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DEVELOPMENT OF MIXED-CONDUCTING DENSE CERAMIC MEMBRANES FOR  
HYDROGEN SEPARATION\*

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# DEVELOPMENT OF MIXED-CONDUCTING DENSE CERAMIC MEMBRANES FOR HYDROGEN SEPARATION

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## INTRODUCTION

The Office of Fossil Energy (FE) in the U.S. Department of Energy (DOE) sponsors a wide range of research, development, and demonstration programs to maximize the use of vast domestic fossil resources and ensure a fuel-diverse energy sector while simultaneously responding to global environmental concerns. DOE/FE implements its programs through DOE's Federal Energy Technology Center (FETC). The development of cost-effective membrane-based reactor and separation technologies is of considerable interest for applications in advanced coal-based power and fuel production technologies.

DOE is formulating a program, called "Vision 21," which is aimed at developing very highly efficient power and coproduction technologies that discharge almost no pollutants and close the carbon cycle. As part of this program, high-temperature membranes for separating hydrogen from coal gasification and other partial-oxidation-product streams are being considered. Thin and dense ceramic membranes, fabricated from mixed protonic and electronic conductors, provide a simple and efficient means for separating hydrogen from gas streams. Mixed-conducting membranes transport via ion and electron conducting mechanisms [1,2]. Hydrogen separation is achieved in a nongalvanic mode, without the need for an external power supply to drive the separation and thereby offers potential economic advantages over existing technologies. In the early 1980s, Iwahara et al. [3-5] first reported protonic conduction in SrCeO<sub>3</sub> materials. Later, the BaCeO<sub>3</sub> system was extensively studied because of its relatively higher conductivities [6-9]. But all of these known materials exhibit low electronic conductivities and are therefore unsuitable for nongalvanic hydrogen separation.

A hydrogen-permeable membrane must exhibit high electronic and protonic conductivities, with the ratio between the two approximating unity. We began to develop a mixed-conducting ceramic membrane to transport hydrogen by first characterizing the transport properties of BaCe<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3- $\alpha$</sub>  (BCY) by impedance spectroscopy, gas permeation, and open-cell voltage (OCV) measurements. Based on the results obtained on the BCY sample, we have developed a novel composite system that operates in a nongalvanic mode, and preliminary measurements indicate that hydrogen permeation is several times faster than that observed for BCY. This paper will describe synthesis, characterization, and performance evaluation of the mixed-conducting dense ceramic membranes intended for hydrogen separation applications.

## EXPERIMENTAL

We synthesized BaCe<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3- $\alpha$</sub>  (BCY) via solid-state reactions of appropriate amounts of BaCO<sub>3</sub>, CeO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>. The details of sample preparation conditions were outlined in Ref. 10. Impedance spectra were measured in the frequency range of 13 MHz-5 Hz and ionic transference numbers were derived from OCV after two sides of the specimen were exposed to various gaseous

environments [10]. Hydrogen permeation was measured in the setup shown schematically in Fig. 1, with N<sub>2</sub>-4% H<sub>2</sub> gas as feed stream and argon as the sweeping gas. All of the permeation measurements were made under ambient gas pressures.

## RESULTS AND DISCUSSION

The total conductivity of BCY was low in pure argon, even at high temperatures ( $\geq 600^\circ\text{C}$ ), but increased slightly with the addition of  $\approx 2\%$  water vapor. The total conductivity of BCY was found to be much higher in pure oxygen than in pure argon, but the effect of water vapor depended on temperature. At low temperatures, addition of water vapor increased total conductivity. At high temperatures, however, total conductivity decreased slightly when water vapor was added. Total conductivity increased from  $\approx 5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$  at  $600^\circ\text{C}$  to  $\approx 2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$  at  $800^\circ\text{C}$ . The total ionic transference number in hydrogen/water vapor environments decreased from 0.90 to 0.80 when temperature increased from 500 to  $800^\circ\text{C}$ . The protonic transference number decreased, whereas the electronic transference number increased with increasing temperature. The protonic transference number decreased from 0.87 to 0.63, whereas the oxygen transference number increased from 0.03 to 0.15 as temperature increased from 600 to  $800^\circ\text{C}$ .

