353b Hydrogen Purification for Fuel Cells by Carbon Dioxide Removal Membrane Followed by Water Gas Shift Reaction

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Hydrogen is receiving increasing attention worldwide not only because of its role as an important raw material in chemical and petroleum industries, but also because of its prospect as a primary energy carrier in the 21st century. For many applications, especially for proton-exchange membrane fuel cells (PEMFC), the CO concentration of hydrogen-rich gas mixture must be reduced to ppm levels to avoid poisoning anode catalysts. In the commercial scale, most feasible strategies to generate hydrogen from hydrocarbon fuels consist of a reforming step followed by the water gas shift (WGS) and a CO clean-up step. The current known approaches for CO clean-up include methanation and preferential oxidation, both of which consume a significant amount of hydrogen. In this study, a process combining CO_2 removal using a polymeric membrane with subsequent CO conversion using water gas shift reaction was developed to purify hydrogen. This process converts CO to H_2 instead of consuming H_2 and removes more than 93.5% of the total CO_2 (for the synthesis gas consisting of 17% CO_2 and 1% CO), which makes subsequent CO_2 concentration and sequestration possible.

We have synthesized CO_2-selective polymer composite membranes with high CO_2 permeability and CO_2/H_2 selectivity in temperatures ranging from 50^{o}C to 150^{o}C. A rectangular flat-sheet membrane cell with well-defined countercurrent gas flows was used to study the CO_2 removal. A feed gas consisting of 17% CO_2, 1.0% CO, 45% H_2, and 37% N_2 was used to simulate the synthesis gas from autothemal reforming of natural gas with air. With this membrane cell running at 120^{o}C, the CO_2 concentration in the gas mixture was reduced from 17% to as low as 30 ppm. The CO_2 data have been in good agreement with model predications for the feed flow rates ranging from 10 to 130 cc/min. Then, another feed gas of 53.9% H_2, 0.1% CO_2, 1.2% CO, and 44.8% N_2 was used to simulate the synthesis gas from the CO_2-removal step. With this feed gas, a conventional low temperature water-gas-shift reactor packed with commercial Cu/ZnO catalyst was operated at 130 to 160^{o}C to shift CO to H_2. With more than 99% CO_2 removed in the synthesis gas, the reversible WGS was shifted forward so that the CO concentration was decreased from 1.2% to less than 10 ppm (dry), which is the requirement for PEMFC. The WGS reactor had a GHSV of 7650 h^{-1} at 150^{o}C and the H_2 concentration in the outlet was more than 54.7% (dry).