

Short communication

Power output and load following in a fuel cell fueled by membrane reactor hydrogen

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Received 21 January 2003; accepted 31 January 2003

Abstract

Hydrogen for current polymer electrolyte membrane (PEM) and alkaline fuel cells must be supplied with not more than a few tens of ppm of CO or CO₂, respectively. If the hydrogen is generated, as it is used, it must be produced efficiently over a broad fuel cell demand range, and follow load changes on the order of seconds. We generated hydrogen for a broad variety of demands from a 1.09/1 molar mix of methanol/water using a commercial water–gas shift catalyst and a membrane reactor. The reactor output hydrogen was fed directly into a PEM fuel cell. Demand was varied between 0 and 0.9 A/cm², both in flow through operation and in dead-end operation. We found power densities virtually identical to those with bottled gas. We also demonstrated inherent load following on a time scale $\leq 2000 \mu\text{s}$.

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Keywords: Polymer electrolyte membrane; Water–gas shift catalyst; Membrane reactor hydrogen

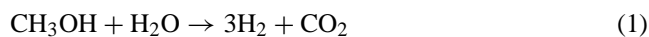
1. Background

Fuel cells in 1 W–100 kW sizes are being considered for near term service in several remote and mobile applications where they provide quiet operation, high reliability and (potentially) high energy density (Wh/lb): advantages that justify the current high price of fuel cells. Hydrogen delivery for these applications must be high density (energy/weight ≥ 1 Wh/g) and must be able to follow a varying load with only a few minutes lag at most. The hydrogen must be delivered relatively pure, containing a few tens of ppm CO or CO₂, respectively, depending on whether the fuel cell is an acidic polymer electrolyte membrane (PEM) or an alkaline cell [1]. Direct methanol PEM fuel cells are an attractive, longer range PEM option, but current designs appear to lag hydrogen fed cells in efficiency, cost and delivered power density.

Small scale generation of hydrogen appears to require more than a scaled down version of large hydrogen plants; miniature petrochemical designs cost and weigh too much per unit of hydrogen output. Efficiency is decreased significantly by the need to follow a load while maintaining hydrogen purity, and by the increased fraction of energy lost

to heat shedding, and for control, startup and shutdown [2]. A recent paper on autothermal reforming with partial oxidation purification, a major direction for fuel cell hydrogen generation, showed that this design could not reliably maintain < 25 ppm CO concentrations when faced with a varying load [3]. In the present paper, we examine fuel cell behavior in response to a varying load when fed with dry hydrogen generated from methanol–steam reforming in a membrane reactor. This is a technique developed over the past few years at REB Research [4,5]. We fed a nearly stoichiometric mixture of methanol and water to a REB reactor, and fed the hydrogen output directly into a T/J Technology PEM fuel cell to test predictions that hydrogen purity and fuel cell electric output are inherently maintained over a varying load.

The membrane reactor design used in this study is shown in schematic in Fig. 1, and is described previously [4,5]. In the reactor, the methanol–water mixture is converted to hydrogen over conventional water gas shift catalyst (Cu/ZnO from Sudchemie) via the reaction:



While hydrogen is formed by this reaction it is extracted through a metal membrane within the reaction zone. This hydrogen removal drives the reaction further to completion than it would in a non-membrane reactor, and increases the effective catalyst activity by increasing the reactant concentration and residence time.

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Our reactor used a REB Research's palladium-coated metal sandwich membrane that is effectively 100% selective to hydrogen. This membrane should insure that any hydrogen that passes the membrane is >99.9999% pure independent of any hydrogen back-pressure changes caused by varying fuel cell demand. Since this is a higher purity than typical of bottled hydrogen we wanted to see if this would result in increased power from the fuel cell. That is, would we see a voltage versus current density curve exceeding that for operation with bottled hydrogen. We also hoped to be able to run the hydrogen into the fuel cell in a dead-end mode, that is without the typical, periodic bleed of hydrogen from the fuel cell, necessary to remove CO₂, CO and unreacted fuel from typical reformat hydrogen. We also hoped to avoid the air bleed upstream of the fuel cell that is typically required to reduce carbon buildup on the fuel cell catalysts.

