Novel, Ceramic Membrane System For Hydrogen Separation

Final Report

Reporting Period: Sep. 30, 2009 – Dec. 31, 2012

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Report Date: August 13, 2013

DOE Award Number: DE-FE0001045

Submitted by:

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This material is based upon work supported by the Department of Energy under Award Number(s) DE-FE0001045

Abstract

Separation of hydrogen from coal gas represents one of the most promising ways to produce alternative sources of fuel. Ceramatec, teamed with CoorsTek and Sandia National Laboratories has developed materials technology for a pressure driven, high temperature proton-electron mixed conducting membrane system to remove hydrogen from the syngas. This system separates high purity hydrogen and isolates high pressure CO_2 as the retentate, which is amenable to low cost capture and transport to storage sites.

The team demonstrated a highly efficient, pressure-driven hydrogen separation membrane to generate high purity hydrogen from syngas using a novel ceramic-ceramic composite membrane. Recognizing the benefits and limitations of present membrane systems, the all-ceramic system has been developed to address the key technical challenges related to materials performance under actual operating conditions, while retaining the advantages of thermal and process compatibility offered by the ceramic membranes. The feasibility of the concept has already been demonstrated at Ceramatec. This project developed advanced materials composition for potential integration with water gas shift rectors to maximize the hydrogen production.

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Executive Summary

Separation of hydrogen from coal gas represents one of the most promising ways to produce alternative sources of fuel. Ceramatec, teamed with CoorsTek and Sandia National Laboratories has developed materials technology for a pressure driven, high temperature proton-electron mixed conducting membrane system to remove hydrogen from the syngas. This system will separate high purity hydrogen and isolate high pressure CO_2 as the retentate, which is amenable to low cost capture and transport to storage sites.

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Major tasks included: (1) design of a membrane separation wafer material for operation at conditions typical of coal gasification process temperature, pressure, and gas composition; (2) optimization of membrane materials for high protonic conductivity, and high pressure differential; (3) evaluation of the mechanical and thermomechanical properties of the membrane materials; (4) development of effective ceramic-to-metal seals; (5) testing and optimization of hydrogen separation efficiency; (6) modeling, design, fabrication, and optimization of wafer stacks for desired hydrogen flux; (7) cost analysis of wafer fabrication and detailed specification of manufacturing capital and operating costs; (8) long-term testing and (9) preliminary evaluation of sulfur tolerance.

Among the key objectives proposed, the following were demonstrated:

A) *Effective membrane proton conductivity of 0.02 S/cm at ~ 600 °C, corresponding to >150 scfh/ft^2 wafer hydrogen separation;*
B) *Preliminary wafer design (layer thickness, channel dimensions) for < $200/ft^2 fabrication feasibility; and,*
C) *Mechanical strength evaluation of sintered membranes.*

Project Objectives

Separation of hydrogen from coal gas represents one of the most promising ways to produce alternative sources of fuel. Ceramatec, teamed with CoorsTek and Sandia National Laboratories is developing a pressure driven, high temperature proton-electron mixed conducting membrane system to remove hydrogen from the syngas. This system will separate high purity hydrogen and isolate high pressure CO_2 as the retentate, which is amenable to low cost capture and transport to storage sites.

The team plans to demonstrate a highly efficient, pressure-driven hydrogen separation module that will separate high purity hydrogen from syngas using a *novel ceramic-ceramic composite membrane*. The ceramic composite, consisting of a proton and an electron conducting dual phase, patented by Ceramatec has been shown previously to be hydrogen selective. The objectives of the three year project are: a) improve membrane proton conductivity through dopant modification; b) measure hydrogen flux at relevant temperature range, pressure, and composition conditions; and c) scale up membrane device to demonstrate a prototype that allows meaningful extrapolation of performance data and process economics to larger commercial systems. To achieve these objectives, Sandia National Laboratories will perform mechanical testing of bar and membrane samples to provide estimation of device reliability; and CoorsTek, a multinational ceramic manufacturing company, will perform cost analysis to select cost effective manufacturing technique. Chevron, who is a member of Ceramatec's oxygen separation membrane research alliance has shown interest in this technology and will be a candidate for potential commercial partnership.

The team combines Ceramatec's strength in ionic conducting ceramic membrane research with CoorsTek's ceramic manufacturing capability and Sandia's materials characterization competence to provide an innovative solution to separate hydrogen from syngas without the use of precious metals.

Overview of Technical Concept

DOE is interested in technologies for hydrogen separation that do not use expensive and strategic precious metal. This can be achieved by the use of proposed all-ceramic composite membrane. The syngas from the coal based facilities, rich in hydrogen and CO_2 and at high pressure is ideally suited for hydrogen separation. The proposed concept utilizes a pressure driven, high temperature proton conducting membrane system to remove hydrogen from the syngas. The process will essentially isolate high pressure CO_2 as the retentate to allow for low cost capture and transport to storage sites.

The team intends to demonstrate a highly efficient, pressure-driven hydrogen separation module that will generate high purity hydrogen from coal-based syngas using a novel ceramic-ceramic composite membrane.[1] Recognizing the benefits and limitations of present membrane systems, the all-ceramic system has been developed to address the key technical challenges related to materials performance under actual operating conditions, while retaining the advantages of thermal and process compatibility offered by the ceramic membranes. The feasibility of the concept has already been demonstrated at Ceramatec, where supported membranes thin enough to achieve high hydrogen fluxes have been fabricated. This project seeks to address the remaining technical hurdles that will need to

be overcome in order to achieve commercially viable hydrogen flux at practical temperatures and pressures and to demonstrate a scaled up hydrogen separation membrane device.

Project Scope

Ceramatec, Inc., teamed with CoorsTek and Sandia National Laboratories, will accomplish project objectives over a three-year period by utilizing a multi-stage work scope. Major tasks include: (1) design of a membrane separation wafer material for operation at conditions typical of coal gasification process temperature, pressure, and gas composition; (2) optimization of membrane materials for sulfur tolerance, high protonic conductivity, and high pressure differential; (3) evaluation of the mechanical and thermomechanical properties of the membrane materials; (4) development of effective ceramic-to-metal seals; (5) testing and optimization of hydrogen separation efficiency; (6) modeling, design, fabrication, and optimization of wafer stacks for desired hydrogen flux; (7) cost analysis of wafer fabrication and detailed specification of manufacturing capital and operating costs; and (8) long-term testing (>1,000 hours) of multi-wafer stacks at realistic syngas composition and operating temperatures and pressures.

Development Need

Modern gasifier and water-gas shift (WGS) reactor technology produce synthesis gas, a mixture primarily of H_2, CO, and CO_2. Advances in hydrogen membrane separation technologies have the potential to reduce costs, improve efficiency, and simplify hydrogen production technologies.[2] Desirable membrane characteristics include: high hydrogen flux at low pressure drops, contaminant tolerance especially sulfur and CO; low cost; and operating temperatures of 250 – 600°C. The membrane system alternative to precious metal membrane that has been extensively evaluated is cermet membrane, a ceramic – metal composite. In general Ni is used as the metallic component although Pd has been evaluated also. Table 1 shows the reported performance of cermet membrane[2] and 2015 DOE target.[3,4]

Table 1. Technical Targets: Proton Transport Cermet Membranes for Hydrogen Separation and Purification			
Performance Criteria	**Units**	**Cermet Status**	**2015 Target**
Flux (for 100 psi ΔP hydrogen partial pressure)	scfh/ft^2	~ 220	200 (in 2010) 300
Cost	$/ft^2 of membrane	<200	<$100
Durability	Years	<1(estimated)	>5
ΔP Operating Capability	psi	100	400-1000
Hydrogen Purity	% of total (dry) gas	>90%	99.99%
Sulfur tolerance	ppmv	~ 20	> 100
Temperature	°C	300 – 400	250 - 550

However, available literature data on cermet (possibly containing Ni or Pd) is shown to provide a flux of ~ 40 scfh/ft^2 (20 cm^3/min-cm^2) at 900°C.[5] *Major challenges still remain in demonstrating higher flux at the lower temperature (550°C to 600°C) using non-precious metal based membranes that is contaminant tolerant.*

Under this program, Ceramatec is investigating the use of a pressure driven, high temperature hydrogen ion conducting membrane device to remove hydrogen from the syngas. An overview of present membrane technology is given in the Appendix.

Technical Concept and Approach

Significant technical work has been performed in the hydrogen membrane area with DOE's support[6] and on-site NETL research. Our proposed concept differs significantly in regards to the membrane materials. A novel, dense, ceramic-ceramic composite mixed protonic/electronic conductor membrane developed at Ceramatec under a previous DOE project[7] has been the foundation of the current project.

In a pressure driven system, both hydrogen ions and electrons generated by dissociation of H$_2$ molecules at the high-pressure surface must be transported through the membrane to recombine at the low-pressure surface. Since these two are parallel kinetic processes, the overall kinetics are limited by the slowest process. In the case of a conventional mixed conducting single-phase membrane, the paths for proton conduction and electron conduction are the same. The proton flux (j_{H+}) through a membrane of thickness L, where the primary charge carrying species are H$^+$ and e$^-$ can be shown as:

$$j_{H^+} = \frac{1}{L}\left[-\frac{kT}{2e^2} \int_i^o \left(\sigma t_{H^+} t_{e^-} \right) d\ln p_{H_2} \right] \qquad (1)$$

where k is the Boltzman constant, T is the absolute temperature in Kelvin, e is the magnitude of the electronic charge, σ is the total conductivity, p_{H2} is the partial pressure of hydrogen and t_{H+} and t_{e-} are the transference numbers of H+ ions and electrons through the membrane. The hydrogen flux thus depends on having high conductivity for both species. The electronic conductivity of perovskites is the limiting factor for use as pressure-driven hydrogen separation membranes. For example, the electronic conductivity of SrCe$_{1-x}$Y$_x$O$_{3-\delta}$ is shown to be 2 to 3 orders of magnitude lower than its protonic conductivity at 800°C.[8]

Our approach is to separate the conduction paths for H$^+$ ions and electrons through the incorporation of a *ceramic second phase* to short-circuit the electron flow-paths. This approach essentially eliminates the combined dependence of hydrogen flux on electronic and proton conductivities.

In addition to being a good electronic conductor at these temperatures, the material chosen as the second phase should also possess good thermomechanical and thermochemical stability (with ambient gases and the proton conducting perovskite) at conditions involving high temperatures (membrane operating temperature to sintering temperature) and pressures > 300 psi. Further, the material must be relatively cost-effective and easily processed to meet DOE cost goals. A ceramic-ceramic composite material has been developed, in which independent migration of proton and electron species occurs through an interpenetrating network of proton and electron conducting ceramic phases.

