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DEVELOPMENT OF PROTON-CONDUCTING MEMBRANES FOR SEPARATING HYDROGEN FROM GAS MIXTURES*

S. E. Dorris and U. Balachandran
Energy Technology Division
Argonne National Laboratory
Argonne, IL 60439-4838

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DISCLAIMER

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S. E. DORRIS (CERAMIST) AND U. BALACHANDRAN (CERAMIST)
ENERGY TECHNOLOGY DIVISION
ARGONNE NATIONAL LABORATORY
9700 SOUTH CASS AVENUE
ARGONNE, IL 60439-4838

Introduction

Petroleum refineries around the world consume major amounts of hydrogen during the hydrogenation, desulfurization, and denitrogenation of fuels, and the hydrogen requirements at refineries are growing as crude-oil feedstocks become heavier with higher levels of sulfur and heavy metals and demand shifts to lighter, high-value finished products [1]. Coal liquefaction, both direct and indirect, also relies on a plentiful supply of hydrogen. While the demand for hydrogen is increasing, a major source of hydrogen in oil refineries, catalytic reforming, is being curtailed. In as much as catalytic reforming, which converts saturated-ring hydrocarbons into aromatics, is now out of favor because of demands for lower-aromatic fuels, the demand for hydrogen derived from other sources such as syngas, coal gas, etc. has increased.

Irrespective of the source and processes involved in hydrogen production, there is a need to efficiently separate hydrogen from product gas streams in a cost-effective manner. Abrado and Khurana [2] note that the recovery of hydrogen with current technology is generally not economical for gas streams that are at pressures below 150 psig and contain <50% hydrogen. Typically, such low-pressure/low-concentration streams are sent to the refinery fuel gas header and are valued as fuel. The difference between the value of hydrogen as fuel gas and the incremental cost of deliberately producing additional hydrogen provides the economic incentive for hydrogen recovery. Petroleum refineries currently employ cryogenics, pressure swing adsorption (PSA), and membrane systems for hydrogen recovery; however, each of these technologies has limitations. Cryogenic separation is generally used only in large-scale facilities with liquid hydrocarbon recovery because its capital cost is high. 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. In addition, current membrane systems are susceptible to chemical damage from H_2S and aromatics and have limited temperature tolerance.

Thin, dense ceramic membranes fabricated from mixed protonic/electronic conductors offer an alternative to existing methods of hydrogen recovery and provide a simple, efficient means of separating hydrogen from gas streams. In addition to providing high-purity hydrogen, the membranes would shift equilibrium-limited reactions toward hydrogen production and away from formation of undesirable by-products by selectively removing hydrogen from product streams. 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 external electrodes, circuitry, and/or power supply). This paper describes a recently initiated program to develop such membranes for separating hydrogen, and presents a review of the literature on mixed protonic/electronic conductors that may serve as suitable membrane materials.

Literature Review

Acceptor-doped $SrCeO_3$ was the first ceramic reported to exhibit proton conduction [3]. Since its discovery, proton conduction has been demonstrated in numerous other acceptor-doped cerates and zirconates, $AB_{1-x}M_xO_{3-\delta}$ (where A = Ca, Ba, or Sr; B = Ce or Zr; and M = a divalent or trivalent cation of Ca, Y, Yb, In, Nd, or Gd) [4-9]. In atmospheres free of proton sources such as H_2 or H_2O, the dominant charge carriers are electron holes and oxygen ions, whereas protons dominate at low to moderate temperatures in the presence of H_2 or H_2O. In H_2 at several hundred degrees Celsius, conductivity is almost purely protonic and ranges up to $\approx 10^{-2}\ \Omega^{-1}\text{-cm}^{-1}$ [10]; at temperatures near 1000°C, conductivity approaches $10^{-1}\ \Omega^{-1}\text{-cm}^{-1}$, with protons, electron holes, and oxygen ions all contributing to conduction. The conductivities of representative proton conductors are shown in Fig. 1. $BaCeO_3$-based ceramics exhibit some of the highest conductivities, and cerates generally exhibit higher conductivities than zirconates. However, material with the highest total conductivity may not necessarily be the most appropriate for separating hydrogen, because operation of the membrane in a non-Galvanic mode requires both electronic and protonic conductivities, and transference numbers for the various charge carriers vary from system to system. For example, the transference number for protons in a $SrCeO_3$-based material is higher, while its total conductivity is lower than that of a $BaCeO_3$-based material.