Dead-end operation is possible because the non-hydrogen components exit the reformer separately from the hydrogen via the raffinate stream in Fig. 1. This should be more efficient than operation with the bleeds since all the hydrogen is used to generate power, and should avoid MEA failure associated with periodic temperature rises [1]. Further, dead-end operation should eliminate the need for proportional bleed

control and valving that adds weight and robs power from the fuel cell, and should make hydration and voltage control easier since there is not a periodic drop in pressure and power.

Membrane reactor hydrogen in the dead-end mode, should result in inherent, instantaneous load following in the reformer, where hydrogen output follows electrical load. In dead-end mode, a change in hydrogen demand at the fuel cell should change the hydrogen pressure at the fuel cell, and this should feed back through the membrane reactor. A change in fuel cell load, thus directly affects, after a slight lag, hydrogen partial pressure in the reactor and this affects the rate of reaction. The greater the power demand, the lower the hydrogen pressure, and the faster the reaction in the membrane reactor [4]. One of the authors, REB, has postulated that the preferred heating mechanism for a membrane reactor is to burn the waste gas [4,5], supplementing this with combustion of raw feed. With proper insulation, the chemical energy of the waste gas returns to the methanol–water. It can be shown that complete cycle thermal efficiencies in excess of 90% are possible for a broad range of waste gas compositions containing 0–25% of the hydrogen generated. Within this range load following should not result in a loss of efficiency.

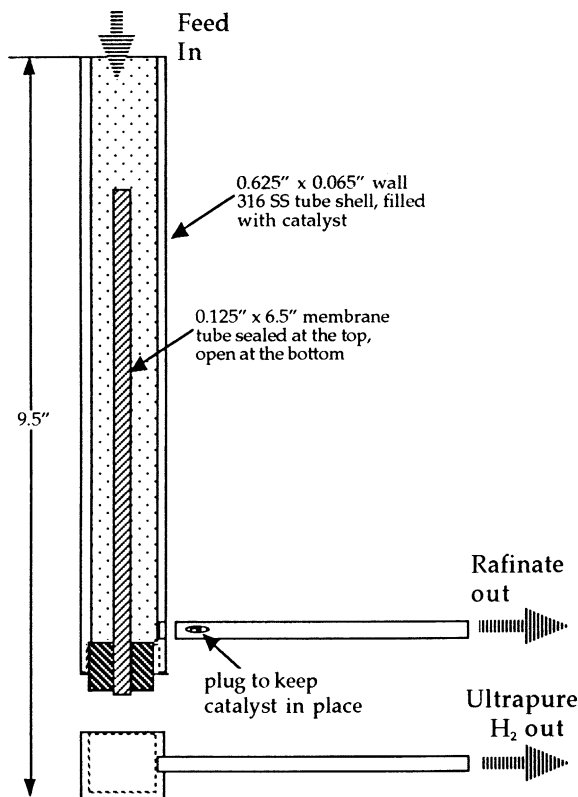


Fig. 1. Membrane reactor, exploded view. Contains one high temperature tube: 0.125 in. OD \times 6.5 in. long (6 in. [15 cm] above the side arm). Gas connection to upper end via Swagelok. Catalyst (24–100 mesh) was inserted at the top next to the membranes. Heating was provided by heating tape on outside, but can be provided by burning waste gas. Operation at 260 °C, 260 psig.

2. Experimental

For these experiments, the REB Research and Consulting (<http://www.rebresearch.com>) membrane was incorporated into one tube membrane reactor as shown in Fig. 1. The reactor was 1/2 in. (1.3 cm) in diameter and 9.5 in. (24 cm) tall containing one membrane tube 6.5 in. (16.5 cm) tall by 1/8 in. (0.32 cm) diameter plus 17 cm³ of Sudchemie methanol reforming catalyst T-2617. The reactor was wrapped with 300 W heating tape (<http://www.omega.com>) and heated to a nominal 260 °C (outside temperature). Temperatures were measured by a K thermocouple (Watlow Inc.) and controlled to ± 1 °C by a PID controller (Fuji Electric).