Advantages of all-ceramic composite membrane

The primary benefit in selecting a ceramic second phase as the electronic conductor arises from the thermochemical compatibility of the two phases. By the appropriate selection of compositions, the thermal expansion coefficient of the two phases can be matched to allow for thermal cycling of the membrane device. Unlike a cermet composite, the all-ceramic composite is not subjected to dewetting of the second phase during fabrication and device operation and does not promote formation of carbon filaments in the presence of CO and CO_2. In addition to the lower cost of the second phase material, traditional ceramic processing techniques such as tape casting and air sintering can be used to fabricate the composite membrane devices. Thus, the hydrogen membrane devices fabricated using ceramic composite materials can be low-cost.

Materials Selection

The cerate based perovskite materials such as $SrCeO_3$ and $BaCeO_3$ have been extensively characterized for hydrogen conductivity. Thus, they make good candidates as the primary ion-conducting phase. By themselves these perovskite phases exhibit very low electronic conduction, and thus require addition of an electronically conductive second phase. However, the selection of a second ceramic phase that is an electronic conductor in reducing atmosphere is a challenge. In addition, it would be beneficial if the second phase helps overcome the stability issues that have been hindering the potential use of cerate materials in hydrogen separation application. One of the fundamental limitations encountered in the use of cerate materials is their inherent instability in CO_2 and H_2O containing atmospheres. The cerate perovskite materials dissociate according to:

$$ACeO_3 + CO_2 = ACO_2 + CeO_2 \qquad [1] \qquad\qquad ACeO_3 + H_2O = A(OH)_2 + CeO_2 \qquad [2]$$

where A is Ba or Sr. One approach to reduce the tendency for these materials to react with CO_2 or H_2O is to add the reaction product CeO_2 to the perovskite phase. This should favor the equilibrium of the reactions to maintain the desired phase. An intimate and well-dispersed mixture of the two phases is less likely to react with CO_2 or H_2O than the baseline perovskite.

Doped ceria compositions have been evaluated as a solid electrolyte material for oxygen separation[9-12] and solid oxide fuel cell[13-16] applications due to their high oxygen ion conductivity. While they function well as an oxygen conductor in air for oxygen separation, their applicability in fuel cell application is compromised by their mixed conducting property in the low oxygen partial pressures (pO_2) of fuels. In fact, the electronic conduction of ceria compositions is an order of magnitude higher in hydrogen than their oxygen ion conductivity in air.[17] The mixed conductivity in ceria results from the oxygen non-stoichiometry in low pO_2. In reducing atmospheres, the ceria phase reduces according to:

$$2CeO_2 = Ce_2O_3 + \tfrac{1}{2} O_2 \qquad\qquad\qquad [3]$$

Using Kröger-Vink notation, it can be written,

$$4\ O_O + 2\ Ce_{Ce} = 2\ Ce'_{Ce} + 3\ O_O + V_O^{\cdot\cdot} + \tfrac{1}{2} O_2 \qquad\qquad [4]$$

$$Ce'_{Ce} = Ce_{Ce} + e' \qquad\qquad\qquad [5]$$
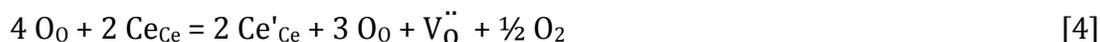
While the mixed conduction is detrimental to fuel cell application, the high electronic conductivity of doped ceria in low pO_2 conditions can be exploited in hydrogen separation membrane technology. The thermochemical (both phases are in thermodynamic equilibrium), thermal expansion and processing compatibilities of the two oxides in the composite make perovskite-ceria combination ideally suitable for the mixed conducting membrane application.

While our previous work focused on developing the composite for 900°C operation, under the proposed program additional optimization is necessary to provide high hydrogen flux under operating conditions of ~600°C. These optimized mixed-conducting composite membranes will allow pressure-driven hydrogen separation at 300 - 600°C at *higher hydrogen flux* than are possible with single phase membranes, *higher stability* than ceramic-metal composite, and *higher selectivity* (>99.9%) than molecular sieve membranes. The basic concept is illustrated in 1(a), and a possible component design is shown in 1(b).

Prior Work at Ceramatec

Hydrogen Flux Measurement

Under the DOE-funded program, the feasibility of the ceramic-ceramic composite for pressure driven hydrogen separation was successfully demonstrated. The material demonstrated good mixed-conducting properties to allow a flux at 900°C of ~2.8 scfh/ft² through a 500-μm thick freestanding membrane and ~ 40 scfh/ft² through a 35-μm thick supported membrane at a hydrogen partial pressure ratio of about 2 (2). Assuming the transport is controlled by bulk properties, this flux is equivalent to ~140 scfh/ft² through a 10-μm thick membrane under the same conditions. Pressure dependence of the hydrogen flux was also tested at lower temperatures (3). Extrapolating the data, one can estimate a flux of 20 cc/cm²-min (~ 40 scfh/ft²) can be achieved using a 10-μm thick membrane at ~ 600°C. Thus, *the focus of the present research would be to increase the flux about three-fold at 50 to 100°C lower temperature.*

(a) (b)
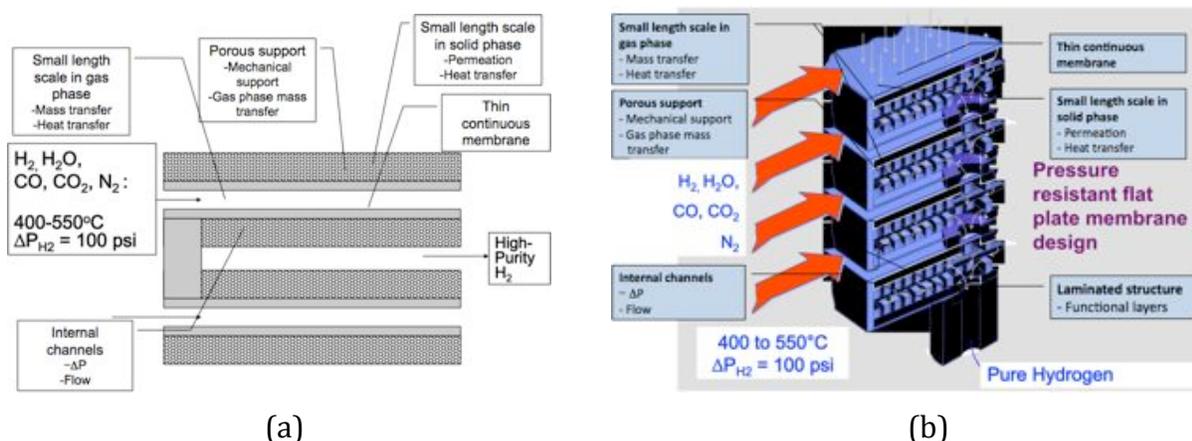
1. (a) Illustration of a thin membrane supported on porous ceramic;
(b) Device design.
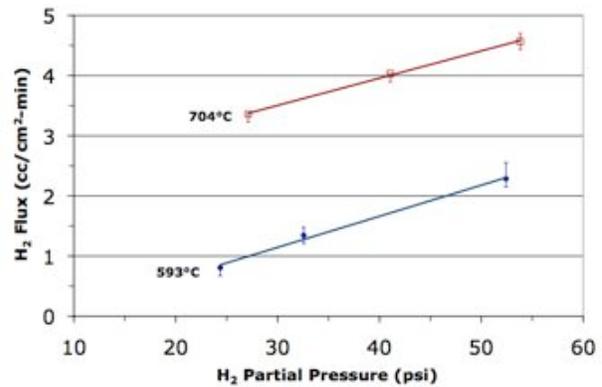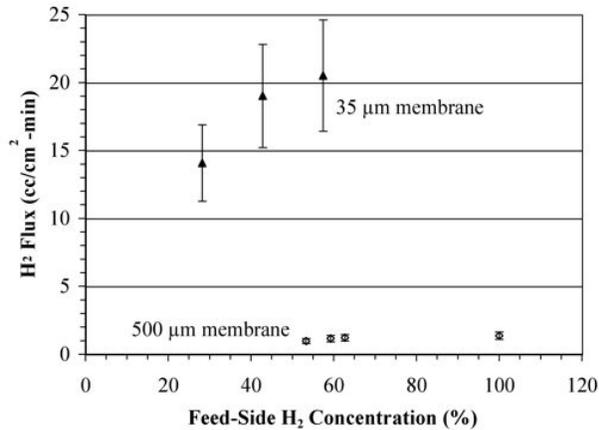
2. Concentration-driven H_2 flux at 900°C
(Feed side: H_2, balance N_2)

3. Pressure-driven H_2 flux (~50μm thick)
(Feed side: H_2, CO, CO_2, CH_4)

Material Stability Evaluation

It was demonstrated that the composite material has <u>increased thermochemical stability in CO_2 containing atmospheres</u> compared to conventional proton conductors (see Figures 4 and 5). The composite showed negligible carbonate formation after 4-hr after a 4-hr exposure to syngas at 900°C.

Prior fabrication technology for tape casting of thin layers, lamination, and sintering of complex geometries, developed under a DOE funded membrane program, was used to fabricate the composite ceramic proton-electron conducting membrane. 6 shows the sintered structure of a ~ 25 micron (1 mil) thick, dense composite layer supported on a thicker (200 micron) porous layer. The channel structure for gas flow, formed by dense layers on top and bottom is also seen in the Figure. A single wafer module based on the membrane technology was also fabricated, shown in 7.

Material Strength Measurement

Strength bars were fabricated using Barium cerate by itself and two composites (60:40 cerate to ceria and 40:60 cerate to ceria). The test conditions and results are shown in 8. A 40% ceria degrades strength only marginally, but high Weibull modulus is retained. With the supported structure, a slight decrease in strength should not be detrimental.

