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

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ABSTRACT

During this quarter catalyst stability studies were performed on Eltron's composite layered membranes. In addition, permeation experiments were performed to determine the effect of crystallographic orientation on membrane performance. Sintering conditions were optimized for preparation of new cermets containing high permeability metals. Theoretical calculations were performed to determine potential sulfur tolerant catalysts. Finally, work was continued 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 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.

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# 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, SCI

### I. Composite Layered Membranes with High Hydrogen Permeability – Eltron

During this reporting period effort was focused on variables related to catalyst deposition. The stability of composite layered membranes under hydrogen separation conditions has been described in detail in previous reports. Data shows long term membrane stability under expected operating conditions. Of equal importance is the chemical and mechanical stability of as deposited catalysts prior to being subjected to hydrogen separation conditions. Deposited catalysts were tested with respect to thermal gradients, variable gas flow rates, and gas composition. Results showed that catalyst layers deposited under appropriate conditions were highly stable to temperature and gas composition fluctuations.

Ambient pressure testing was performed on composite layered membranes with different crystallographic orientations. Reports in the literature have discussed the possibility that preferred crystallographic orientation within a hydrogen separation membrane may affect performance. Four membranes were tested with different crystallographic orientations determined by X-ray diffraction. Under ambient pressure conditions no significant difference was observed in performance. All membranes had a permeation rate of 21-23 mL•min$^{-1}$•cm$^{-2}$ at 400$^{o}$C.

### II. Multi-Phase Ceramics and Cermets – CoorsTek

CoorsTek continued developing the processing conditions necessary to sinter cermets containing high permeability metals. Starting material purity was verified and several different ceramic phases were tested. Sintering conditions were optimized for maximizing density of both ceramic and metal phases. Results showed that higher surface area starting materials led to dense cermets at lower sintering temperatures. In addition, sintering tests showed that higher sintering temperatures did not affect phase formation in the cermet. Samples will be prepared for permeation testing at Eltron Research, Inc.

### III. Membrane Coatings and Catalysts –SCI

SCI is currently developing sulfur tolerant catalysts for the retentate side of the hydrogen separation membrane. Work was continued on optimizing a dip-coating procedure for uniformly coating an alloy of 80 weight percent palladium and 20 weight percent copper onto a hydrogen separation membrane surface.

Theoretical calculations were performed to determine the energy of sulfide formation on several potential metal catalyst surfaces under the expected temperature range of 320-440$^{o}$C. Calculations were performed for metals exposed to 10, 100, and 1000 ppm $H_2S$. Results showed that unalloyed iridium possessed the highest tolerance to sulfur without bulk sulfide formation. Calculations showed that the other unalloyed metals including Pd, Cu, Pt, Ru, Rh, and Ga all formed one or more stable bulk sulfides in the presence of $H_2S$ in concentrations as low as 10 ppm.

## *Task 3 High Pressure Hydrogen Separation*

**Contributors**: Eltron

High pressure testing is currently 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 continued on key documentation including a mechanical report, a process and control report, and a matrix evaluating Eltron's family of hydrogen separation membranes. These reports will be finalized during the next quarter and included 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 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. Eltron Research Inc. has ordered materials for scale-up manufacture of composite layered membranes to be used in Task 9.

## *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 $cm^2$. Based on the current long term studies the scale-up separation unit will initially be tested at $400^oC$ and pressures up to 300 psig.

## SUMMARY AND CONCLUSIONS

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

1. Variables related to catalyst deposition were investigated in order to maximize catalyst stability under hydrogen separation conditions.
2. Ambient pressure experiments were performed on membranes with varying crystallographic orientations. Results showed that crystallographic orientation of the membrane did not affect hydrogen permeation.
3. Sintering conditions for new cermet membranes were optimized.
4. Theoretical calculations were performed for determining the stability of metal sulfide phase formation on catalyst surfaces.
5. Engineering documentation for a hydrogen separation unit utilizing Eltron's membrane technology was developed.
6. Work was continued on the construction of a scale-up hydrogen separation unit.

## OBJECTIVES FOR NEXT REPORTING PERIOD

During the final reporting period of this project all Tasks will be completed and documented. Eltron will perform hydrogen permeation experiments on new cermets and the scale-up demonstration unit will be tested. CoorsTek will sinter cermets for testing at Eltron Research, Inc. Sud Chemie will complete catalyst development including determining the sulfur tolerance of prepared Pd/Cu catalysts. NORAM will complete all engineering documentation and issue final drafts to Eltron Research, Inc.

