MIXED CONDUCTING MEMBRANES FOR PRESSURE-DRIVEN HYDROGEN SEPARATION FROM SYNAGS

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Introduction

Integrated Gasification Combined Cycle (IGCC) systems show tremendous potential for very efficient, environmentally friendly power generation. In IGCC systems, a combined cycle is employed in which syngas (CO+H₂) is used to drive a gas turbine and the exhaust gases are then used to heat water/steam to generate superheated steam that drives a steam turbine. IGCC systems typically operate at efficiencies higher than 40%, whereas coal-burning plants that employ flue gas desulfurization processes reach a maximum efficiency of 34%. A number of demonstration projects, such as the Wabash River Coal Gasification Repowering Project in Indiana and the Pinon Pine IGCC Power Project in Nevada, have been carried out as part of the Department of Energy (DOE) Coal Technology Program.²,³

Despite the significant potential of IGCC systems, economic considerations still limit their wide-spread commercial applicability. Fortunately, the total hydrogen in raw syngas is usually greater than 200% of the required amount. Thus, one critical advance that would significantly enhance the commercial viability of IGCC systems is the recovery of hydrogen fuel from syngas as a by-product. There are a number of technologies and combinations of technologies being considered as alternatives for recovery of hydrogen from syngas. These technologies include membrane separation, pressure swing adsorption (PSA), methanation and nitrogen wash techniques. Each of these techniques has its strong points, and the choice of the specific technique is usually dictated by the economics of the process and the purity of hydrogen desired. Since ultra-high purity (>99%) H₂ is a high value commodity, a technique that could generate such a high purity gas stream would be most attractive from an economic standpoint.

Technical Approach

Membrane separation, especially with ceramic membranes that separate H_{2} by selectively transporting H^+ ions (protons), offers the potential for generation of very high purity hydrogen (>99.9%), and is clearly superior in this regard compared with the other techniques mentioned above. Studies at SK Corporation in Ulsan, Korea have shown that the highest purities attainable by other techniques such as PSA, methanation and nitrogen wash techniques are only 97%, 85% and 97% respectively.⁴

A high-temperature, pressure-driven membrane-based separation system would be ideal for separation of hydrogen from the hot, high-pressure syngas stream typical of IGCC systems. Ceramic membranes are the only alternatives for operation under the high-temperature, high-pressure environment expected in IGCC systems, and can be designed to have very good thermomechanical and thermochemical stability under IGCC operating conditions. Our approach is to use a dense ceramic mixed-conducting membrane that can generate a stream of very high-purity H₂. The proposed concept, when fully developed, will be compatible with the temperature and pressure conditions in IGCC systems and thus will be amenable for process and physical system integration.

One category of ceramic membranes that has received a good deal of attention in the preceding decade is mixed proton/electronic conducting perovskite type oxide ceramics. The stoichiometric chemical composition of perovskites can be represented as ABO₃, where A is a bivalent ion (A²⁺) such as calcium, magnesium, barium or strontium and B is a tetravalent ion (B⁴⁺) such as cerium or zirconium. While simple perovskites such as barium cerate (BaCeO₃) and strontium cerate (SrCeO₃) have some proton conductivity, it is now well known that doping these perovskites at the B sites can significantly enhance their protonic conductivities. The most common examples are structures of the form AB_xD_{1-x}O₃, formed by doping ABO₃ with trivalent ions such as yttrium (Y³⁺) and ytterbium (Yb³⁺). For example, BaCe₀.₉₅Y₀.₀₅O₃₋δ has been shown to have a proton conductivity as high as 1.27 × 10⁻² S/cm at 800°C in a H₂/H₂O atmosphere. In a pressure driven system, both hydrogen ions and electrons generated by dissociation of H₂ molecules at the high-pressure surface must be transported through the membrane to recombine at the low-pressure surface of the membrane. Since these two are parallel kinetic processes, the overall kinetics are limited by the slowest process. In the case of a conventional mixed conducting membrane, the paths for proton conduction and electron conduction are the same. However, the electronic conductivity of mixed perovskites is very low and therefore is usually the limiting factor to these materials being used effectively as pressure-driven hydrogen separation membranes. For example, Phillips et al have shown that the electronic conductivity of SrCe₀.₇₅Y₀.₂₅O₃₋δ was 2 to 3 orders of magnitude lower than its protonic conductivity at 800°C.⁵ Our approach is to increase the electronic conductivities of these perovskite-based membranes through compositional and microstructural modifications.

