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

Type of Report: Quarterly

Reporting Period Start Date: January 1, 2005

Reporting Period End Date: March 31, 2005

Principal Authors:

Eltron: Carl R. Evenson, Anthony F. Sammells, Richard T. Treglio, Adam E. Calihman

ANL: U. (Balu) Balachandran

CoorsTek: Richard N. Kleiner, James E. Stephan, Frank E. Anderson

Süd Chemie: Chandra Ratnasamy, Mahendra Sunkara, Jyothish Thangla

NORAM: Clive Brereton, Warren Wolfs, James Lockhart

Date Report was Issued: April 30, 2005

DOE Award Number: DE-FC26-00NT40762

Name and Address of Submitting Organization:

Eltron Research Inc., 4600 Nautilus Court South, Boulder, CO 80301-3241

TABLE OF CONTENTS

	<u>Page</u>
Disclaimer	3
Abstract	4
Executive Summary	5
Introduction.....	6
Experimental.....	6
Results and Discussion	7
Tasks 1 & 2 Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes	7
Task 3 High Pressure Hydrogen Separation.....	9
Task 4 Thin-Film Hydrogen Separation Membranes	10
Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit	10
Task 6 Membrane-Promoted Conversion of Alkanes to Olefins.....	10
Task 7 Catalyst Membrane Compositions for Scale Up.....	10
Task 8 Manufacturing Processes for Demonstration-Scale Hydrogen Separation Membranes.....	10
Task 9 Fabrication and Evaluation of Demonstration-Scale Hydrogen Separation Unit	11
Summary and Conclusions	11
Objectives for Next Reporting Period.....	12
Open Items or Cooperative Agreement Changes.....	12
Time Lines	12

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

During this quarter long term and high pressure hydrogen separation experiments were performed on Eltron's composite layered membranes. Membranes were tested at 400°C and a 300 psig feed stream with 40% hydrogen for up to 400 continuous hours. In addition membranes were tested up to 1000 psig as demonstration of the ability for this technology to meet DOE goals. Progress was made in the development of new hydrogen separation cermets containing high permeability metals. A sulfur tolerant catalyst deposition technique was optimized and engineering work on mechanical and process & control reports was continued.

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 long term and high pressure permeation experiments, processing of new cermets, development of sulfur tolerant catalysts, and mechanical concepts for inclusion of a hydrogen separation device based on Eltron's composite layered membrane technology into an IGCC power plant.

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 long term and high pressure hydrogen separation experiments were performed on Eltron's composite layered membranes. Membranes were tested at 400°C and a 300 psig feed stream with 40% hydrogen for up to 400 continuous hours. In addition membranes were tested up to 1000 psig as demonstration of the ability for this technology to meet DOE goals. Progress was made in the development of new hydrogen separation cermets contain high permeability metals. A sulfur tolerant catalyst deposition technique was optimized and engineering work on the mechanical and process & control reports was continued.

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

Long term permeation data was collected for composite layered membranes. Membranes were tested at 400°C with a 300 psig 40% H₂ feed stream and an ambient pressure 100% H₂ permeate stream. Figure 1 is a plot of permeation vs. time for a membrane tested under these conditions for 240 continuous hours. Permeation initially was 135 mL•min⁻¹•cm⁻², and after 240 hours the permeation was still greater than 80 mL•min⁻¹•cm⁻². After 240 hours the membrane was brought back to ambient conditions and examined with X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD and SEM showed that the membrane was intact and no undesired phase formation was present. A second membrane was run under equivalent conditions for over 400 hours. After 400 hours the permeation was greater than 50 mL•min⁻¹•cm⁻².

Figure 1. Composite layered membrane tested at 400°C and 300 psig for 240 continuous hours.

Composite layered membranes were also tested up to 1000 psig. These high pressure experiments were designed to demonstrate the ability to operate Eltron's composite layered membranes under DOE's expected IGCC operating conditions. Figure 2 shows a plot of hydrogen permeation versus the partial pressure difference across the membrane. A hydrogen permeation of $101 \text{ mL} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ was measured at 1010 psig. Flow rates and temperature were not optimized for this demonstration test. It is expected that under appropriate operating conditions higher permeation values can be obtained.

Figure 2. H₂ permeation at 420°C versus the partial pressure difference across a 0.250 mm membrane. The total pressure differential was 1010 psi. The straight line represents the flux predicted based on Sieverts' Law.

