $SrCo_{0.5}FeO_x$ powder with a mean particle size of approximately 0.3 μm, and consisting of essentially single-phase perovskite SCFO as produced. A doctor blade technique using a paste made from the aerosol powder and 400 MW polyethylene glycol (PEG) was adopted as the standard method for membrane fabrication. The majority of work in the second year consisted of sintering studies on the supported membranes.

This doctor blade application method yielded individual layers of 20-30 μm thickness prior to sintering, which provided sintered membranes of 5-10 μm thickness. The particle layer before sintering is continuous, uncracked and highly porous. After heating to 800 °C, relatively little densification of the film is observed, consistent with the support sintering results; however, rapid sintering occurs above 900 °C, accompanied by cracking or opening up of the film. In air, plate-shaped grains develop, which retain significant open porosity (apparent by SEM) to temperatures above 1150 °C, whereas nitrogen sintering retains approximately equiaxed particle structure leading to elimination of porosity in the film at approximately 1050 °C. The observed microstructures of the films were consistent with those seen in sintering studies of the porous supports. The films, which start as SCFO perovskite phase prior to sintering (i.e. as-produced SCFO powder), evolve to a composite mixture of layered perovskite and CoO after sintering in N_2 at 1050 °C. This phase mixture is consistent with literature reports for successful thick-wall membranes of this composition.[10,11]

Thus, we have been successful at demonstrating the fabrication of dense supported membrane materials of the desired phase and thickness without densifying the underlying support, and have advanced the understanding how to achieve these important objectives. Unfortunately, the conditions that lead to a high degree of film densification also cause development of large cracks and open areas in the film as shrinkage occurs in the film. This critical issue can be addressed by reducing stress development in the membrane layer that inevitably occurs as the layer tries to shrink. One possible strategy to accomplish this was investigated. By using additives to the porous support, it was shown that sintering temperatures very near the point of partial melting of the film could be employed without densification of the support. The presence of a significant amount of liquid phase should enable stress in the film to be dissipated without cracking. Though the strategy of inhibiting support densification was successfully demonstrated, the films retained a porous open structure, and research will be continued on this strategy in the last year of the project.

The apparatus to investigate the MOCVD defect mending strategy was assembled and investigation into the strategy initiated. An appropriate metal organic precursor, $Fe(tmhd)_3$, was identified, and technique to attach SCFO membranes to alumina tubes using a silver paint was found. Initial experiments were successful in depositing iron oxide on one side of the membrane; however, better control of the pressures will be needed to control deposition so that only open pores and defects are blocked. Work on this technique will continue in the third year of the project.

To summarize the overall progress on the project, we are progressing steadily toward achieving the objectives of the project. The major issues to focus on in the final year are film cracking and the MOCVD mending. The cracking problem is critical to overall success of the project. We will continue to explore support modification and liquid-assisted sintering of the film. We will also explore more sophisticated ceramic paste formulations (combinations of dispersant, binder and plasticizer), exploiting methods that have been used for tape casting. We also hope to demonstrate that the understanding we have gained on support and film processing can be extended to other ceramic membrane compositions.

EXPERIMENTAL

The details of support fabrication were provided in the previous annual report. Briefly, commercially-obtained $SrCo_{0.5}FeO_x$ powder (Prax Air) was pressed and sintered to provide 0.5 inch diameter disks that were strong but retained approximately 45% porosity. The standard support fabrication procedure that was adopted involved uniaxial pressing of powder in a 0.5 in. die at 64 MPa, followed by sintering in air at 1050 °C (2 hr soak and 5 /min ramp rate). Sintering in N_2 was also investigated, as explained in the previous annual report; however, air sintering was adopted as the standard procedure for most of the results being reported here. The ultrafine powder used to fabricate the ceramic membrane layer was synthesized using aerosol pyrolysis. A TSI 3076 aerosol generator was used with air or N_2 carrier/atomizing gas (35 psig, 1.5 slpm) to create an aerosol from an aqueous metal nitrate solution containing the metals in the desired ratio. The aerosol was carried through a three-zone Lindbergh furnace with 3 ft. heated length. The tube diameter (15 cm) provided a residence time of approximately 2.4 min. at 700 °C, which was the temperature adopted for the majority of powder syntheses. Though both N_2 and air were investigated as carriers in powder synthesis, relatively little difference was found and air became the standard procedure for most of the membrane fabrication reported in this report.

