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Electrochemical hydrogen pump for recirculation of hydrogen in a fuel cell stack

FRANO BARBIR[1],* and HALUK GÖRGÜN[2]
[1]*United Nations Industrial Development Organization-International Centre for Hydrogen Energy Technologies (UNIDO-ICHET), Sabri Ülker Sk. 38/4, Cevizlibağ Zeytinburnu, 34015, Istanbul, Turkey*
[2]*Department of Electrical Engineering, Yıldız Technical University, Beşiktaş, 34349, Istanbul, Turkey*
*(*author for correspondence, tel.: + 90-212-4164848, fax: + 90-212-4168945, e-mail: barbir@unido-ichet.org)*

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Abstract

The objective of this work is to evaluate the use of an electrochemical hydrogen pump for recirculation of hydrogen in a fuel cell stack. The hydrogen pump needed about 130 mV at 0.5 A cm^{-2}, primarily because of the cell resistance (0.18 Ω cm^2). This voltage loss was higher than a fuel cell voltage gain resulting from hydrogen recirculation. However, if one pumping cell is used for 10 active cells this means 13 mV loss per cell (or about 2%) which may be an acceptable voltage penalty. A stack with hydrogen recirculation should operate with less voltage fluctuation and should need purging less often than a stack operating with a dead-end mode of hydrogen supply. An additional benefit of hydrogen purification may be achieved in the systems with a fuel processor where operation in a dead-end mode is not possible. Attention must be paid to water management when designing and operating a hydrogen pump within a fuel cell stack.

Nomenclature

b	Tafel slope, V per decade
F	Faraday constant, 96,485 C mol^{-1}
i	current density, A cm^{-2}
I	current, A
i_0	exchange current density, A cm^{-2}
$\dot{m}$	mass flow rate, g s^{-1}
M	molecular mass, g mol^{-1}
n	number of electrons, 2
N	number of cells in stack
P	pressure, kPa
R_Ω	areal resistance, Ω cm^2
R	gas constant, 8.314 J g^{-1} mol^{-1}
S	stoichiometric ratio
T	temperature, K
V	potential, V
W	power, W

1. Introduction

An electrochemical cell, a fuel cell or an electrolyzer, may also be used to pump hydrogen through a proton exchange membrane [1–3]. On the anode side hydrogen is split into its constituents, protons and electrons, just like in a fuel cell anode process (Figure 1). Electrons travel through electrically conductive parts of the cell and through the external circuit to the cathode side and protons go through the proton exchange membrane. On the cathode side protons and electrons combine and form hydrogen just like in an electrolyzer cathode process. Of course, an external DC power source is needed to get this process going.

With this simple process, it is possible to pump hydrogen from a low pressure side to a high pressure, or to selectively pump hydrogen from a mixture of gases. There are several possible applications for such pumping, such as:

- Hydrogen compression for storage,
- Hydrogen purification,
- Hydrogen recovery/separation/extraction,
- Recirculation of hydrogen in a fuel cell stack.

Sedlak et al. [1], in their pioneering work, proposed the use of this concept for hydrogen recovery and hydrogen purification. Rohland et al. [2], proposed the use of an electrochemical hydrogen compressor in an automotive fuel cell system with a methanol reformer. The compressor is used for both pumping of hydrogen into a storage tank as well as for purification, particularly during the start up period. Stroebel et al. [3], characterized a PEM electrochemical compressor used to pressurize hydrogen up to 40 bar. Eissman et al. [4],

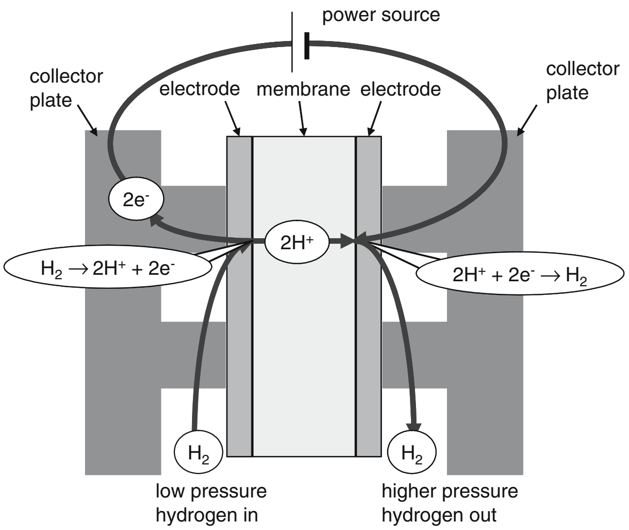

Fig. 1. Principle of hydrogen pumping across the proton exchange membrane.

patented an electrochemical cell for purification of hydrogen in a fuel cell system with a reformer, where hydrogen from a reformer or from a fuel cell exhaust is pumped and simultaneously purified.

