Title: Advanced Hydrogen Transport Membranes for Vision 21 Fossil Fuel Plants

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TABLE OF CONTENTS

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ABSTRACT

During this quarter composite layered membrane size was scaled-up and tested for permeation performance. Sintering conditions were optimized for a new cermet containing a high permeability metal and seals were developed to allow permeability testing. Theoretical calculations were performed to determine potential sulfur tolerant hydrogen dissociation catalysts. Finally, work was finalized on mechanical and process & control documentation for a hydrogen separation unit.

EXECUTIVE SUMMARY

Eltron Research Inc. and team members CoorsTek, Süd Chemie, Argonne National Laboratory, and NORAM are developing an environmentally benign, inexpensive, and efficient method for separating hydrogen from gas mixtures produced during industrial processes, such as coal gasification. This project was motivated by the National Energy Technology Laboratory (NETL) Vision 21 initiative, which seeks to economically eliminate environmental concerns associated with the use of fossil fuels. Currently, this project is focusing on four basic categories of dense membranes: i) mixed conducting ceramic/ceramic composites, ii) mixed conducting ceramic/metal (cermet) composites, iii) cermets with hydrogen permeable metals, and iv) layered composites containing hydrogen permeable alloys. Ultimately, these materials must enable hydrogen separation at practical rates under ambient and high-pressure conditions, without deactivation in the presence of feedstream components such as carbon dioxide, water, and sulfur.

This report contains results for scale-up permeation testing of composite layered membranes, processing of new cermets, development of sulfur tolerant catalysts, and engineering documentation for a hydrogen separation unit.

INTRODUCTION

The objective of this project is to develop an environmentally benign, inexpensive, and efficient method for separating hydrogen from gas mixtures produced during industrial processes, such as coal gasification. Currently, this project is focusing on four basic categories of dense membranes: i) mixed conducting ceramic/ceramic composites, ii) mixed conducting ceramic/metal (cermet) composites, iii) cermets with hydrogen permeable metals, and iv) layered composites with hydrogen permeable alloys. The primary technical challenge in achieving the goals of this project will be to optimize membrane composition to enable practical hydrogen separation rates and chemical stability. Other key aspects of this developing technology include catalysis, ceramic processing methods, and separation unit design operating under high pressure. To achieve these technical goals, Eltron Research Inc. has organized a consortium consisting of CoorsTek, Süd Chemie, Inc. (SCI), Argonne National Laboratory (ANL), and NORAM.

During this quarter composite layered membrane size was scaled-up and tested for permeation performance. Sintering conditions were optimized for a new cermet containing a high permeability metal and seals were developed to allow permeability testing. Theoretical calculations were performed to determine potential sulfur tolerant hydrogen dissociation catalysts. Finally, work was finalized on mechanical and process & control documentation for a hydrogen separation unit.

EXPERIMENTAL

The Experimental Section of the first quarterly report (January 1, 2001) contained detailed descriptions of equipment and procedures to be used over the duration of this program. The specific aspects presented were: (a) preparation of ceramic powders, (b) preparation of composite materials, (c) fabrication of tube and disk membranes, (d) construction and operation of ambient-pressure hydrogen separation units, (e) construction and operation of high-pressure hydrogen separation units, (f) hydrogen transport and ambipolar conductivity measurements and calculations, and (g) fabrication of thin film ceramics. For brevity, these general issues will not be repeated. However, modification of equipment or methods, as well as any other experimentally relevant issues, will be reported in the Results and Discussion section under their corresponding Tasks as outlined in the original proposal.

RESULTS AND DISCUSSION

Tasks 1 & 2 Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes

Contributors: Eltron, CoorsTek

I. Composite Layered Membranes with High Hydrogen Permeability – Eltron

Scale-up verification of composite layered membrane hydrogen separation performance was demonstrated as discussed under Task 9.

II. Multi-Phase Ceramics and Cermets – CoorsTek

CoorsTek continued developing the processing conditions necessary to sinter a new cermet referred to as EC101 containing high permeability metal and ceramic phases. Sintering conditions were optimized for maximizing density of both ceramic and metal phases. Sintering temperature was varied between 1450 and 1800^{o}C under different sintering atmospheres. Results showed that sintering at higher temperatures led to samples with less than 1% porosity. Brazing was investigated in an effort to form leak-free seals for accurate permeability testing.

III. Membrane Coatings and Catalysts –SCI

Thermodynamic calculations were performed on potential hydrogen dissociation catalysts for hydrogen separation in sulfur containing feed streams. Results showed that, as expected, the noble metals had the highest tolerance to sulfide formation.

Several different catalysts were prepared and tested for sulfur resistance in hydrogen containing feed streams. Membranes were exposed to 5-30 ppm H_2S and the permeability compared to equivalent membranes not exposed to H_2S. Results showed that palladium copper alloy catalysts were more sulfur tolerant than pure palladium catalysts. Energy Dispersive X-ray Analysis, XPS, and X-ray diffraction were used to confirm the presence of sulfur on membrane surfaces following testing.

