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TABLE OF CONTENTS

	<u>Page</u>
Disclaimer	3
Abstract	4
Introduction	5
Experimental	6
Results and Discussion	6
Tasks 1 & 2 Preparation, Characterization, and Evaluation of Hydrogen Transport Membranes	6
Task 3 High Pressure Hydrogen Separation	14
Task 4 Thin-Film Hydrogen Separation Membranes	15
Task 5 Construction and Evaluation of Prototype Hydrogen Separation Unit	16
Task 6 Membrane-Promoted Conversion of Alkanes to Olefins	16
Summary and Conclusions	16
Objectives for Next Reporting Period	17
Open Items or Cooperative Agreement Changes	17
References	18
Timelines	19

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ABSTRACT

Eltron Research Inc., and team members CoorsTek, Süd Chemie, and Argonne National Laboratory 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. This objective is being pursued using dense membranes based in part on Eltron-patented ceramic materials with a demonstrated ability for proton and electron conduction. The technical goals are being addressed by modifying composite membrane composition and microstructure to maximize hydrogen permeation without loss of material stability. 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.

During this quarter, a composite metal membrane based on an inexpensive hydrogen-permeable metal achieved permeation rates in excess of 25 mL/min/cm². Preliminary attempts to incorporate this metal into a cermet were successful, and a thick cermet membrane (0.83 mm) with 40 vol.% metal phase achieved a permeation rate of nearly 0.4 mL/min/cm². Increasing the metal phase content and decreasing membrane thickness should significantly increase permeation, while maintaining the benefits derived from cermets. Two-phase ceramic/ceramic composite membranes had low hydrogen permeability, likely due to interdiffusion of constituents between the phases. However, these materials did demonstrate high resistance to corrosion, and might be good candidates for other composite membranes. Temperature-programmed reduction measurements indicated that model cermet materials absorbed 2.5 times as much hydrogen than the pure ceramic analogs. This characteristic, in addition to higher electron conductivity, likely explains the relatively high permeation for these cermets. Incorporation of catalysts with ceramics and cermets increased hydrogen uptake by 800 to more than 900%. Finally, new high-pressure seals were developed for cermet membranes that maintained a pressure differential of 250 psi. This result indicated that the approach for high-pressure seal development could be adapted for a range of compositions. Other items discussed in this report include mechanical testing, new proton conducting ceramics, supported thin films, and alkane to olefin conversion.

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. This objective will be accomplished by employing dense ceramic and composite membranes based in part on Eltron-patented materials¹⁻³ with a demonstrated ability for rapid hydrogen ion and electron conduction. The primary technical challenge in achieving the goals of this project will be to optimize membrane composition and microstructure 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), and Argonne National Laboratory (ANL).

Currently, this project is focusing on three basic categories of membranes: i) ceramic/ceramic composites ii) high-temperature ceramic/metal composites (cermets), and iii) intermediate-temperature cermets. A comparison of these membranes is presented in Table 1. The ceramic/ceramic composites demonstrate the lowest hydrogen permeation rates, with a maximum of approximately 0.1 mL/min/cm² for 0.5-mm thick membranes at 800 to 950°C. Under equivalent conditions, cermets achieve a hydrogen permeation rate near 1 mL/min/cm², and the metal phase also improves structural stability and surface catalysis for hydrogen dissociation. Furthermore, if metals with high hydrogen permeability are used in cermets, permeation rates near 4 mL/min/cm² are achievable with relatively thick membranes. Intermediate-temperature cermets are more difficult to fabricate and the characteristics of these materials have not yet been thoroughly determined. However, at this time experimental data indicate that an order of magnitude improvement in hydrogen permeation relative to high-temperature analogs at temperatures near 400°C is possible. Consequently, these membranes will be more compatible with upstream desulfurization systems.

During this quarter, a composite metal membrane based on an inexpensive hydrogen-permeable metal achieved permeation rates in excess of 25 mL/min/cm². Preliminary attempts to incorporate this metal into a cermet were successful, and a thick cermet membrane (0.83 mm) with 40 vol.% metal phase achieved a permeation rate of nearly 0.4 mL/min/cm². Increasing the metal phase content and decreasing membrane thickness should significantly increase permeation, while maintaining the benefits derived from cermets. Two-phase ceramic/ceramic composite membranes had low hydrogen permeability, likely due to interdiffusion of constituents between the phases. However, these materials did demonstrate high resistance to corrosion, and might be good candidates for other composite membranes. Temperature-programmed reduction measurements indicated that model cermet materials absorbed 2.5 times as much hydrogen than the pure ceramic analogs. This characteristic, in addition to higher electron conductivity, likely explains the relatively high permeation for these cermets. Incorporation of catalysts with ceramics and cermets increased hydrogen uptake by 800 to more than 900%. Finally, new high-pressure seals were developed for cermet membranes that maintained a pressure differential of 250 psi. This result indicated that the approach for high-pressure seal development could be adapted for a range of compositions. Other items discussed in this report include mechanical testing, new proton conducting ceramics, supported thin films, and alkane to olefin conversion.