Membrane layers were initially deposited by several methods, as outlined in a previous report. For the membrane fabrication reported here (i.e. that past years work), a doctor blade procedure was used with a paste made from the aerosol-derived powders and 400 MW polyethylene glycol (PEG). The paste was made by dispersal of the powder into polyethylene glycol (PEG; MW=400) to provide a paste which was approximately 20 wt% solid. A fixed amount of the paste was spread uniformly across the surface of the support using a razor blade edge.

A series of experiments was conducted in which a modified composite MgO/ $SrCo_{0.5}FeO_x$ support was used. For these supports, MgO powder (Ube, 0.2 μm mean particle size with some particles up to 1 μm) was mixed by mortar and pestle with varying amounts of $SrCo_{0.5}FeO_x$ powder prior to pressing and sintering. The support sintering procedure was the same as for the pure $SrCo_{0.5}FeO_x$ porous supports (2 hour soak at 1050 °C in air, with 5 °C/min ramp rates).

An apparatus was assembled for using metal organic chemical vapor deposition (MOCVD) to mend defective membranes. The experimental arrangement, depicted in Fig. 1, allows for a disc-shaped membrane to be exposed to a vapor-phase MOCVD precursor on one side, and to a CVD co-reactant on the opposite side. By proper control of the pressure on both sides, an appropriate combination of pressure driven flow and diffusion should be possible so that the deposition location can be controlled. The 0.5 inch membrane discs were adhered to 0.5 inch diameter alumina tubes using a silver ink. Ceramic cements were also tried, but they typically led to fracture of the ceramic membrane when thermally curing the cement. The two-part silver ink (METECH 3145-DST) was processed by applying and drying a layer of each part, followed by firing at might be 800 °C for 20 min (5 °C/min ramp). The compound $Fe(tmhd)_3$ (Alfa Aesar) (tmhd = tetramethylheptanedionate) was used as the MOCVD precursor.

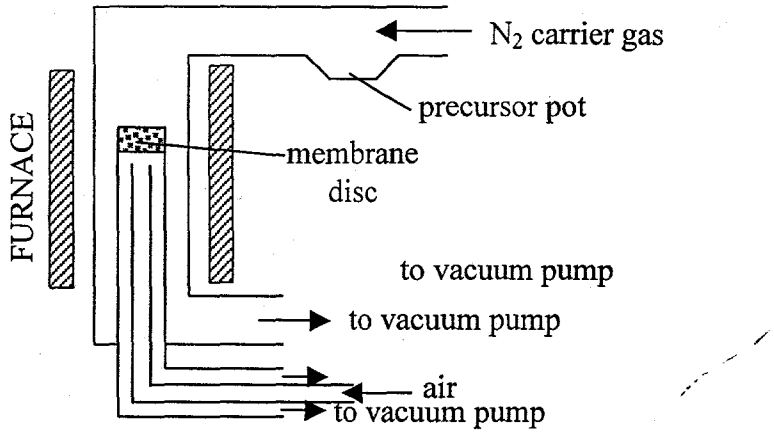

Fig. 1. Experimental arrangement for MOCVD mending of defective membranes.

RESULTS AND DISCUSSION

Building on the previous year's work, densification studies on $SrCo_{0.5}FeO_x$ supports were completed in air and nitrogen. The results show that comparable levels of densification are achieved at approximately 50 °C lower in nitrogen than in air (Fig. 2). It was found that reasonably strong porous supports could be fabricated at approximately 1050 °C while retaining close to 45% porosity in the supports. As noted in a previous report, the microstructure in very different for air and N_2 sintering. With air sintering, large plate-shaped grains are formed, whereas grains remain more equiaxed with N_2 sintering. The crystalline phase content also depended on the sintering atmosphere, as reported in the first year report, with air sintering leading to the desired layered perovskite structure and N_2 sintering leading to a mixture of several phases (brownmillerite, CoO, and layered perovskite). Based on these results, the standard procedure for supports was adopted as sintering at 1050 °C in air for 2hr with ramp rate of 5 °C/min.

