ANL/ET/CP-96705

CONF-980746--

Development of Proton-Conducting Membranes for Hydrogen Separation*

U. (Balu) Balachandran (u_balachandran@qmgate.anl.gov; 630-252-4250)
J. Guan (se_dorris@qmgate.anl.gov; 630-252-5084)
S.E. Dorris (se_dorris@qmgate.anl.gov; 630-252-5084)
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439

July 1998

RECEIVED
AUG 13 1998
OSTI

Invited paper for presentation at the Advanced Coal-based Power and Environmental Systems '98 Conference, Morgantown, WV, July 21-23, 1998.

* Work supported by the U.S. Department of Energy, Federal Energy Technology Center, under Contract W-31-109-Eng-38.

Development of Proton-Conducting Membranes for Hydrogen Separation*

U. (Balu) Balachandran (u_balachandran@qmgate.anl.gov; 630-252-4250)
J. Guan (se_dorris@qmgate.anl.gov; 630-252-5084)
S.E. Dorris (se_dorris@qmgate.anl.gov; 630-252-5084)
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439

Introduction

The Office of Fossil Energy (FE) at DOE sponsors a wide range of research, development, and demonstration programs to maximize the use of vast domestic fossil resources and to ensure a fuel-diverse energy sector while responding to global environmental concerns. The development of cost-effective membrane-based reactor and separation technologies is of considerable interest for applications in advanced coal-based power and fuel technologies. Because concerns over global climate change are driving nations to reduce carbon dioxide emissions, hydrogen is considered the fuel of choice for both electric power and transportation industries. While it is likely that renewable energy sources will ultimately be used to generate hydrogen, fossil-based technologies will be utilized to generate the hydrogen in the interim.

Outside of direct coal liquefaction, three major industrial areas currently produce and use large volumes of hydrogen, although other areas such as hydrogen-fueled vehicles and indirect coal liquefaction may develop into major users. At present, petroleum refining and the production of ammonia and methanol collectively consume about 95% of all deliberately manufactured hydrogen in the U.S., with petroleum refining accounting for about 70%. As crude oil quality deteriorates and restrictions on sulfur, nitrogen, and aromatic levels become increasingly stringent, refinery hydrogen needs will continue to increase, all while hydrogen sources such as naphtha reforming become more scarce due to reduced aromatic allowances in products. In this climate of growing demand and dwindling sources, membrane technology may reduce refining costs and help retain domestic refining capacity by integrating hydrogen separation and purification into the shift conversion process (thereby facilitating hydrogen production) and by recovering hydrogen from streams where recovery is currently not economical due to low concentration, low pressure, or other factors.

Petroleum refineries currently employ cryogenics, pressure swing adsorption (PSA), and membrane systems for hydrogen recovery. Each of these technologies has limitations: cryogenics is generally used only in large-scale facilities with liquid hydrocarbon recovery, because of its high capital cost; and PSA typically recovers less of the feedstream hydrogen and is limited to modest temperatures. Currently used membrane systems are susceptible to chemical damage from H_2S and aromatics and have limited temperature tolerance. Following is a description of efforts at

Argonne National Laboratory to develop dense ceramic membranes as a simple and efficient alternative method for hydrogen recovery.

Objective

The objective of this project is to develop dense ceramic membranes that can efficiently and economically separate hydrogen from gaseous mixtures (e.g., syngas, coal gas, etc.). Toward this end, materials with suitable electronic and protonic conductivities will be identified, and methods for fabricating thin, dense ceramic membranes from such materials will be developed. The chemical and mechanical stability of the membranes will be determined to estimate the expected lifetime of the membranes. Scoping-level evaluations will be performed to identify potential applications of proton membrane technology. Areas that will be evaluated include overall market scale, typical site operating scale, process integration opportunities and issues, and alternative-source economics.