Table 1.
Summary of Hydrogen Separation Membrane Characteristics.

Composite Membrane	Thickness (mm)	Temperature (°C)	Separation Rate (mL/min/cm²)	Ambipolar Conductivity (S/cm)	Permeability (mol·m/m²/s/Pa^{0.5})
Ceramic/ceramic	0.1 to 0.5	800 to 950	- 0.1	1 x 10 ⁻⁴ to 5 x 10 ⁻³	N/A
High-temp. cermet	0.1 to 0.5	800 to 950	- 1.0	2 x 10 ⁻⁴ to 1 x 10 ⁻²	N/A
High-temp. cermet w/ H ₂ -perm metal	0.1 to 0.5	600 to 950	- 4	N/A	- 10 ⁻⁸ 600 to 950EC
Intermed.-temp. composite membrane	0.05 to 0.5	300 to 500	>15 (Anticipated)	N/A	- 10 ⁻⁷ 380 to 450EC

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, ANL

I. Cermets Containing Metals with High Hydrogen Permeability – Eltron

Cermets containing H₂ permeable metals demonstrate significantly higher permeation rates than other analogs, and potentially operate at temperatures more compatible with gas cleanup technologies. Unfortunately, many of these metals and alloys are very expensive. Membranes currently under development attempt to overcome these limitations either by minimizing the metal content, or focusing on much less expensive metals and alloys. Preliminary results for the former type of membrane were described in the previous report, and consist of a graded structure where the metal phase primarily is restricted to a thin film on one surface. This arrangement is analogous to

a supported thin metal film membrane, except that the metal film is very well integrated with the support and the membrane is prepared using conventional ceramic processing methods.

Development of inexpensive membranes with H₂ permeable metals was initiated by first testing the permeation characteristics of the metal phase alone. The best results to date are shown in Figure 1. These results were for a 0.13-mm thick composite metal membrane (not a cermet) and were obtained using a low to intermediate temperature flange for sealing. At only 400°C, this membrane permeated nearly 20 mL/min/cm² of H₂ (corrected for STP) with no leak. Permeation increased steadily to 24.6 mL/min/cm² at 470°C; however, due to the nature of the sealing flange, higher temperatures were not tested.

Figure 2 shows results for the same sample at 400°C as a function of the Ar sweep rate. Permeation increased steadily with sweep rate between 144 to 568 mL/min. At the highest sweep rate tested, a maximum permeation rate of 27 mL/min/cm² was achieved. Results for this metal composite membrane corresponded to a maximum diffusivity of - 1 x 10⁻⁶ m²/s, a permeability of - 2 x 10⁻⁷ mol·m/m²/s/Pa^{0.5}, and an apparent activation energy of - 21 kJ/mol.

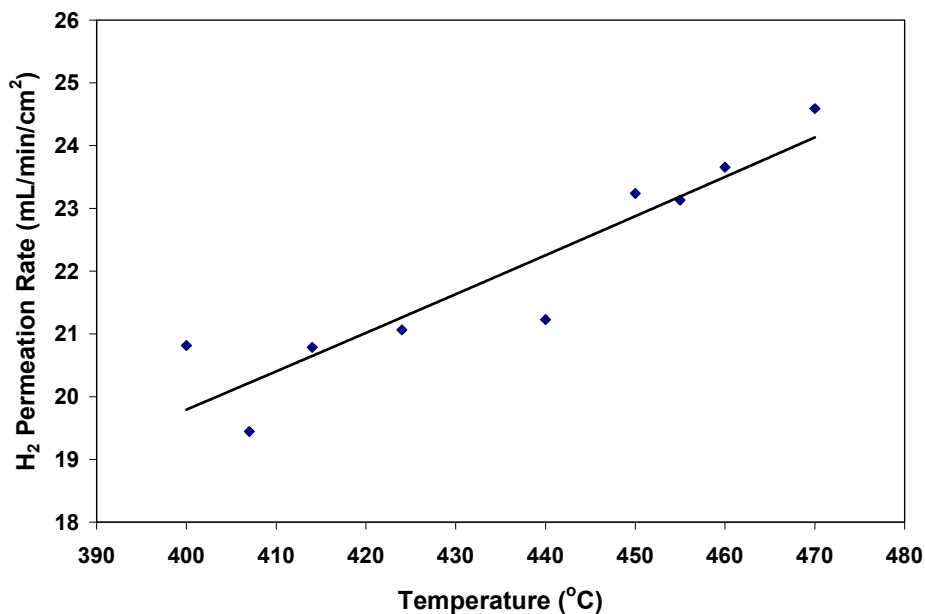


Figure 1. Hydrogen permeation rate as a function of temperature for a composite metal membrane. The permeation rate was corrected for standard temperature and pressure. The feed gas was - 170 mL/min 80/20 H₂/He and the sweep gas was - 250 mL/min Ar.