In a fuel cell system, hydrogen may be supplied either in a dead-end or a flow-through mode [5]. The former is possible only with very pure hydrogen and nevertheless requires periodic purging of the fuel cell anode side. The latter results in unused hydrogen at the fuel cell exhaust, which can be used either in a burner or, if it is a pure hydrogen system, it may be pumped back to the fuel cell inlet, using a passive (ejector) or an active device (pump or a compressor). The objective of this work is to evaluate the use of an electrochemical (PEM) hydrogen pump for recirculation of unused hydrogen from the fuel cell exhaust back to the fuel cell inlet, as proposed by Barbir et al. [6]. This can be applied not only in a system with pure hydrogen but also in a system with reformate gas, since the PEM hydrogen compressor would also work as a purifier.

2. Theoretical background

Theoretically, the required potential for hydrogen pumping across the membrane in an electrochemical cell is given by the Nernst equation:

$$V_{\text{theor}} = \frac{RT}{nF}\ln\left(\frac{P_2}{P_1}\right) \tag{1}$$

where P_2/P_1 is the pressure ratio across the membrane. The potential is clearly a function of the pressure ratio. For example, for $P_2/P_1 = 10$, the resulting voltage is $V = 29$ mV.

The hydrogen mass flow rate is proportional to current, according to Faraday's law:

$$\dot{m} = \frac{MI}{nF}. \tag{2}$$

Power required for hydrogen pumping is simply a product of current and voltage. The theoretical power is then:

$$W_{\text{theor}} = IV_{\text{theor}}. \tag{3}$$

By combining Equations (1)–(3) an expression for theoretical power needed to pump hydrogen at rate m is obtained:

$$W = \frac{\dot{m}RT}{M}\ln\left(\frac{P_2}{P_1}\right). \tag{4}$$

However, actual cell voltage will always be higher than that predicted by the Nernst equation, due to unavoidable losses, such as activation overpotential and ohmic resistance.

$$V = V_{\text{theor}} + V_{\text{act}} + V_{\text{ohm}} \tag{5}$$

where:

$$V_{\text{act}} = \text{activation polarization}, \quad V_{\text{act}} = b\log\left(\frac{i}{i_0}\right) \tag{6}$$

$$V_{\text{ohm}} = \text{ohmic losses}, \quad V_{\text{ohm}} = iR_{\Omega}. \tag{7}$$

Activation polarization for hydrogen oxidation and hydrogen evolution is relatively small. Stroebel et al. [3] found that the polarization of hydrogen evolution on the cathode of a PEM hydrogen compressor is slightly larger than that of hydrogen reduction on the cathode.

3. Experimental set-up

An off-the-shelf fuel cell, with 50 cm^2 active area, made by Fuel Cell Technologies, Inc., with a membrane electrode assembly (MEA) supplied by 3M (28 μm perfluorosulfonic acid membrane with 1000 EW and with total Pt catalyst loading of 0.8 mg cm^{-2}) was connected to a hydrogen bottle through a pressure regulator (Figure 2). The other side of the cell was connected to a backpressure regulator so that a desired pressure might be achieved and maintained. The line connecting the two sides of the fuel cell was used for initial purging of the cell, first with nitrogen and then with hydrogen. A controllable DC power supply was connected to the bus plates of the fuel cell. It was operated in a constant current mode. Pressure on the high pressure side was maintained by a backpressure regulator and verified by a pressure transducer. This set-up (Figure 2) was used to characterize the cell as a hydrogen pump, i.e., voltage was measured as a function of current.