Approach

The literature on mixed electronic/protonic conductors was surveyed to identify suitable candidate materials. $SrCe_{1-x}M_xO_{3-\delta}$ and $BaCe_{1-x}M_xO_{3-\delta}$ (where M is a fixed-valent dopant such as Ca, Y, Yb, In, Nd, or Gd) were selected for further investigation on the basis of their reported total conductivities and proton transference numbers. $SrCeO_3$- and $BaCeO_3$-based powders with various dopants and dopant concentrations were synthesized via solid-state reaction, then pellets were uniaxially pressed and sintered.

The transport properties of pellets with various compositions were investigated by impedance spectroscopy, open-cell voltage (OCV), and gas permeation measurements. After a material with a favorable combination of proton conductivity and transference number was identified, its ability to transport protons was demonstrated with a hydrogen pump and water vapor electrolyzer (Fig. 1) in which $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (BCY) served as the electrolyte and porous Pt as the electrodes. Because the results to this point indicated that the electronic conductivity was insufficient for nongalvanic hydrogen separation, BCY-containing composite membranes (referred to as ANL-1) were fabricated with increased electronic conductivity.

Nongalvanic permeation of hydrogen through ANL-1 membranes was measured with the setup shown in Fig. 2. A membrane was secured with a sealant to one end of a support tube. The tube was placed in a furnace where hydrogen-containing "feed gas" was passed over one side of the membrane while argon "carrier gas" flowed over the opposite side. The gas concentrations were analyzed with a gas chromatograph that was periodically calibrated with standard gases. Gas leakage through the setup was tested by replacing the hydrogen feed gas with helium and measuring the helium concentration in the carrier gas.

Little information is available on the chemical and mechanical stability of proton-conducting materials, so chemical stability was studied by in-situ measurements of the conductivity of pellet samples immersed in various gases and by X-ray diffraction analysis of powder samples after their exposure to the gases. The mechanical properties of membrane materials will be evaluated by conventional methods; if necessary, second-phase materials will be added to improve their mechanical strengths.

Because nongalvanic separation of hydrogen was demonstrated with ANL-1 membranes, procedures are being developed to fabricate these materials into a convenient reactor design. These efforts presently focus on the extrusion and tape casting methods. Hydrogen permeation rate increases as the membrane thickness decreases, so the fabrication procedures will be optimized to minimize membrane thickness. Techniques to braze ANL-1 membranes to Inconel alloy tubes to form leak-tight seals are also being developed. Process issues and economics will be evaluated as technical progress warrants.

Project Description

In its "Vision 21" program, the U.S. Department of Energy (DOE) aims to develop highly efficient power and cogeneration technologies that close the carbon cycle and discharge almost no pollutants. A likely modular component of the Vision 21 coproduction plant is an integrated gasification combined cycle (IGCC) that is ideally suited for cogenerating electricity and high-quality transportation fuel or other high-value chemicals. In an IGCC system, coal and other carbonaceous feed stocks are partially combusted at elevated temperatures and pressures to produce synthesis gas ("syngas"), a mixture of carbon monoxide and hydrogen. High-temperature membranes are being considered for use in the IGCC to separate hydrogen from coal gasification and other partial-oxidation-product streams. However, current membrane systems have several limitations: for example, they are susceptible to chemical damage from H_2S, CO, and aromatics; have limited temperature tolerance; undergo phase transformations that threaten their mechanical stability; have poor selectivity for hydrogen; and are costly.

Thin, dense ceramic membranes fabricated from mixed protonic/electronic conductors provide a simple and efficient means for separating hydrogen from gas streams. Because such membranes contain no interconnected porosity, the only species that pass through them are those that participate in conduction. As a result, selectivity for hydrogen is very high. Also, because the membrane is a mixed conductor, hydrogen separation is achieved in a nongalvanic mode, (i.e., without the need for electrodes or an external power supply to drive the separation), thereby offering potential economic advantages over some existing technologies. Because the membranes are made from ceramic materials, they are more tolerant of high temperatures and may be more resistant to chemical degradation.