The specific technical hurdles that need to be overcome prior to commercial scale demonstration of the membrane technology are listed below:

1) Membrane materials optimization for specific operation conditions;
2) Ceramic-to-metal seal development;
3) Long-term stability studies on membrane devices, and component design and materials optimization to maximize device life under operation conditions; and
4) Sub-commercial scale demonstration of commercial level hydrogen flux.
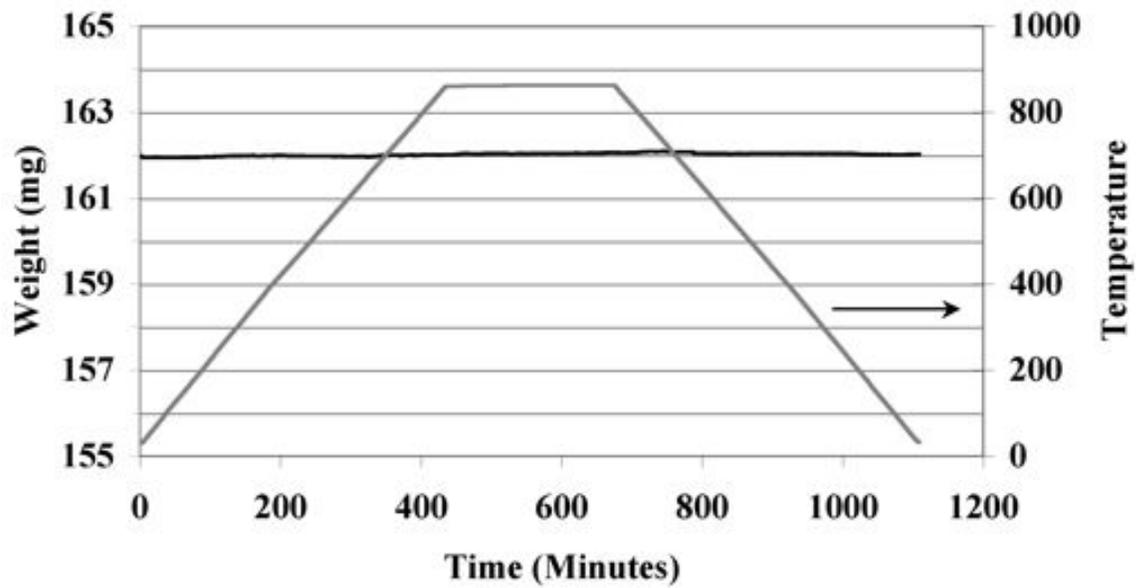
4. Thermogravimetry of composite powder sample showing no weight gain as a result of exposure to syngas
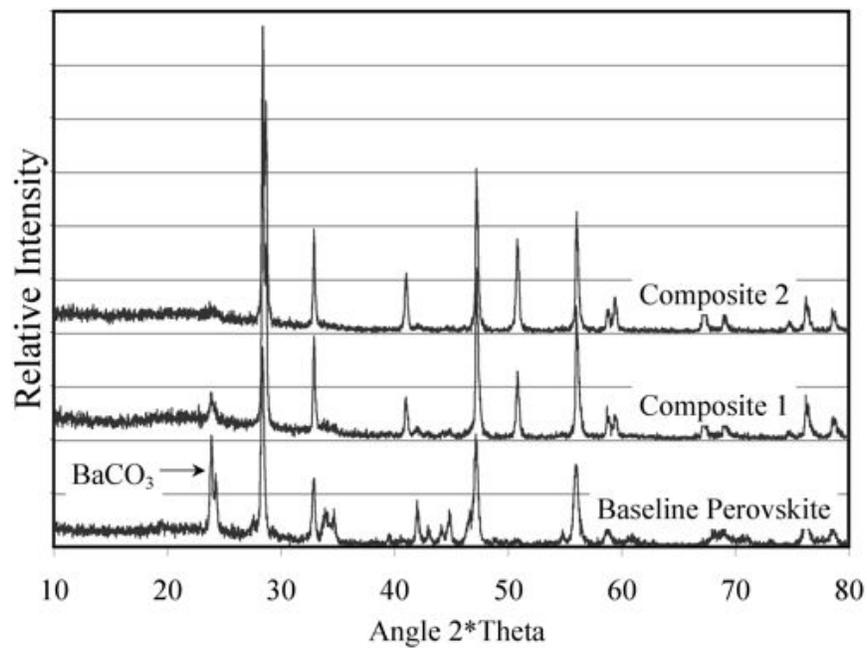
5. X-ray diffraction pattern of baseline $BaCeO_3$ and the composite exposed to syngas (in powder form) at 900°C
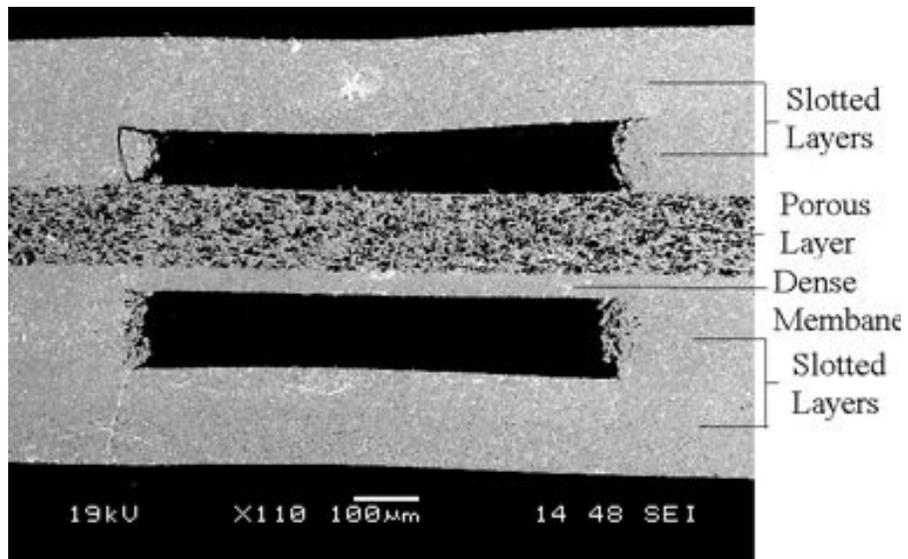
6. Sintered membrane structure

7. Full Size Membrane (~ 5 x 5 inch)

a) Ba-Cerate only Loading Rate: 20 MPa/s; Relative Humidity: 50% Weibull modulus=22, Characteristic Strength=95 MPa	b) Composite 1 60 % Ba-Cerate- 40% Ceria composite; Loading Rate: 20 MPa/s; Relative Humidity: 50% Weibull modulus=17.9, Characteristic Strength=81 MPa
c) Composite 2 40 % Ba-Cerate- 60% Ceria composite; Loading Rate: 20 MPa/ s; Relative Humidity: 50% Weibull modulus=6.7, Characteristic Strength=92 MPa Low strength sample (marked by arrow) appears to be a pre-existing crack	d) Summary of Strength Data

8. Strength Test Results of Proton conductor and Composite Materials

Technical Progress

High-Temperature, High-Pressure Membranes for Hydrogen Separation

Goals and Objectives

The overall project goal is to develop a ceramic membrane hydrogen separation system that can extract over 200 scfh/ft^2 of hydrogen from syngas at >99.5% separation efficiency at typical coal gasification conditions with a projected manufacturing cost of less than $100/ft^2, without the use of precious metals. A prototype of the device will be operated continuously for at least 1,000 hours to demonstrate design suitability.

In order to achieve the above goals, the objectives for the three-year project are:

- Improve membrane proton conductivity through dopant modification;

- Measure hydrogen flux at relevant temperature, pressure, and gas composition conditions; and

- Scale up membrane devices to demonstrate a prototype that allows for meaningful extrapolation of performance data and process economics to larger commercial systems.

Wafer design for membrane separation unit

The wafer design targeted in the previous DOE program was specifically intended for pressure-driven separation of hydrogen at 900°C from coal-derived syngas in IGCC systems and requires modifications for efficient performance at the target lower temperatures (~ 600°C). Ceramatec has well established process models and design tools that were used to reevaluate the device design. The parameters for the design study included operating conditions (pressure, temperature and gas composition) typical for coal gasification processes, and membrane material properties (target proton conduction and prior strength results).

Wafer Design
Task Highlights:
- A preliminary wafer design has been established with dual active surfaces.

- The thicknesses of the individual layers within the membrane have been established.

- The calculated stresses within the wafer are within design allowance suggesting high reliability.

Accomplishments:
Sub-Task 1.1 Definition of Performance Metrics

Objective: Define and document the performance metrics for the hydrogen separation wafer. This includes the primary metrics as defined in the SOPO and the secondary objectives such as mechanical stress limits and internal pressure drop.

Synopsis: Primary Metric – Flux: The initial flux target for the hydrogen membrane is 150 scfh of hydrogen per square foot of membrane while operating at 600°C with a hydrogen feed pressure of 100 psi.

Secondary Metric – Stress: Early developments of the hydrogen membrane materials produced the strength data whereby design allowables could be estimated. Based on a Ba-Cerate Ceria composite, the following weibull strength properties were achieved:

s_0 = 81 MPa [Characteristic Strength of dense material]

s_0 = 16.2 MPa [Characteristic Strength of porous material – estimated from Trostel and Rice models for 30% porous materials]

m = 17.9 [weibull modulus]

Assuming wafer failure criteria of 1^{-10}, an allowable design stress can be calculated based on the formula and yields the allowable design stresses for the dense and porous materials:

$$\sigma_{allowable} = \sigma_0 \left(\ln(\frac{1}{1-f}) \right)^{1/m}$$

Dense allowable stress: $s_{allowable}$ = 22.4 MPa

Porous allowable stress: $s_{allowable}$ = 4.5 MPa

Secondary Metric – Pressure Drop: Although this metric is yet to be determined, it seems reasonable as an initial objective to maintain this loss to about 1% of the hydrogen feed pressure of 100 psi. This yields an internal pressure drop of 1 psi or about 50 torr. Process and flow models will be used to determine the impact and feasibility of this target.

Sub-Task 1.2 Membrane Preliminary Design

Objective: Develop a preliminary design whereby the primary metric (hydrogen flux) can be attained and the design can be analyzed to assure the secondary metrics (stress and pressure drop) can be met.

Synopsis: High fluxes will require very thin membranes. Earlier studies demonstrated membranes as thin as 35 microns. However, with hydrogen feed pressure of 100 psi, this thin membrane will require a porous support. Likewise these high fluxes (and low pressure drops) require relatively large open channels for the collection of the hydrogen product. The supported membrane and the open channel design leads to a layered wafer design whereby a porous support can feed transitional channels which communicate to open radial channels for gas collection. This staged porous/channel configuration accommodates both the mechanical stress issues and the internal pressure drop issues.

Large surface area wafers increases the hydrogen production per component, yet requires long radial flow paths and increasingly large channels for the accumulated product. Both of these tend to limit the surface area of an individual wafer in order to minimize mass and cost of the ceramic membrane.

It is assumed that the application of this technology is for large-scale production of hydrogen as might be found downstream of a coal-derived syngas process. This in turn would require large surface areas of membrane. Hence, the membranes or wafers should be easily assembled into arrays of parallel and serial configurations. In heat exchangers this is accomplished using bundles of staggered finned tubes. Likewise, these membranes

can be stacked into modules where the wafers act as fins in a cross-flowing feed gas extracting out pure hydrogen.

The basic repeat unit within this modular stack is the wafer. The wafer is comprised of an external dense membrane to separate the hydrogen out of the feed stream, porous layers to provide mechanical support to the thin membrane, and channeled layers whereby the hydrogen product can be collected to a central manifold. As both the top side and the bottom side are exposed to the feed gases, both sides contain the separation membrane and create a nearly symmetric assembly of layers through the thickness.

Sub-Task 1.3 Mechanical Design

Objective: Through mechanical stress modeling, determine the minimum feature size of the various layers within the membrane such that design stresses are not exceeded.

