

CHARACTERIZATION OF PEM ELECTROCHEMICAL HYDROGEN COMPRESSORS

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ABSTRACT

This research work concerns the development and characterization of an electrochemical hydrogen-compressor (HC) based on proton exchange membrane (PEM) technology. In a HC device, pure hydrogen (or hydrogen-containing mixtures) is supplied to the anode, and pure (99.7% and more) pressurized (potentially several hundred bars) hydrogen is collected at the cathode. HCs can be used to extract hydrogen from different gaseous mixtures and waste gases (for example, from outlet gases of fuel cells, products of organic fuel conversion). Results reported in this communication concern the role of various operating parameters (water vapor partial pressure, current density, operating temperature) on the maximum output pressure which can be reached with such HCs. A model, which takes into account the effect of hydrogen back diffusion due to the pressure gradient, has been developed. Experimental compression up to 28 bars has been measured.

1. INTRODUCTION

In a hydrogen compressor (HC) device, pure hydrogen (or hydrogen-containing mixtures) is supplied to the anode, and pure (99.7% and more [1]) hydrogen, possibly pressurized [2, 3], is collected at the cathode. The following electrochemical reactions are taking place:

anode reaction: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$;

cathode reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$;

overall cell reaction: $\text{H}_2 \rightarrow \text{H}_2$.

HCs can potentially be used to extract hydrogen from different gaseous mixtures and waste gases (for example, from outlet gases of fuel cells, products of organic fuel conversion) and to produce purified and compressed hydrogen. In such systems, the low-pressure hydrogen input can be pressurized up to several hundred bars (using the series connection of several cells) without additional energy inputs.

Electrochemical hydrogen compression has been studied by different research groups. Research activities on hydrogen electro-transport in PEM cells started at RRC “Kurchatov Institute” *ca.* 20 years ago [4]. Later, research group from “Center for Solar Energy and Hydrogen Research” in Baden-Wuerttemberg (Ulm, Germany) demonstrated the possibility to compress hydrogen using Nafion 117 membrane up to 43 bar [2]. The maximum pressure difference achieved by authors of paper [3] using Nafion 105, 115 and 117 membranes was *ca.* 54 bar. They concluded that using improved cell design, it could be possible to reach pressures above 100 bars. According to patent [5], pressures of up to 12 000 psi (857 bar) can be reached using multi-cell assemblies. More recently, an Italian research group has studied the galvanostatic and tensiostatic mode of hydrogen pump operation using Nafion 117 membrane [6] at atmospheric pressure. Other studies in Canada [7, 8] have been reported on the hydrogen pump, however without consideration on high-pressure operation. Concerning the purity of hydrogen obtained using hydrogen pump, it was shown by Lee et al [1], that 99.72% hydrogen purity can be obtained using Nafion 115 membrane and a two-stage separation process from $\text{H}_2/\text{N}_2/\text{CO}_2$ mixture. According to [9], Mitsubishi Corporation has developed a high-pressure prototype electrolyser able to operate at a maximum pressure of 350 bar. It thus seems possible to reach similar pressure levels with the HC, using the same membrane and properly supported anodic electrode. However, it can be expected that such high pressures will not be easy to reach in one single step and that multi-cell systems connected in series will be required. The purpose of the work reported here is to

estimate the maximum output pressure that can be reached, to provide data on the kinetics of the compression process and to determine the best operating conditions for single-cell HCs.

2. EXPERIMENTAL DETAILS

The experimental PEM-HC used in this work is pictured in figure 1. This prototype was designed and manufactured at Kurchatov Institute. Briefly, it consists of an electrochemical cell clamped between an upper and a lower stainless steel (grade 12X18H10T or SS316) cover vessel, both designed for high pressure operation. On top of the upper cover vessel, a manometer (visual control) and a pressure sensor (remote control) are positioned. Both cover vessels are equipped with electric heaters and electronic temperature regulators for temperature management. The electrochemical cell consists of two (stainless steel SS316) flanges. The solid polymer electrolyte (SPE) is an ion-exchange membrane (Nafion 117 from DuPont de Nemours, USA), pressed between two fluoroplastic gaskets. An anodic current collector made of hydrophobic porous carbon-paper, and a cathodic current collector made of porous titanium, are pressed on both sides of the SPE. Each current collector is surface-covered with an appropriate catalytic layer made of platinum nanoparticles ($1 \text{ mg}\cdot\text{cm}^{-2}$) and 25 wt. % of ion-exchange resin.