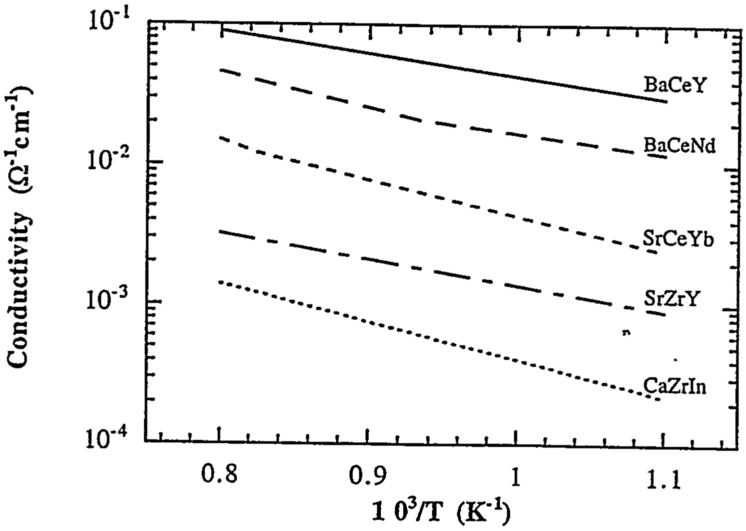

Fig 1.
Electrical conductivity of representative perovskite-type mixed electronic/protonic conductors in H_2. BaCeY = $BaCe_{0.8}Y_{0.2}O_{3-\delta}$, BaCeNd = $BaCe_{0.9}Nd_{0.1}O_{3-\delta}$, SrCeYb = $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$, SrZrY = $SrZr_{0.95}Y_{0.05}O_{3-\delta}$, CaZrIn = $CaZr_{0.9}In_{0.1}O_{3-\delta}$. Adapted from Ref. [10].

The incorporation of protons in proton conductors can be described [7, 11, 12] by the following reactions:

$$H_2O + V_O^{\cdot\cdot} + O_O^x = 2OH_O^{\cdot} \quad (1)$$

$$H_2 + 2O_O^x + 2h^{\cdot} = 2OH_O,^{\cdot} \quad (2)$$

where $V_O^{\cdot\cdot}$ represents doubly ionized oxygen vacancies, $OH_O^{\cdot}$ signifies an oxygen ion-proton pair, O_O^x are oxygen ions on oxygen sites, and $h^{\cdot}$ are electron holes. These reactions suggest that the protons are intimately associated with oxide ions rather than occupying lattice positions, and it has been proposed [13] that proton conduction proceeds when protons hop between oxide ions. Other equilibria that play a role in defining the concentrations of charge carriers as a function of temperature and gas phase composition are

$$1/2\ O_2 + V_O^{\cdot\cdot} = 2h^{\cdot} + O_O^x \quad (3)$$

and

$$2H_2 + O_2 = 2H_2O. \quad (4)$$

As the defect concentrations vary with temperature and atmosphere, the charge carrier that dominates conduction also varies. Assuming a defect structure based on the above equilibria, Labrincha et al. [5] fitted their electrical conductivity data for $SrZr_{0.84}Y_{0.16}O_{2.92}$ to the following equation:

$$\sigma = \sigma_O{}^{2-} + \sigma_p(pO_2)^{1/4} + \sigma_{H^{\cdot}}/(1+pH_2/pH_2O)^{1/2}, \quad (5)$$

