

# **Supported Dense Ceramic Membranes for Oxygen Separation**

Annual Report

Period Starting: June 25, 2000

Period Ending: June 24, 2001

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March 2003

DOE Award No.: DE-AC26-98FT40120

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## ABSTRACT

This project addresses the need for reliable fabrication methods of supported thin/thick dense ceramic membranes for oxygen separation. Some ceramic materials that possess mixed conductivity (electronic and ionic) at high temperature have the potential to permeate oxygen with perfect selectivity, making them very attractive for oxygen separation and membrane reactor applications. In order to maximize permeation rates at the lowest possible temperatures, it is desirable to minimize diffusional limitations within the ceramic by reducing the thickness of the ceramic membrane, preferably to thicknesses of 10  $\mu\text{m}$  or thinner. It has proven to be very challenging to reliably fabricate dense, defect-free ceramic membrane layers of such thickness. In this project we are investigating the use of ultrafine  $\text{SrCo}_{0.5}\text{FeO}_x$  (SCFO) powders produced by aerosol pyrolysis to fabricate such supported membranes.  $\text{SrCo}_{0.5}\text{FeO}_x$  is a ceramic composition that has been shown to have desirable oxygen permeability, as well as good chemical stability in the reducing environments that are encountered in some important applications. Our approach is to use a doctor blade procedure to deposit pastes prepared from the aerosol-derived SCFO powders onto porous SCFO supports. We have previously shown that membrane layers deposited from the aerosol powders can be sintered to high density without densification of the underlying support. However, these membrane layers contained large-scale cracks and open areas, making them unacceptable for membrane purposes. In the past year, we have refined the paste formulations based on guidance from the ceramic tape casting literature. We have identified a multicomponent organic formulation utilizing castor oil as dispersant in a solvent of mineral spirits and isopropanol. Other additives were polyvinylbutyral as binder and dibutylphthalate as plasticizer. The nonaqueous formulation has superior wetting properties with the powder, and presumably evolves less tensile stress during drying. Membrane layers have been first made from the commercial SCFO powder to accelerate evaluation of the new formulations, since the aerosol power synthesis process is time consuming. We found that, with appropriate levels of the dispersant, we could increase the powder loading in pastes made from the commercial SCFO powder up to 43 wt%. This, combined with the attributes of the other additives, has allowed us to prepare sintered supported membranes with no evidence of cracking. However, the membranes prepared from the relatively coarse commercial powder did not sinter to the high density level (at 1100  $^{\circ}\text{C}$  in  $\text{N}_2$ ) that we had observed with the aerosol-derived powder. This is the current status of the project. The future efforts will be focused toward evaluation of the new paste formulation with aerosol-derived SCFO powder. We anticipate that some adjustments, particularly to the dispersant levels, will be needed for the high specific area aerosol powders.

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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. The potential impact of such membranes for high-temperature applications such as partial oxidation reactors and oxidative reformers is widely recognized.<sup>1-4</sup> 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).<sup>4-9</sup> The Sr-Co-Fe-O family of perovskite-related phases are one of the highly promising materials for dense ceramic oxygen-transporting membranes.<sup>4,9</sup> 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 broad 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<sup>10,11</sup> 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<sup>10,11</sup> 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<sub>0.5</sub>FeO<sub>x</sub> powder (Prax-Air), and the same overall composition is being used for the dense membrane layer. The SrCo<sub>0.5</sub>FeO<sub>x</sub> 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<sub>2</sub>).<sup>4,9,12-14</sup>

In the previous project years, we have reported on the fabrication of the porous support, fabrication of the aerosol-derived SCFO powder, and our first results depositing membranes from that powder using a doctor blading procedure with pastes prepared using various diluents with the aerosol powder. The best and most extensive results reported previously were obtained using polyethylene glycol (MW 400) as the diluent with SCFO powder loadings of 15-20 wt%. The effect of sintering atmosphere and temperature was explored. This procedure typically led to sintered membrane layers that were 5-10 μm in thickness. Those results demonstrated that a high level of densification of the membrane top layer could be obtained without densification of the porous support. Such densification was achieved by sintering under nitrogen at temperatures of 1050 °C or higher. However, the membrane layer densification led to large scale cracks and openings in the membrane. Significant defects and cracks can not be tolerated in a functional dense ceramic membrane.