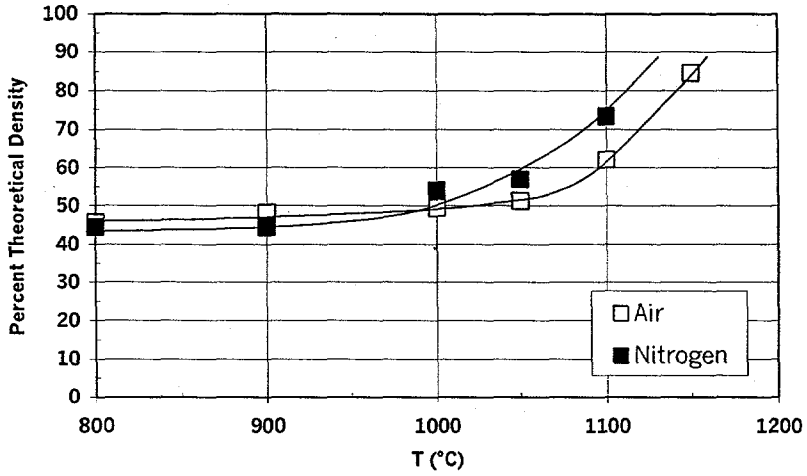

Fig. 2. Densification of $SrCo_{0.5}FeO_x$ supports as a function of sintering temperature and atmosphere.

A major part of the effort in the past year has been on the sintering behavior of thick films deposited from the aerosol-derived powder. The aerosol-derived powder produced at 700 °C in either air or nitroge, was essentially single phase perovskite $Sr(Co,Fe)O_{3-x}$ as produced (Fig,.3). It was somewhat surprising that the layered perovskite or brownmillerite phases that were seen with sintering of the SCFO supports did not appear in the as-produced powders, especially since the overall composition of the powders is not consistent with single phase $S(Co,Fe)O_{3-x}$. This indicates that the simple perovskite structure is kinetically preferred, and that the reactor residence time is sufficient to develop crystalline perovskite but not sufficient to allow the layered structures to evolve.