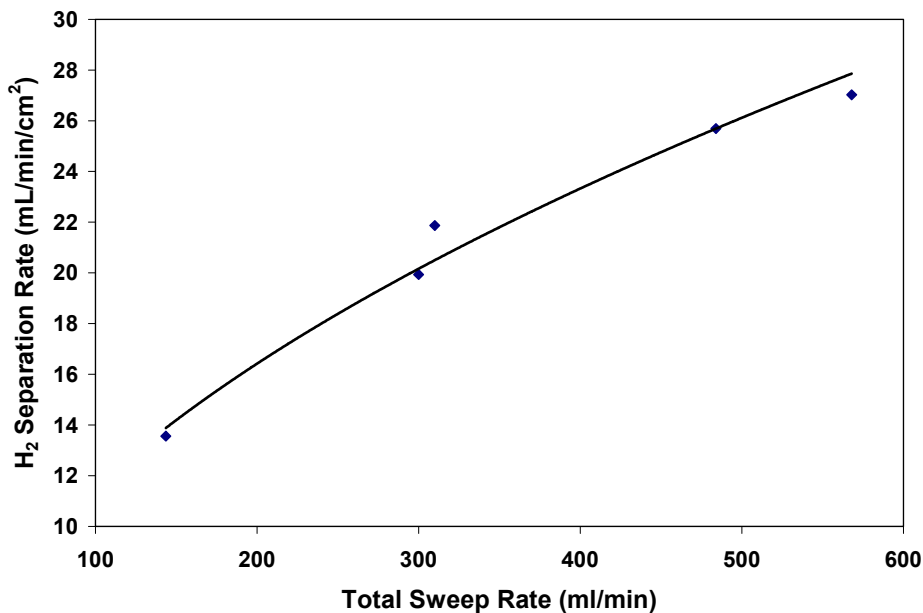


Figure 2. Hydrogen permeation rate dependence on sweep gas rate for a metal composite membrane at 400°C. The permeation rate was corrected for standard temperature and pressure. The feed gas was - 170 mL/min 80/20 H₂/He and the sweep gas was Ar.

Unlike expensive H₂ permeable metals (*e.g.*, Pd and its alloys), incorporation of the above material into a cermet is difficult due to metal reactivity. The first attempts to produce cermet analogs resulted in structurally stable membranes; however, in addition to the ceramic and metal phases, undesired oxide and carbide phases also were present. Adjusting the sintering conditions and atmosphere improved the membrane compositions, and most of the residual undesired phases were limited to the membrane surface. Slight sanding of the surfaces nearly eliminated evidence of these phases in the XRD patterns.

Figure 3 contains H₂ permeation data as a function of time for a cermet represented as CER3/60 vol.% Metal-2, where CER3 is a ceramic with negligible proton conductivity or H₂ permeation and Metal-2 is the primary component of the composite metal membrane in Figures 1 and 2. The membrane was 0.83 mm thick and did not contain a catalyst to promote H₂ dissociation or protect the surface. Only results at high-temperature were obtained (750°C) and the data shows a substantial decrease in permeation from 0.37 to 0.21 mL/min/cm² over 193 minutes of testing. Post-run XRD analysis revealed dramatic changes to both the feed and sweep sides of the membrane, which explain the loss of permeation. Specifically, the sweep side demonstrated a reduction in the metal-to-ceramic ratio and a significant quantity of the oxide of the metal phase (likely from a leak in the system). The feed side also showed a reduction in the metal-to-ceramic ratio, as well as the presence of numerous unidentified peaks. These peaks did not appear to be associated with common hydrides or oxides of the metal phase. SEM analysis of the membrane before and after permeation measurements corroborated the XRD results and demonstrated major morphological changes, including an increase in surface roughness and extensive micro-cracks. These results highlight the reactivity of the metal phase and underscore the need for a

protective/catalytic surface coating with this category of membrane. Also, it is likely that this test temperature was much too high for this category of materials.

A second set of membranes were prepared with only 40 vol.% Metal-2, and the membranes were coated with a 0.1- μ m thick Pd layer on each side. XRD analysis confirmed the presence of the ceramic and metal phases, in addition to a significant quantity of an undesired carbide. For this sample, testing was initiated at 700°C and permeation measurements were obtained as the membrane cooled at 1°C/min. The results are shown in Figure 4. A direct comparison to the above membrane was not possible since testing was performed at a lower temperature (*i.e.*, 700 instead of 750°C). However, the maximum permeation rate of 0.18 mL/min/cm² was roughly two times lower than the analog with 60 vol.% metal. This permeation rate corresponded to an apparent diffusivity 2.8×10^{-8} m²/s, a permeability of 4.1×10^{-9} mol·m/m²/s/Pa^{0.5}, and activation energy of 53 kJ/mol. Despite the Pd coating, post run XRD analysis indicated formation of oxides of the metal phase on both sides of the membrane, and a hydride of the metal phase on the H₂ feed side. Subsequent SEM/EDX analysis revealed that the 0.1- μ m Pd film was not sufficient to cover the membrane surface.