The reactor was fed with reagent grade methanol (Aldrich) mixed with a water purchased at the local supermarket (Absopure[®] Steam Distilled Drinking Water) to form a 1:2 by volume water methanol mixture, equivalent to 1.09 mol H₂O/mol CH₃OH. The slight excess of water over the 1:1 molar ratio in Eq. (1) is thought to be beneficial to prevent coking. The methanol–water was premixed and held in a polyethylene tank before being used. A medical dosing pump (Pulsafeeder, Pulsatron Inc.) took the methanol–water from the tank at a constant flow rate 1 cm³/min $\pm 5\%$, and fed it to a copper tube 1/8 in. (0.32 cm) diameter and 5 feet (1.5 m) long that served as a boiler before entering the reactor. Pressure in the reactor was maintained by a check valve (Swagelok) on the off-gas stream set to 265 psi (18 MPa), and was measured by a (US Gauge) pressure gauge ± 5 psi (35 kPa) accuracy. In order to maintain temperature uniformity in the boiler and reactor, the copper tube boiler was

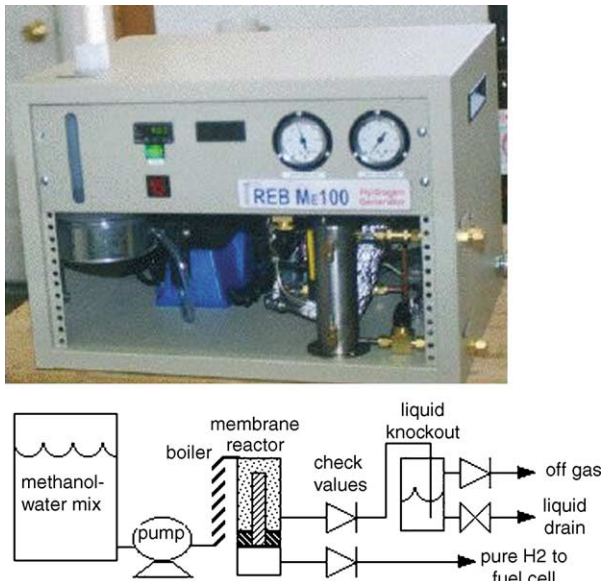


Fig. 2. Experimental reformer setup and flows.

wrapped around the reactor beneath the main insulation (Zirtek Inc., ceramic covered with aluminum foil) with only a thin layer of insulation between the boiler and the heat tape. Wrapping the boiler tube around the reactor eliminated the need for a second controller and heater loop.

Hydrogen production upstream of the fuel cell was measured by a mass flow meter (Aalborg) calibrated against a bubble flow meter. Exiting hydrogen passed a check valve (Swagelok) set to 1 psi (7 kPa) to prevent hydrogen suck back in the event of an unplanned shutdown. After passing the reactor check valve, waste gas entered a knockout drum to collect liquids, water and unreacted methanol. From there, vapors exited the system through a third check valve set at 1 psi (7 kPa). (see Fig. 2). For brevity we refer to the experimental reformer as the Me100 because it is a methanol–water reformer that includes a 100% selective membrane.

Hydrogen from the Me100 was fed directly, dry, into a T/J Technology fuel cell with 5 cm² active area operated at 50 °C. The fuel cell membrane was Nafion 117 coated with T/J–PtRuMo/C catalyst, 0.53 mg/cm², at the anode and a Pt/C catalyst, 0.48 mg/cm², at the cathode. Oxygen flow was maintained at 100 kPa and 100 ml/min throughout. For comparison tests, the fuel cell was also fed bottled hydrogen (Airgas). A constant flow of each, of 85 ml/min was maintained by use of a software adjusted mass flow controller (Alltech Associates Inc.) downstream of the fuel cell. The hydrogen pressure was about 100 kPa at the fuel cell, both with the Me100 and the bottled hydrogen source, but was not controlled directly in any way. We used dry hydrogen and a 50 °C operating temperature to make the tests more sensitive to CO poisoning and at the same time more typical of the likely operation of small portable fuel cells. Humidification generally improves PEM fuel cell performance [8]. Power curves, voltage versus current density as shown