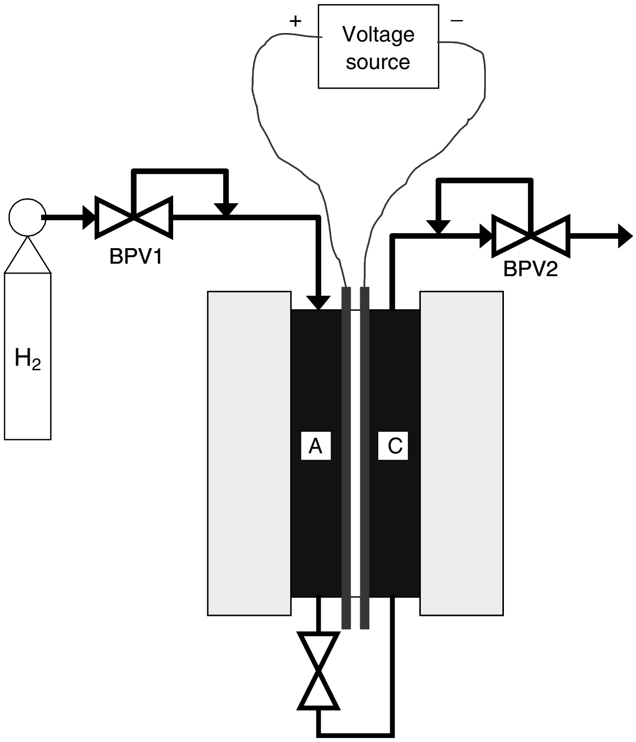

Fig. 2. Schematic of a PEM fuel cell connected as a hydrogen pump.

This hydrogen pump cell was then connected to an identical fuel cell in such a way that the hydrogen line from the exhaust of the fuel cell was connected to the anode of the pump (low pressure side), and the cathode of the pump (high pressure side) was connected to the fuel cell inlet with a "T" fitting (Figure 3). Both anode and cathode of the pump were equipped with a purge valve to allow purging during the initial set-up as well as during normal operation if necessary.

Electrically, the pump cell was connected in series with the load. This means that the rate of hydrogen pumping was identical to the hydrogen consumption rate in the fuel cell, which means that in this case the fuel cell operated with a hydrogen stoichiometric ratio of 2. The working pressure of the pump was essentially equivalent to the pressure drop through the fuel cell. The pressures at the fuel cell inlet and outlet were measured by pressure transducers. In order to better characterize the pump cell, its resistance was measured continuously using a high frequency milliohm meter measuring impedance at 1 kHz.

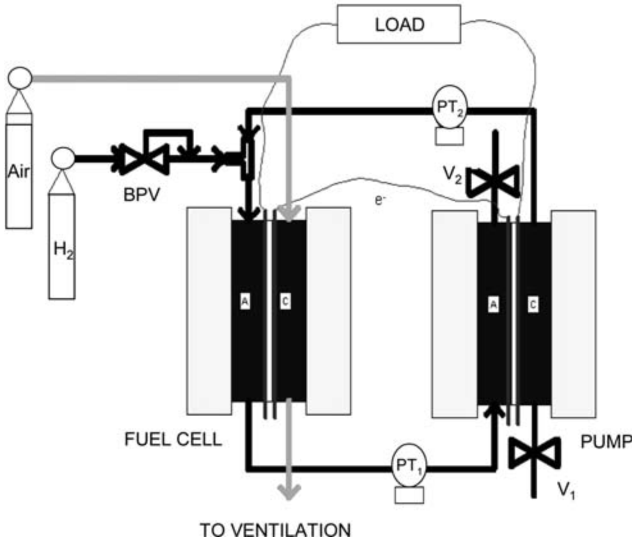

Fig. 3. Schematic diagram of a PEM hydrogen pump used to recirculate hydrogen in a fuel cell.

4. Results and discussion

Figure 4 shows how the pump cell responded to a stepwise increase in the hydrogen pumping rate which, in this configuration, was directly proportional to the electrical current drawn from the fuel cell. The pump cell voltage seems to be directly proportional to current (Figure 5) which, according to Equation (5), means that the Ohmic losses are predominant. Indeed, the voltage losses due to cell resistance, which were measured independently (on average 0.18 Ω cm^2) are much higher than the activation polarization and the calculated Nernst potential, from Equation (1), as shown in Figure 6. The activation polarization in Figure 6 was calculated by simply deducting the measured ohmic losses (*iR*) and the calculated Nernst potential from the measured cell voltage. Not surprisingly, relatively good curve fitting was achieved by a logarithmic expression, as it should be proportional to a logarithm of current, according to Equation (6). This activation polarization includes both anode and cathode, and it is similar in magnitude to that found by Stroebel et al. [3].