Synopsis: Based on beam analyses and the channel spans of the preliminary design, the thicknesses of the various layers can be estimated in order to maintain stresses below the design allowables. For example, the dense membrane and porous support form a composite layer which is required to withstand the pressure loads as it spans the First Slotted (S1) layers. Likewise, the first S1 layer is required to span the width of the Second Slotted (S2) layers. And again, the S2 layer is required to span its mirrored S2 layer at the wafer mid-plane. A simplified sketch of this internal repeat unit is shown in 9.
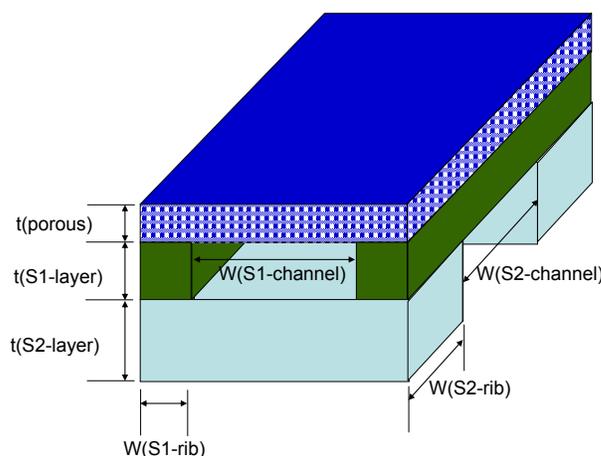
9. Internal Structure Analyzed for Stress Minimization

Based on these beam analyses the thicknesses of the various layers were estimated.

Membrane materials optimization and advanced characterization

The target operating conditions of membrane devices are considerably lower in temperature than our previous intended application. In addition, the sulfur tolerance requirements are expected to vary with the composition of the coal. Therefore, effort will be directed at (1) evaluating the sulfur tolerance of candidate membrane materials and/or selecting membrane materials with greater sulfur tolerance, and (2) identifying and optimizing materials with higher protonic conductivity at lower temperatures (e.g. 350-600°C) than currently known materials. The Ceramatec team is fully aware of prior research attempts to improve proton conductivity of perovskite materials by doping and

the difficulties encountered. Thus, several approaches will be used in parallel to maximize the probability of success of the project.

The primary approach will be to evaluate the effect of various dopants on the proton conductivity of the perovskite. Since our research efforts in developing high proton conductivity materials for 900°C operation, we have extended our investigation into properties at lower temperatures and with the use of modified dopants, i.e. substitutional cations in the Ce-site of the perovskite. Those results are briefly summarized below.

Enhancing Proton Conductivity
Perovskite Composition
Prior work in our laboratory showed that A doping on the Ce-site increases the protonic conductivity of $BaCeO_3$ much more than the traditional Y or Yb doping. Previously we evaluated the effect of modifiying dopants. The purpose of modified dopant is two-fold: substituting a more expensive dopant and potential improvement in conductivity and stability. Eight formulations were synthesized as listed in Table 2. X-ray diffraction patterns (10) showed essentially single phase for all compositions.

Table 2. Compositions Evaluated

	Total Dopant
Formulation 1	0.1
Formulation 8	0.2
Formulation 3	0.1
Formulation 4	0.2
Formulation 5	0.15
Formulation 6	0.15
Formulation 7	0.1
Formulation 8	0.2

Focus was given to determining the conductivity in hydrogen (essentially the proton conduction) at 800°C. The conductivity data are plotted in 11. Based on these results the following trend was observed: At similar dopant level, A doping gives higher conductivity; and modified doping increases the conductivity at a fixed total doping. Some scatter in the data comes from slightly different densities of these various compositions.
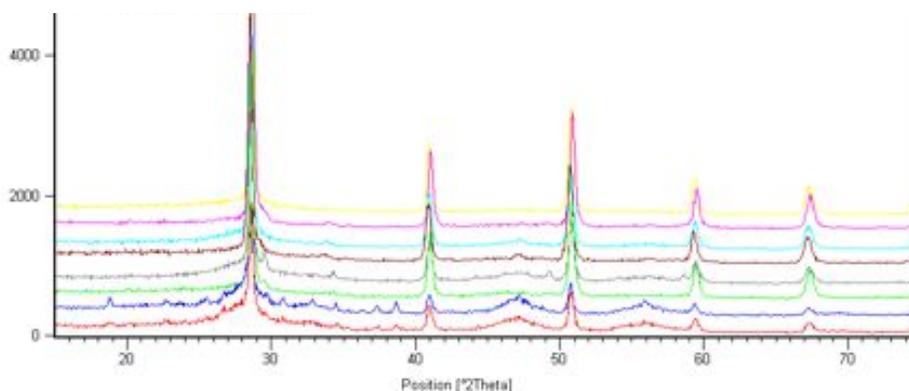
10. Powder X-ray Diffraction Pattern for Various Compositions
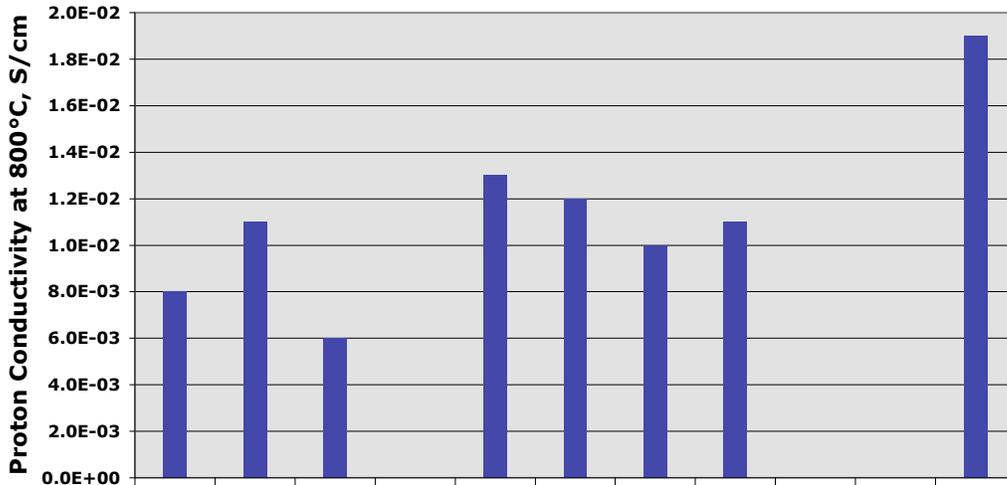
11. Conductivity Measured in Hydrogen for Various Compositions

With A doped (0.3 level) BaCeO$_3$, the conductivity was measured over a range of temperature (12). Even at a temperature of 700°C, the proton conductivity is about 0.014 S/cm.
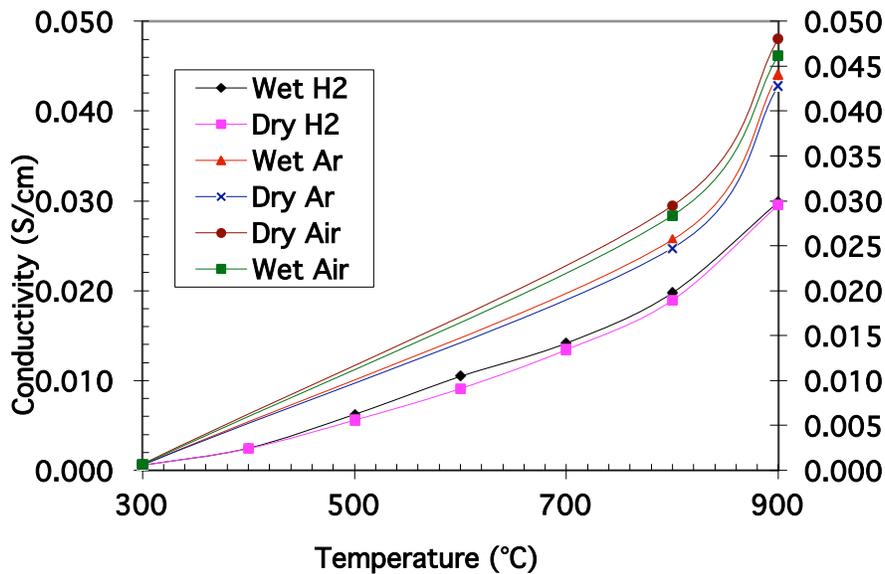
12. Conductivity of 0.3 A-doped Composition at Low Temperatures

Transference Number

Perovskite proton conductors are complex in terms of their conduction mechanism. In oxygen containing atmospheres they are oxygen-electron mixed conductors; in inert atmosphere such Argon they are predominantly electronic conductors; and in hydrogen containing atmospheres they are proton-electron mixed conductors. Determination of proton transference number is not only complicated, the value also depends on the gas atmosphere used for the measurement. Typically, one can measure the conductivity in air,

argon, and hydrogen and assume all conduction in air is oxygen and electronic and all in hydrogen is protonic and electronic to estimate the proton ion transference number. The generally assumed mechanism of proton transport in these materials is the association of H^+ with the 'electron holes'. Thus, a significant portion of the electronic conduction in air becomes the proton conduction in hydrogen. The ratio of conductivity in hydrogen to that in air then will approximate the proton transference number. In such method, the calculated proton transference number is shown in Table 3.

Table 3.Proton Transference Number from Measured Conductivity

Dopant level in $BaCeO_3$	t_{proton}
0.1	0.50
0.2	0.61
0.1	0.50
0.2	0.68
0.15	0.54
0.15	0.52
0.1	0.53
0.2	0.60

Once again, the protonic transference number, t_p increases as a function of total dopant concentration.