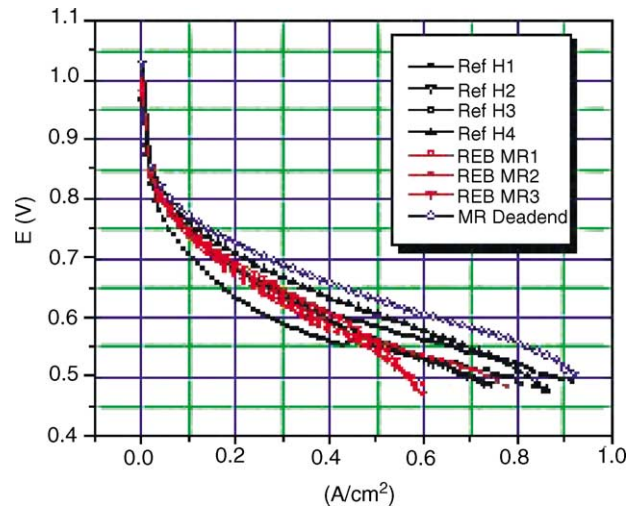


Fig. 3. Performance curve with non-humidified bottled H₂ and non-humidified REB membrane, Me100 membrane reactor output with a T/J Technology PEMFC at 50 °C, IR corrected.

in Fig. 3 were measured using a PC controlled Scribner 890B Fuel Cell Test Station. The power curve experiment sequences took approximately 15 min each, and so provided a first demonstration of load following. To measure fuel cell response at higher cycle times, Fig. 4, a HP load bank, HP 6060B, was changed between 0.1 and 1 A over 1 ms (1000 μ s) with a cycle that repeated over 10 ms.

Several tests were run with the membrane reactor hydrogen in dead-end mode, that is without any hydrogen bleed from the fuel cell. In dead-end mode the hydrogen flow to the fuel cell is controlled by hydrogen use at the cell. No effort was made to adjust the methanol–water feed to maintain a constant hydrogen pressure at the fuel cell, and as a result the hydrogen pressure rose as high as 275 kPa during electric load tests.

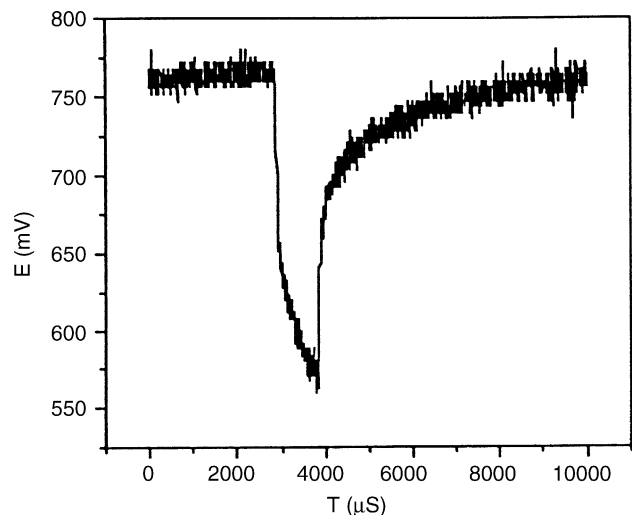


Fig. 4. Voltage response of T/J PEMFC at 50 °C powered by a REB Me100 membrane reactor H₂ generator. The current pulsed from 0.1 to 1 A with 100 Hz and 10% duty cycle, no IR correction.