Perovskite-type oxides such as $SrCeO_3$ and $BaCeO_3$ exhibit significant proton conductivities in hydrogen-containing atmospheres when oxygen vacancies and other charged defects are introduced by the partial substitution of trivalent cations for Ce [1]. Because of their high proton conductivities, these materials are suitable for galvanic applications such as fuel cells and hydrogen pumps [2-4]. However, to be suitable for nongalvanic hydrogen separation with high permeability and selectivity to hydrogen, both the electronic and protonic conductivities of the material must be high and approximately equivalent. In addition, the materials must exhibit high catalytic activity for the oxidation and evolution of hydrogen at the solid/gas interfaces. While doped $SrCeO_3$ and $BaCeO_3$ are good proton conductors in hydrogen-containing atmospheres, their electronic conductivities and interfacial catalytic activities are inadequate for nongalvanic separation of hydrogen [5,6]. Based on the transport properties of doped $BaCeO_3$ and $SrCeO_3$, we have developed a novel composite system (referred to as ANL-1) that exhibits sufficient electronic conductivity in the bulk and high catalytic activity at the solid/gas interfaces and is therefore suitable for separating hydrogen from gas mixtures in nongalvanic operation.

Results

Transport Properties of Doped BCY

Of the materials studied to this point, BCY exhibited the highest total conductivity in hydrogen ($\approx 4.2 \times 10^{-2}\ \Omega^{-1}cm^{-1}$). Open-circuit voltage measurements on hydrogen concentration cells in the temperature range of 600-800°C showed that its proton transference number was about 0.8-0.95. While the conductivity and transference numbers are encouraging, both hydrogen pump and water vapor electrolyzer experiments show that hydrogen can be generated from the cathode only by applying a DC current through the BCY membranes, i.e., the monolithic BCY membranes did not transport hydrogen nongalvanically.

Shown in Fig. 3 is the hydrogen evolution rate as a function of applied current at 600 and 800°C for the hydrogen pump experiment. The theoretical values calculated from the applied current density using Faraday's law are also shown for reference. When the applied current was low (<22 mA/cm^2), the current efficiency was close to unity, which agrees well with the high proton transference numbers, but the current efficiency dropped significantly at higher current densities. The decrease in current efficiency was more evident at high temperature (800°C) than at low temperature (600°C).

Very dry hydrogen (dew point < -40°C) was obtained by electrolyzing water vapor. As shown in Fig. 4, the current efficiencies were lower than those observed in hydrogen pumping. The low current efficiencies suggest that oxygen ion and electron conduction were significant during water vapor electrolysis. Electron holes may have been formed in a reaction of the oxygen vacancies with the oxygen, which might remain locally at the anodic interface with a relatively higher pressure as a by-product of the water vapor electrolysis:

$$\frac{1}{2}O_2 + V_O^{\bullet\bullet} \rightarrow O_O^{\times} + 2h^{\bullet}$$

Stability with H_2O, CO_2, and H_2S

In-situ measurements of the conductivity of BCY showed that the material has adequate stability in atmospheres containing water vapor at moderate pressures (<0.07 atm) and temperatures (500-800°C). X-ray diffraction analysis of powders after exposure to water vapor revealed no appreciable decomposition of the material. The effect of H_2O on hydrogen permeation remains to be studied.

Thermodynamic data suggests that BCY is unstable in high concentrations of CO_2 (BCY was calculated to be unstable at $>1.5 \times 10^{-5}$ atm at 600°C and at >0.0155 atm at 850°C). However, resistance measurements on BCY in an atmosphere containing 1% CO_2 showed that the materials has limited tolerance to CO_2 at elevated temperatures. The bulk resistance of BCY pellets increased 1% after their exposure to 1% CO_2-N_2 at 850°C for 100 h while it increased by 5% after exposure at 600°C for 100 h (Fig. 5). X-ray diffraction analysis of powder samples showed only slight decomposition to carbonates and oxides during this exposure. A hydrogen separation experiment with an ANL-1 membrane used a feed gas of 66 mol.% H_2, 33 mol.% CO, and 1% CO_2 and showed no decrease in hydrogen permeation rate with time during ≈48 h at 750-850°C.

