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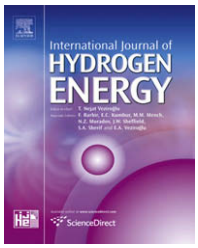

Proton exchange membrane (PEM) electrolyzer operation under anode liquid and cathode vapor feed configurations

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ABSTRACT

Proton exchange membrane (PEM) electrolysis is a potential alternative technology to crack water in specialty applications where a dry gas stream is needed, such as isotope production. One design proposal is to feed the cathode of the electrolyzer with vapor phase water. This feed configuration would allow isotopic water to be isolated on the cathode side of the electrolyzer and the isotope recovery system could be operated in a closed loop. Tests were performed to characterize the difference in the current–voltage behavior between a PEM electrolyzer operated with a cathode water vapor feed and with an anode liquid water feed. The cathode water vapor feed cell had a maximum limiting current density of 400 mA/cm^2 at 70 °C compared to a current density of 800 mA/cm^2 for the anode liquid feed cell at 70 °C. The limiting current densities for the cathode water vapor feed cell were similar to those predicted by a water mass transfer model. It is estimated that a cathode water vapor feed electrolyzer system will need to be between 5 and 8 times larger in active area or number of cells than an anode liquid feed system.

1. Introduction

Commercially available PEM electrolyzers can generate H_2 pressures of up to 200 psi and have production rates from 400 to 7900 kg/yr [1]. These units have the advantages of producing high purity hydrogen (99.999%) at high conversion efficiency (95%). Fast response time as well as the ability to accept variations in load makes the technology desirable for on-demand delivery and combining with photovoltaic power sources [2]. Disadvantages of operation include high capital cost and the hydrogen production costs. The production costs are dependent on the cost of electricity. A large energy supply is often needed due to high anode overpotentials [3]. In certain specialty applications, such as isotope separation, a dry gas supply is needed and the capital and energy costs have less effect on the relative efficiency of the system.

One of the technological issues with the use of a PEM electrolyzer in isotope separation is the development of an overall system design that will maintain the oxygen and hydrogen streams separate, maintain a closed loop hydrogen system, and allows easy integration of the electrolyzer. One design option for the isotope recovery system that would meet these criteria is to feed water vapor to the PEM electrolyzer on the cathode side of the membrane. In order to keep the hydrogen contained in a closed loop, hydrogen gas would be used as the carrier for the isotopic water vapor. Oxygen gas would be produced at the anode and be exhausted by natural convection or be removed by a sweep gas, such as nitrogen. A proposed operating configuration, using tritiated water, is shown in Fig. 1, where T represents the hydrogen isotope tritium. The water vapor would diffuse across the membrane and be oxidized at the anode to produce oxygen gas. The

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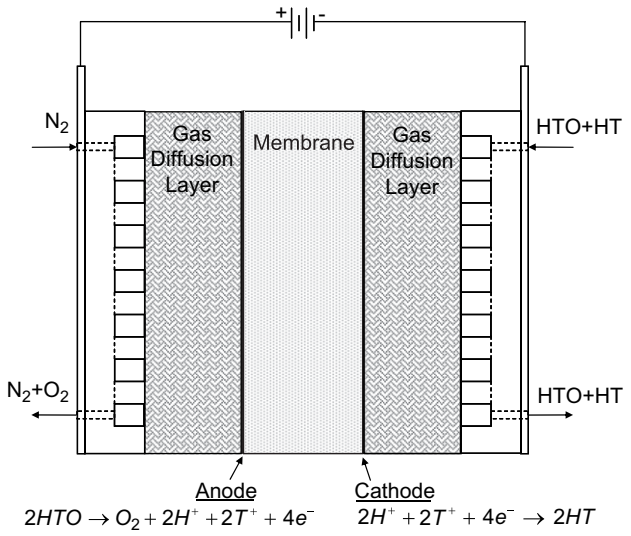

Fig. 1 – Illustration of a cathode water vapor feed PEM electrolyzer, where T represents tritium, an isotope of hydrogen.