Meeting Target Conductivity Through Doping

With a target conductivity of 0.02 S/cm at 600°C in order to meet the required hydrogen flux, additional compositions were prepared based on the earlier indication that modified dopants tend to increase the conductivity. We have previously established that A doping improves the proton conductivity of $BaCeO_3$ composition and that a different dopant further enhances the conductivity. The evaluation thus centered on adding the second dopant. The charts (13) below show the conductivity data from representative samples.
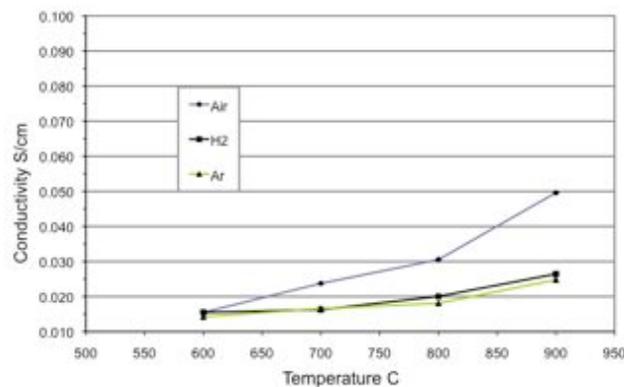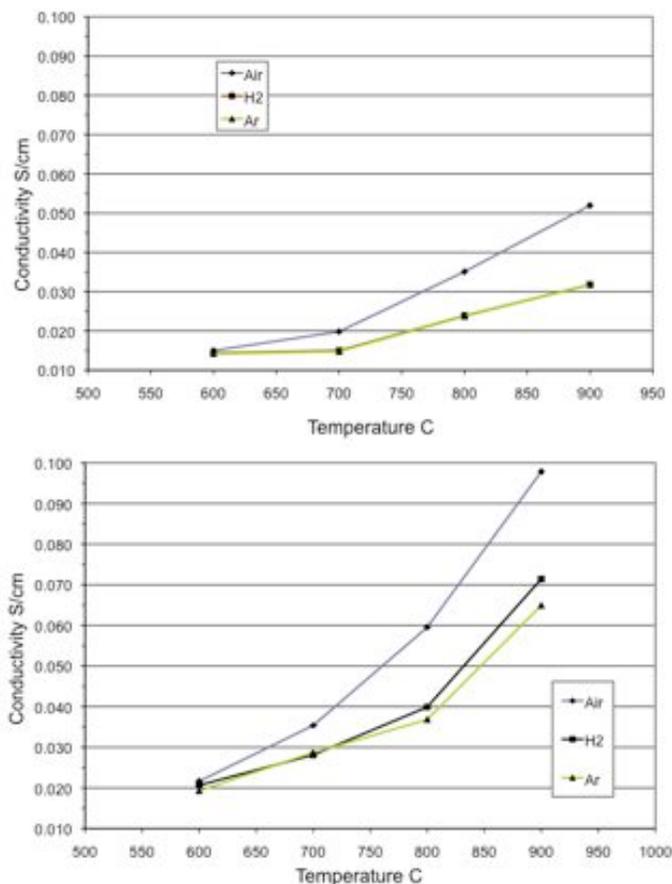
13. Conductivity of doped $BaCeO_3$ compositions in wet Ar, Air, H_2 atmospheres

From the above figure, it is evident that the conductivity in wet hydrogen for a doped $BaCeO_3$ meets the target conductivity set as the milestone for this year. While it is likely that not all the contribution to conduction will be protonic, prior results in our laboratory and those in the literature show that at 600°C these materials are predominantly protonic. Experiments are in progress to separate contributions to conductivity of these compositions from various species, i.e. hydrogen, electrons, and oxygen.

Mechanical and thermomechanical property evaluation (Sandia National Labs.)

Another vital requirement for functional device design is a clear understanding of the mechanical and thermomechanical properties of membrane materials. As mentioned before, due to a delay in the start of the project at Sandia National Laboratory, the testing of strength bars of compositions selected under the current project is moved to year 2. However, Sandia and Ceramatec has mechanical property information from prior test results on similar materials set and the lessons from the results are discussed below.

The following materials were strength tested:
- Composition 2 – $Ba_{.92}Ce_{.70}A_{.3}O_{3-\partial}$ with no composite Ceria added,
- Composition 4 – $Ba_1Ce_{.70}A_{.3}O_{3-\partial}$ with 40 vol%$Ce_{.80}A_{.20}O_{2-\partial}$, and
- Composition 5 – $Ba_{.92}Ce_{.70}A_{.30}O_{3-\partial}$ with 40 vol%$Ce_{.80}A_{.20}O_{2-\partial}$

In addition, billets of pure Cerium oxide, sintered to 80% and 95% density were also fabricated and strength tested for comparison. Composition 1-$Ba_1Ce_{.70}A_{.30}O_{3-\partial}$ with no composite Ceria added did not survive the initial sintering process, while composition 3 $Ba_1Ce_{.70}A_{.30}O_{3-\partial}$ with 60 vol%$Ce_{.80}A_{.20}O_{2-\partial}$, fractured during machining.

The strength testing was accomplished at ambient, under a controlled humidity of 50%, using ASTM-B four point bend bars, with an outer loading span of 40 mm, and an inner span of 20 mm. Between 15-30 samples for each material were fractured. The strength distributions, fitted to a two parameter Weibull distribution are shown in 14.
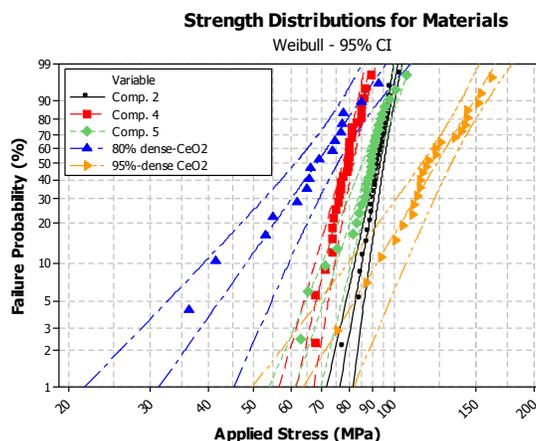
14. Strength distributions for various Ba-Ce compositions, and of ceria of different sintered density.

After fracture of the samples, examination of each sample was conducted to pinpoint the location of failure. For compositions 2 and 4, about 1/3 of the samples failed from edge flaws while the rest failed from surface defects, while for Composition 5 most of the failures were from surface flaws, with a few volume-initiated failures. In all three cases, the edge and surface initiated strengths were similar. From the strength results, it appears that the addition of the ceria to the Barium Cerate slightly degrades the strength. It is also clear that the strength distributions of the materials are bracketed by the high density (95%) and the low density (80%) ceria material. Representative fracture origins in the ceria material are shown in 15. It is apparent that pores, due to either incomplete sintering, or due to defect incorporation during powder pressing, are responsible for low strengths in the materials.

Tape casting process that will be used to make the membrane may eliminate some of the flaws in pressed / sintered components. Several sintering cycles will be evaluated prior to fabricating the next set of strength bar specimens. The new set of strength data will be used to revise the wafer design and to guide the sintering conditions of tape cast laminates.
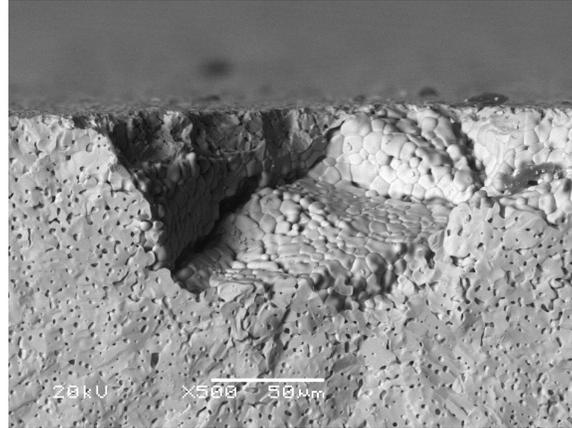
15. Failure origin in 95% dense ceria: surface pore due to poor sintering

15 kg of doped $BaCeO_3$ of higher conductivity composition and doped CeO_2 composite powder were prepared. The powder was finely milled to 1 – 5 µm and combined with 2% PEOX binder and then passed through a 150 mesh screen prior to pressing. This powder was then used to produce 40 billets (2.5 x 2.5 x .25) inches. The billets were uniaxially pressed to 8000 psi in an automatic hydraulic press. The billets were then sintered at 1560 °C over 5 days. These were then sent to Sandia National Labs to be machined into bars for strength testing. In addition, 30 machined bars were returned to us by Sandia for hydrogen reduction. The bars were reduced in batches of 6 at 600 C for 3 hrs. The bars were then returned to Sandia for testing.

Strength test results from the two batches that were sent to Sandia National Laboratory are summarized below. The set of samples for lot 2 used improved sintering technique and likely had fewer and/or smaller flaws and hence higher average strength. For both lots, the reduction slightly lowered the strength.
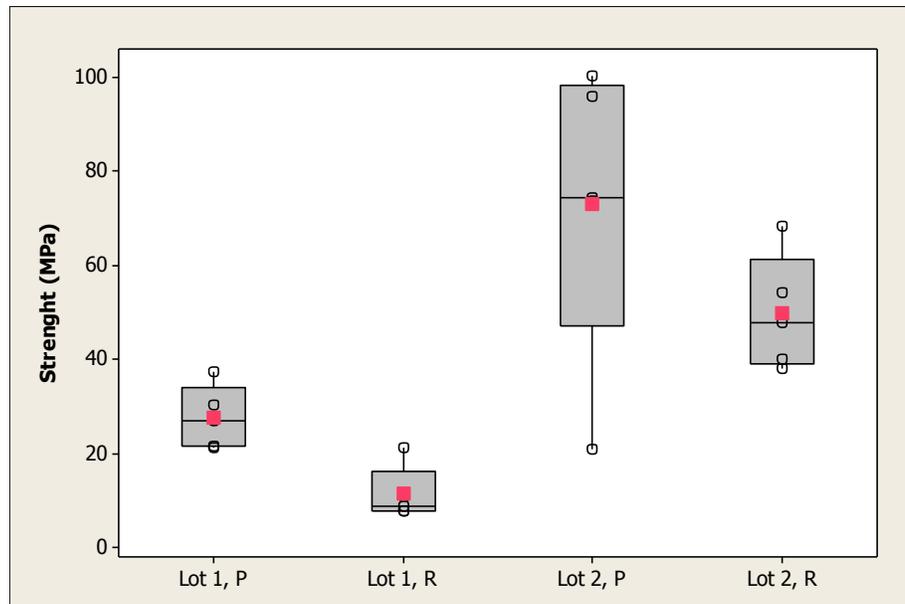
2. Strength Test Results from Bar Samples

P = Pristine (as sintered and machined); R = Sintered bars that were reduced in flowing hydrogen

Ceramic to metal seal development

From previous experience, one of the primary challenges in functional device development is the development of effective ceramic-to-metal seals that permit system manifolding by joining the central ceramic component that carries the high-purity hydrogen to external metallic tubing. Hermetic ceramic-to-ceramic sealing using a transient liquid phase method has been developed for ITM syngas modules and a similar strategy will also need to be evaluated for hydrogen module fabrication. Initial screening of three different glasses was done. The material designated Q-glass shows promising initial results with the least cracks. Proper sealing temperature profile may reduce the cracks even further to provide a good seal. Additional work is needed to identify a thermally compatible manifold and an appropriate seal material.