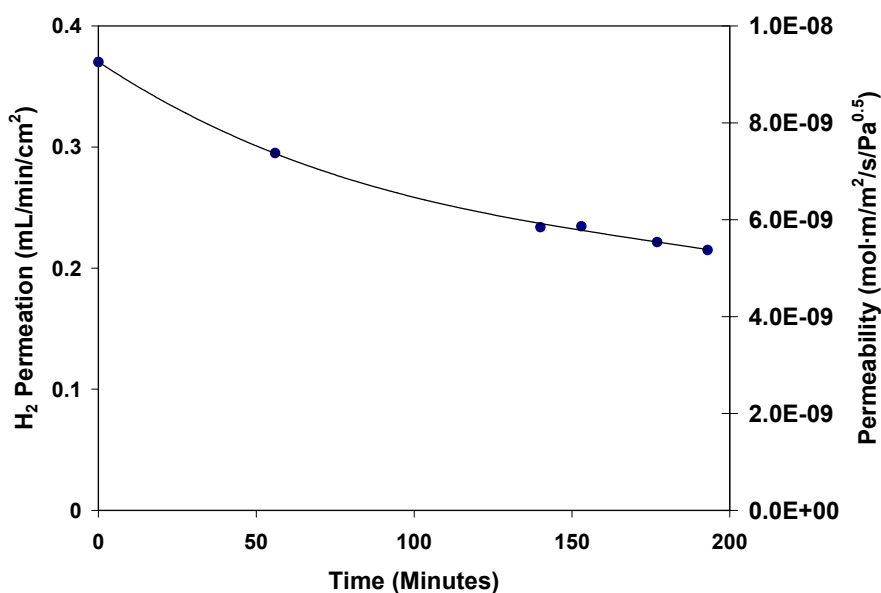


Figure 3. Hydrogen permeation as a function of time at 750°C for a 0.83-mm thick cermet represented as CER3/60 vol.% Metal-2. The membrane did not contain a catalyst. The feed gas was 80 mL/min 80/20 H₂/He and the sweep gas was - 110 mL/min Ar.

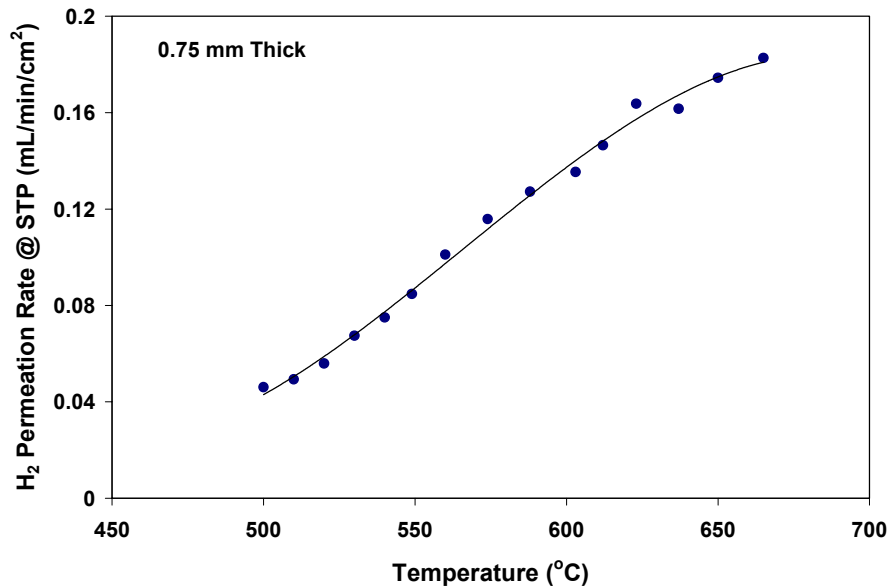


Figure 4. Hydrogen permeation rate as a function of temperature for a 0.75-mm thick membrane with the composition CER3/40 vol.% Metal-2. The membrane contained a 0.1- μ m thick Pd layer on each side. The feed gas was 80/20 H₂/He at 80 mL/min and the sweep gas was Ar at - 111 mL/min. Permeation rates were corrected for standard temperature and pressure.

II. Two-Phase Ceramic/Ceramic Composites – CoorsTek, Eltron

Effort was continued optimizing the fabrication of two-phase ceramic/ceramic composite membranes represented as AB_{0.8}B^c_{0.2}O_{3- δ} /CER1 and AB_{0.8}B^c_{0.2}O_{3- δ} /CER2. Although these materials demonstrate lower H₂ permeation than other membranes under development, results from these studies are indicating that a significant increase in ceramic chemical stability can be achieved with this approach (discussed below). Hence, stabilized ceramics identified by these efforts have good potential for cermets.