No decrease in hydrogen permeation rate was noted in BCY pellets exposed to 250 ppm of H_2S/balance hydrogen for 48 h at 750°C. Future experiments will study the effects of H_2S, H_2O, and CO_2 on hydrogen permeation rate over longer periods of time.

Hydrogen Permeation

Because the mixed-conducting membrane transports only those gas species that participate in its conduction processes, the selectivity of the membrane for hydrogen is expected to be 100%. Selectivity was demonstrated by feeding one side of the membrane with a gas mixture containing 66 mol.% H_2, 33 mol.% CO, and 1% CO_2 and analyzing the concentration of hydrogen in the argon carrier gas on the opposite side of the membrane. Gas concentrations were measured by gas chromatography. Only hydrogen was detected in the argon carrier gas, showing that only hydrogen diffused through the membrane. As temperature increased from 750 to 850°C, the hydrogen permeation rate through the membrane (thickness ≈1.6 mm) increased from 0.21 to 0.29 scc cm^{-2} min^{-1}.

The rate-limiting steps for hydrogen permeation were determined by investigating the dependence of permeation rate on membrane thickness. Figure 6 shows the permeation flux through ANL-1 membranes with 4% H_2/balance N_2 as the feed gas (flowing at 86 $cm^3 min^{-1} cm^{-2}$) and Ar as carrier gas (flowing at 43 $cm^3 min^{-1} cm^{-2}$). Hydrogen permeation rates increased with temperature and were approximately proportional to the inverse of membrane thickness (0.095 to 0.205 cm) at a given high temperature (800°C), with a slope close to $(E_N \sigma_{amb})/2F$, where E_N is the Nernst potential, σ_{amb} is ambipolar conductivity, and F is Faraday's constant. This suggests that the permeation is limited by bulk properties for samples under these conditions. However, at low temperatures (<650°C), the flux data showed significant deviation from this relationship, suggesting that interfacial resistance, rather than bulk properties, is more significant at low temperatures. Analysis showed that interfacial resistance was a strong function of temperature, decreasing dramatically when temperature rose from 600 to 800°C. The permeation rate for BCY (thickness ≈ 2 mm) was measured by short-circuiting its two platinum electrodes (Fig. 6). This figure shows that the hydrogen flux through ANL-1 was increased by a factor of ≈2 relative to that of short-circuited BCY.

As evident in Fig. 6, hydrogen permeation can be improved by reducing the membrane thickness, especially at high temperatures. A considerable increase in the permeation rate is also expected by increasing the operating temperature and hydrogen partial pressure across the membranes. With an increase in partial pressure across the membrane, the Nernst Potential (i.e., the driving force) will be increased; an increase in operating temperature will not only enhance the Nernst potential but also improve the catalytic activity at the interface and the proton conductivity in the bulk. Figure 7 shows the permeation rates through a membrane 1.6 mm thick with 100% H_2 as the feed gas (flowing at 190 $cm^3min^{-1}cm^{-2}$) and Ar as the carrier gas (flowing at 85 $cm^3min^{-1}cm^{-2}$). The hydrogen permeation rate under these conditions increased from 0.42 $cm^3min^{-1}cm^{-2}$ at 750°C to 1.15 $cm^3min^{-1}cm^{-2}$ at 900°C.

Application

Dense, mixed-conducting ceramic membranes show promise for efficiently and cost-effectively separating hydrogen from gas mixtures. As part of the DOE Vision 21 program, these membranes are being developed to separate hydrogen from coal gasification, water gas shift reaction, and other partial oxidation product streams. The separated hydrogen is envisioned to be utilized in a fuel cell that achieves very high efficiency while simultaneously concentrating CO_2 for possible sequestration, chemical fixation, or utilization. Advantages of the mixed-conducting membranes over some existing hydrogen recovery methods include its high selectivity for hydrogen, its nongalvanic operation, and its ability to withstand high temperatures. In addition, preliminary tests suggest that the mixed-conducting membrane may provide greater resistance to chemical degradation.