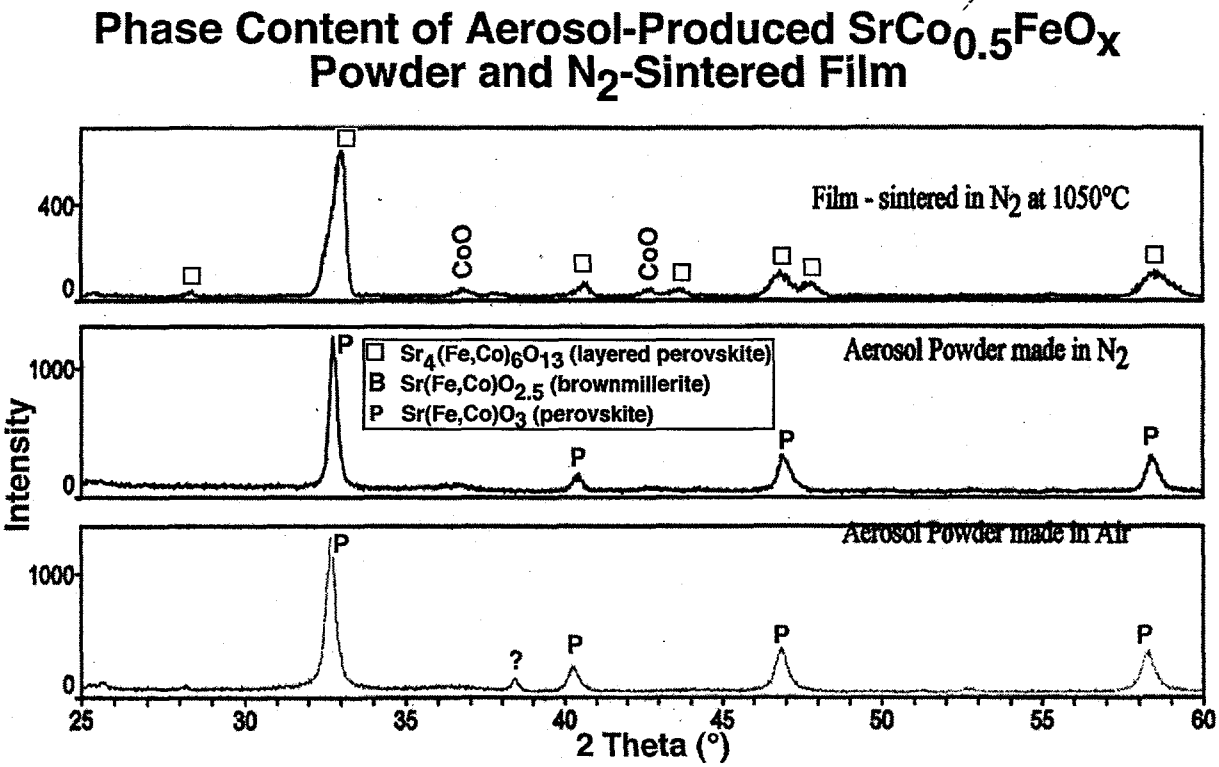

Fig. 3. X-Ray diffraction result for $SrCo_{0.5}FeO_x$ powders made by aerosol pyrolysis using air an N_2 as carrier gas, and for $SrCo_{0.5}FeO_x$ film after sintering in N_2. Film was produced using powder produced in air with support sintered in air.

For film deposition, the work in the past year has centered mainly on the use of a PEG paste, as described in the Experimental section. The application of a single layer of the paste by the manual doctor blade method led to a layer that was typically 20-30 μm thick before sintering and uncracked (Fig. 4). In the "before calcination" image in Fig. 4, the powder particles have a very thick coating of PEG around them. In the images taken after calcination at 800 °C, the PEG has been completely removed, and there has been some particle–particle necking; however, relatively little shrinkage appears to have yet occurred. This is consistent with the shrinkage (densification) profiles determined for the SCFO supports (Fig. 2). Thus the images at 800 °C are a good indication of the particle films after PEG removal but before significant densification.

There is little or no cracking evident in the films at this stage, and the cross-sectional micrograph shows that the particles are still loosely packed with very high porosity in the film.