The challenge in fabricating this category of membranes is to achieve a dense membrane without migration of constituents between the two phases. Such migration of cations can compromise both the proton and electron conductivity of the material, and dramatically reduce H₂ permeation. As indicated in the previous report, this problem has impeded development of the material represented as AB_{0.8}B^c_{0.2}O_{3- δ} /CER1. Numerous batches were prepared with varying quantities of each phase and with an excess of the B^c dopant in an effort to minimize migration; however, none of these approaches were successful. For this composition, the main problem is migration of the perovskite B-site cation into the CER1 phase. Although the resulting membrane is mechanically stable, a maximum H₂ permeation of only 0.027 mL/min/cm² for a 0.2-mm thick membrane was achieved.

Alternatively, a second composition represented as $AB_{0.8}B^c_{0.2}O_{3-\delta}$ /CER2 demonstrated no interdiffusion, and rough measurements using an ohmmeter indicated good electrical conductivity. Unfortunately, constituents of the CER2 phase react with the membrane seal material and no permeation test have been successful to date. To overcome this problem, a compression flange system was tested; however, the membranes cracked under mechanical pressure. O-rings with much higher malleability were purchased and it is anticipated that these will enable testing of this composition during the next reporting period.

III. Membrane Mechanical Testing and Chemical Stability – CoorsTek

Mechanical tests were performed on model proton-conducting ceramics and cermets to establish a baseline for mechanical properties and assess the effect of adding a metal phase on material strength. Table 2 presents a summary of four-point bend flexural strength and Weibull modulus measurements for the ceramic $AB_{0.8}B^c_{0.2}O_{3-\delta}$ and the corresponding cermet $AB_{0.8}B^c_{0.2}O_{3-\delta}$ /40 wt.% Metal-1. These results indicated that addition of the metal phase significantly increased material strength and improved the Weibull Modulus (a measurement of the flaw distribution within the material). Considering the much higher H_2 permeation of cermets relative to ceramics, these results were very encouraging.

Resistance to corrosion from water was measured for selected compositions by boiling samples in deionized water for two hours and measuring the sample weight loss. The results are summarized in Table 3. The sample with the worst corrosion resistance was the pure ceramic $AB_{0.8}B^c_{0.2}O_{3-\delta}$. The cermet analogs also showed substantial corrosion, however, the weight loss was not as high as expected based on corrosion for the ceramic. This result indicated that the metal phase had a slight stabilizing effect on the ceramic. The $AB_{0.8}B^c_{0.2}O_{3-\delta}$ /CER1 sample was very stable and demonstrated only a 0.24-% weight loss, and the $AB_{0.8}B^c_{0.2}O_{3-\delta}$ /CER2 demonstrated no weight loss. Considering that this latter sample consisted of distinct $AB_{0.8}B^c_{0.2}O_{3-\delta}$ and CER2 phases, the high stability was surprising.

These data were used to design a set of experiments to determine the minimum amount of the CER phase that can be added to stabilize the parent ceramic. Results from these tests will be presented in the next report.

Table 2.
Summary of Mechanical Testing of Model Ceramic and Cermet Materials.

Composition	Test	Microbars (2 mm x 1.5 mm)	Minibars (4 mm x 3 mm)
$AB_{0.8}B^c_{0.2}O_{3-\delta}$	4-Pt. Bend Flexural Strength (MPa)	72.4	67.7
$AB_{0.8}B^c_{0.2}O_{3-\delta}$ /Metal-1		153	149
$AB_{0.8}B^c_{0.2}O_{3-\delta}$	Weibull Modulus	14.0	N/A*
$AB_{0.8}B^c_{0.2}O_{3-\delta}$ /Metal-1		20.4	15

*Not calculated due to the small number of samples.

For the ceramic, eight microbars and four minibars were tested. For the cermet, 20 microbars and 10 minibars were

Table 3.
Weight Loss for Selected Membrane Samples after Boiling in Water for 2 Hours.

Composition	Initial Weight (g)	Final Weight (g)	Weight Loss (%)
$AB_{0.8}B^c_{0.2}O_{3-\delta}$	1.8357	0.5316	71.0
$AB_{0.8}B^c_{0.2}O_{3-\delta}/44$ wt.% Metal-1	1.9188	1.6116	16.0
$AB_{0.8}B^d_{0.2}O_{3-\delta}/44$ wt.% Metal-1	1.9032	1.5759	17.2
$AB_{0.8}B^c_{0.2}O_{3-\delta}/CER1$	1.8962	1.8917	0.24
$AB_{0.8}B^c_{0.2}O_{3-\delta}/CER2$	1.8977	1.8977	0.00

IV. Evaluation of New Proton Conducting Ceramics – ANL

ANL is contributing to this project by looking for new proton conducting materials with improved properties. Cerate-based perovskites exhibit high proton conductivity in hydrogen-containing atmospheres at elevated temperatures,⁴ however, they easily decompose in the presence of CO₂ at low temperatures (below 800°C) and hence lose their proton conduction.⁵ Lack of good mechanical properties is another factor that hinders the application of cerate-based materials. To develop a more rugged alternative to the cerates, Eltron and ANL are studying acceptor-doped titanates because they may have better mechanical strength and better stability in CO₂-containing atmosphere. While these compounds do not possess high proton conductivity because of their very low proton concentrations, the diffusivity of protons in these compounds is extremely high.⁶ Therefore, although these materials may not yield high hydrogen fluxes, the results from this study may give useful information to engineer new formulations with both high hydrogen flux and good stability.