In the past years effort, the emphasis was on eliminating cracking in the sintered membrane layer, primarily by investigating new paste formulations and sintering cycles. We chose to do this initially using the commercial powder for the membrane layer, rather than the aerosol-derived powder. This was done to speed up evaluation of the new formulations, since the low production rate of our aerosol powder apparatus was significantly limiting the rate at which we could prepare and evaluate new membrane samples. The use of the commercial powder, which is much coarser in particle size than the aerosol powder, sped up our evaluations of new formulations considerably, and also revealed the substantially higher sinterability of the ultrafine aerosol-derived powders.

Nonaqueous pastes or inks are often used in ceramic tape casting formulations because of superior wetting of the particles, and lower surface tension during drying. In addition, traditional ceramic tape casting, a process analogous to our doctor blade procedure, employs other additives to aid in particle dispersal (dispersant), green body strength (binder), and cracking resistance (plasticizer).<sup>15,16</sup> We found, based on reported tape casting formulations,<sup>15</sup> a new multicomponent formulation that allowed us to increase the powder (commercial SCFO) fraction of the paste from <20 wt% to 43 wt% while maintaining acceptable viscosity for blading. This formulation employed castor oil as dispersant in a solvent mixture of mineral spirits and isopropanol. Polyvinylbutyral was added as a binder and dibutyl phthalate was used as plasticizer. A new multi-segment sintering cycle was also employed to provide time for the organic additives to evolve during sintering. Results obtained using this formulation with the commercial powder showed complete elimination of cracking in membrane layers sintered in N<sub>2</sub> at temperatures up to 1100 °C. However, membrane layers prepared using the commercial powder were significantly less dense at these sintering conditions than those prepared previously with aerosol-derived powder. This is attributed primarily to the particle size, and demonstrates the potential superiority of the ultrafine aerosol-derived powders for low-temperature sintering.

The current status of the project is that we are preparing a new supply of aerosol SCFO powder, in order to evaluate the new multicomponent organic paste formulation with aerosol powder. The aerosol powder has substantially higher specific surface area associated with the smaller particle size. Thus, we expect that adjustments in the formulation will need to be made to achieve good dispersion of the powder, and acceptable viscosity for spreading. These tasks, with determination of appropriate sintering conditions for the new formulation, will be the focus of the work for the remainder of the project.

## EXPERIMENTAL

The details of support fabrication were provided in the previous annual reports. Briefly, commercially-obtained SrCo<sub>0.5</sub>FeO<sub>x</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 reports. Over the past year, we have exclusively used a doctor blade procedure with a paste made up of SCFO powder, either from the commercial source or produced by our aerosol pyrolysis process, combined with organic and/or aqueous additives. The investigations over the past year focused on primarily two paste formulations, summarized in Table 1. For the PEG paste, the paste was made by dispersal of the powder into polyethylene glycol (PEG; MW=400) to provide a paste that was approximately 20 wt% solid. For the multicomponent organic formulation, castor was used as a dispersant, and was mixed well with the powder first before adding the solvent and additives. This mixing order allowed us to obtain up to 43 wt% powder paste that still had acceptable viscosity for spreading. For all formulations, a fixed amount of the paste was spread uniformly across the surface of the support using a razor blade edge to give the green film

Table 1. Paste formulations used for doctor blade membrane deposition .

Simple Organic Formulation	Multicomponent Organic Formulation
Powder: 20 wt% (aerosol powder) Solvent/Binder/Dispersant: 80 wt% 400 MW Polyethylene Glycol (PEG)	Powder: 43 wt% (commercial powder) Solvent: 39 wt% 2:1 mineral spirits:isopropanol Dispersant: 3 wt% castor oil Binder: 5 wt% polyvinyl butyral Plasticizer: 10 wt% dibutyl phthalate

Some experiments were continued into the the use of metal organic chemical vapor deposition (MOCVD) to mend defective membranes. The apparatus and procedure used for these experiments was described in the previous annual report.

## RESULTS AND DISCUSSION

We have previously reported on our success in fabricating and sintering SCFO films from aerosol powders on porous supports under different atmospheres. A high degree of densification

of the supported film (without densification of the support) could be obtained by sintering in  $N_2$  at temperature in the 1050 – 1100 °C range. However, the film shrinkage during densification led to the formation of very large open cracks, that might more accurately be described as canyons, in the films (see Fig. 1). The emphasis in the investigations of the past year was on strategies to control the large scale cracking that was in the films.