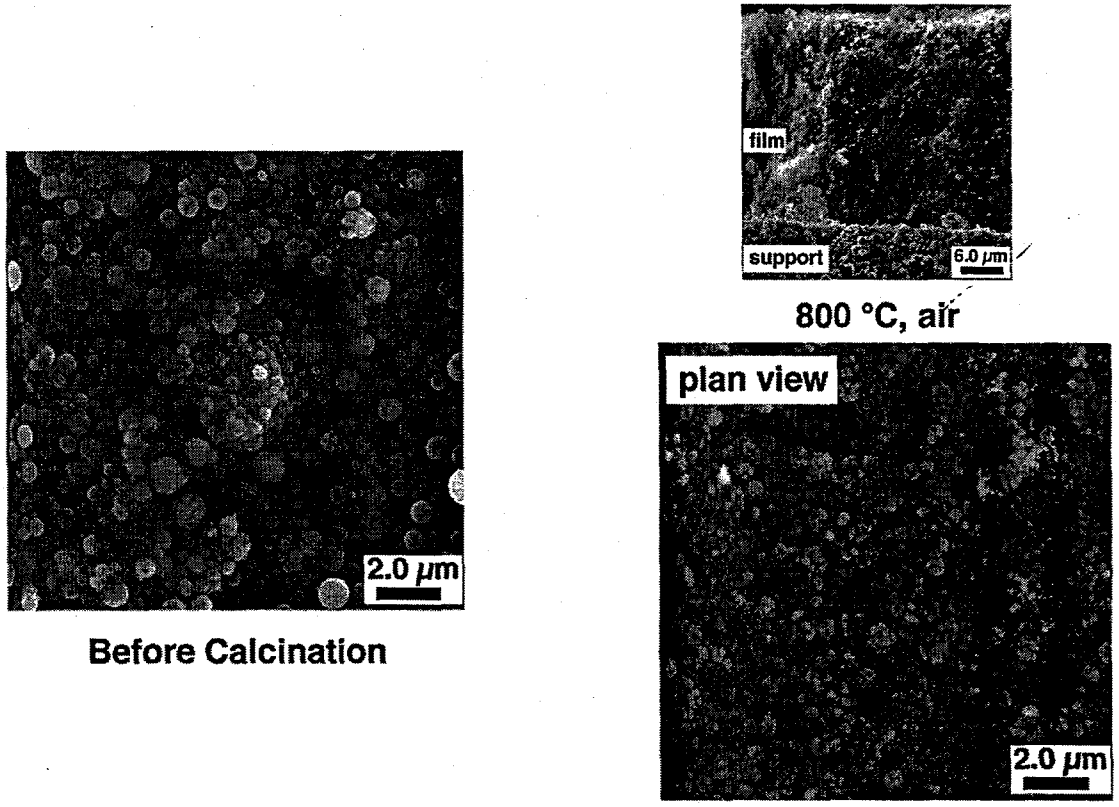

Fig. 4. Scanning electron micrographs of $SrCo_{0.5}FeO_x$ films after application of PEG paste ("before calcination"), and after calcining to 800 °C in air.

Quantitative evaluation of the film densification/shrinkage was not done as a function of temperature, however SEM images reveal that significant sintering occurs for temperatures above 900 in air or N_2 (Figs. 5 and 6). Relatively little densification occurred in the supports at this temperature, which shows the enhanced sintering of the ultrafine aerosol powder. It is also interesting that pronounced growth of plate-shaped grains begins to occur at approximately 900 °C for air sintering (Fig. 6). On the support sintering studies, we have determined that these plate-shaped grains are characteristic of the layered perovskite stucture. Thus 900 °C is the approximate temperature where the perovskite structure begins to form the layered structures in the time scales of our sintering experiments.

With the use of higher sintering temperatures, the areas of film continued to densify displaying microstructures that depended on atmosphere in much the same way that was seen with the supports (i.e. plate shaped grains in air and equiaxed grains in N_2). Furthermore, N_2-sintered film material became fully dense (by SEM observation) at a sintering temperature of approximately 1050 °C, whereas the air-sintered films were not dense at that temperature (Figs. 5 and 6). However, in both cases, pronounced cracking had occurred during densification, leading to the large areas of open underlying support that can be seen in the lower magnification

image in Fig. 7. It is noteworthy that the film material can be densified completely without densifying the underlying support, which is one of the major objectives in the project; however, the uncovered support areas make the supported film from being functional as a membrane.

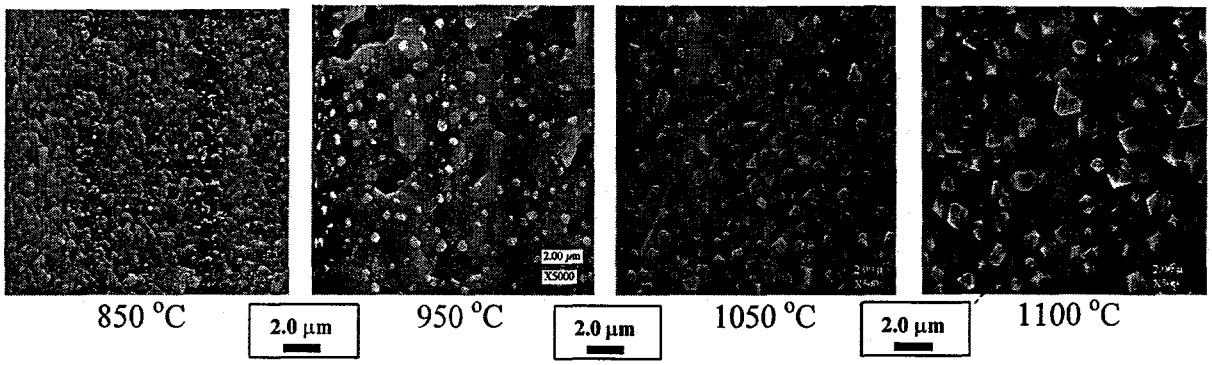

Fig. 5. Scanning electron micrographs of $SrCo_{0.5}FeO_x$ films sintered in N_2 at several temperatures.

