II.B.2 Inorganic Membrane Porous Support Tube Fabrication

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Objectives

Develop versatile and flexible technology to fabricate support tubes suitable for microporous and dense membrane layers.

- Determine source for uniform spherical metal powders.
- Determine best materials of construction for compatibility with target operating environments and suitability for application of membrane layer(s).

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Fuel Processor Capital Costs
- B. Operation and Maintenance
- C. Feedstock and Water Issues
- E. Control and Safety
- G. Efficiency of Gasification, Pyrolysis, and Reforming Technology
- AB. Hydrogen Separation and Purification

Approach

- Identify materials suitable for support tube fabrication.
- Obtain spherical metal powder samples.
- Characterize powder samples for size distribution and morphology.
- Form tubes from candidate powders.
- Perform sintering trials to determine optimum sintering conditions.
- Characterize sintered support tubes for pore size distribution and surface roughness.
- Test support tubes for suitability with microporous and/or dense membrane layers.

Accomplishments

- Potential support tube materials have been identified and include 300 and 400 series stainless steels, iron aluminide, and Hastelloy X.
- Gas (argon or helium) atomized powders have been identified to have the greatest potential for hydrogen membrane supports (powders are spherical and size distribution can be controlled). A narrow size

distribution of particles can result in a narrow pore-size distribution and a smooth surface for application of either palladium or microporous separative layers.
- Support tube forming process parameters are being established, and pilot sintering trials are in progress.

Future Directions

- Obtain spherical powder samples suitable for support tube fabrication from Ames Laboratory.
- Complete forming and sintering trials of support tubes using Ames powder.
- Fully characterize support tubes.
- Work with collaborators to deposit Pd-Ag membranes and evaluate membrane performance.
- Evaluate composite membrane materials to reduce interactions between support and membrane.

Introduction

One of the essential elements for economical and large-scale hydrogen production is the effective and efficient separation of hydrogen from the gas mixtures in which it is contained. These gas mixtures may include, for example, reformed natural gas and coal-derived synthesis gas. The temperatures and pressures of these gas mixtures are often high, which presents issues with respect to the robustness of the separation devices.

Approach

The Oak Ridge National Laboratory (ORNL) has developed a versatile membrane fabrication process for membrane support tubes and microporous (<2 nm pore diameter) membranes. This task will be directed to the development of support tubes using ORNL technology suitable for application of microporous membranes and dense membranes (i.e., Pd or proton conductors) for hydrogen separation.

The need is for effective and durable hydrogen separation and purification membranes with high flux rate and lower cost. The objective is to develop the fabrication techniques to produce robust, porous support tubes suitable for microporous (<2 nm diameter) or dense, e.g., palladium, membranes. The consensus is that hydrogen separation membranes will be composite structures, i.e., thin membranes on strong support structures. Also, the quality of the membrane layer, either microporous or dense, is dependent on the quality of the support tube. A uniform pore size with a high degree of surface smoothness is required for application of these layers. The thickness required to achieve a leak-free dense palladium membrane is dependent on the largest pore that the layer needs to span. Thus, if the average pore size of a support is 5 µm but the distribution of pores varies from 1 µm to 15 µm, the layer needs to be applied thick enough to span 15-µm pores, which will be approximately three times thicker than required to span 5-µm pores. The pore size distribution of the support tube is very dependent on the size distribution of precursor powder. Therefore, early work will focus on evaluation of metal powder samples and the fabrication of tubes. These tubes will be characterized for uniformity of pore size and surface roughness in order to correlate tube properties with powder characteristics so that we can better predict which powders will yield the best quality support tubes. The support tubes must be able to withstand transmembrane pressures of 20-30 atm (2-3 MPa) at temperatures of 500-700°C. Lastly, the support tubes must be rugged and able to operate for extended periods at temperatures of 500-700°C in the presence of H_2, CO_2, CO, CH_4, H_2O, and trace amounts of H_2S.

Results

Potential support tube materials have been identified and include 300 and 400 series stainless steels, iron aluminide, and Hastelloy X. Samples of metal powders made by both water atomization and gas atomization were obtained and characterized. Gas (argon or helium) atomized powders were mostly spherical, while water atomized powders were very irregular in shape. Support tubes were formed and sintered. Resulting tubes were characterized using gas flow measurements and scanning electron microscopy (SEM). SEM micrographs indicated a more uniform-looking surface for the tubes made from gas atomized powder. Cursory tests done by applying a ceramic membrane layer to these tubes revealed that the membranes applied to tubes made from gas atomized powder had fewer leaks. Gas atomized powders have been identified to have the greatest potential for hydrogen membrane supports (powders are spherical and size distribution can be controlled). A narrow size distribution of particles can result in a narrow pore-size distribution and a smooth surface for application of either palladium or microporous separative layers.

Conclusions

Gas atomized metal powder was shown to result in support tubes having a more uniform surface when compared to tubes made from water atomized powder. Initial evaluation using thin microporous layers indicates that the tubes made from the gas atomized powder result in fewer leaks in the final membrane layer.

FY 2004 Publications/Presentations

1. Tim Armstrong, Brian Bischoff, Roddie Judkins, E. Andrew Payzant, and Scott Speakman, *Development of Supports and Membranes for Hydrogen Separation*, Presented at the 2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Annual Program Review in Philadelphia, May 2004.