where $\sigma_O{}^{2-}$, σ_p, and $\sigma_{H^{\cdot}}$ are the conductivities associated with oxygen ions, electron holes, and protons, respectively. The resulting conductivities yielded the variation in transference numbers as functions of pO_2 as shown in Fig. 2. Protons clearly dominate conduction in this material up to moderately high oxygen pressure (≈0.001 atm O_2), with electron holes becoming dominant at higher partial pressures of oxygen (pO_2). Because a goal of this project is to develop membranes that operate in a non-Galvanic mode, membrane materials will need sizable protonic and electronic conductivities ($\approx 10^{-2}\ \Omega\text{-cm})^{-1}$, with their transference numbers being comparable in size. Variation of the dopant composition and concentration may allow the relative contributions of the charge carriers to be tailored for the present application. For example, Labrincha et al. [5] show that electronic conduction is suppressed by substituting lanthanum for strontium in $SrZrO_3$, and Iwahara et al. [13] show that the total conductivity of $BaZr_{0.95}M_{0.05}O_{3-\delta}$ varies by approximately one order of magnitude across the series M = Ga, In, Nd, Dy.

In addition to having high protonic and electronic conductivities, materials for hydrogen-separating membranes must have sufficient mechanical integrity and be chemically stable under

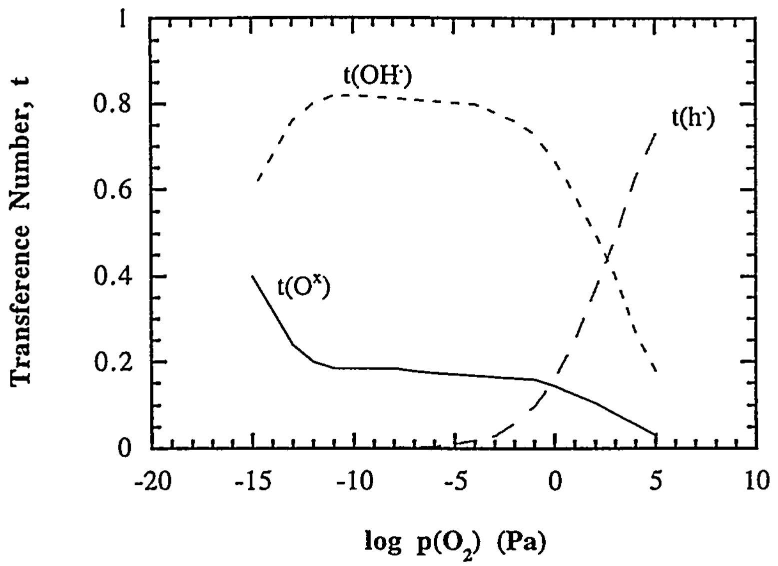

Fig. 2.
Predicted effects of oxygen partial pressure on the transference numbers of electron holes, t(h$^\cdot$), oxygen-ions, t(O^x), and protons, t(OH$^\cdot$), in $SrZr_{0.84}Y_{0.16}O_{2.92}$ at 800°C. Adapted from Ref. [5].

highly reducing conditions. On the basis of published thermodynamic data, Yokokawa et al. [14] determined that $SrCeO_3$ should be unstable, decomposing into SrO and Ce_2O_3, only under the most extreme conditions, e.g., above 1000°C at $pO_2 < 10^{-20}$ atm. This determination was experimentally corroborated by Bonanos et al. [4], who found that reduction of $SrCeO_3$ was not a problem in prototype fuel cells and water electrolyzers, and concluded, on the basis of lengthy conductivity measurements, that $BaCeO_3$-based materials should be even more stable.