protons and cations produced by the reaction would be conducted back to the cathode and reduced to form isotopic hydrogen gas. When an electrolyzer in this configuration is operated such that it electrolyzes all the isotopic water that crosses the membrane, the isotopic water and hydrogen gas should be confined to the cathode side of the electrolysis cell. Operating the cathode water vapor feed in this mass transport limited condition will limit the reaction rate in the cell to the rate of water diffusion from the cathode to the anode minus the rate of water electroosmotic drag from the anode to the cathode. The cathode water vapor feed configuration is significantly different than traditional PEM electrolyzer operation with a feed of liquid water to the anode [4]. With a liquid feed of water to the anode, the reaction rates in the cell at a given cell voltage are limited more by the kinetics of the reactions and the ohmic losses in the membrane and are not significantly limited by mass transfer.

Previous research on vapor electrolysis has been limited to high temperature solid oxide electrolyzers operating at the anode [5–7]. While this work focuses on the experimental comparison of a cathode water vapor feed electrolyzer with a traditional anode liquid feed system at 80 °C or below using PEM based electrolysis. These experimental results are compared with a model for mass transfer in a cathode water vapor feed electrolyzer that was developed in previous work [8]. Models of the cathode water vapor feed electrolyzer performance were developed using physics that are well accepted in PEMFC systems [9]. Polarization (current–voltage) testing of a single electrolysis cell is performed to compare the steady-state performance of a cathode water vapor feed cell with an anode liquid feed cell for design purposes. The polarization of a cathode water vapor feed electrolyzer was characterized for different cell temperatures at 100% relative humidity for the cathode feed gas. For comparison, an identical cell was operated with an anode liquid water feed at different cell temperatures and water flow rates.

2. Experimental

2.1. Cathode water vapor feed operation

A bench scale PEM electrolyzer in cathode water vapor feed configuration was tested to determine the electrochemical performance of the cell. Nitrogen was used as the carrier gas for water vapor to the cathode. The dry flow rate of nitrogen for all cathode water vapor feed experiments was 1000 sccm. When using a 1000 sccm carrier gas flow rate, water vapor was carried into a cell at a rate well above 1.3 stoich at all temperatures. Nitrogen was humidified using a Nafion® tube humidifier from Fuel Cell Technologies. The humidifier temperature and water level were controlled throughout the experiments. The humidifier temperature was set to the desired dewpoint for each experiment. All cathode water vapor feed experiments were performed at 100% relative humidity (RH). To prevent condensation, a heated transfer line carried the gas from the humidifier to the electrochemical cell. Before entering the cell, the dewpoint of the inlet gas was measured using a humidity sensor from Vaisala HMT 334 humidity sensor. The humidity sensor was mounted in a heated and insulated T fitting that was thermostated at 75 °C. The outlets of the cell were at atmospheric pressure. The cell exhaust was vented into a fume hood with adequate ventilation to maintain the atmospheric concentration of hydrogen well below 1%. The cathode water vapor feed equipment described above was integrated and assembled by Giner Electrochemical Systems, Inc. and operation of the system was controlled using a LabView™ program. All tests were run with DI water as a surrogate for tritiated water.

2.2. Anode liquid feed operation

In the anode liquid feed configuration, water was fed to the anode of the electrolyzer from a temperature controlled water reservoir. A Thermo Scientific NESLAB 7 constant temperature bath was used as the water reservoir. Water was pumped from the reservoir to the cell using a Watson–Marlow 403U/R1 peristaltic pump. Flexible tubing with a 1/16″ bore was used for delivery of the water to the cell. With this size tubing, the pump accurately delivered water flow rates between 2 ccm and 11 ccm as per the manufacturer's directions. During anode liquid water feed experiments, nitrogen with a 25 °C dewpoint was flowed through the cathode. The dry nitrogen flow rate during these experiments was 500 sccm. The heated transfer line was heated to 75 °C to keep water from condensing.

2.3. Electrochemical cell

The cells tested had a 50 cm^2 circular active area cell and were prepared by Giner Electrochemical Systems, Inc. The cell housing was made out of aluminum and was heated by silicone heating pads placed on the outside of the cell. The heating pads were circular and of similar size as the active area. The temperature of the cell was monitored by a thermocouple within the cell housing. The Membrane Electrode Assembly (MEA) in the cell had 2 mg/cm^2 of Pt catalyst at the