MEMBRANE FUEL PROCESSOR FOR HYDROGEN GENERATION: REACTOR AND PROCESS ISSUES

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Introduction

Hydrogen-fed proton exchange membrane (PEM) fuel cells offer a modular source of power for stationary and mobile applications spanning power stations, remote sensors, soldier-power, and vehicles. Energy density and safety considerations rule out the storage and supply of hydrogen, so the widespread deployment of PEM fuel cells requires efficient, on-demand production of high purity hydrogen from liquid fuels. Technology under development involves a sequence of reaction and purification steps, typically involving fuel reforming, water gas shift conversion, and preferential oxidation.[1, 2] These steps involve multiple units with different operating conditions and catalysts, adding undesirable complexity, weight, volume, and complexity.

In this study we evaluate the use and feasibility of a catalytic membrane reactor to generate high purity hydrogen for supply to a PEM fuel cell. The use of hydrogen-permselective membranes in fuel processing has been the focus of recent patent activity.[3] The basic concept is depicted in **Figure 1**. A liquid fuel is fed to a catalytic reactor wherein the desired chemistry is carried out. The catalyst is in the form of particles or impregnated in the wall of the porous tube. The surface of the tube is coated with a hydrogen permselective membrane such as a Pd-based alloy or a molecular sieving oxide. As hydrogen is generated it is removed through the membrane to the permeate side which is maintained at atmospheric pressure (with or without sweep gas). Elevated pressure reaction provides a trans-membrane driving force for permeation of hydrogen. Removal from the reaction zone of high purity hydrogen through the permselective membrane drives the reforming to high conversion while rejecting CO, a fuel cell poison. We consider several hydrogen producing reaction systems, including:

- Direct methanol decomposition
  $CH_3OH \rightarrow 2\,H_2 + CO$
- Methanol steam reforming
  $CH_3OH + H_2O \leftrightarrow 3\,H_2 + CO_2$
  $CO + H_2O \leftrightarrow H_2 + CO_2$
  $CH_3OH \leftrightarrow 2\,H_2 + CO$
- Iso-octane steam reforming

We also consider oxidative decomposition and autothermal reforming which involve the co-feed of air with the fuel. Controlled oxidation provides the requisite energy to drive the endothermic reactions, avoiding the need to supply external energy.

Model Framework and Evaluation Strategy

We developed mathematical models of the packed-bed membrane reactor (PBMR) and catalytic membrane reactor (CMR). The PBM model was applied to the methanol decomposition system while the CMR model was applied to the methanol steam reforming. Where possible, we used literature kinetics and transport parameters. Details of the model are discussed elsewhere.[4] The feasibility of the membrane fuel processor is determined by calculating several performance metrics, including hydrogen utilization and productivity, device volume and membrane cost. We also developed a process-level model in which we evaluate the complete fuel processor and PEM fuel cell system. Key process issues such as energy integration, water management, and overall efficiency, are evaluated for the conventional fuel processor and membrane fuel processor systems.

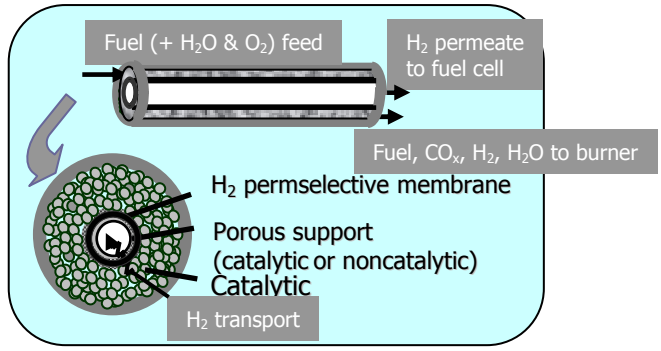

Figure 1. The membrane fuel processor involves feed of fuel to catalytic zone with hydrogen removal to atmospheric pressure stream for direct feed into fuel cell.

Results and Discussion

Methanol Decomposition. The direct decomposition of methanol to hydrogen is attractive for several reasons. Methanol is a liquid at ambient conditions and has a reasonable ratio of hydrogen to carbon. Moreover, the decomposition occurs at relatively low reaction temperature and involves a single reactant. The PBMR model considered a Pd film on the outside surface of macroporous supports (hollow tube or fiber). In the simulations we consider a defect-free Pd film thickness ranging from 1 to 100 μm deposited on commercially available ceramic hollow fibers, which afford high surface to volume. We assume isothermal operation with the permeate hydrogen at 1 atm pressure. Reaction occurs on supported Pd particles and on the Pd membrane surface, following the kinetics provided by Hara et al.[5] We account for the site coverage by adsorbed product CO which blocks hydrogen dissolution and permeation.

Figure 2 shows the results of a simulation of the PBMR for a 10-μm thick Pd membrane supported on a hollow fiber (outer diameter 1 mm; wall thickness 0.1 mm; length 1 m). At high flow rate (high GHSV) the hydrogen production is limited by low methanol conversion. Since the hydrogen permeate is maintained at 1 atm, hydrogen may back diffuse to the reaction side at the front of the reactor. As the GHSV is decreased, the methanol conversion and hydrogen partial pressure increase. The hydrogen partial pressure exhibits a maximum at an intermediate GHSV, signaling the transition to a second regime of reduced hydrogen generation. A low feed rate limits the hydrogen productivity; here the hydrogen partial pressure approaches that of the permeate (1 atm).

