TITLE: SUPPORTED DENSE CERAMIC MEMBRANES FOR OXYGEN SEPARATION

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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

Porous substrates (discs) have been fabricated from commercially-purchased powder with compositions of $SrCo_{0.8}Fe_{0.2}O_x$ and $SrCo_{0.5}FeO_y$ (compositions which lead to different perovskite-related phases). The sintering of these powders to provide substrates possessing acceptable porosity and strength has been evaluated, and appropriate standard preparation methodologies have been determined. While both of the above compositions are known for high oxygen permeability, $SrCo_{0.5}FeO_y$ is more stable under reducing conditions and less prone to the volatile loss of cobalt during sintering, and was therefore chosen for the initial film depositions. Deposition of $SrCo_{0.5}FeO_y$ films upon these porous substrates has been carried out by several methods using submicron powders produced by aerosol pyrolysis in our laboratory. The aerosol production of $SrCo_{0.5}FeO_y$ powder has been investigated, and the effect of synthesis temperature and gas atmosphere on particle morphology and crystalline phase content evaluated. As-produced

powder possesses x-ray diffraction patterns consistent with reported patterns for the layered $SrCo_{0.5}FeO_y$ structure. Typical particle size of the aerosol-derived powder is approximately 0.2 µm.

Two methods of film deposition have been attempted: direct deposition of a slurry of the ultrafine aerosol powder onto the porous substrate, and doctor blading of a paste made from the aerosol powder and polypropylene glycol (PPG). Slurry deposition provides micron-thick layers, and requires multiple deposition-sintering cycles to provide layers of the desired thickness for subsequent membrane densification. The paste method provides membrane layers of 5 - 10 µm thickness in a single deposition, although cracking is evident, apparently due to stress accompanying the loss of PPG. Sintering studies of the supported films has just begun.

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

- thorough study of sintering behavior of supported $SrCo_{0.5}FeO_y$ films deposited by doctor blading, focusing on the effects of atmosphere (O_2 partial pressure) and temperature profile.
- characterize effect of film sintering and subsequent annealing procedures on crystalline phase content
- 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)
- begin evaluation of MOCVD mending strategy

ARTICLES, PRESENTATIONS, AND STUDENT SUPPORT

Journal Articles (peer reviewed)

- none published or submitted at this time

Conference Presentations

- none derived from this grant at this time

Pending Conference Presentations (Submitted)

- D. Xia, R. Chitthuri, and T. L. Ward, The Use Of Aerosol Processing and Chemical Vapor Deposition in the Fabrication of Dense Mixed-Conducting Ceramic Films, submitted for presentation at the Engineering Foundation Conference on Vapor Phase Synthesis of Materials III, July 18-23, 1999, Porvoo, Finland.
- D. Xia and T.L. Ward, Nonporous Thick-Film Ceramic Membranes for High-Temperature Oxygen Separation Applications, submitted for presentation at the 1999 Annual Meeting of the American Institute of Chemical Engineers, Oct. 31-Nov. 5, 1999, Dallas, TX.

Also Note: the principal investigator has served or will serve as a chair of several directly relevant sessions at national meetings in the past and upcoming year:

- Recent Developments in New Membrane Materials I; 1998 Annual Meeting of the American Institute of Chemical Engineers; Nov. 15-20, 1998, Miami Beach, FL.
- Pressure Driven Membrane Based Processes in the Petroleum and Chemical Industries; 1999 Spring National Meeting of the American Institute of Chemical Engineers, March 14-18, 1999, Houston, TX.
- Recent Developments in New Membrane Materials I; 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)