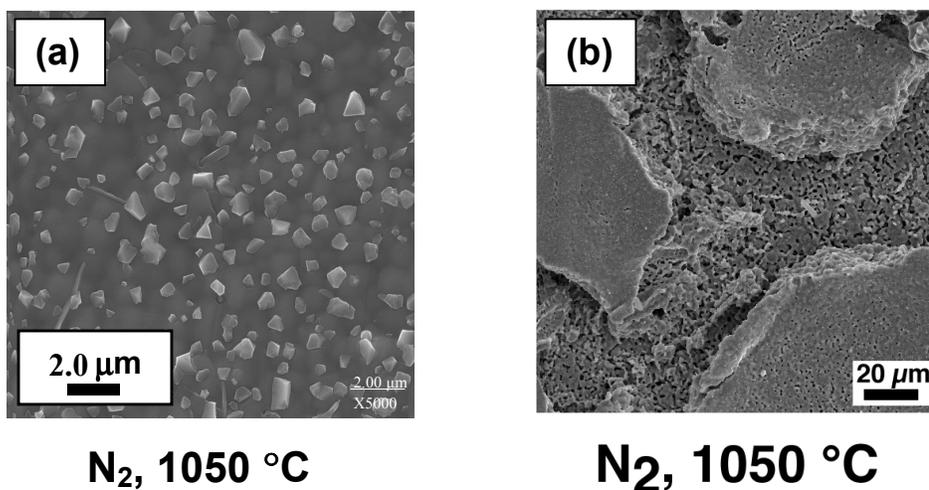


Fig. 1. Scanning electron micrographs showing highly densified supported SCFO membrane layers (a), with large open cracks between the densified regions apparent at lower magnification (b). Membranes were obtained by deposition of paste from aerosol derived powder and PEG.

A number of strategies were considered to minimize crack formation in the sintered supported films. These included: use of other dispersants and additives to improve the mass loading of the pastes and plasticity of the green films, modified powder characteristics, and modified thermal processing cycles. Our primary emphasis was on changing the paste formulation to allow higher mass loading of powder, thus reducing the overall porosity introduced during burnout/sintering. Upon reviewing literature related to screen printing and tape casting of ceramic films, we found that organic solvent-based ink formulations often offered considerable advantages. Because of good solubility, it becomes easy to incorporate organic additives such as dispersants, plasticizers, and binders. Furthermore, surface tension during drying is normally greatly reduced for organic solvents, helping to reduce cracking during drying. The formulation presented in Table 1 was adopted and investigated in comparison to the previously used aqueous and PEG-based pastes. This was done using the commercial SCFO powder rather than our aerosol-derived powder in order to save time in preliminary evaluation of the new formulation, since the synthesis of sufficient aerosol-derived powder for paste formation is a time-consuming process.

Green films were deposited by spreading of the paste over the pre-sintered porous SCFO support using hand-held single-edge razor blade. Based on previous results that showed superior sintering behavior in nitrogen, only nitrogen was used for sintering. A staged sintering procedure (Fig. 2) was used to provide soak times at two intermediate temperatures to allow sufficient time for solvent and heavier organics to evolve. This thermal cycle was different from previously reported membrane fabrication. Fig. 3 shows the much improved uniformity obtained after sintering films made from pastes with higher loading of the commercial SCFO powder

(sintering at 1050 °C in N<sub>2</sub>). The figure also shows an image of a film prepared from aerosol powder sintered under the same conditions. The aerosol film layer sintered to much higher density, but developed massive cracks and flaws. The difference between the sintered commercial powder films and the aerosol powder film could be attributed to both particle size and paste formulation effects. The aerosol-powder film was prepared from a simple PEG paste.

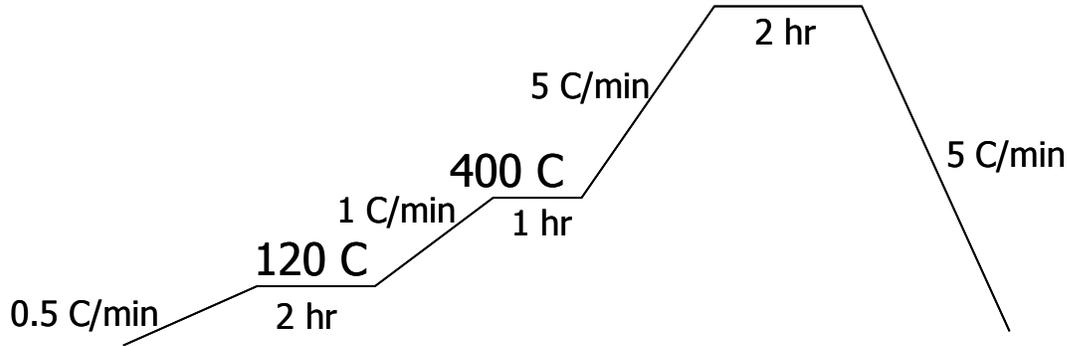


Fig. 2. Thermal cycle used for sintering the membranes deposited from the multicomponent organic paste formulation.