E glass	E glass-dye check
Q glass	Q glass-dye chck
S glass	
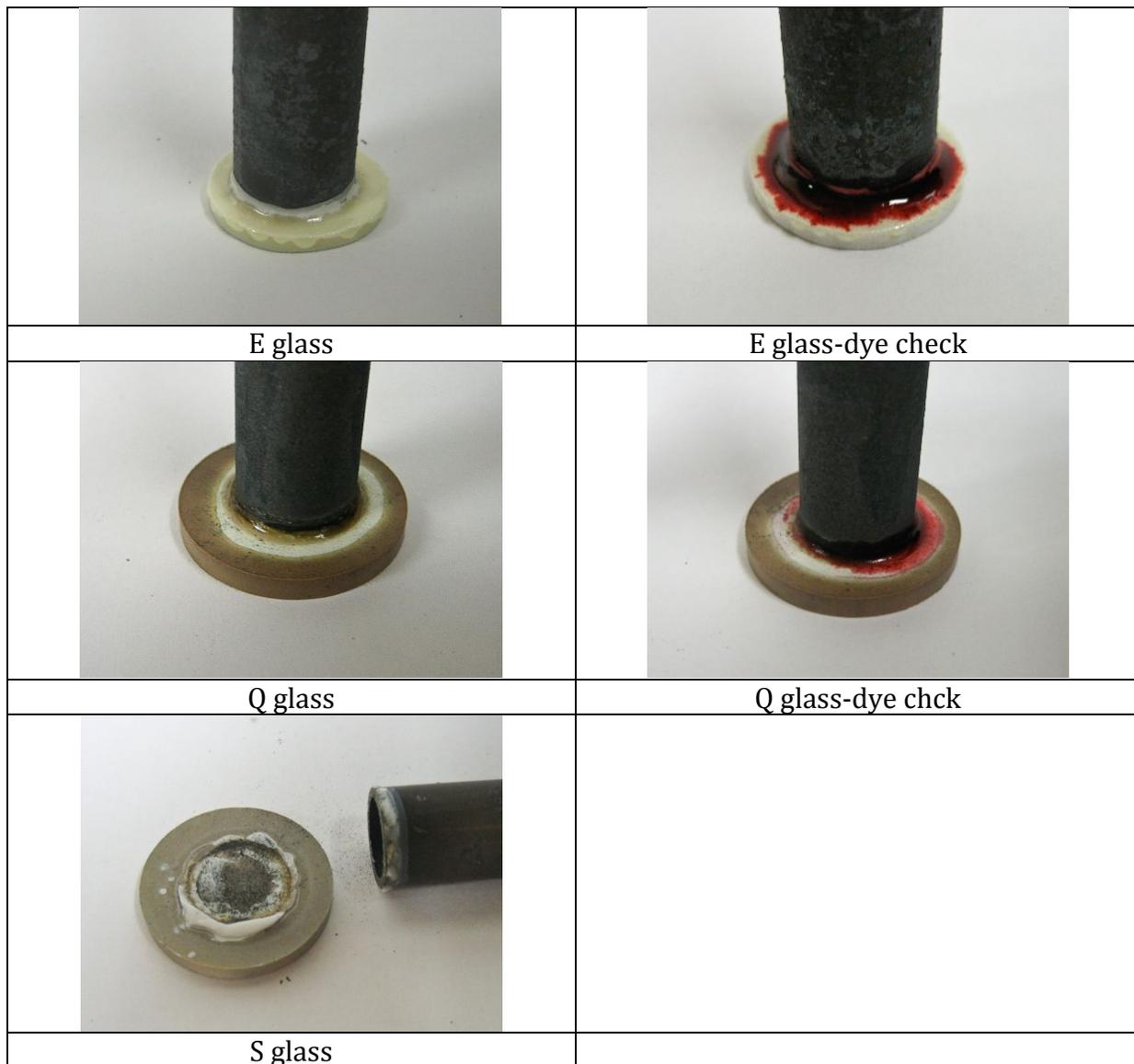
16. Photographs of seals using three different glass materials

Task 5 Wafer Fabrication Cost Analysis

Based on the tape casting and lamination process that will be used for wafer fabrication, an analysis is performed to determine the cost per square foot of membrane. The cost model for the Proton Membrane project was built using a multi-step approach. First, the process flow was generated to ensure all process steps required to build the membranes and modules were included.

In performing the flow sheet analysis, a number of processes were assumed to be slightly different from our current practice as the process is scaled to a manufacturing size process, rather than a research / pilot scale process. Our current equipment and process does not allow us to be able to slit or punch tape while it is being cast. It is, however, an industrial standard practice to perform these tasks on the tape caster, so they were included in the tape casting process on the projected flow sheet.

After the flow sheet was finished, a cost model was built around the processes with input from an industry consultant. The areas reviewed were:

- Yield assessment

  o Current yield levels of similar products were analyzed and reviewed.
  o Yields of similar other industries were reviewed based on experience of consultants as well as engineers and managers within Ceramatec who have worked in other industries.

- Equipment required

  o Risk levels were associated based on how different the proposed process was from what is currently being practiced
  o Budgetary quotes were received for the equipment
  o Expected "uptime" of equipment was based on industry standard and Ceramatec history for the different pieces of equipment
  o Replicates of equipment were based on required uptime given the plant would be operational 24x5 with the exception of furnace-based processes that are expected to operate 24x7

- Personnel required

  o Expected productivity of operators using the commercial-size equipment was estimated based on input from comparable industries.
  o All estimates were based on employees being fully trained, but not yet improving efficiencies due to the learning curve with the equipment and processes.

Once all the yields, equipment, and personnel were assessed, the cost model generated the expected cost per module and the associated cost per wafer based on Prime Cost, Prime Costs with Benefits, and Total Cost (which includes equipment depreciation).

To determine labor and equipment requirements, an estimate of 500 modules per year of production was used. Modifying this level of production will affect cost based on equipment utilization and expected operator productivity. Based on these expected yields, a cost was generated for the modules built with 144 wafers per module. These costs were

calculated both with and without capital depreciation involved. The capital depreciation is calculated based on a 10-year straight-line depreciation.

Based on this estimate, Phase I target fabrication cost can be achieved.

Permeation Testing

The test set up for permeation testing was been built and a schematic is shown below in 17. Photographs of the test rig are shown in 18. Hydrogen permeation tests were conducted using dense, composite disks of about 500 μm thick.
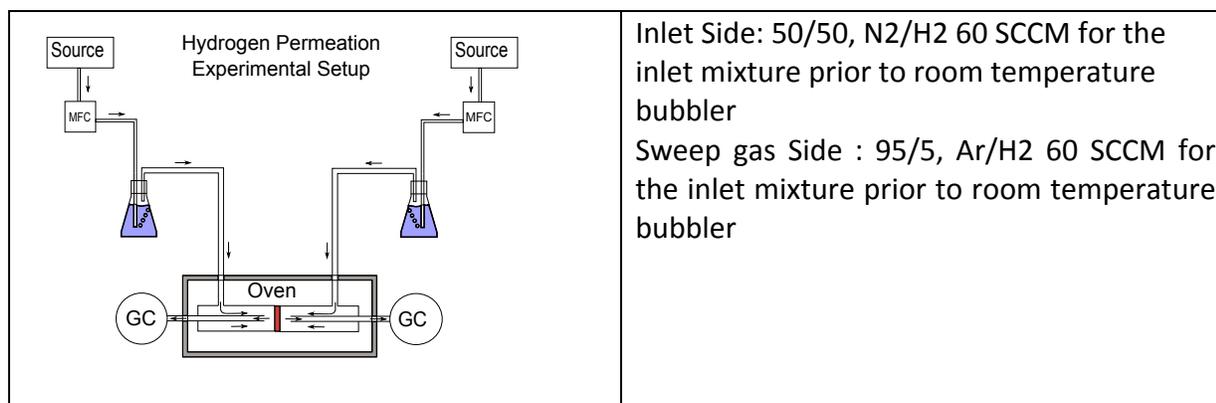
Hydrogen Permeation Experimental Setup Source MFC Source MFC Oven GC GC	Inlet Side: 50/50, N2/H2 60 SCCM for the inlet mixture prior to room temperature bubbler Sweep gas Side : 95/5, Ar/H2 60 SCCM for the inlet mixture prior to room temperature bubbler
17. Permeation test set up	

18. Permeation test set up

Hydrogen permeation has been observed and measured over a range of temperatures. The use of copper gaskets to provide a mechanical seal against the membrane has proven functional however not ideal. A small amount of leak across the membrane has been detected. A material balance has been used to determine the quantity of hydrogen permeating through the membrane in spite of a detected leak. This set up while not perfect allows us to measure permeation at ambient pressure. The results of this effort are shown in 19.

Effect of surface catalyst on the membrane permeability was also tested. A thin, porous layer of Pd/Au was deposited on both surfaces of the membrane. In one test, an increase in flux of ∼ 30% was observed, although the results in subsequent tests were inconsistent.
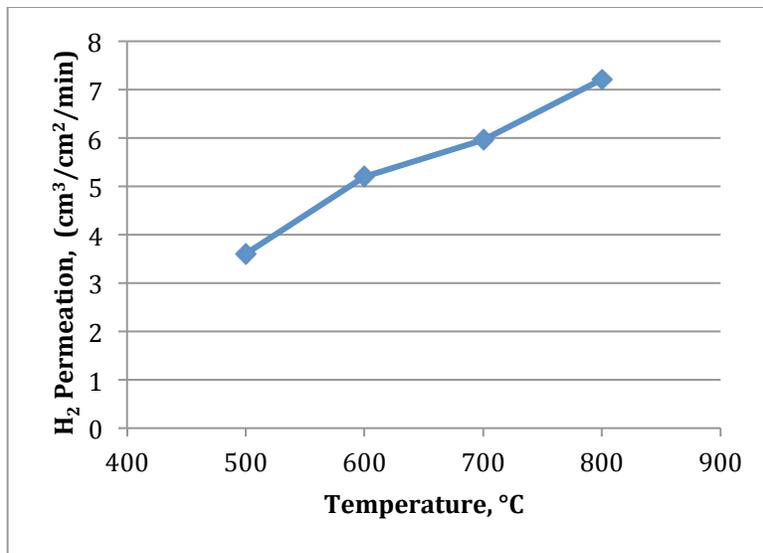
19. Measured Hydrogen Flux

Modified Gas Separation Test Device

The rig shown in 18 was modified to have a vertical rig that allows for balanced compression from both sides as shown in 20. Swagelok VCR face seal fittings, which offer the high purity of a metal-to-metal seal, providing leak-tight service from vacuum to positive pressure, were used to separate the feed (H2) and carrier gases (Ar). The seal on a VCR assembly is made when the gasket is compressed by two beads during the engagement of a male nut or body hex and a female nut. The Silver foil was chosen as the gasket material for its CTE match, operating temperature, and malleability.
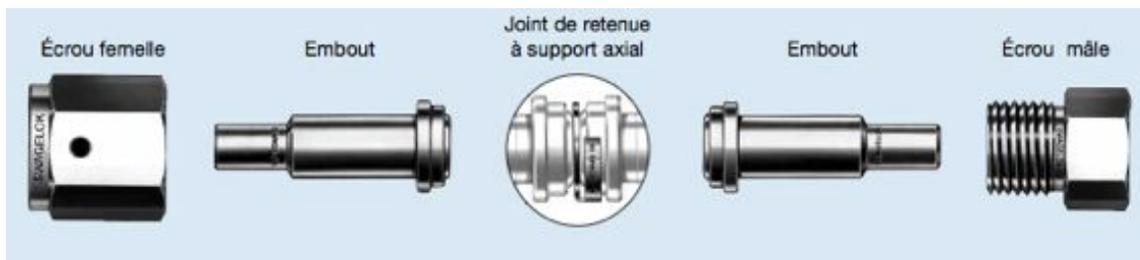
20. Permeation Test Rig Design Modification