II. Multi-Phase Ceramics and Cermets – CoorsTek

CoorsTek is currently focusing on the processing conditions necessary to sinter cermets containing high permeability metals. Variables under consideration include ceramic phase and particle size, weight percent metal phase, sintering temperature and time, and sintering atmosphere. Variables are being optimized for appropriate phase formation and density. High density cermets have been processed as shown in Figure 3. Distinct metallic and ceramic phases are present and a clean interface was found between the ceramic and metal phases. X-ray diffraction shows the appropriate metal and ceramic phases.

Figure 3. x200 SEM image of a cermet containing a high hydrogen permeability metal.

III. Membrane Coatings and Catalysts –SCI

SCI is currently developing sulfur tolerant catalysts for the retentate side of the hydrogen separation membrane. A dip-coating procedure was developed for coating an alloy of 80 weight percent palladium and 20 weight percent copper onto a hydrogen separation membrane surface. Following dip-coating the alloy was allowed to form at 400°C for four hours. SEM analysis showed a uniform coating and EDAX analysis confirmed the correct alloy formation.

Task 3 *High Pressure Hydrogen Separation*

Contributors: Eltron

Key results for high pressure hydrogen separation are discussed under Task 1.

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

Previous reports detailed NORAM's effort in drafting a report entitled "Criteria for Incorporating Eltron's Hydrogen Separation Membranes into Vision 21 IGCC Systems and FutureGen Plants". During this reporting period work was continued on three additional key documents including a mechanical report, a process and control report, and a matrix evaluating Eltron's family of hydrogen separation membranes. All four of these reports will be included as appendices in the 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 new cermets based on high permeability metals that have acceptably high permeation rates. In addition, 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 cermetes based on high permeability metals also have potential; however, these cermetes 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 cermetes. CoorsTek is in the process of installing a Loomis close one-end extruder for manufacture of cermet tubes. Eltron's current work in Task 8 is focused on identification of materials and manufacturing processes for composite layered membranes. A variety of suppliers and processing techniques are under consideration.

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

Work was continued on the design and construction of a scale-up hydrogen separation unit. The appropriate plumbing has been installed and the necessary safety systems are under development. The reactor design will allow incorporation of membranes with surface areas ranging from 50 to 200 cm². Based on the current long term studies the scale-up separation unit will initially be tested at 400°C and pressures up to 300 psig.

SUMMARY AND CONCLUSIONS

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

1. Composite layered membranes were tested at 400°C and 300 psig of a 40% hydrogen feed stream for up to 400 hours. Permeation greater than 50 mL•min⁻¹•cm⁻² was observed after 400 hours.
2. Permeation of composite layered membranes was measured at pressures up to 1010 psig.
3. Processing conditions for new high permeability cermetes was further developed.
4. A dip-coating procedure was finalized for deposition of a sulfur resistant catalyst on the surface of a hydrogen separation membrane.
5. Two engineering reports were drafted detailing mechanical concepts and process & control issues necessary for inclusion of composite layered hydrogen separation membranes in gasified coal power plants.
6. Construction of a scale-up hydrogen separation reactor was continued and safety issues were addressed.

OBJECTIVES FOR NEXT REPORTING PERIOD

During the next reporting period additional long term permeation experiments will be performed to address membrane stability and the demonstration scale hydrogen separation unit will continue to be constructed. CoorsTek will continue optimizing the processing conditions necessary for production of dense cermets. SCI will test sulfur tolerant catalysts for permeation under ideal conditions and in the presence of sulfur. Finally, NORAM will prepare the final draft of mechanical and process & control reports.

OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

None.

TIME LINES

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

Task 6 Membrane-Promoted Conversion of Alkanes to Olefins												
Tasks	Months	0	6	12	18	24	30	36	42	48	54	60
<ul style="list-style-type: none"> • Lab-Scale Reactor Construction (Eltron) • Catalyst Development (Eltron, SCI) • Membrane Reactor Evaluation (Eltron) 		<p>—▲ Completed</p> <p>_____▲ Completed</p> <p>_____▲ Completed</p>										

[illegible]

Tasks	Months	0	6	12	18	24	30	36	42	48	54	60
• Manufacturing Processes for Ceramic and Cermet Membranes <i>(CoorsTek)</i>												
• Manufacturing Processes for Composite Metal Membranes <i>(Eltron)</i>												

[illegible]