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron

High pressure testing was focused on testing a scaled-up hydrogen separation composite layered membrane as discussed in Task 9.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: CoorsTek, Eltron

No actions were performed on this task during this quarter.

Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit

Contributors: NORAM

During this reporting period work was completed on key engineering documentation including a mechanical report, a process and control report, and a matrix evaluating Eltron's family of hydrogen separation membranes. The key results of these documents will be included in the project final report.

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins

Contributors: Eltron

No actions were performed on this task during this quarter.

Task 7 Catalyst Membrane Compositions for Scale Up

Testing during the past year focused on layered composite membranes. Results for these materials were compiled and compared to all the categories of membranes developed under this program. Based on hydrogen permeation rates, mechanical stability, and economics, the results to date clearly indicated that the layered composites have the greatest potential for scale up and commercial viability. In terms of ceramics and cermets, effort now is being focused on a cermet containing a high permeability metal. Cermets may provide chemical and mechanical stability advantages and have potential as protective/catalytic layers in the layered composite membranes.

Task 8 Manufacturing Processes for Demonstration-Scale Hydrogen Separation Membranes

CoorsTek has developed a thin film deposition procedure for the application of BCY / Ni thin films ranging from 10 to 100 μm onto the inner surface of a tubular support. Variables optimized in this procedure include sintering temperature, time, and atmosphere. This procedure is easily adaptable to manufacturing scale; however, the permeability of BCY / Ni materials will limit its commercial potential. New cermets based on high permeability metals also have potential; however, these cermets are in an early stage of development. The developed procedures for BCY/Ni thin film deposition will easily be adaptable to the new class of cermets. CoorsTek has installed a Loomis extruder for manufacture of cermet tubes. Trial tubes were prepared and sintered. As discussed below, Eltron Research Inc. has demonstrated scale-up testing of composite layered membranes.

Task 9 Fabrication and Evaluation of Demonstration-Scale Hydrogen Separation Unit

During this quarter permeation testing was performed on scaled-up composite layered membrane with a surface area of 31.7 cm^2. This represents a fifteen fold scale-up compared to our standard 2 cm^2 membrane size. A reactor was constructed including appropriate furnace elements, plumbing, and analysis to accommodate this size membrane. Permeation testing was performed at 420^{o}C and at pressures up to 150 psig. A hydrogen helium feed stream up to 12.5 L/min was fed to the retentate side of the membrane and argon was used on the permeate side of the membrane to facilitate GC analysis. Permeation results are shown in Figure 1. Results showed a maximum permeation up to 51 $mL{\bullet}min^{-1}{\bullet}cm^{-2}$ which can be extrapolated to a hydrogen separation rate of 0.46 lbs H_2 / day. Figure 1 shows that the membrane was limited by gas phase diffusion. Fluid dynamic calculations and improved hardware design will lead to improved performance.

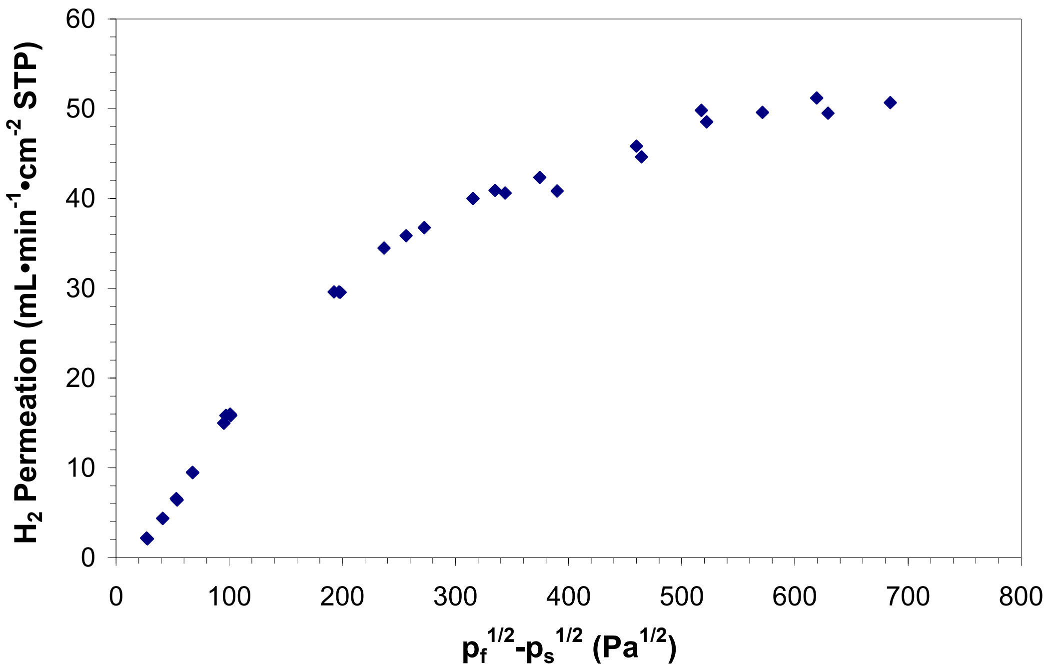


Figure 1. Plot of permeation vs. the difference in the square roots of the hydrogen partial pressure across the membrane.