Titanate ceramics were synthesized using two different dopants over a wide concentration range, and XRD analysis indicated that these materials were single phase. Total conductivity was measured under a variety of atmospheres using a four-point DC method. The range of total conductivity measured for these samples was between 10⁻³ and 10⁻¹ S/cm. The samples with the higher presumed proton conductivity showed poor stability under reducing conditions, and crumbled after prolonged exposure to a H₂/N₂ atmosphere. The second category of materials appeared stable under reducing conditions and had a maximum total conductivity of - 5 x 10⁻² S/cm. However, based on the conductivity dependence on atmosphere, it is likely that these materials had low proton conductivity. These experiments will be repeated during the next reporting period using similar materials with a different perovskite A-site cation. Additionally, investigation of the effect of cermet grain size on conductivity will be initiated.

V. Membrane Surface Catalysis – SCI

Surface catalysis has not demonstrated an effect on H₂ permeation rates for any of the materials tested to date. Within the membrane thickness range evaluated, it is likely that for ceramic materials the permeation process was completely limited by diffusion through the bulk. Cermet membranes demonstrated much higher permeation; however, the metal phase had good catalytic

properties and, again, no improvement in permeation was achieved by adding surface catalysts.

The difficulty in preparing, handling, and testing thin film membranes makes routine evaluation of catalysts impractical. Accordingly, potential catalysts now are being evaluated using temperature-programmed reduction (TPR) measurements on catalyst-impregnated membrane precursor powders. Results from these tests will be used to facilitate the design of composite catalysts with high H₂ uptake and dissociation, as well as stability under operating conditions.

Figure 5 shows the TPR data for precursor powders of the ceramic AB_{0.8}B^c_{0.2}O_{3-δ} and the corresponding cermet AB_{0.8}B^c_{0.2}O_{3-δ}/44 wt.% Metal-1 without any added catalyst. The effect of the metal phase was apparent by a dramatic increase in the H₂ uptake and a sharp peak centered at 212°C. Samples of these powders were impregnated with Pt, Pd, Cr, and Ni and the TPR results are summarized in Table 4. Initially, addition of Pt had little effect on H₂ uptake relative to the catalyst-free powder, and Pd only increased uptake slightly. More significant gains were achieved using Cr and Ni catalysts, which increased uptake by 98 and 168%, respectively. However, when Cl-based precursors were used, H₂ uptake increased more than three-fold for Pt and nearly an order of magnitude for Pd. The sample impregnated with 0.25 wt.% Pd using the chloride precursor absorbed 2248 F mol of H₂ per gram of catalysts, corresponding to a 951% increase relative to the catalyst-free powder. The catalyst-free cermet had a very high H₂ uptake of 538.8 F g/mol, which partly explains the relatively high H₂ flux with this material. Moreover, addition of 0.25 wt.% Pd to this sample resulted in the highest H₂ uptake of 5070 F mol/g.

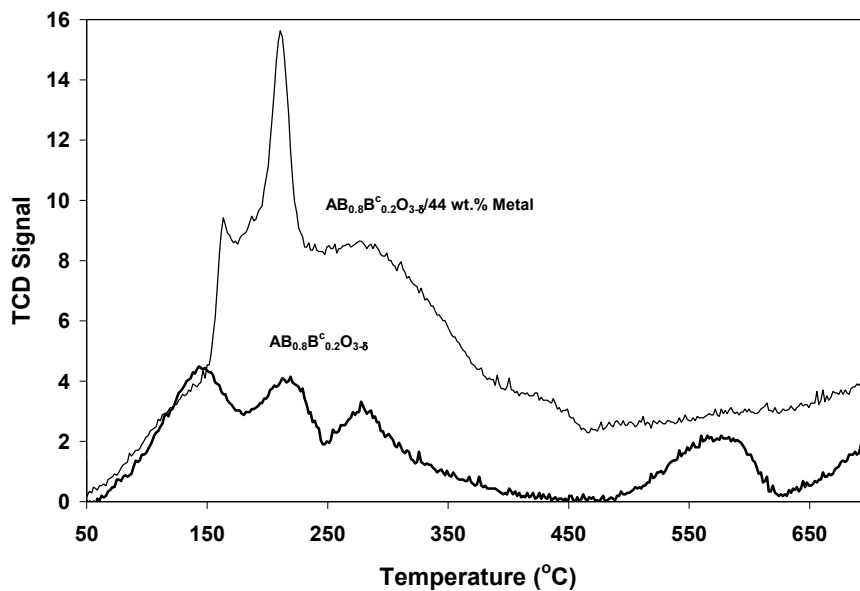


Figure 5. TPR results for ceramic and cermet membrane precursor powders without catalyst.