Determination of the production rate of hydrogen provides guidance on determining feasibility of methanol decomposition. **Figure 3** shows the dependence of the PBMR productivity on the hydrogen utilization over a range of reactor temperatures. The productivity exhibits a maximum at an intermediate utilization; the maximum underscores the aforementioned behavior at extremes in the space velocity. Since a 50 kW_e fuel cell requires nominally 0.4 mole H_2/s, these productivities are too low (e.g. 500 liter reactor volume at 80% hydrogen utilization). Our simulations of oxidative

decomposition show that external heating can be avoided but it comes at the expense of hydrogen utilization.

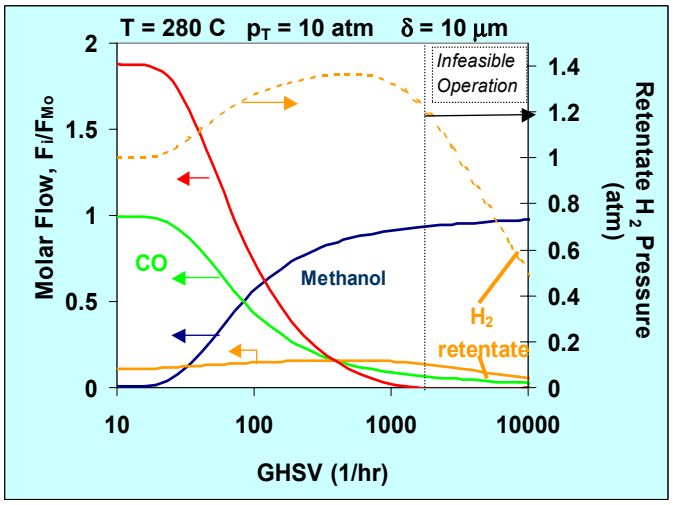

Figure 2. Dependence of the species molar flow rates and retentate hydrogen partial pressure on space velocity (GHSV) for methanol decomposition carried out at 10 atm and 280 C, using a 10 µm thick, supported Pd membrane.

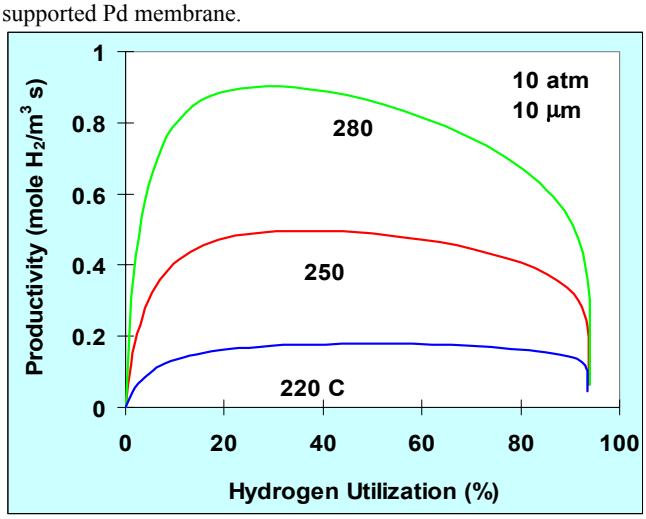

Figure 3. Dependence of the production rate of hydrogen on hydrogen utilization for methanol decomposition.

Methanol Reforming. Steam reforming of methanol is more attractive than decomposition because of the reduced CO production and the higher catalytic rates. We carried out the steam reforming of methanol in a CMR comprised of hollow fiber membranes impregnated with methanol synthesis catalyst (Cu/ZnO) and coated with a Pd-based membrane. We used a comprehensive catalytic kinetic model that accounts for methanol reforming, water gas shift, and methanol decomposition.[6] The CMR model accounts for multi-component transport and reaction within the catalytically active support as well as site blockage by adsorbed CO. In the first set of simulations we assumed isothermal operation with permeate hydrogen maintained at 1 atm. We are currently evaluating alternative configurations, including coupled autothermal reforming and membrane fuel processing.

Figure 4 shows representative results for reaction carried out at 280 C and 5.2 bar total pressure with a methanol to water feed ratio of 0.93 and a 10 µm thick Pd membrane. The simulations reveal a productive membrane processor. The device volume needed for a 50 kW_e PEM exhibits a local minimum at an intermediate space velocity. For example, at a hydrogen utilization of 75% the requisite reactor volume is about 15 liters. While additional volume would be needed for external energy supply, these results are encouraging.

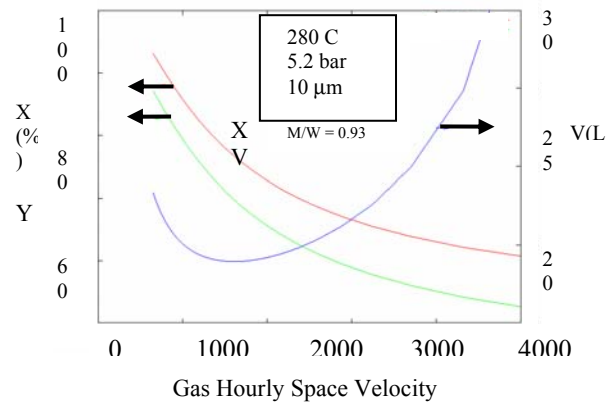

Figure 4. Simulated performance of methanol reforming in membrane processor.

Process Level Issues. We are also evaluating process-level issues of the membrane fuel processor/PEM system, focusing on energy integration, water management, sweep gas use, and overall efficiency. Process simulations of methanol and iso-octane based reforming reveals that complete fuel conversion and hydrogen recovery is unnecessary because the retentate can be combusted to provide the requisite heat for fuel vaporization and endothermic reforming. A comparison of the membrane fuel processor to the conventional system comprising reforming, WGS, and preferential oxidation reveals some notable advantages. For example, the membrane reactor delivers high purity hydrogen to the fuel cell. There are additional process simplifications regards water management and sweep gas utility.

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