SUMMARY AND CONCLUSIONS

Conclusions based on the work performed during this quarter are summarized as follows:

1. Scale-up hydrogen permeation testing was demonstrated on a membrane with a surface area of 31.7 cm^2 and a permeation rate of 51 $mL \bullet min^{-1} \bullet cm^{-2}$.
2. Work was continued developing the processing conditions and sealing mechanisms for EC101 cermet membranes.
3. Thermodynamic calculations were performed on several different hydrogen dissociation catalysts in sulfur containing feed streams to determine catalyst tolerance to sulfide formation. Permeation testing in H_2S containing feed streams demonstrated the palladium copper catalysts were more sulfur tolerant than pure palladium.
4. Engineering concepts and designs were finalized. Full engineering documentation will be summarized in the final report.

OBJECTIVES FOR NEXT REPORTING PERIOD

A no-cost extension was obtained to finalize cermet development at CoorsTek. During the extension period of the contract, CoorsTek will continue the work it has initiated on a single cermet composition referred to as EC101. This cermet was chosen to evaluate key manufacturing variables and demonstrate ability to fabricate thin cermet disks (13-15 mils). Work will also continue on development of a cost-effective extrusion manufacturing process for these materials. Eltron Research Inc. will monitor cermet development progress and test appropriate materials. All other milestones and tasks have been completed.

OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

As mentioned above, a no-cost extension was obtained to finalize cermet development at CoorsTek.

TIME LINES

The time lines separated into each task are presented below, with markers indicating overall progress for each subtask.

Tasks 1 & 2
Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes

Tasks	Months: 0 6 12 18 24 30 36 42 48 54 60
• Baseline Evaluation of Established Membranes *(Eltron, CoorsTek)*	Completed
• Preparation, Characterization, and Testing of Novel Ceramic and Cermet Composites *(Eltron, CoorsTek, ANL)*	Completed
• Advanced Issues for Optimization of Ceramic and Cermet Composites *(ANL, CoorsTek, Eltron)*	Extension
• Development of New Metal Composite Membranes *(Eltron)*	Completed
• Development of Catalysts and Surface Coatings *(Eltron, SCI)*	Completed