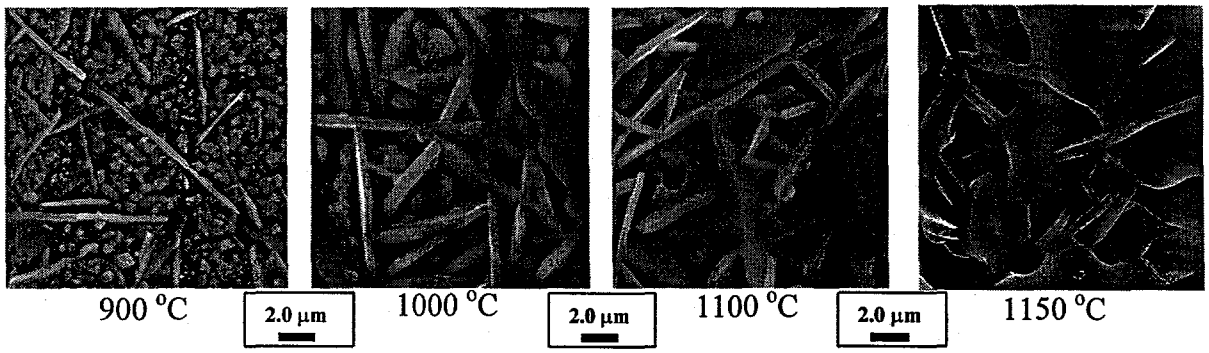

Fig. 6. Scanning electron micrographs of $SrCo_{0.5}FeO_x$ films sintered in air at several temperatures.

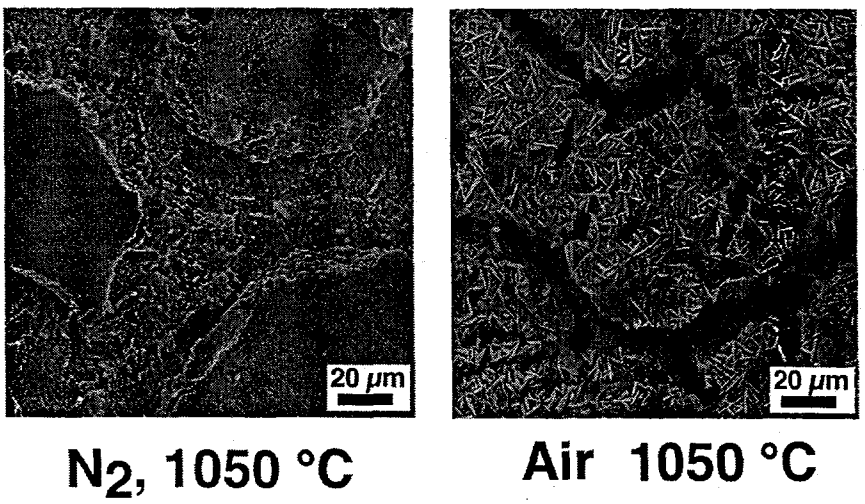

Fig. 7. Relatively low magnification scanning electron micrographs of $SrCo_{0.5}FeO_x$ films sintered in N_2 and air at 1050 °C.

The crystalline phase evolution of the films that occurred with sintering was also investigated to a limited extent. Using grazing angle XRD, the XRD pattern of a film sintered in N_2 at 1050 °C was shown in Fig. 3. This shows that the film is a mixture of layered perovskite and CoO, possible also containing some of the cubic perovskite since its peaks overlap with the layered perovskite. This multiphase mixture is consistent with literature reports for this composition,[10,11] although it is not consistent with our results for supports sintered in N_2, which displayed a composite mixture of phases consisting primarily of the brownmillerite phase, but without the layered perovskite. In this case, the support had been pre-sintered in air and was in the layered perovskite phase before membrane deposition. It is interesting and fortuitous that, after conducting the film sintering in N_2, the phase content remained as layered perovskite rather than converting to brownmillerite.