The design is developed that the membrane can be attached to Ag foil gasket (washer shape) and the entire unit is placed to VCR fittings. Upon fitting the gasket (21) is compressed to make seals but the membrane is not disturbed.
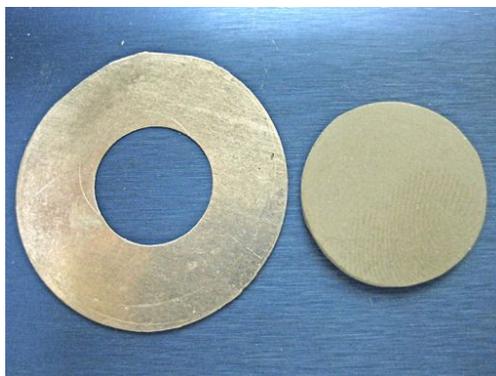
21. Gasket Seal for Membrane Permeation Testing

Several materials were tried to attach BCY membrane to Ag. Selected materials should offer CTE match, gas tight seal, tolerant to reducing environment, and mechanical strength enough to withstand gas pressure. The range of materials tried were variation of Ag based with an oxide flux (typically CuO) added.

Thin layer of Ag/oxide paste was applied to BCY membrane perimeter and the Ag gasket was placed. The sample was fired at 953°C for 30 minutes. The seal shown in 21 passed the dye check and pressure test (up to 10 psi)
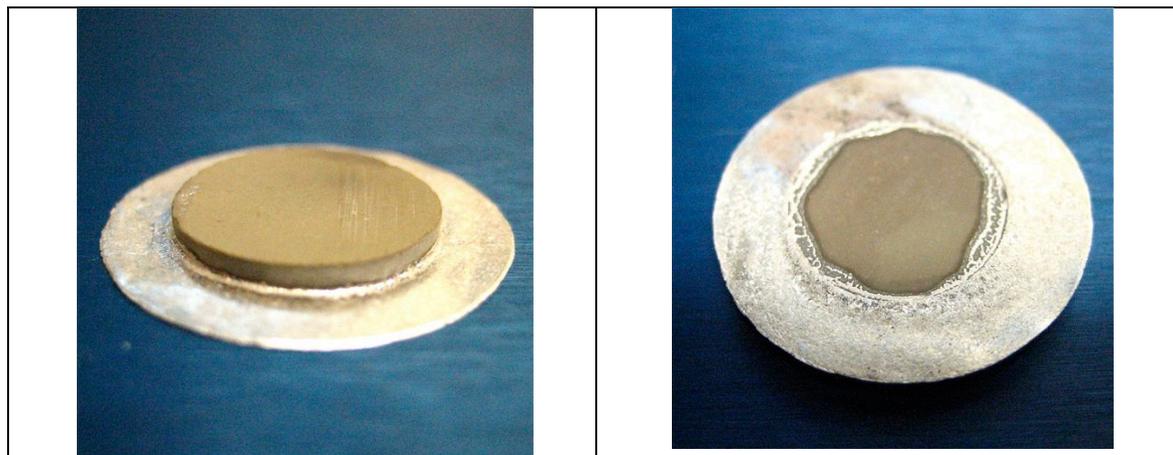
22. Ag foil sealed Membrane

Test and Analysis

BCY sample was placed into VCR fittings and applied 10psi pressure on one side for the leak test. Heated up the furnace to 600°C and started measuring H_2 concentration by GC

Upstream gas: 50% H_2 in N_2 (through the H_2O bubbler)
Downstream gas: 5% H_2 in Ar (through the H_2O bubbler)

Test 1:
Sweep gas (downstream): 4.97% H_2, 95.03 % Ar (measured)

Testing Temperature: 600°C
Sweep Gas Flow Rate: not measured
Sample Size: 3/8" diameter

applied pressure (psi)		concentration (%)		
upstream	downstream	H_2	N_2	Ar
10	5	11.02	0.00	82.48
10	10	9.90	0.00	84,80
15	10	23.88	21.67	55.06

It appeared the seal broke when 15psi (upstream) was applied.

Subsequent test (Test 2) using a new membrane showed excellent seal characteristics. No N_2 cross over from feed side to permeate side was observed.

Test 2:
Feed gas (downstream): 4.96% H_2, 94.52% Ar (measured)
Testing Temperature: 600°C
Downstream Gas Flow Rate 35cc/min
Sample Size: 5/16" diameter; 1.23 mm thick

Applied pressure (psi)		Concentration (%)			
Upstream	Downstream	H_2	N_2	Ar	H_2 Permeation Rate, sccm/cm^2
0	0	7.18	0.00	84.13	2.52
5	0	7.07	0.00	85.34	2.33
5	5	6.35	0.00	90.06	1.39
10	5	6.43	0.00	88.32	1.56
10	10	5.74	0.00	92.83	0.72
15	10	6.03	0.00	92.48	0.98
15	15	5.43	0.00	93.00	0.45

The measured hydrogen permeation rate is identical to the previous measurement (5 sccm/cm^2 for a 0.5 mm thick membrane).

Several samples of thick pellets and thin, supported membranes were tested. The following Table 4 shows the results from a thin ($\sim$ 50 µm) membrane. Baseline leak was characterized by using N_2 as the upstream gas and Ar-5%H_2 as the downstream. It appears that the membrane has some leak as measure by the presence of N_2 in the downstream gas.

As expected, when the upstream gas had hydrogen present the downstream concentration of hydrogen increased. Additional tests where the thin membrane is completely dense is needed to quantify the permeation rate of thin membranes.

Addition of H_2S to the feed gas does not appear to degrade the performance.

Table 4.Thin supported membrane

Temp	Upstream Gas	Downstream Flow Rate (cc/min)	H2%	Ar%	N2%
600	N2	34	5.33	93.88	0.92
600	N2	34	5.26	91.33	0.89
600	N2	34	5.21	93.07	0.92
600	50% H2/N2	34	6.16	93.08	0.93
600	50% H2/N2	34	6.14	92.44	0.89
600	50% H2/N2	34	6.1	91.81	0.87
600	50% H2/N2	17	7.17	92.22	1.56
600	50% H2/N2	17	6.96	91.14	1.41
600	50% H2/N2	17	7.01	90.54	1.43
600	N2	17	5.38	92.6	2.06
600	N2	17	5.28	92.46	2.06
600	N2	17	5.19	92.04	2.01
600	50ppm H2S	34	6.4	91.76	1.66
600	50ppm H2S	34	6.42	91.76	1.57
600	50ppm H2S	34	6.43	91.62	1.56
600	50ppm H2S	17	7.54	89.46	1.87
600	50ppm H2S	17	7.61	89.46	1.81
600	50ppm H2S	17	7.59	88.94	1.75

Results from a thicker (unsupported) membrane are shown below in Table 5. No nitrogen leak was detected in the downstream when the feed gas was 50%H_2-bal N_2.

Table 5.Thick membrane

Temperature, °C	Upstream Flow Rate (cc/min)	H2	Ar	N2
400	17	4.90	93.26	0.00
400	17	4.90	94.34	0.00
400	34	4.88	92.24	0.00
400	34	4.88	93.63	0.00
400	74	4.90	94.16	0.00
400	74	4.90	93.86	0.00
500	17	4.86	94.08	0.00
500	17	4.86	93.66	0.00
500	34	4.87	94.34	0.00
500	34	4.87	91.60	0.00
500	74	4.88	94.19	0.00
500	74	4.88	94.02	0.00
600	17	5.84	94.53	0.00
600	17	5.78	92.77	0.00
600	17	5.79	91.27	0.00

600	34	5.51	90.20	0.00
600	34	5.51	92.99	0.00
600	34	5.50	93.39	0.00
600	74	5.21	92.46	0.00
600	74	5.21	93.16	0.00
600	74	5.21	92.60	0.00

A thick membrane with a surface catalyst was also tested. The results are shown in Table 6. In this case, a slight leak as indicated by the presence of N_2 is observed. Again, no major effect due to presence of H_2S is noted (Table 7). The actual H_2S amount reaching the membrane may be smaller than the inlet gas due to the fact the gases were humidified prior to reaching the membrane.

Table 6.Thick membrane with surface catalyst (Pd/Au)

Upstream Gas	Upstream Flow Rate (cc/min)	Downstream Concentration, %		
		H2	Ar	N2
N2	34	5.33	93.88	0.92
N2	34	5.26	91.33	0.89
N2	34	5.21	93.07	0.92
50% H2/N2	34	6.16	93.08	0.93
50% H2/N2	34	6.14	92.44	0.89
50% H2/N2	34	6.1	91.81	0.87
50% H2/N2	17	7.17	92.22	1.56
50% H2/N2	17	6.96	91.14	1.41
50% H2/N2	17	7.01	90.54	1.43
N2	17	5.38	92.6	2.06
N2	17	5.28	92.46	2.06
N2	17	5.19	92.04	2.01
50ppm H2S	34	6.4	91.76	1.66
50ppm H2S	34	6.42	91.76	1.57
50ppm H2S	34	6.43	91.62	1.56
50ppm H2S	17	7.54	89.46	1.87
50ppm H2S	17	7.61	89.46	1.81
50ppm H2S	17	7.59	88.94	1.75

Table 7.Effect of H_2S on membrane permeation at 600C

Feed Gas: H_2 via bubbler
Sweep Gas: N_2 via bubbler (50cc/min)
H_2 concentration in   3.25%
permeate stream

Feed Gas: 25ppm H_2S(mix of 50ppm H_2S in
50/50 H_2/CO + Wet H_2)

Sweep Gas: N_2 via bubbler (50cc/min)
H_2 concentration in   2.53%
permeate stream

Feed Gas: H_2 via bubbler
Sweep Gas: N_2 via bubbler (30cc/min)
H_2 permeated   6.73%

Feed Gas: 25ppm H_2S
(mix of 50ppm H_2S in 50/50 H_2/CO + Wet H_2)
Sweep Gas: N_2 via bubbler (30cc/min)
H_2 concentration in   4.89%
permeate stream

Feed Gas: H_2 via bubbler
Sweep Gas: N_2 via bubbler (10cc/min)
H_2 permeated   19.95%

Feed Gas: 25ppm H_2S
(mix of 50ppm H_2S in 50/50 H_2/CO + Wet H_2)
Sweep Gas: N_2 via bubbler (10cc/min)
H_2 concentration in   14.08%
permeate stream

Fabrication of thin supported membrane

As an alternative to tape cast and lamination, a pressing approach is being evaluated to make thin supported membrane. Initial results look promising as shown below in 23. Thicknesses of various layers need to be optimized.