Future Activities

The chemical stability of mixed-conducting ANL-1 membranes in the presence of H_2S, CO_2, and H_2O will be examined by monitoring hydrogen permeation through the membranes for extended periods (several hundred hours). While preliminary results indicate that the ANL-1 membranes are stable for practical purposes during periods of less than 48 h, these results must be confirmed with long-term studies. A focus of future efforts will be on optimizing fabrication procedures to minimize the membrane thickness and thereby increase the hydrogen permeation rate. Performance of the membranes in separating hydrogen from high-pressure gas streams will be evaluated by using FETC's in-house R&D facilities.

Potential applications for mixed-conducting membrane technology will be evaluated. Areas to be evaluated include overall market scale, typical site operation scale, process integration opportunities and issues, and alternative-source economics.

Acknowledgment

This work has been supported by the U.S. Department of Energy's Federal Energy Technology Center, under Contract W-31-109-Eng-38 with Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL, 60439-4838 (FWP 49601). The technical program manager at FETC is Dr. Arun C. Bose.

References

[1]. H. Iwahara, T. Yajima, and H. Uchida, Solid State Ionics, **70/71**, 267 (1994).

[2]. N. Taniguchi, E. Yasumoto, and T. Gamo, J. Electrochem. Soc., **143**, 1886 (1996).

[3]. J. Langguth, R. Dittmeyer, H. Hofmann, and G. Tomandl, Chemie Ingenieur Technik, **69**, 3197 (1997).

[4]. H. Iwahara, T. Yajima, T. Hibino, and H. Ushida, J. Electrochem., 140, 1687 (1993).

[5]. J. Guan, S. E. Dorris, U. Balachandran, and M. Liu, Solid State Ionics, **100**, 45 (1997).

[6]. J. Guan, S. E. Dorris, U. Balachandran, and M. Liu, J. Electrochem. Soc., **145**, 1780 (1998).

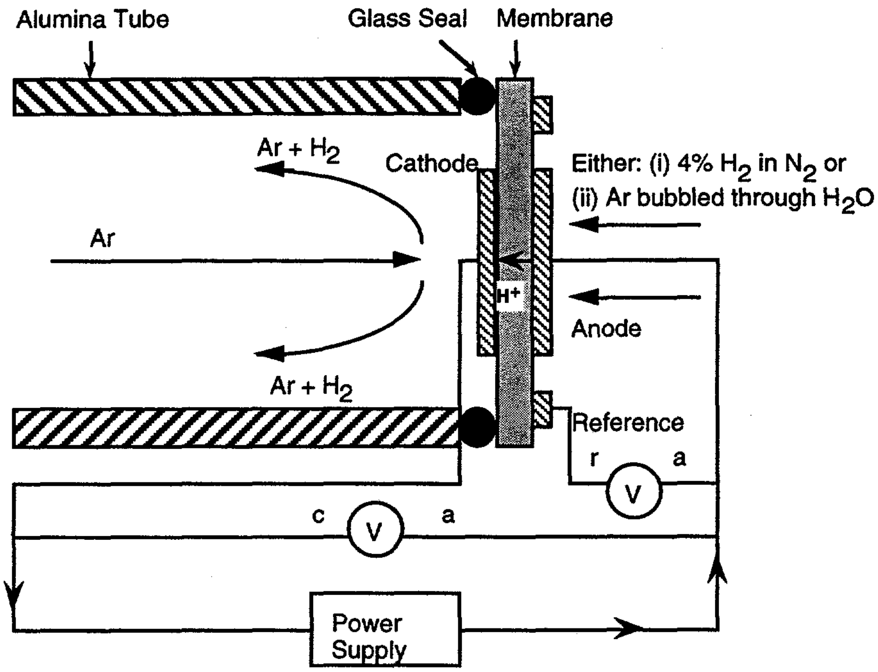

Fig. 1. Schematic illustration of hydrogen pumping and water vapor electrolysis.