The Nernst potential is almost negligible because of the very small pressure drop through the fuel cell (order of magnitude of 7 kPa at maximum flow rate). The pressure drop is directly proportional to the hydrogen flow rate (Figure 7), reflecting a laminar flow regime in the fuel cell channels.

Data in Figures 4–7 appear to be somewhat scattered, although it should be mentioned that the number of these data points is very small as compared to the overall number of data points. The reasons for these "excursions" are not well understood. They may be related to accumulation of inerts, including water, on the low pressure side of the pump at low current densities or lack of water at higher current densities (also indicated by scattered resistances at higher current densities). Presence of most likely liquid water may be indicated by scattered pressure drop data in Figure 7. These phenomena will be further investigated in future studies. In any case, attention must be paid to water management when designing and operating a hydrogen pump within a fuel cell stack.

If the pump cell potential is deducted from the fuel cell potential the net potential is obtained, as shown in Figure 8. The voltage spent on pumping hydrogen

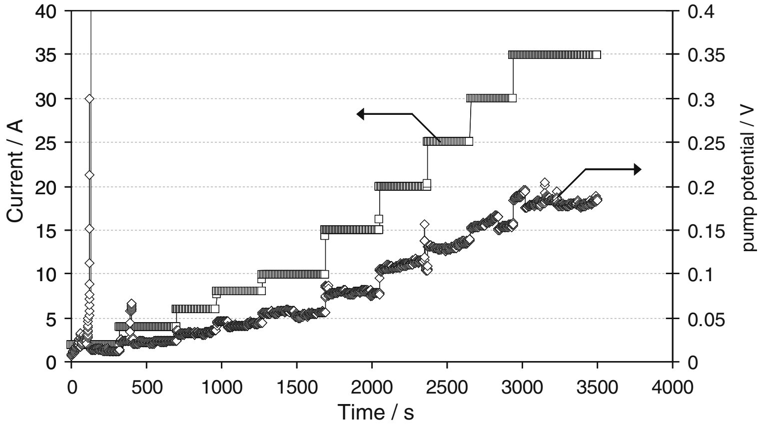

Fig. 4. Electrochemical hydrogen pump potential over time as a function of step-wise increase in current.

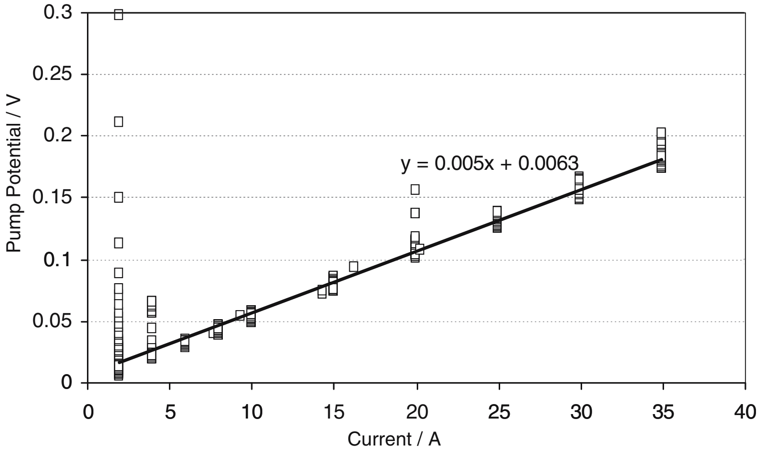

Fig. 5. Hydrogen pump potential as a function of hydrogen pumping rate.

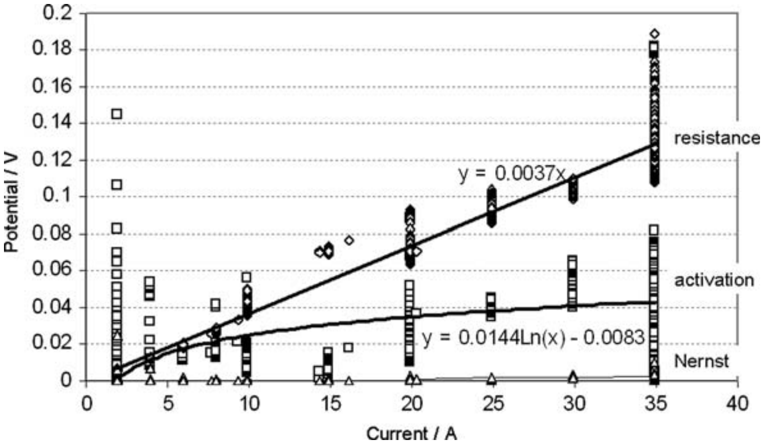

Fig. 6. Components of electrochemical pump voltage (resistance was independently measured, Nernst potential was calculated as a function of pressure, and activation polarization is then calculated by deducting these two from the measured cell voltage).