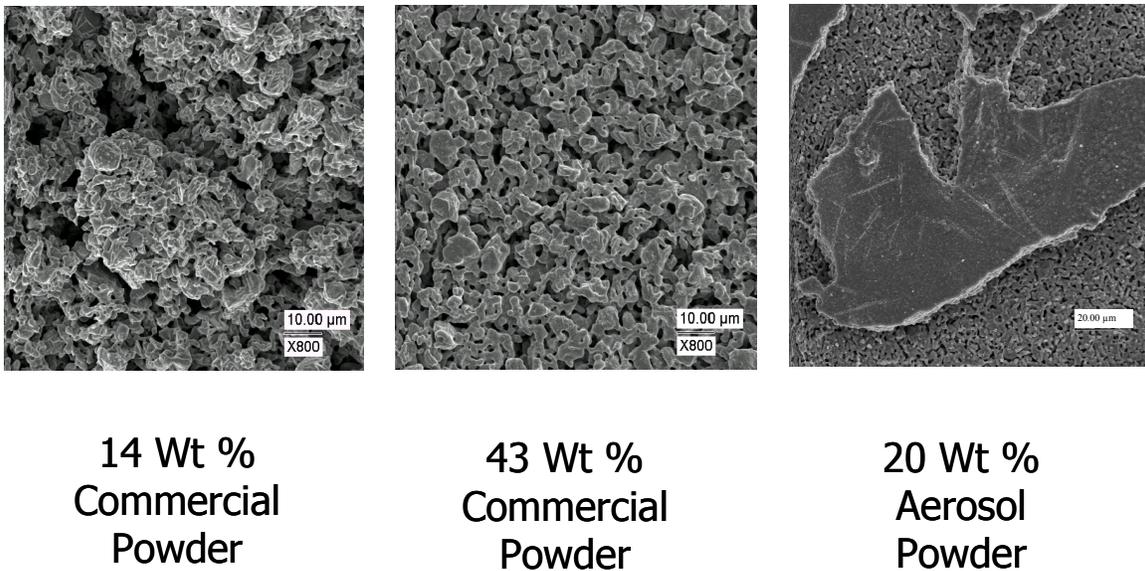


Fig. 3. SEM micrographs showing the sintered structure of SCFO films made from commercial SCFO pastes with low (14 wt%) and high (43 wt%) powder loading. The dramatic difference in sintering behavior between aerosol powder and the commercial powder can be seen comparing to the third image that shows the dense but highly cracked film layer obtained after sintering a 20 wt% aerosol powder paste. All films were sintered at 1050 °C in nitrogen.

Fig. 4 shows additional plan-view SEM images of membrane top layers made from the commercial SCFO powder after the staged sintering procedure. We found no evidence of cracks or opening developing in the membrane layer at any sintering temperature investigated using the new formulation with commercial SCFO powder. However, it is again noted that the membrane layer sintered at 1100 °C in Fig. 4 still has dramatically more residual porosity than the sintered

areas of the top layer in Fig. 1 (from aerosol-derived SCFO powder). This dramatically shows the sintering advantages of the aerosol-derived powder. The distinction between the membranes prepared from aerosol powder and the commercial powder is further demonstrated in Fig. 5. The figure shows the micrographs of the two powders, revealing the much smaller size and spherical morphology of the aerosol powder, as well as the large-scale and small-scale microstructure of the films prepared from the two pastes. It is apparent from the large area views that cracks are not significant in the commercial powder membranes, while, at the micron scale, the microstructure for the two powders is very similar.