The results above show that the thick films can be processed to give the layered perovskite phase mixture that is desired for membrane applications. It has also been demonstrated that the aerosol-derived powder can be processed and densified as films without densifying the underlying porous support of the same composition. However, the large-scale cracking and opening of the membrane films during sintering is a critical problem that must be overcome. Our current analysis of the cracking problem is as follows. During thermal processing of the paste-derived films, the first physical occurrence is removal of the volatile dispersant (PEG), which leaves behind substantial remnant porosity in the film. Film densification requires sufficient shrinkage to eliminate this remnant porosity as well as the normal interparticle porosity. The shrinkage accompanying densification is naturally three dimensional; however, if the film is bonded to the substrate, shrinkage in the plane of the film is "constrained", leading to tensile stress development in the film. This stress leads to cracking. Once cracking has generated film islands, these islands are more free to shrink, leading to the highly dense islands seen in the N_2 sintered sample in Fig. 5. There is an inherent dilemma in the inevitable generation of stress during densification films, which must be done to provide useful membranes.

One strategy that we have investigated to overcome this dilemma is to sinter the films at a temperature very near the melting point. If the films are more liquid-like, then they should be able to flow in response to stress, rather than be forced to crack or delaminate from the support. However, sintering near the melting point would also densify the underlying support if some strategy is not employed to inhibit support sintering, a fact which we confirmed by experiment. We attempted to inhibit support sintering by mixing MgO powder with the SCFO support powder prior to support sintering. MgO has a very high melting point (2852 °C), and should sinter minimally at the melting temperature of the SCFO phases, which is around 1200 °C. In addition, MgO has been found to be chemically nonreactive with the SCFO phases.[3] Thus, the effect of adding varying amounts of MgO to the support was investigated. The addition of 40 wt% MgO to the support served to inhibit densification of the support at 1200 °C where film and support would have been fully sintered and indistinguishable in the absence of the MgO (Fig. 8). With MgO added to the support, film sintering was conducted at temperatures as high as 1400 °C. At sintering temperatures of 1200 and 1300 °C the support densification appears inhibited and the film remains clearly distinct from the support (Fig. 8). However, although the film shows rounding of feature indicative of partial melting, it retains what appears to be an open network structure. This may indicate that complete melting does not occur, or that wetting of

the porous support below somehow prevents the formation of a contiguous film. This strategy has clearly achieved part of its intended results; however, we need to do further work to understand why films do not become contiguous under these conditions, and to ascertain whether this strategy can lead to viable dense membranes.