The chemical stability of hydrogen membrane materials in the presence of CO_2 poses a concern that is potentially more serious than the problem of reduction, because alkaline earth carbonates are extremely stable. On the basis of thermodynamic data [15], $SrCeO_3$- and $BaCeO_3$-based materials are expected to react to form alkaline earth carbonates at temperatures < 1200°C in 1 atm CO_2; however, studies of $BaCe_{0.8}Gd_{0.2}O_{2.9}$ in artificial fuel-gas mixtures that contain 8% CO_2 and in prototype fuel cells [16, 17] show that the cerates have a limited tolerance to CO_2 at elevated temperatures. At 800°C, $BaCe_{0.8}Gd_{0.2}O_{2.9}$ appeared, by X-ray diffraction, to be stable up to 0.2 atm of CO_2. This apparent discrepancy between experiment and theoretical prediction of cerate stability may or may not result from slow kinetics of decomposition, as concluded by Scholten et al. [15], but it clearly demonstrates the importance of determining the stability limits of candidate materials under actual operating conditions. In comparison to cerates, zirconates are expected to be more resistant to reaction with CO_2 and have greater mechanical strength [10]. Considering the questionable stability of cerates in the presence of CO_2, zirconates warrant investigation as suitable hydrogen-separating membranes despite the fact that they are expected to have lower conductivities than the cerates. Considering the conductivity, strength, and stability requirements, the following materials have been selected for evaluation as hydrogen-permeable materials: $SrCe_{1-x}M_xO_{3-\delta}$, $BaCe_{1-x}M_xO_{3-\delta}$, $CaZr_{1-x}M_xO_{3-\delta}$, $SrZr_{1-x}M_xO_{3-\delta}$, and $BaZr_{1-x}M_xO_{3-\delta}$, where M will be a fixed-valent cation such as Ca, Y, Yb, In, Nd, or Gd.

Approach

The expertise to develop hydrogen-permeable membranes is closely related to that used in developing oxygen-permeable membranes for gas-to-liquid fuel conversion where oxygen-permeable membranes separate oxygen from the nitrogen in air, allowing high-purity oxygen to react with methane and form syngas in the presence of a catalyst. Because the oxygen-permeable membrane transports electrons in addition to oxygen ions, it operates without electrodes or external power supply. Consequently, the process is energy efficient and reduces the cost of converting methane to syngas by ≈50% when compared with the cost of steam reforming or partial oxidation.

To be suitable as a hydrogen-permeable membrane, a material must exhibit suitable electronic and protonic conductivities, have sufficient mechanical integrity to withstand normal operating stresses, and be chemically stable under a wide range of gas atmospheres. Initially, based on the literature regarding mixed electronic/protonic conductors, five candidate materials were identified for further development. Now, procedures for synthesizing and sintering dense specimens will be established, and their ionic and electronic conductivities will be measured.

Although numerous materials are reported to exhibit mixed electronic/protonic conduction, the appropriate balance between electronic and protonic conduction has not been demonstrated (for the present application, the levels of protonic and electronic conductivity should be approximately equal). Based on a preliminary study of the selected materials, the compositions will be modified or additional compositions will be selected on the basis of thermodynamic and point-defect chemistry principles. Materials with a total conductivity of $\approx 10^{-2}$-10^{-1} $(\Omega\text{-cm})^{-1}$ and comparable protonic and electronic conductivities will be selected for further evaluation. In particular, their stability limits will be determined. At the same time, their mechanical properties will be evaluated and improved with second-phase additions when necessary.

After identifying mechanically and chemically stable materials with sufficient electronic and protonic conductivities, the materials will be fabricated into thin, tubular membranes and the hydrogen flux will be measured under simulated operating conditions. Based on data from these studies, a prototype process will be designed and the associated economics will be assessed with respect to size of plant, temperature range of operation, and energy and mass balances. In addition, potential applications of proton membrane technology will be evaluated in terms of overall market scale, typical of scale site operation, process integration opportunities and issues, and alternative-source economics. These efforts will be coordinated with efforts at the Pittsburgh Energy Technology Center (PETC) to examine similar issues in the context of direct and indirect coal liquefaction. Process issues and economics will continue to be evaluated as technical progress warrants.

Conclusions

Dense ceramic membranes made from mixed protonic/electronic conductors are permeable only to hydrogen, and in principle, provide a simple, efficient means of separating hydrogen from gas mixtures. At a time when world demand for hydrogen is growing, such proton-conducting membranes have the potential to significantly alter the economics of hydrogen separation and purification processes and thus improve the economic viability of processes that utilize hydrogen, such as some refinery operations and direct and indirect coal liquefaction. This paper describes a recently initiated program to develop materials and fabrication processes to separate hydrogen with dense ceramic membranes in a non-Galvanic mode of operation (i.e., without electrodes or external power supply).

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