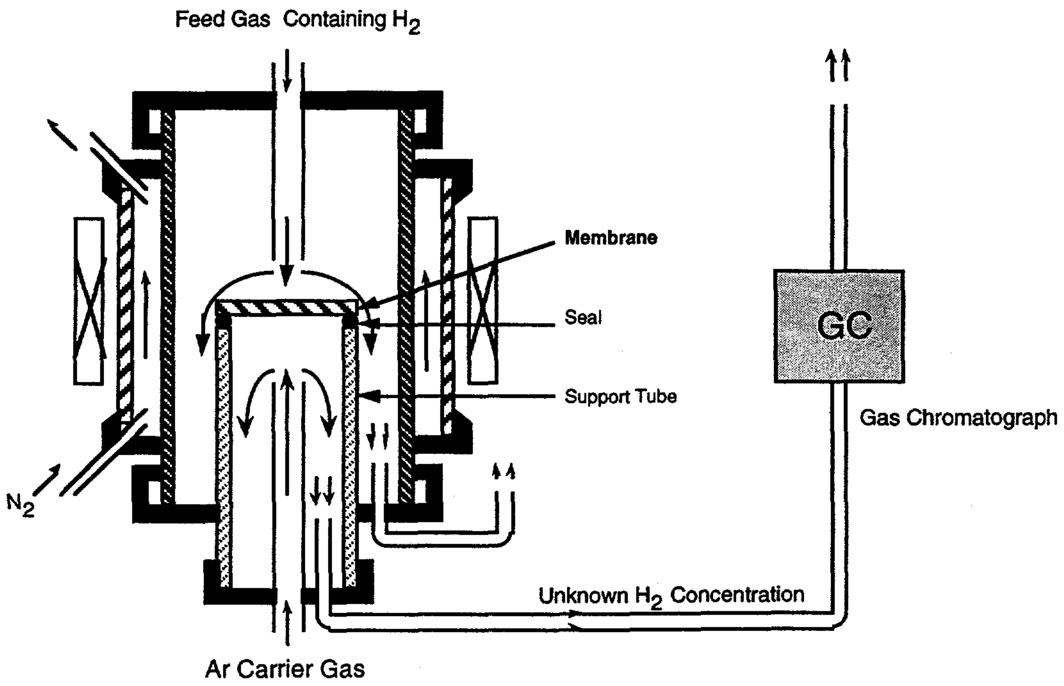

Fig. 2. Schematic illustration of setup for hydrogen separation.

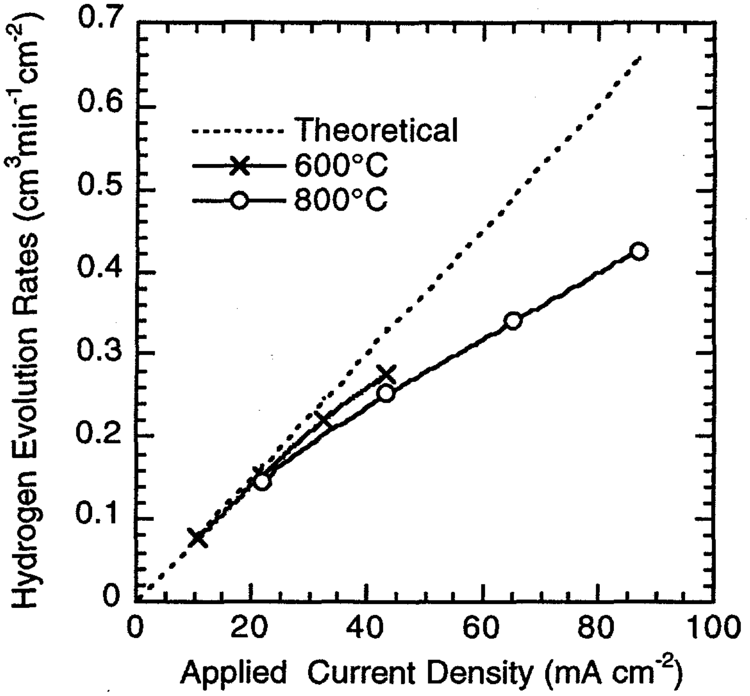

Fig. 3. Hydrogen pumping rates as a function of current density and temperatures.