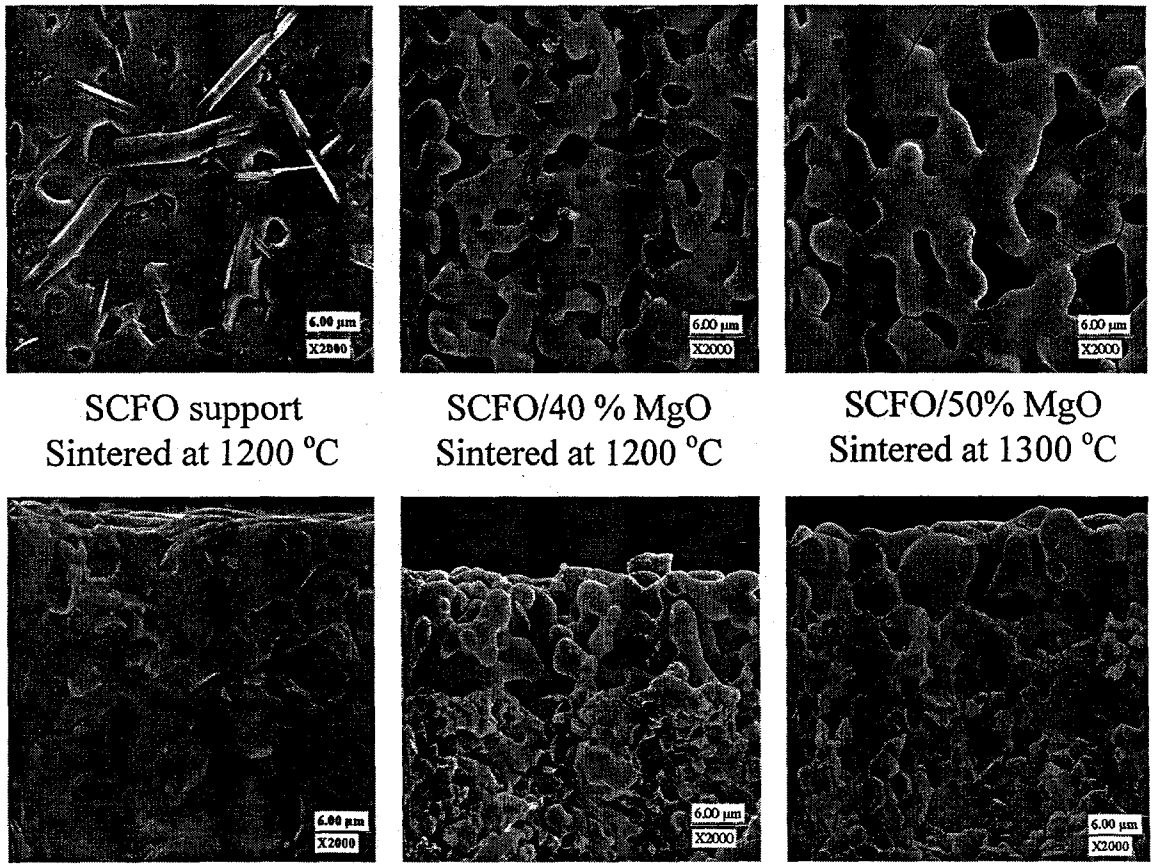

Fig. 8. Sintering of $SrCo_{0.5}FeOx$ films on composite MgO/SCFO supports compared to sintering on a pure SCFO support.

In the past year, research was also initiated on the metal organic chemical vapor deposition (MOCVD) mending strategy that was outlined in the original project proposal. The idea, briefly, was to conduct an MOCVD reaction within defects of a membrane such that the defects would be blocked by a chemically compatible material. The strategy was to use a reaction that required a co-reactant (such as H_2 or O_2) in addition to the metal organic precursor, and to control contact of the reactants using counter-directional convection or diffusion such that deposition only occurs in the pores or defects. The exeperimental apparatus that has been used was depicted in Fig. 1 in the Experimental section. It has been demonstrated that the compound $Fe(tmhd)_3$ (tmhd=tetramethylheptanedionate) has appropriate properties for this strategy. We have found that it can be sublimed readily at 200 °C using a N_2 carrier gas, and will react to produce iron oxide at 280 – 300 °C in the presence of O_2, but is stable to well over 300 °C in the absence of oxygen. Experiments have been conducted at varying the pressure difference across the membrane to get an appropriate balance between transport of precursor/carrier and oxygen

so that deposition occurs in the region of the membrane layer. Thus far, we have obtained iron oxide deposition on the membrane surface and on the reactor walls on the precursor side. Thus, further work is needed to properly identify the pressure conditions that will give deposition within the membrane layer itself.

CONCLUSION

At the end of the second year of this project we now have a good understanding of how to produce suitable porous $SrCo_{0.5}FeO_x$ supports and $SrCo_{0.5}FeO_x$ powders for thick (~10 μm) film membranes. We understand how atmosphere (oxygen content) effects sintering rate as well as phase development. Air processing promotes formation of the desired layered perovskite phase; however the grain morphology of that phase is highly eccentric plates that are difficult to densify. Processing in N_2 allows more rapid densification at lower temperatures, but may lead to formation of the undesired brownmillerite phase. The brownmillerite composite phase mixture may be convertible into the desired layered perovskite mixture after densification, but we have yet to demonstrate this. In addition, we have found that a support that is primarily layered perovskite can help inhibit the brownmillerite phase formation when sintering the film in N_2. We have been able to fabricate supported films the desired membrane composition on a porous substrate of similar composition without densifying the support, which is one of the main challenges in fabrication of these membranes. The main obstacle that we have failed thus far to solve is the densification of the membrane layers without cracking or opening up of the film. The use of additives to inhibit densification of the support successfully enabled use of higher film sintering temperatures. However, the films retained a porous morphology even at temperatures near or above the temperature of partial melting. The major portion of future work in this project will explore further the concept of inhibited support sintering, as well as investigated more sophisticated ceramic paste formulations for the membrane layer. In particular, combinations of dispersant, binder and plasticizer that are typically used for tape casting will be investigated. We also hope to demonstrate that the understanding we have gained on support and film processing can be extended to other ceramic membrane compositions.

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