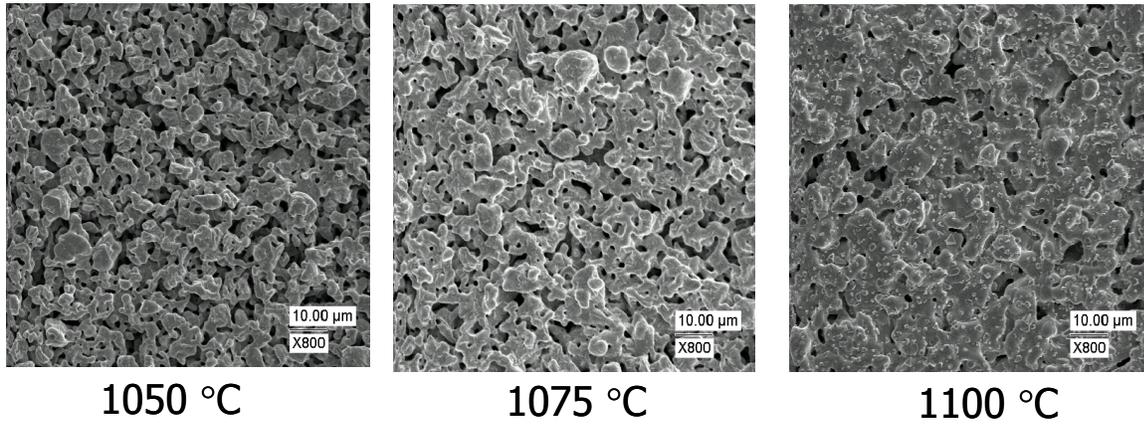


Fig. 4. Plan-view scanning electron micrographs of top-layers deposited using the multicomponent organic paste (43 wt% powder) and sintered in nitrogen at the temperature indicated.

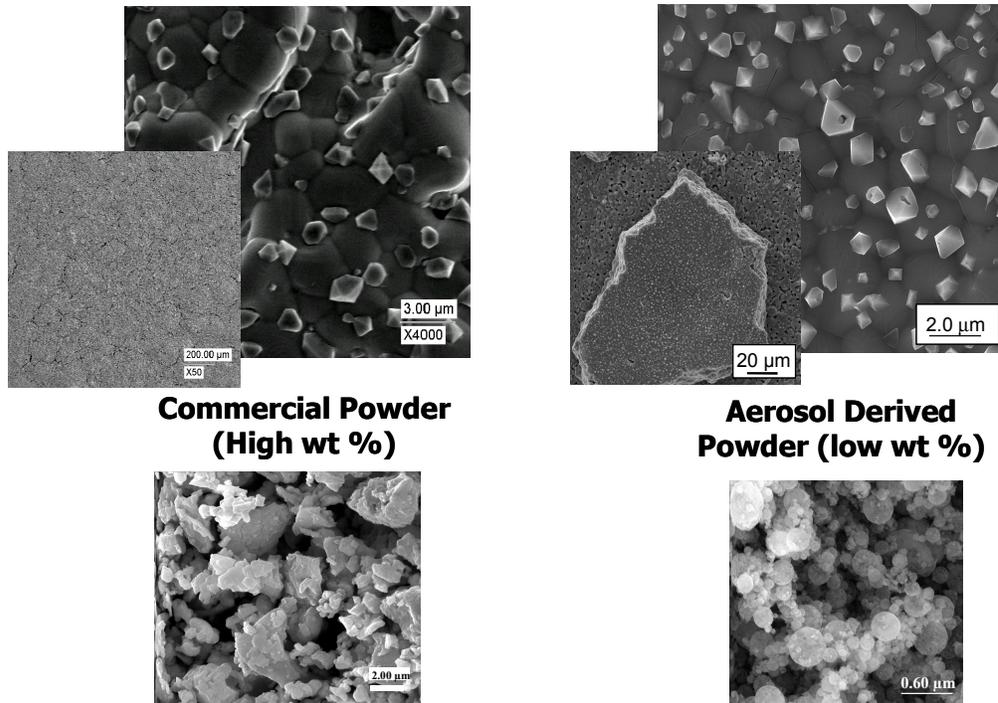


Fig. 5. SEM micrographs comparing aerosol-derived and commercial SCFO powders, along with the large-scale and micron-scale microstructure of sintered membrane layers derived from them. Membranes were sintered at 1100 °C in nitrogen.

## CONCLUSION

The sintering advantages offered by the aerosol-derived powder are impressive, and the superiority of the multicomponent paste formulation is also apparent. The new paste formulation is very attractive for testing on aerosol powder. Thus the immediate future work will involve using the multicomponent organic paste formulation with high powder loading of the aerosol powder. Based on the results presented here, this should produce higher quality supported membranes that we have been able to produce thus far. In addition, we will then be able to make a more direct assessment of the role of powder versus paste formulation and sintering cycle in determining the final extent of sintering and cracking.

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