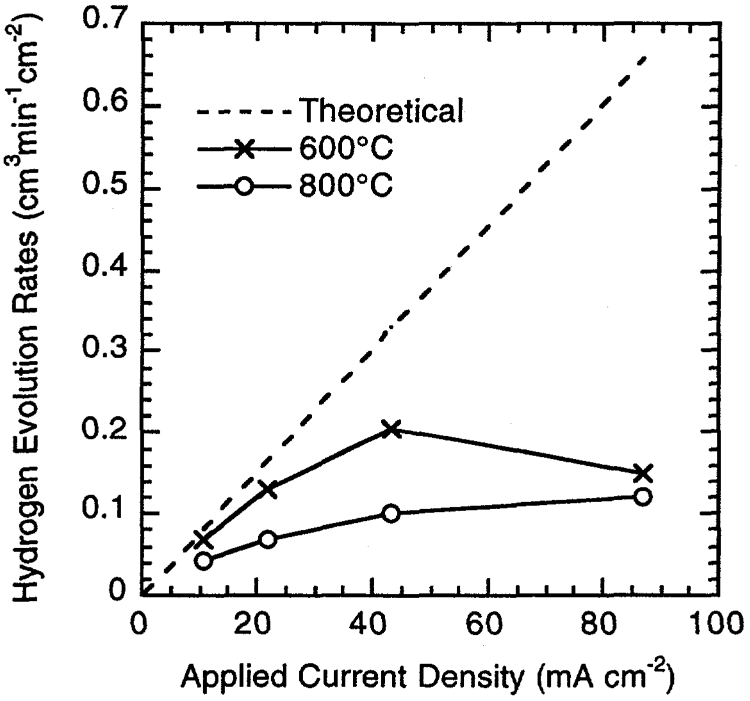

Fig. 4. Hydrogen evolution rates during water vapor electrolysis.

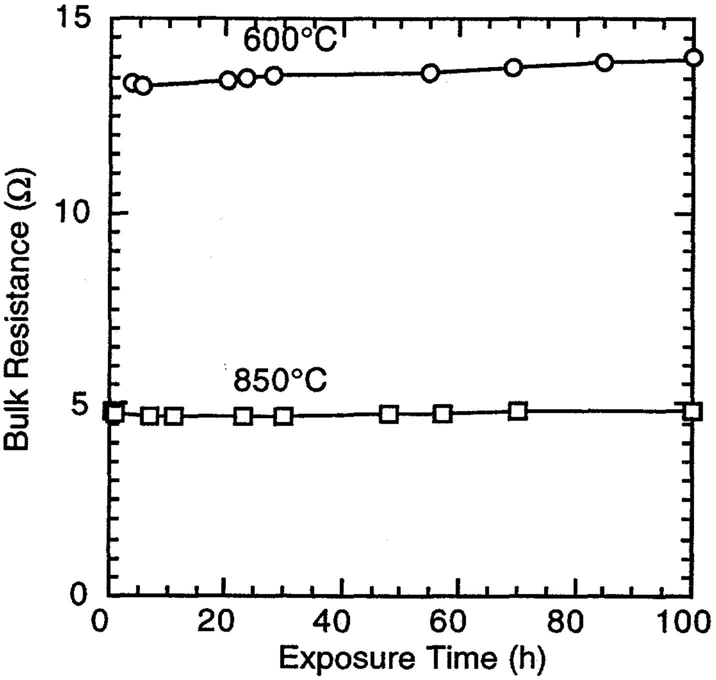

Fig. 5. Bulk resistance of BCY as a function of exposure time in 1% CO_2-N_2 at 600 and 800°C.

