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Development of Proton-Conducting Membranes for Separating Hydrogen from Gas Mixtures*

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DISCLAIMER

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ABSTRACT

The production, cleanup, compression, and circulation of hydrogen are critical to direct coal liquefaction processes. Bechtel International, in a study performed for the U.S. Department of Energy, estimated that about 40% of the capital cost of a coal liquefaction plant would be for the air separation, gasification, and gas cleanup/by-product recovery sections of the plant. A hydrogen-permeable ceramic membrane would have the potential to reduce the size, complexity, and cost of the shift converter units in primary hydrogen production by selectively removing hydrogen from the equilibrium-limited shift reactor, thus reducing the number of stages and the need for carbon dioxide removal. In the liquefaction section, these

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membranes would allow recovery of high-purity hydrogen directly from the overhead gas streams from high- and intermediate-pressure vapor/liquid separators, avoiding much of the gas cleaning, drying, and conditioning required to purify recycled hydrogen with the conventional technology.

Outside of direct coal liquefaction, three major areas currently produce and use large volumes of hydrogen, and several other areas such as hydrogen-fueled vehicles and indirect coal liquefaction may develop into major users. At present, the three major areas (petroleum refining, ammonia manufacture, and methanol manufacture) collectively consume about 95% of all deliberately manufactured hydrogen in the U.S., with petroleum refining taking about 70%. As crude oil quality continues to deteriorate and allowable levels of sulfur, nitrogen, and aromatics in engine and burner fuels continue to decrease, refinery hydrogen needs will continue to increase while sources such as naphtha reforming become more scarce due to reduced aromatics in products. The potential of membrane technology both to recover hydrogen from streams where it is currently not economical due to low concentration, low pressure, or other factors, and to facilitate hydrogen production by integrating hydrogen separation and purification into the shift conversion process, may reduce refining costs and help retain domestic refining capacity and operation.

Petroleum refineries currently employ cryogenics, pressure swing adsorption (PSA), and membrane systems for hydrogen recovery; each of these technologies, however, has limitations. Cryogenic separation is generally used only in large-scale facilities with liquid hydrocarbon recovery, due to its high capital cost. PSA typically recovers less of the feed-stream hydrogen and is limited to modest temperatures. Current membrane

systems create a large pressure drop that requires substantial gas recompression, are susceptible to chemical damage from H_2S and aromatics, and have limited temperature tolerance.

Thin and dense ceramic membranes fabricated from mixed protonic/electronic conductors can provide a simple, efficient means of separating hydrogen from gas streams and offer an alternative to existing methods of hydrogen recovery. Because mixed electronic/protonic conductors internally transport not only hydrogen (and thus provide the means to separate hydrogen from other gaseous components) but also electrons, hydrogen separation could be achieved in a non-Galvanic mode of operation (i.e., without the need for external electrodes, circuitry, and/or power supply).

To be suitable as a hydrogen-permeable membrane, a material must exhibit sufficiently high electronic and protonic conductivities, and these conductivities must be approximately equal to one another to maximize hydrogen permeation through the material. In addition, the material must have sufficient mechanical integrity to withstand normal operating stresses and must be chemically stable under a wide range of gas atmospheres. This talk will summarize results obtained in Argonne's effort to develop material for use as a hydrogen separation membrane.

Of various materials reported to be proton conductors, the cerates generally exhibit the highest conductivities. The transport properties of $BaCe_{0.95}Y_{0.05}O_{3-\alpha}$ (5%-BCY) and $SrCe_{0.95}Y_{0.05}O_{3-\alpha}$ (5%-SCY) were characterized by impedance spectroscopy, gas permeation, and open-cell voltage measurements. The results for 5%-BCY indicate that in an

oxygen/water vapor atmosphere, proton conduction is dominant at low temperatures (500-600°C) while oxygen ion conduction dominates at higher temperatures (700-800°C). In a hydrogen/water vapor atmosphere, proton conduction dominates over the entire temperature range studied (500-800°C); this is desirable for a hydrogen separator. However, compared to the protonic transference number, the electronic transference number is relatively low in a H_2/H_2O atmosphere and must be enhanced in order to maximize the rate of hydrogen permeation.

For 5%-SCY at temperatures ≤600°C, ionic conduction is almost completely protonic, indicating that 5%-SCY should have a significantly greater selectivity for hydrogen permeation than 5%-BCY. Hydrogen permeation through 5%-SCY at 750°C was estimated to be ≈0.05 cm^3(STP) $cm^{-2}min^{-1}$ from protonic conductivity measurements. Our experience suggests that hydrogen permeation can be enhanced by reducing interfacial polarization in the mixed-conducting ceramics. We have developed a novel composite system, and preliminary measurements indicate that hydrogen permeation in this new system is several times faster than that observed in 5%-BCY or 5%-SCY.

In this presentation, we will describe the materials selection, synthesis, characterization, and performance evaluation of mixed-conducting dense ceramic membranes for hydrogen separation applications.

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