through the fuel cell (approx. 130 mV at 25 A or 0.5 A cm^{-2}) can hardly be justified. Performance of the fuel cell at two times the stoichiometric hydrogen flow rate induced by electrochemical pumping did not improve the fuel cell performance by 130 mV as compared to operation with hydrogen dead ended. Figure 9

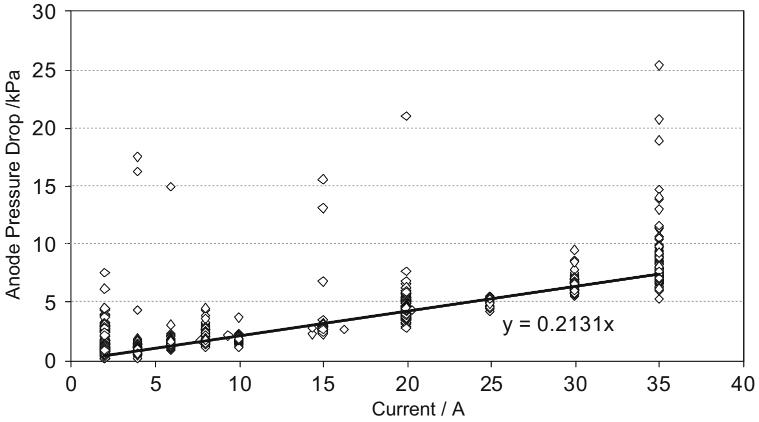

Fig. 7. Anode pressure drop through the fuel cell.

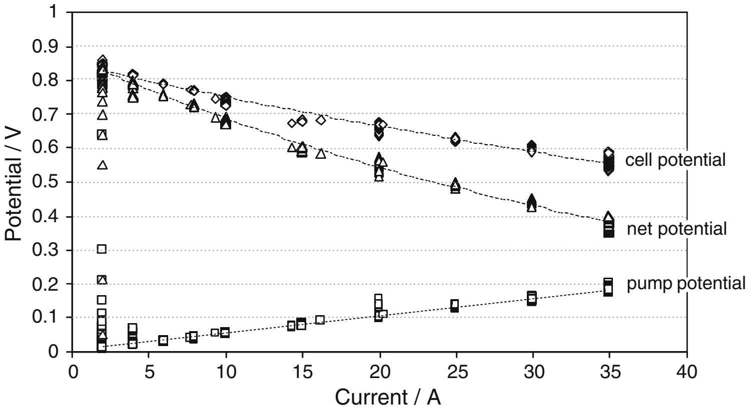

Fig. 8. Polarization curves of fuel cell and pump cell and the resulting polarization curve.

shows the fuel cell performance at various hydrogen stoichiometric ratios. The voltage gain at hydrogen stoichiometric ratio of 1.5 appears to be negligible (< 20 mV). However, a polarization curves do not show how the cell performs over time. A cell operating in dead-end mode needs to be periodically purged in order to remove water and other inerts (such as nitrogen) that may accumulate in the anode compartment. Figure 10 shows that the voltage in a fuel cell operated in dead-end mode begins to decrease sharply after approximately

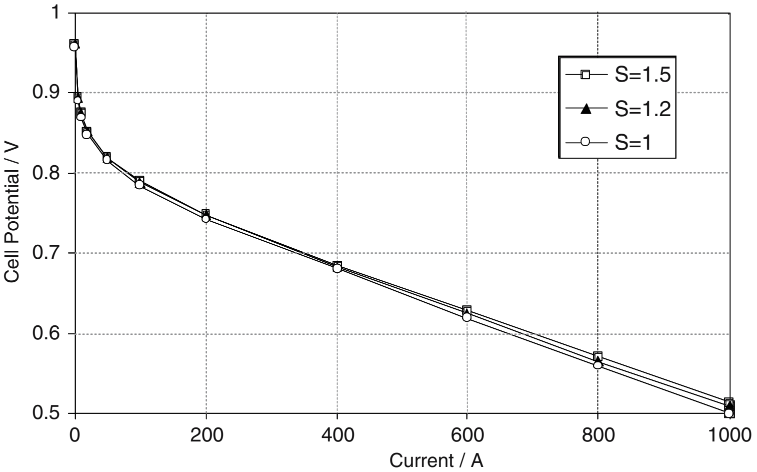

Fig. 9. Fuel cell polarization curves at different H_2 stoichiometry.