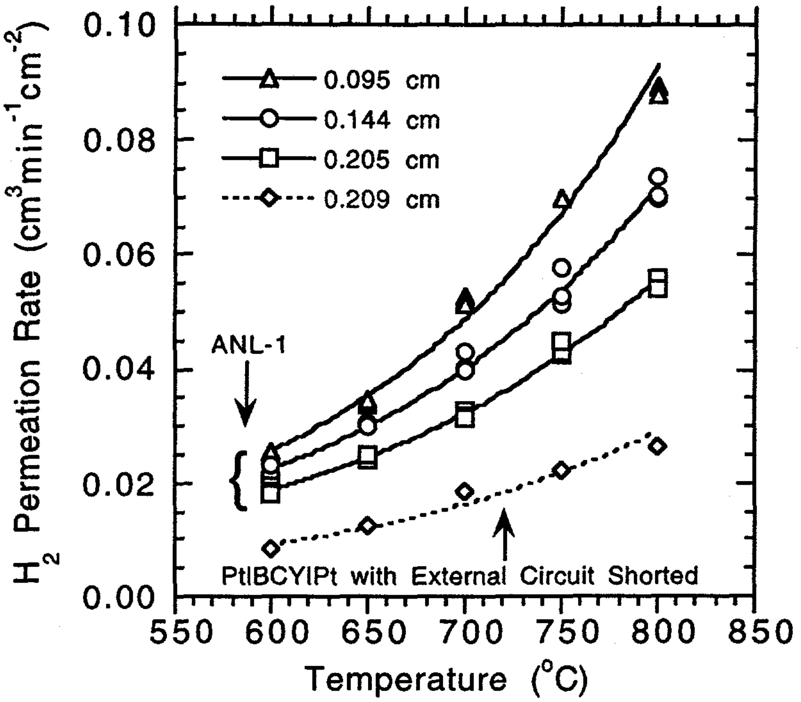

Fig. 6. Temperature and thickness dependence of hydrogen permeation rates through ANL-1 membranes and PtIBCYIPt cell with external circuit shorted.

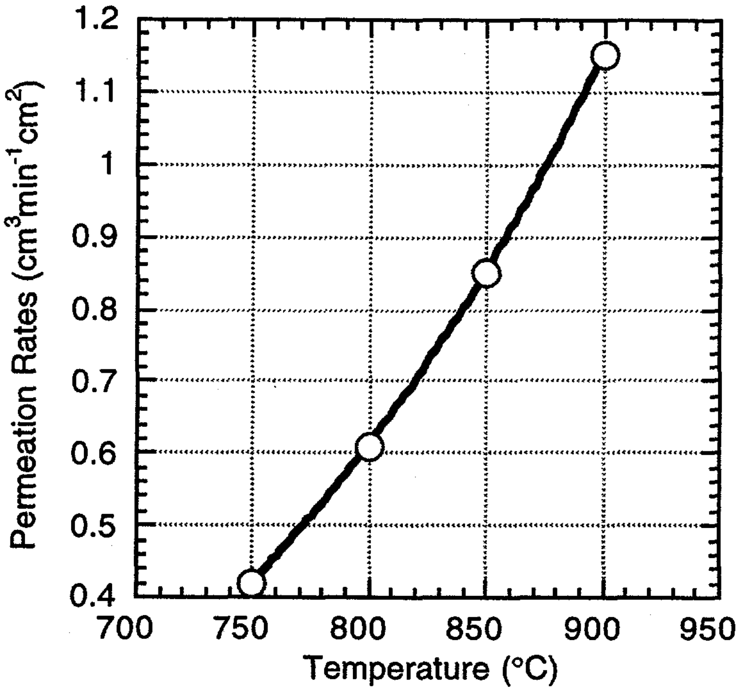

Fig. 7. Hydrogen permeation rate at high temperature at 100% hydrogen feeding.