3. Results

We found a startup time in the order of 5 min. The temperature was constant with time $\pm 1^\circ\text{C}$, but varied along the length of the reactor by $50\text{--}60^\circ\text{C}$ with the maximum reactor temperature in the middle. If this variation were caused by endothermicity, the temperature should have been a minimum in the center of the reactor, Amphlett et al. [6]. Further, a 50°C gradient is more than could be explained by the heat of reaction and the heat of boiling given the high thermal conductivity of the copper boiler tube. We thus attribute the temperature gradient to heat loss at the ends of the reactor. At these operating conditions with the Sudchemie catalyst, the Me100 produced a maximum of $150\text{ cm}^3/\text{min}$ of hydrogen, or enough to generate 30 amps in a fuel cell. Depending on the pump rate, the off-gas could be made flammable or not, but no effort was made to use heat from burning the waste gases to heat the reactor. A room CO detector used as a safety measure (Nightingale, Inc.) indicated that no measurable CO built up in the lab, but no other effort was made to measure the composition of the off-gas.

The voltage versus current density observed with this set-up is shown in Fig. 3. The results with bottled hydrogen set to 100 kPa using the bleed are shown in black, those with membrane reformer hydrogen set to 0 psig using the bleed are shown in red, and those with reformer hydrogen in dead-end mode (no bleed, varying pressure) are shown in blue. We performed several runs with bottled hydrogen and reformer hydrogen because there was considerable scatter in the performance curves, especially at the start with the bottled hydrogen. This scatter is typical of operation with dry hydrogen, and relates to membrane conditioning/hydration–dehydration effects. The power output is consistent with previous measurements on this fuel cell at 50°C with dry hydrogen in constant bleed mode.

Fig. 3 shows that the performance with bottled hydrogen (black lines) is virtually identical to that with membrane reformer hydrogen (red lines). Studies using Ballard fuel cells show a nearly 75% decrease in power density for even 10 ppm CO [1,7] and results with T/J fuel cells fed impure hydrogen (unpublished) are similar. Fig. 3 shows a slight fall off in voltage with the membrane reactor hydrogen at high currents, but the dead-end performance suggests this may be due to mass transportation differences between the bottle and the reformer. That is, the hydrogen bottle maintains hydrogen pressures better at high fuel cell demands. The Me100 hydrogen pressure in flow through mode is probably lower than that delivered by the cylinder.

The fuel cell power curve with membrane reactor hydrogen in dead-end mode is uniformly higher than with either reformer or bottled hydrogen with a bleed. Dead-end operation is generally not used since it tends to concentrate any impurities in the hydrogen feed. The high observed voltages, especially at middle and high current densities suggests that our reformer hydrogen is essentially 100% pure. That the voltage is higher with reformer gas in dead-end mode that

with cylinder gas and reformer gas in flow through mode is pressure related, at least partially. In dead-end mode, the Me100 hydrogen pressure varied with the load and rose as high as 275 kPa at zero flow. Generally, fuel cell voltages increase with higher hydrogen pressures. Other possible contributors to the increased power curve in Fig. 3 include increased hydrogen humidity as water is not swept from the system with the bleed. Whatever the explanation, dead-end fuel cell operation seems preferable with membrane reactor hydrogen, at least with this type of fuel cell. Dead-end mode might have produced less power had significant amounts of impurities traversed the fuel cell membrane either from the air side or the hydrogen side. Low permeation appears to be typical of Nafion membranes like those used here [8], but is not with all the alternative membranes currently under development.

The experiments in Fig. 3 had a cycle time of about 15 min, and did not show a clear loss of voltage versus steady state; that is it showed load following at this time scale. To measure fuel cell response at higher cycle times, an experiment was performed with membrane reactor hydrogen in dead-end operation, where a HP 6060B load bank was changed between 0.1 and 1 A over 1 ms ($1000\ \mu\text{s}$) with a cycle that repeated every 10 ms. The voltage is shown in Fig. 4 as observed through a Tektronix TDS 210 oscilloscope. The load amperage changes from 0.1 to 1 A at about $3000\ \mu\text{s}$, and changes back to 0.1 A at $4000\ \mu\text{s}$. For the 5 cm^2 fuel cell, this is the equivalent of a change between 0.02 and $0.2\text{ A}/\text{cm}^2$, and based on Fig. 3 we expected steady state voltages of 0.85 and 0.72 V, respectively. The voltages observed in Fig. 4 are somewhat lower, 0.77 V at 'steady state' and $0.02\text{ A}/\text{cm}^2$, and between 0.65 and 0.575 V at $0.2\text{ A}/\text{cm}^2$. This latter voltage is not a steady state, it was still falling by $4000\ \mu\text{s}$. The steady voltage difference between Figs. 3 and 4 seems mostly due to the lack of IR correction in the transient experiments.