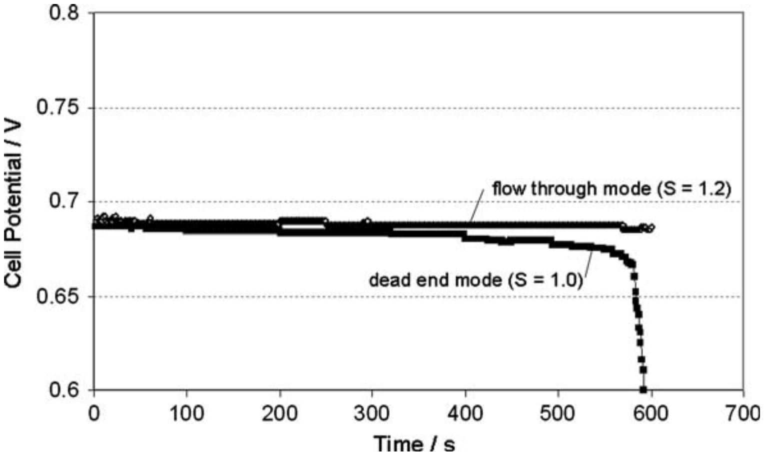

Fig. 10. Fuel cell performance over time in a dead-end and flow through modes.

10 min of quasi-steady state operation. Any hydrogen flow rate above stoichiometric would result in a steady state (as shown in Figure 10).

In this case, one pump cell was used with one fuel cell resulting in a hydrogen flow rate equal to twice the stoichiometric flow rate. However, if one pump cell is used with 10 or five fuel cells the resulting stoichiometry would be 1.1 and 1.2, respectively, and the voltage penalty (loss) due to recirculation would be 13 and 26 mV per cell, respectively (or 2–4% of fuel cell voltage), which may be acceptable, i.e., in the same order of magnitude as the voltage gain in the fuel cell stack due to flow-through regime.

5. Applications

Hydrogen pump cell or cells may be incorporated directly in a fuel cell stack, since they may be exactly the same as the active cells. With an appropriate configuration of internal manifolds it would be possible to accomplish a flow-through regime in active fuel cells while the stack is practically operated in a dead-end mode (see Figure 11) [6]. Hydrogen recirculation results in a smoother operation than operation in a dead-end mode. If necessary, a purge line may also be installed. The desired stoichiometric ratio is achieved by selecting the number of pump cells per active cell:

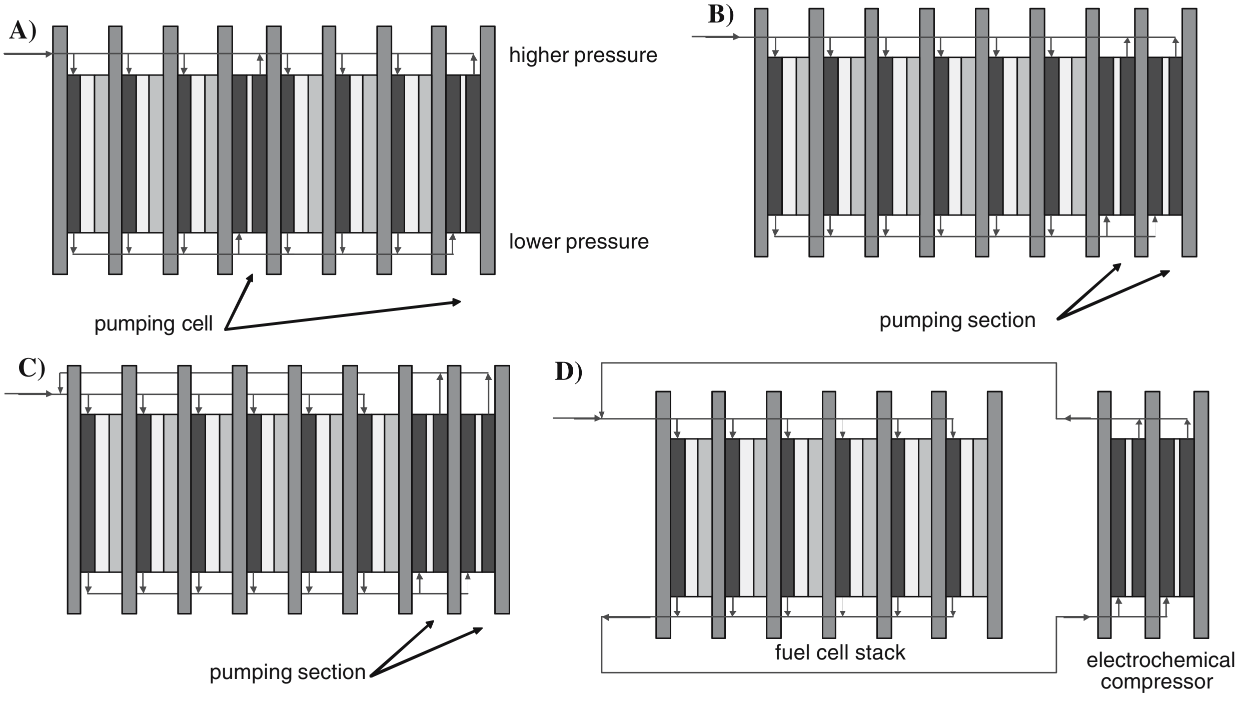

Fig. 11. Stack configurations with electrochemical recirculation of hydrogen (A) with pumping cells distributed throughout the stack, (B) with pumping cells grouped at the end of the stack, (C) with pumping cells grouped at the end of the stack and with a recirculation manifold back to the stack inlet, (D) with an external electrochemical pump connected to the stack.

$$S = 1 + \frac{N_{\mathrm{Pump}}}{N_{\mathrm{Act}}}. \tag{8}$$

When hydrogen is not used as pure gas, such as if hydrogen is coming from a reformer, where hydrogen content in the reformate gas may be approximately 40%, recirculation with a regular pump is not possible because together with hydrogen all other gases would be recirculated back to the fuel cell inlet resulting in reduced hydrogen concentration (some gas from the exhaust would still have to be expelled). However, with the electrochemical hydrogen pump only hydrogen would be recirculated while other gases could be expelled. Typically, fuel cells running on reformate gas need to operate with hydrogen stoichiometry between 1.2 and 1.3 (ideally below 1.1) resulting in hydrogen utilization of about 80%. Higher hydrogen flow rate results in better fuel cell performance (i.e. higher cell potential), but lower overall efficiency due to low fuel utilization. With a built-in electrochemical pump it would be possible to have both higher hydrogen flow rate through individual cells and close to 100% fuel utilization.

Other possible applications of the electrochemical hydrogen compressor include hydrogen purification. A purification cell does not have to be placed at the stack exhaust but it can also be installed between the reformer and the fuel cell stack (as suggested by Eissman et al. [4]) or between the reformer and hydrogen storage (as suggested by Stroebel et al. [3]).

Another variation of hydrogen purification is separation of hydrogen from a gas mixture from which it would be difficult to separate hydrogen by physical methods (for example a mixture of hydrogen and helium).

Hydrogen storage and utilization sometimes requires high pressures (typically from 200 to 350 bar). Theoretically, compression would be possible with an electrochemical cell if designed properly to withstand such high pressures. PEM electrolyzers which can generate hydrogen at > 200 bar have been demonstrated. However, the Nernst potential at these high pressures would not be negligible because, it would be of the same order of magnitude as the ohmic losses, thus resulting in compressor efficiencies of about 50%. The use of thinner membranes (though properly supported to withstand high pressures) would result in lower resistance but would also result in higher hydrogen crossover losses.

6. Conclusions

Electrochemical compression of hydrogen is a known concept. This work describes a built-in electrochemical pump within a fuel cell stack to accomplish recirculation of hydrogen through the active cells of the stack resulting in improved fuel cell performance. The results indicate that the voltage losses due to recirculation of hydrogen may be justified with a better and more stable fuel cell performance. By selecting the number of pump cells per active cells in a stack it is possible to achieve a desired hydrogen stoichiometry. For example one pump cell for each 10 active cells would result in hydrogen stoichiometry of 1.1. The additional benefit of hydrogen purification may be achieved in systems with a fuel processor. Other possible applications of the electrochemical hydrogen compressor include hydrogen separation and high pressure compression.

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