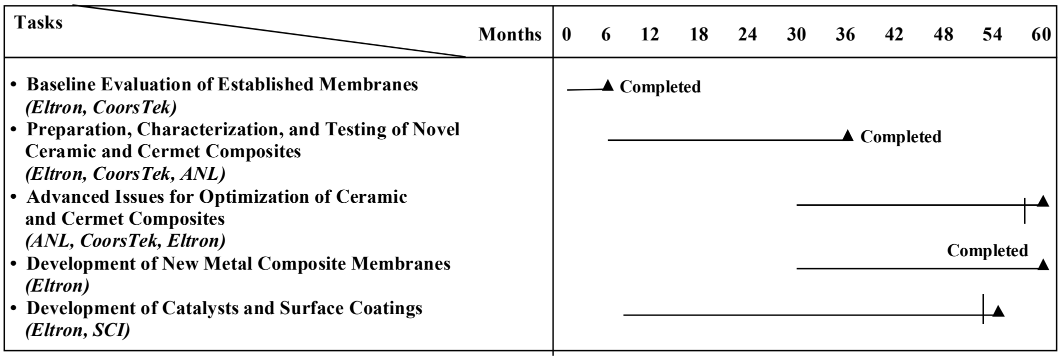
## OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

None.

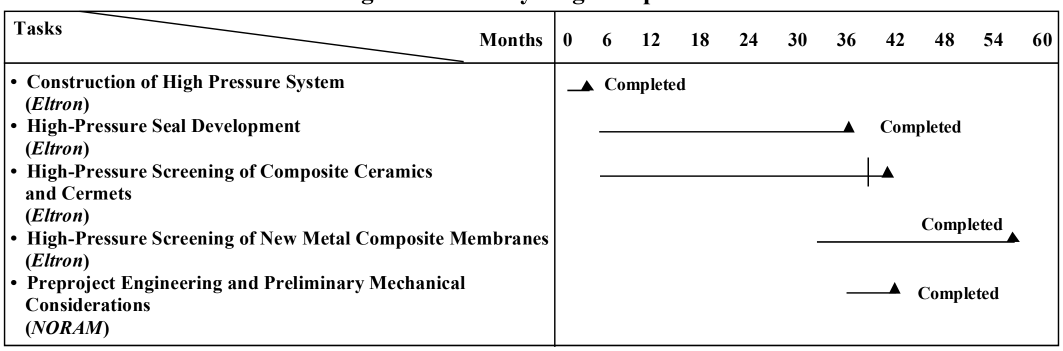
## TIME LINES

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

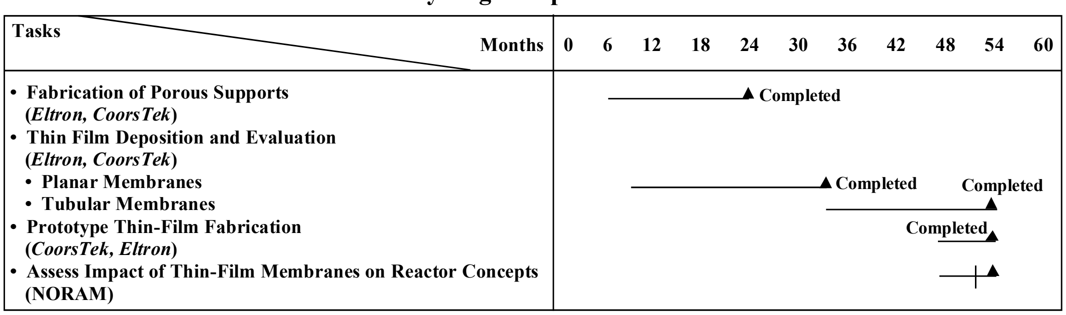
## *Tasks 1 & 2*
## Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes



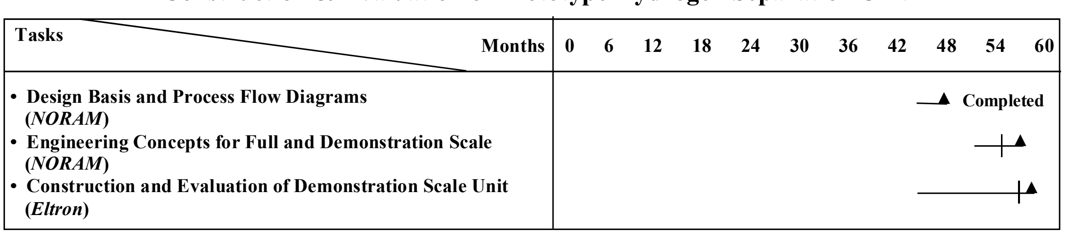

## *Task 3*
## High-Pressure Hydrogen Separation




## *Task 4*
## Thin-Film Hydrogen Separation Membranes




## *Task 5*
## Construction & Evaluation of Prototype Hydrogen Separation Unit



## *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*) | |

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