Full voltage recovery at 0.1 A occurred at about $6000\ \mu\text{s}$, $2000\ \mu\text{s}$ after the initial change. This suggests that the time scale for the voltage recovery in the reformer–fuel cell system is $2000\ \mu\text{s}$. This is good enough for most applications, and is much faster than is seen for load following with a non-membrane reformer [3]. If a faster response than $2000\ \mu\text{s}$ is needed and effort could be made in this direction, perhaps by reducing the capacitance effect of transient charging of a double layer in the fuel cell. Two other changes to increase response are to reduce the buffer effect of hydrogen absorption in the metal membrane and catalyst. This could be done by operating at higher temperatures and with a different catalyst. Another approach is to reduce the length of the hoses between the fuel cell and the membrane reactor; $2000\ \mu\text{s}$ is about the transit time for a sound wave in the 3 m hose between the membrane reactor and the hydrogen.

Fast response minimizes the need for capacitors [9] and makes it easier to design control systems to maintain high efficiency across a broad turndown range.

4. Discussion

The Me100 used here is suited only for laboratory use. Combustible waste gas from the reformer was vented unburned, while electricity was used to heat the reformer. Further, only manual adjustment of the methanol/water flow rate was available, Fig. 2. The next step for REB Research will be to heat the reactor by methanol–water combustion, and after that, to heat it mostly from waste gas combustion. At steady state, burning the waste gas to heat the reactor should provide system efficiencies over 90% of the lower heat value of the methanol–water [6]. Future work will explore how combustion heating affects the way a fuel cell fed with membrane reactor hydrogen follows a changing electrical load. These experiments suggest there will be no problem controlling hydrogen output if reactor heating is provided by methanol combustion, since this should be similar to electrical heating.

Controllability may decrease when heat comes from waste gas combustion since changes in the partial pressure of hydrogen in the reactor in response to changing power demands will result in simultaneous opposite changes in the heat value of the off-gas and in the heat demand of the reactor. This difference is made up with an appropriate methanol burner, and since the time scale for reactor heating appears to be on the order of minutes (seen here during startup), even a simple controller should have no problem maintaining temperature and efficiency over a small range of turn-down. Because of the broad range of hydrogen recoveries that give efficient operation, 0–25% at steady state, we are guardedly optimistic that there is a control scheme to give good stability and high efficiency over a broad range of turn down as well, but we have yet to pick a control strategy to do this.

One control scheme we are considering is to use a pressure sensor within the hydrogen output to control the methanol/water pump delivery rate, adjusting the methanol feed to maintain a hydrogen output pressure of say 10 psig. Our idea is to maintain the reactor at a constant pressure (about 260 psi (18 MPa) seems appropriate) by exhausting waste gas, as done here. Our thought is to send all the waste gas to the burner as in Buxbaum [4,5], and turning on raw methanol–water combustion only when this does not suffice to maintain the reactor temperature within a desired range,

or perhaps when the exhaust from combustion leaves at too low a temperature. Another thought is generally controlling the reactor temperature by the methanol–water pump rate. A third control scheme is to drive the methanol–water pump directly from the mechanical energy within the waste gas, using a non electrical steam–water pump of the sort that is sometimes used to provide feed water to steam engines. This last method removes an energy inefficiency inherent in using electricity to pump the liquid feed when plenty of pressure volume energy is available for free in the waste gas. This pump is likely to make the overall design lighter as well, but it may make it less controllable.

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