For a given total conductivity, ambipolar diffusion flux density reaches its maximum when the ionic transference number equals the electronic transference number [11,12]. The relatively low electronic transfer numbers of this material suggest that electronic transport in the hydrogen/water vapor environments is not adequate to obtain maximum hydrogen flux density. To improve electronic transport, a second phase, with high electronic conduction or proper doping, is needed. Because the electronic transference number is low, the electrodes and external power circuitry (galvanic mode) shown in Fig. 1 are needed for BCY samples to transport hydrogen. The measured hydrogen flux as a function of pumping current in a BCY sample ( $\approx 2$  mm thick) at 600 and  $800^\circ\text{C}$  is shown in Fig. 2 together with the theoretical flux calculated from the Nernst equation.

Recently, we developed a novel composite with improved electronic transport by adding a second phase, with high electronic conduction, and fabricated samples in the thickness range of 200  $\mu\text{m}$  to 2 mm. Hydrogen permeation through these samples was measured in a setup similar to that shown in Fig. 1, but with no electrodes or external power supply (nongalvanic mode). The measured flux as a function of temperature in samples with various thicknesses are shown in Fig. 3. For comparison, the flux measured in an  $\approx 2$ -mm-thick BCY pellet by short-circuiting the two Pt electrodes is also shown in this figure, which shows that the flux is higher in the novel composite samples than in the BCY. At  $800^\circ\text{C}$ , we measured a hydrogen flux of  $0.05 \text{ cm}^3/\text{min}/\text{cm}^2$  in a  $\approx 2$ -mm-thick composite sample, whereas in a BCY sample of the same thickness, we measured only  $0.02 \text{ cm}^3/\text{min}/\text{cm}^2$ . A maximum flux of  $\approx 0.12 \text{ cm}^3/\text{min}/\text{cm}^2$  was obtained in the 200- $\mu\text{m}$ -thick composite sample. We realize that industrially significant hydrogen fluxes have not been obtained (in Fig. 3), but we think the flux can be enhanced significantly by optimizing the amount of second-phase addition, controlling the microstructure, and modifying the surface conditions of the ceramic membrane. Moreover, all gas streams were maintained at ambient pressures in our permeation measurements (for safety reasons) and the flux will increase significantly with an increase in the hydrogen partial pressure differential between the two sides of a membrane.

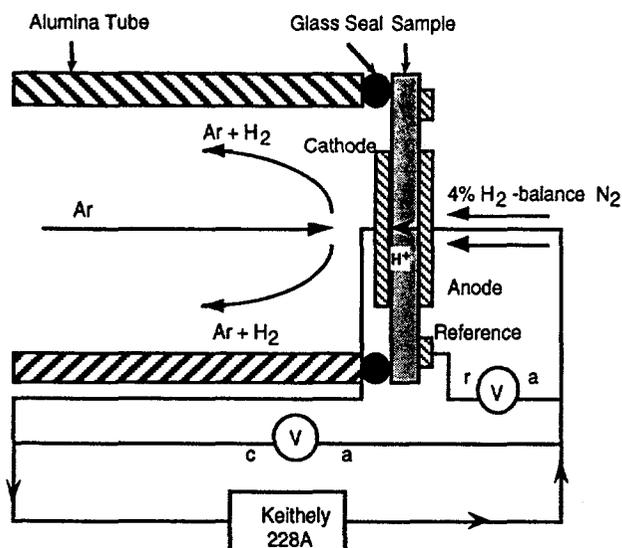


Fig. 1.  
Schematic illustration of setup for testing hydrogen permeation.

