TITLE: SUPPORTED DENSE CERAMIC MEMBRANES FOR OXYGEN SEPARATION

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DOE GRANT NO.: DE-FG2698-FT40120

PERIOD OF PERFORMANCE: June 25, 1999 - June 24, 2000 DATE: April 1999

ABSTRACT

OBJECTIVE

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. Ceramic mixed-conducting membranes separate oxygen with perfect selectivity via ionic oxygen transport through the oxygen vacancies in the crystalline material. The potential impact of such membranes for high-temperature applications such as partial oxidation reactors and oxidative reformers is well recognized. Specific tasks and objectives of the project include:

• explore strategies for the successful fabrication of defect-free thick-film $Sr(Co,Fe)O_x$ membranes on porous supports, emphasizing deposition and subsequent densification of ultrafine powders produced by aerosol methods.

• develop an improved understanding of particle deposition and infiltration into porous granular supports, and the relationship to sintering behavior, film adhesion, and stability.

• explore and demonstrate the use of a novel metal organic chemical vapor deposition technique to mend membrane defects.

ACCOMPLISHMENTS TO DATE

The main accomplishments in the first year of the project were: (1) the establishment of a protocol for making porous $SrCo_{0.8}Fe_{0.2}O_x$ and $SrCo_{0.5}FeO_y$ substrates using commercially purchased powder, (2) production and characterization of ultrafine $SrCo_{0.5}FeO_y$ powder using aerosol pyrolysis, (3) characterization of substrates and powder, and (4) deposition of thick $SrCo_{0.5}FeO_y$ films from the aerosol-derived powder by two methods: direct deposition of a slurry, and doctor blading of a paste made using polypropylene glycol (PPG, MW=400) as a vehicle. Investigation of the sintering behavior of the thick films had just been started. The results demonstrated that $SrCo_{0.5}FeO_x$ powder possessing controlled elemental composition, desired crystalline phase content, and mean particle size of approximately 0.2 µm could be produced using aerosol pyrolysis. Slurry deposition provided micron-thick layers, and required multiple deposition-sintering cycles to provide layers of the desired thickness for subsequent membrane densification. The paste method provided membrane layers of 5 - 10 µm thickness in a single deposition, although cracking was evident after thermal treatment.

In the past year (second project year), the sintering behavior of the supported thick $SrCo_{0.5}FeO_y$ films in N_2 and air was investigated. In addition, investigations into the use of a metal-organic chemical vapor deposition (MOCVD) method to mend defective membranes were initiated. The sintering atmosphere effected the crystalline phase content and film microstructure, as well as the densification behavior. Densification rates of $SrCo_{0.5}FeO_y$ disks were higher in N_2 than air, with comparable levels of density reached at 50-100 °C lower in N_2. In supported films, sintering in N_2 led to highly dense and relatively featureless regions of film separated by large cracks; whereas sintering in air produced a porous film consisting of large platelet-shaped grains and comparatively little cracking. The extensive cracking observed in N_2-sintered samples apparently results from cracking initiated by substrate-constrained sintering, followed by complete densification of isolated film islands at 1000-1100 °C after bonds with substrate have been sheared. X-ray diffraction (XRD) indicated that a perovskite phase is produced in air, while sintering in N_2 produces the desired layered perovskite structure. The differences in crystalline growth habit of the two phases is still not understood, but the highly elongated grain growth of the perovskite phase apparently results in a very open structure with large grain size that is difficult to sinter to high density without melting. Melting is generally not desirable because the porosity of the underlying support (of the same composition) must be maintained. However, we have also explored using another oxide powder (MgO) in the substrate to inhibit sintering while nearly melting the film. The sintering inhibition was substantial, but could not prevent densification near the $SrCo_{0.5}FeO_y$ melting point.

In the MOCVD mending investigations, we have found that $Fe(tmhd)_3$ can be sublimed readily at 200 °C in a N_2 carrier, and will react to produce iron oxide at 280-300 °C in the presence of O_2 but is stable to temperatures above 300 °C in pure N_2. This makes this $Fe(tmhd)_3$/air a candidate system for counterdiffusion MOCVD mending of flaws. Experiments conducted thus far with this combination have led to iron oxide formation on either side of the membrane layer, but the proper pressure balance has not yet been achieved for deposition inside membrane or defect pores.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

The successful development of dense ceramic oxygen-selective membrane technology could impact fossil energy utilization several ways. This technology could replace cryogenic oxygen purification as a source of high-purity oxygen for industrial processing and chemical reactors, providing potentially enormous energy savings. There is also promise of direct integration of such membranes into reactor design to provide energy-efficient membrane reactors. These membranes are a very attractive option for providing oxygen to convert methane to methanol or other products at remote gas fields, allowing transportation and exploitation of an under-utilized fossil energy source. Oxygen-transporting membranes may also lead to new developments in the fuel cell systems, which could include: new electrode materials, new fabrication approaches for thin electrode/electrolyte layers, or use of a compact membrane-based catalytic reformer to produce H_2 for a conventional PEM fuel cell.

PLANS FOR THE COMING YEAR

- more detailed analysis of XRD data with objective of better understanding the development of crystallinity that accompanies densification in different atmospheres and the role of grain growth in inhibiting densification
- further explore multiple deposition cycles to address crack mending
- examine film melting on alternative supports
- continue exploration of the MOCVD mending method
- evaluate compositional and microstructural stability of sintered $SrCo_{0.5}FeO_y$ films at typical membrane operation temperature (including permeation stability is sufficiently defect-free membranes are made)
- use aerosol method to explore alternative membrane compositions and dopants, with permeation characterization using pressed disks rather than films

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

- none published or submitted at this time

Conference Presentations (each with preprint volume)

- T.L. Ward,* D. Xia, and R. Chitthuri, "The Use of Aerosol and Vapor Processing in the Fabrication of Dense Mixed-Conducting Ceramic Films", platform presentation, Vapor Phase Synthesis and Materials III, Engineering Foundation Conference, July 18-23, 2000, Helsinki, Finland.

- T. Ward,* D. Xia, R. Chitthuri, "The Processing and Mending of Dense Thick Film Ceramic Membranea Using Ultrafine Powders", platform presentation, 1999 Annual Meeting of the American Institute of Chemical Engineers, Oct. 31-Nov. 5, 1999, Dallas, TX.

Students Supported Under this Grant

- Deying Xia, M.S. student in chemical engineering (University of New Mexico)
- Rajarao Chitthuri, M.S. student in chemical engineering (University of New Mexico)