Task 3
High-Pressure Hydrogen Separation

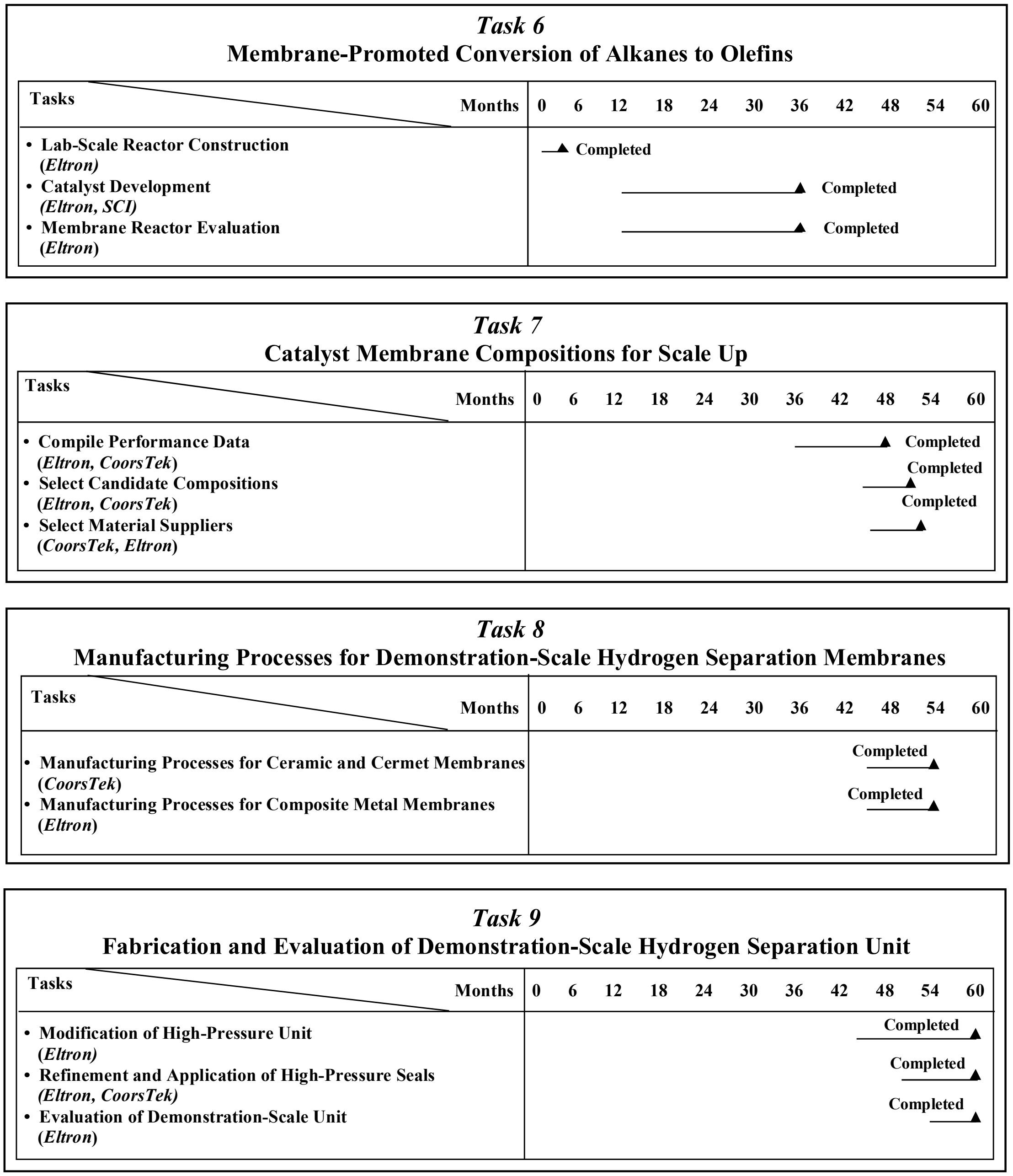
Tasks	Months: 0 6 12 18 24 30 36 42 48 54 60
• Construction of High Pressure System (*Eltron*)	Completed
• High-Pressure Seal Development (*Eltron*)	Completed
• High-Pressure Screening of Composite Ceramics and Cermets (*Eltron*)	Extension
• High-Pressure Screening of New Metal Composite Membranes (*Eltron*)	Completed
• Preproject Engineering and Preliminary Mechanical Considerations (*NORAM*)	Completed

Task 4
Thin-Film Hydrogen Separation Membranes

Tasks	Months: 0 6 12 18 24 30 36 42 48 54 60
• Fabrication of Porous Supports (*Eltron, CoorsTek*)	Completed
• Thin Film Deposition and Evaluation (*Eltron, CoorsTek*)	
• Planar Membranes	Completed
• Tubular Membranes	Completed
• Prototype Thin-Film Fabrication (*CoorsTek, Eltron*)	Completed
• Assess Impact of Thin-Film Membranes on Reactor Concepts (NORAM)	Completed

Task 5
Construction & Evaluation of Prototype Hydrogen Separation Unit

Tasks	Months: 0 6 12 18 24 30 36 42 48 54 60
• Design Basis and Process Flow Diagrams (*NORAM*)	Completed
• Engineering Concepts for Full and Demonstration Scale (*NORAM*)	Completed
• Construction and Evaluation of Demonstration Scale Unit (*Eltron*)	Completed


Task 6
Membrane-Promoted Conversion of Alkanes to Olefins
Tasks
Months 0 6 12 18 24 30 36 42 48 54 60
• Lab-Scale Reactor Construction (Eltron)
Completed
• Catalyst Development (Eltron, SCI)
Completed
• Membrane Reactor Evaluation (Eltron)
Completed
Task 7
Catalyst Membrane Compositions for Scale Up
Tasks
Months 0 6 12 18 24 30 36 42 48 54 60
• Compile Performance Data (Eltron, CoorsTek)
Completed
• Select Candidate Compositions (Eltron, CoorsTek)
Completed
• Select Material Suppliers (CoorsTek, Eltron)
Completed
Task 8
Manufacturing Processes for Demonstration-Scale Hydrogen Separation Membranes
Tasks
Months 0 6 12 18 24 30 36 42 48 54 60
• Manufacturing Processes for Ceramic and Cermet Membranes (CoorsTek)
Completed
• Manufacturing Processes for Composite Metal Membranes (Eltron)
Completed
Task 9
Fabrication and Evaluation of Demonstration-Scale Hydrogen Separation Unit
Tasks
Months 0 6 12 18 24 30 36 42 48 54 60
• Modification of High-Pressure Unit (Eltron)
Completed
• Refinement and Application of High-Pressure Seals (Eltron, CoorsTek)
Completed
• Evaluation of Demonstration-Scale Unit (Eltron)
Completed

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