2000µm core
400µm bond
~2um dense
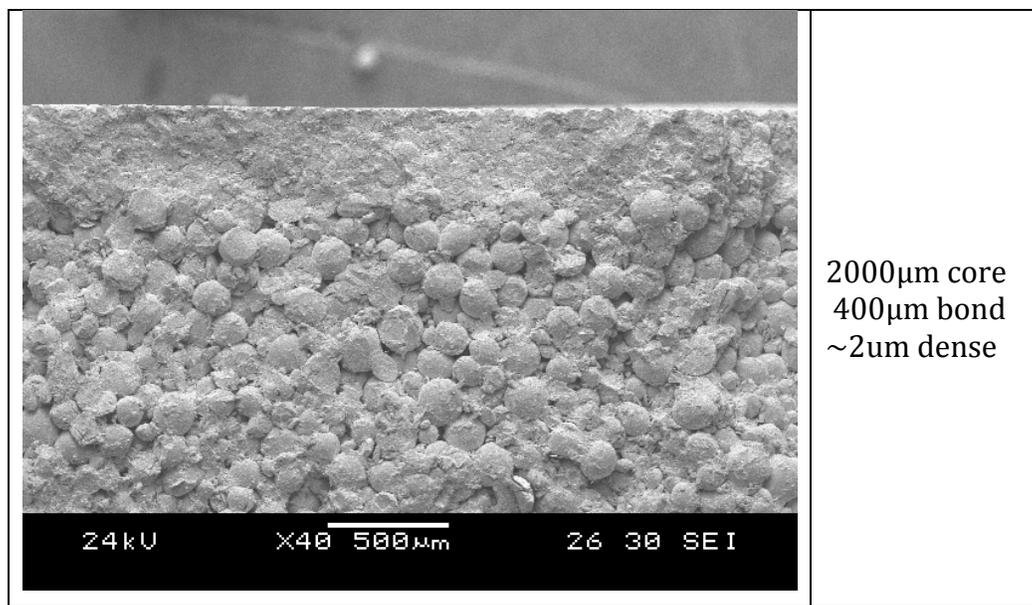
23. SEM micrograph of thin supported membrane (initial trial)

Optimization of Membrane Fabrication Trials

For tape casting, we found that using 1-38 µm powder resulted in the best structure and tape quality. However, during the repeated firing for dense layer coating trials, the through porosity structure began to close in. The part densified considerably (24). In order to lower the driving force for sintering of the porous body, the starting powder was coarsened, crushed and graded to 63-150um, and then combined with 2% PEOX binder, 25 discs were pressed. These discs were then fired to 1650 C over 5 days. These have 35% open porosity. This porosity is maintained even after five full sintering cycles. Flatness is also maintained after repeated firing. The sintered membrane is shown in 25.
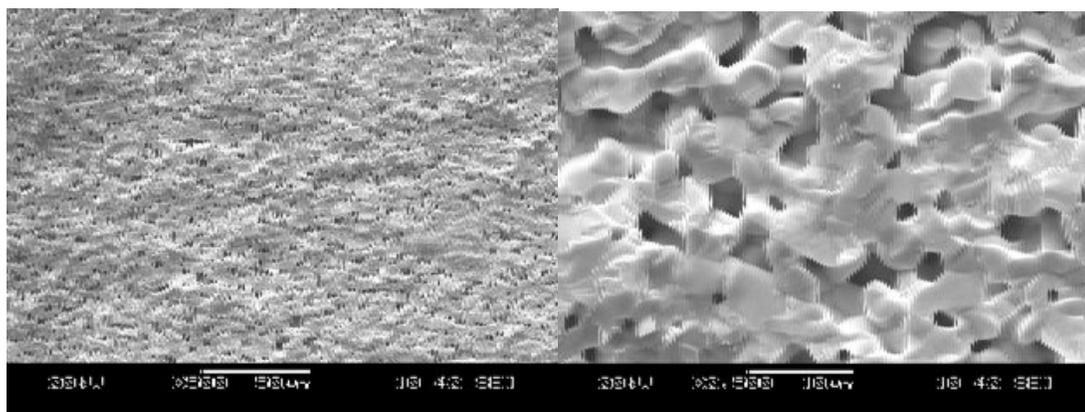
24. SEM cross-section of sintered tape using 1-38um powder
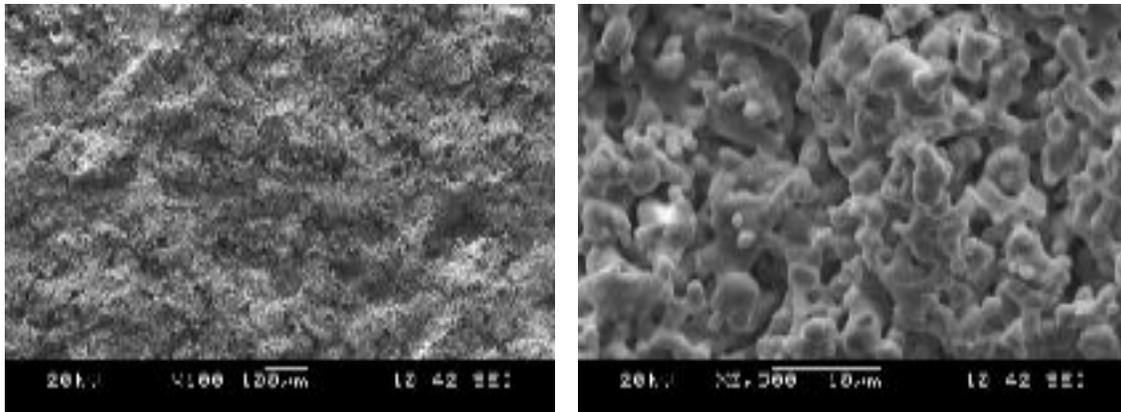
25. SEM cross-section of sintered pressed part using 63-150um powder

Using milled powder of the same composition, this porous substrate was coated with a thin bond layer (D50=10μm) followed by a thin dense layer (D50=3μm). This was done by suspending the milled powder in Butyl Alcohol, then flooding the surface of the part with the suspension. The part is dried then fired to 1560 C over 3 days. The process is repeated for each coating. The cross section of the final sintered body is shown in 26. 27 shows the surface images. There are still some creases that result in porosity. Further sintering trials are needed to improve the density of the surface layer.
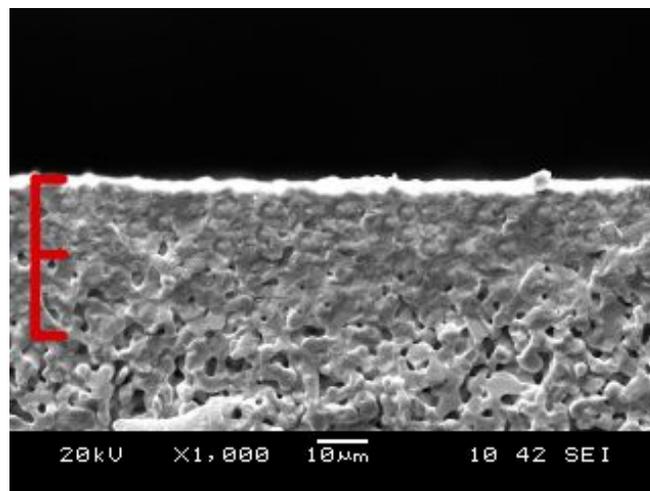
26. SEM cross-section of sintered porous with 15μm dense layer D50=3μm coated on bond layer D50=10μm
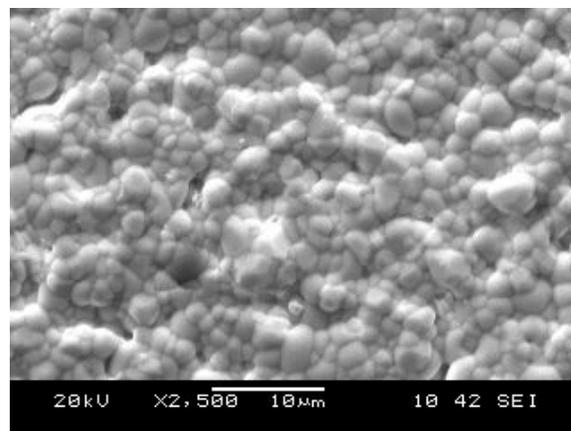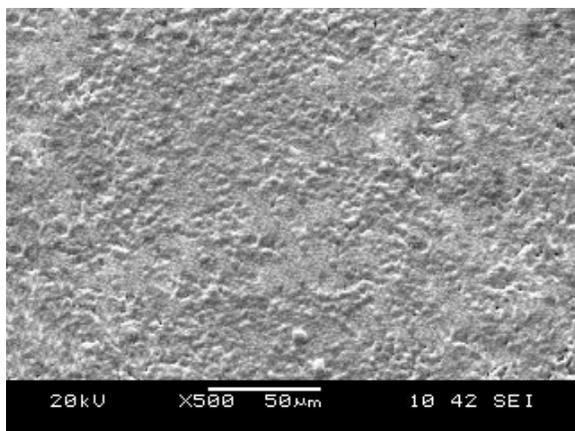
27. Surface SEM of sintered membrane showing dense layer coating with minimal pinholes

Conclusions

The objectives of the three-year project are:

a) Improve membrane proton conductivity through dopant modification;

b) Measure hydrogen flux at relevant temperature range, pressure, and composition conditions; and

c) Scale up membrane device to demonstrate a prototype that allows meaningful extrapolation of performance data and process economics to larger commercial systems.

Measurable goals were set to gauge the project performance. The accomplishments of the project include:

- *Demonstration of effective membrane proton conductivity of 0.02 S/cm at 600°C, corresponding to >150 scfh/ft² wafer hydrogen separation*
- *Preliminary wafer design (layer thickness, channel dimensions) showing < $200/ft² fabrication feasibility*
- *Completion of cost model identifying process yields necessary for meeting the cost goal.*
- *Demonstration of high hydrogen flux using thick membrane*
- *Identification of fabrication pathway for thin, supported membrane device*
- *Preliminary evaluation of negligible effect of H_2S on membrane performance*

However, additional work is required to demonstrate the scale up process and test devices of meaningful size. Ceramatec intends to continue the scale up process with non-federal sources of funding.

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