Table 4.
H₂ Uptake Calculations Based on TPR Results for
Selected Membrane Materials and Catalysts.

Sample	Catalyst	H₂ Uptake (F mol/g)	Change from Bare Material (%)
AB _{0.8} B ^c _{0.2} O _{3-δ}	None	213.9	–
AB _{0.8} B ^c _{0.2} O _{3-δ}	0.25 wt.% Pt	200.7	- 6.20
AB _{0.8} B ^c _{0.2} O _{3-δ}	0.25 wt.% Pd	254.3	18.9
AB _{0.8} B ^c _{0.2} O _{3-δ}	0.25 wt.% Cr	423.5	98.0
AB _{0.8} B ^c _{0.2} O _{3-δ}	0.25 wt.% Ni	573.2	168
AB _{0.8} B ^c _{0.2} O _{3-δ}	0.25 wt.% Pt (chloride precursor)	900.4	321
AB _{0.8} B ^c _{0.2} O _{3-δ}	0.25 wt.% Pd (chloride precursor)	2248	951
AB _{0.8} B ^c _{0.2} O _{3-δ} / 44 wt.% Metal-1	None	538.8	–
AB _{0.8} B ^c _{0.2} O _{3-δ} / 44 wt.% Metal-1	0.25 wt.% Pd	5070	841

Task 3 High Pressure Hydrogen Separation

Contributors: Eltron

Operation of dense ceramic hydrogen separation membranes at high temperatures and pressures requires a chemically resistant seal with similar mechanical and expansion characteristics as the membrane material. Seal materials are being developed and tested using a closed-one-end tube configuration. Seal formation was achieved by ramping the cell assembly up to 1000°C in 10% H₂/90% N₂ and holding for a period of time. The assembly then was cooled to 800°C, for seal evaluation. To date, high-pressure seals focused on ceramic membranes only, and a seal was maintained at a differential pressure of - 250 psi for 2000 hours before termination of the test. To determine the versatility of the approach, a seal was developed during this reporting period for cermet membranes. Multiple tests were performed using the AB_{0.8}B^c_{0.2}O_{3-δ}/44 wt.% Metal-1 cermet composition and seals were routinely maintained at pressures in excess of 200 psi, with a maximum of 250 psi during a 72-hour test.

Task 4 Thin-Film Hydrogen Separation Membranes

Contributors: Eltron, CoorsTek

Efforts to fabricate thin films were continued using $AB_{0.8}B^c_{0.2}O_{3-\delta}$ /44 wt.% Metal-1 cermet as a model material. Membranes were fabricated with two and three thin film layers tape cast on porous supports; however, only the three-layer samples were sufficiently dense to achieve acceptable seals for testing. Figure 6 shows results for a 1.9-mm thick sample with a 0.1-mm thick membrane. Although this thickness was within the range routinely achieved by grinding standard membrane samples, the H_2 permeation rate was about three times lower than the best results for this composition. This decreased performance might be the result of resistance through the porous support.

CoorsTek focused on optimizing the binder burnout step during thin film fabrication, and successfully produced defect-free parts. Furthermore, CoorsTek also continued efforts to mechanically generate very thin membranes by experimenting with precursor particle sizes and annealing steps. To date, membranes as thin as 50 Fm were successfully fabricated using this approach. It is anticipated that these structures either will be coupled to a support structure or the method will be applied to reduce the thickness of layered structures.