In addition to being a good electronic conductor at these temperatures, the membrane material should also possess good thermomechanical and thermochemical stability at testing conditions involving temperatures as high as 900°C and high pressures of up to 5-10 atm. It has been reported that barium and strontium cerates are thermochemical unstable in H₂O and CO₂ containing atmospheres, due to carbonate formation as indicated in Equation (2).

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\text{BaCeO}_3 + \text{CO}_2 \rightarrow \text{BaCO}_3 + \text{CeO}_2 \quad (2)
\]

We are also addressing methods of increasing the thermochemical stability of the cerate-based membranes in CO₂-containing atmospheres. A membrane system that displays good mixed conductivity and thermochemical stability has been chosen for a proof-of-concept demonstration using said perovskite-ceria composite mixed conducting membranes for pressure-driven gas separation.

Experimental Approach

Membrane materials were synthesized with optimized compositions for mixed conductivity and thermochemical stability, using conventional powder processing routes. The powders were uniaxially pressed with appropriate binder additions in the shape of bars for conductivity measurements and as pellets for thermochemical stability measurements in simulated syngas. The bars and pellets were subjected through a prescribed sintering schedule and the densities of the sintered parts were measured through an Archimedes measurements, to ensure that the porosities in all parts was less than 1%, and that the densities corresponded to expected values for the chosen compositions. The specimens were studied by x-ray diffraction and scanning electron microscopy respectively to ensure that the targeted phases and microstructures were obtained in the sintered pellets.

The conductivity of the baseline cerate compositions and the modified compositions were evaluated using a conductivity test station, which is schematically shown in Figure 1. The apparatus has the ability to measure conductivities of bar specimens in various dry or wet gases. Conductivities of various bar specimens were measured at 800°C, 850°C and 900°C in wet hydrogen, and dry argon so that the protonic and electronic conductivities of the material could be assessed.

Membrane material stability under conditions expected in an IGCC system will be tested using a simulated syngas produced by steam reforming of natural gas. A mixture of steam/methane (2:1 ratio), and carbon dioxide (CO₂/CH₄=1.4) calculated to match the carbon/hydrogen ratio found in IGCC syngas, will be passed over a commercial nickel steam reforming catalyst at 800°C and 7.8 bar. Space velocity of less than 500 volume methane (stp conditions) per volume catalyst per hour will be used. This is low enough that the reformate composition is expected to closely match the equilibrium composition (1.5% CH₄, 21.4% CO₂, 15.3% CO, 36.2% H₂, 1.1% N₂, 24.5% H₂O) calculated for a steam/CO₂ reforming natural gas.

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BaCeO₃-Based protonic conductivities of separation at 800-900 oC, resulting in a very high purity hydrogen developed. These membranes will allow pressure-driven hydrogen.

A novel, dense, mixed-conducting ceramic membrane is being developed. These membranes will allow pressure-driven hydrogen separation by use of these mixed conducting membranes. The electronic conductivity and thermocatalytic stability of candidate membranes materials under simulated operating conditions will be evaluated. The performance of the membrane as a mixed ionic-electronic conducting membrane will be evaluated through feasibility studies of pressure-driven hydrogen separation from simulated syngas. This hydrogen separation technique is expected to have a major impact on enhancing the commercial feasibility of IGCC systems.

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References