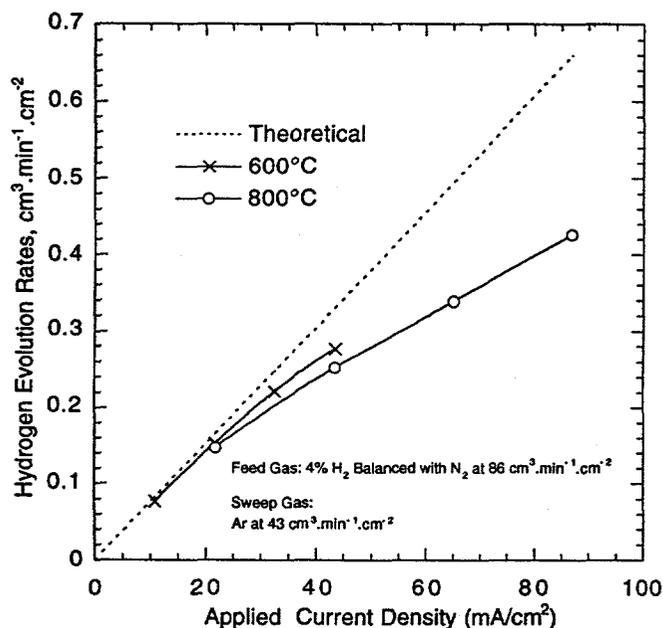


Fig. 2.  
Hydrogen flux through a 2-mm-thick BCY sample as a function of pumping current at 600 and 800°C.

## CONCLUSIONS

The electronic transference numbers of BCY were relatively low when compared with the protonic numbers. At 800°C, a hydrogen flux of only 0.02 cm<sup>3</sup>/min/cm<sup>2</sup> was obtained in an ≈2-mm-thick BCY sample by short-circuiting the two Pt electrodes. We have developed a novel composite system with improved electronic transport, and preliminary measurements indicate that the new membrane materials can be used in a nongalvanic mode to separate hydrogen from gas mixtures. A maximum flux of 0.12 cm<sup>3</sup>/min/cm<sup>2</sup> has been measured at 800°C in the composite material operated in the nongalvanic mode. Currently, work is underway to further enhance the hydrogen flux in the composite membrane materials.

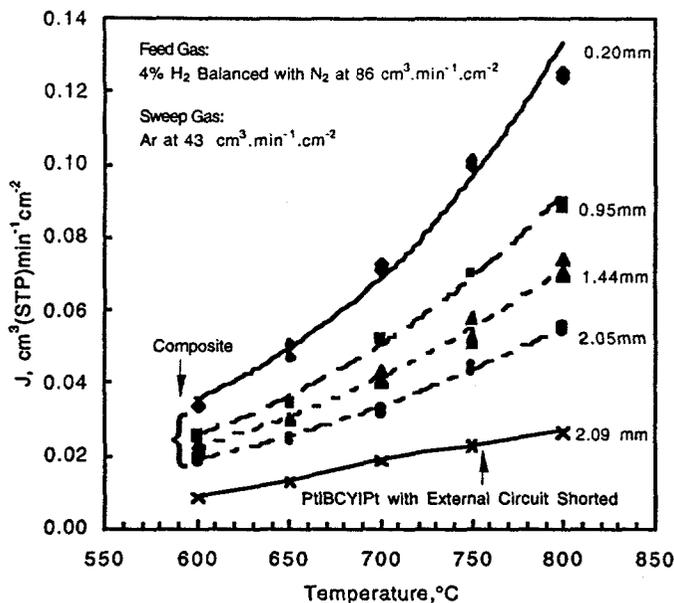


Fig. 3. Hydrogen flux in novel composite in nongalvanic mode as a function of temperature. Flux measured in BCY in short-circuit condition (with two platinum electrodes) is shown for comparison.

#### ACKNOWLEDGMENT

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