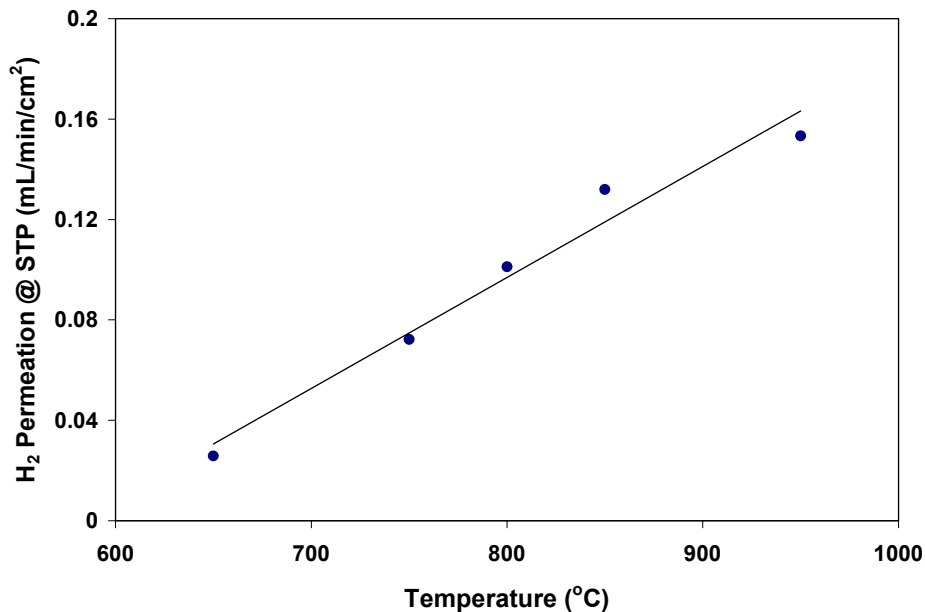


Figure 6. H_2 permeation as a function of temperature for a 0.1-mm thick three-layer tape cast membrane on a porous support. The membrane composition was $AB_{0.8}B^c_{0.2}O_{3-\delta}$ /44 wt.% Metal-1. The feed gas was 80/20 H_2 /He and the sweep gas was Ar. Gas flow rates were between 80 and 110 mL/min.

Task 5 *Construction and Evaluation of Prototype Hydrogen Separation Unit*

Contributors: Eltron, CoorsTek

Limited actions related to prototype device design and identification of test conditions were continued. Also, thin-walled tube membranes were fabricated for testing in the high-pressure separation unit.

Task 6 *Membrane-Promoted Conversion of Alkanes to Olefins*

Contributors: Eltron

Conversion of propane to propene was monitored at 650°C using a 0.21-mm thick cermet membrane represented as $AB_{0.8}B^c_{0.2}O_{3-\delta}/60$ vol.% Metal-2. The membrane was coated with a Pt catalyst to promote dehydrogenation. The feed gas was 80 mL/min of 10% propane (bal. Ar) and 15 mL/min He. Using 120 mL/min Ar on the membrane permeate side, conversion of propane was only 18.5% and the propene yield was only 4.4%. H_2 permeation through the membrane resulting from propane dehydrogenation was approximately 0.014 mL/min/cm². These low values reflect the very low membrane surface area (0.42 cm²) and catalyst content relative to the membrane cell volume, propane concentration, and gas flow rates. Switching the sweep gas to 80 mL/min air and 40 mL/min Ar increased the propene concentration by only 3.4%, corresponding to a propene yield of 4.6%. This increase in dehydrogenation using air on the sweep side results from the greater driving force for H_2 migration when permeate H_2 is oxidized to H_2O .

Although these results were not compelling, hydrogen from the dehydrogenation of propane did permeate through the membrane and increasing the driving force did affect propene yield. The next experiments will employ larger membrane and catalyst areas and lower feed gas residence times in an effort to amplify the effect of the membrane.

SUMMARY AND CONCLUSIONS

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

- A composite metal membrane based on an inexpensive H_2 -permeable metal achieved permeation rates in excess of 25 mL/min/cm². Preliminary attempts to incorporate this metal into a cermet were successful, and thick cermet membrane (0.83 mm) with 40 vol.% metal phase achieved a permeation rate of nearly 0.4 mL/min/cm². Increasing the metal phase content and decreasing membrane thickness should significantly increase permeation for this category of cermets. However, these materials exhibited poor stability in the absence of a protective surface coating.
- Two-phase ceramic/ceramic composite membranes had low H_2 permeability, likely due to interdiffusion of constituents between the phases. However, these materials did demonstrate high resistance to corrosion from water, and might be good candidates for other composite membranes.

- Preliminary mechanical testing indicated much higher material strength and improved Weibull modulus for cermets relative to ceramics.
- A range of titanate ceramics demonstrated either poor stability in H₂ or negligible proton conductivity.
- TPR measurements indicated that model cermet materials absorbed 2.5 times as much H₂ than the pure ceramic analogs. This characteristic, in addition to higher electron conductivity, likely explains the relatively high permeation for these cermets. Incorporation of catalysts with these ceramics and cermets increased H₂ uptake by 800 to more than 900%.
- New high-pressure seals were developed for cermet membranes that maintained a pressure differential of 250 psi. This result indicated that the approach for high-pressure seal development could be adapted for a range of compositions.
- Supported thin film membranes were successfully fabricated. Only samples with three thin film layers were dense enough to permit testing, and these samples demonstrated permeation rates approximately three times lower than analogous membranes produced by conventional methods.

OBJECTIVES FOR NEXT REPORTING PERIOD

During the next reporting period, effort at Eltron will focus on development of membranes with inexpensive H₂ permeable metals. In particular, the effect of adequate surface coatings will be assessed. Other tasks to be continued during the next quarter include:

- testing of multi-phase ceramics and cermets
- refining manufacturing of selected membrane compositions
- catalyst testing
- membrane stability studies
- testing catalytic membrane reactors for propane dehydrogenation
- outlining requirements for prototype and incorporation into a Vision 21 plant
- mechanical testing of candidate membrane compositions
- development of thin film membranes

OPEN ITEMS OR COOPERATIVE AGREEMENT CHANGES

McDermott Technology, Inc. (MTI) ceased operations on December 31, 2002. Negotiations are underway to transfer MTI's role on this project to SOFCo (also owned by MTI's parent, McDermott).

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