Figure 1. Experimental electrochemical HC.

A schematic diagram of the automated test-bench used for the measurements is pictured in figure 2. A PEM water electrolyser (E) is used to produce the hydrogen which is then used in the HC. Gaseous oxygen and hydrogen produced by E are extracted from the biphasic water-gas mixtures in separators C1 and C2. Oxygen is rejected to the atmosphere, and hydrogen is sent to the HC through valve V3. Hydrogen in excess is rejected through valve V4. Power unit CS2 supplies the electric power to the electrochemical cell of the HC. Before operation, water tanks are filled up with deionized ($18 \text{ M}\Omega\cdot\text{cm}$) water (figure 2). Admission and exhaust chambers of the HC are purged with pure nitrogen stored in reservoir V using the pressure regulator PR. Then hydrogen is injected into the HC and a voltage is applied to the electrochemical cell. Hydrogen is oxidized at the anode and decomposed into protons and electrons. Protons then migrate through the membrane to the cathode where they are reduced into molecular hydrogen. As the reaction proceeds, the pressure in the upper cover vessel gradually increases. The output pressure of the HC is monitored by the PC with the help of pressure sensors, until stationary values are reached.

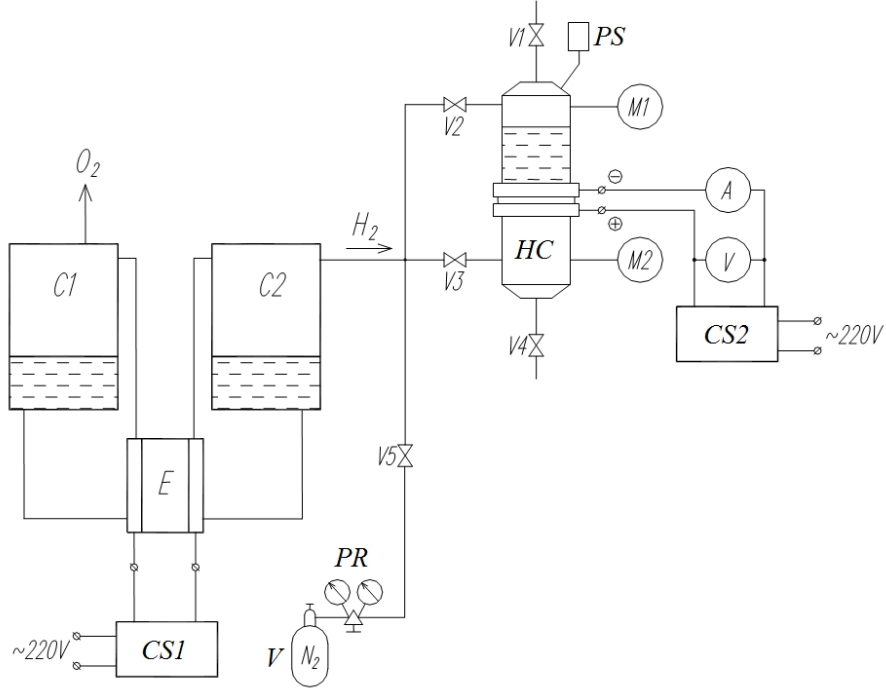


Figure 2. Experimental test-bench. E – electrolyser; HC - hydrogen compressor; C1 - oxygen separator; C2 - hydrogen separator; CS1 - electrolyser current supply; CS2 - hydrogen compressor current supply; V1...V5 – valves; M1, M2 – manometers; V - vessel with inert gas (nitrogen); PR - pressure reducer; PS - pressure sensor; A – amperemeter; V – voltmeter.

3. MODELING

In a first step, the behavior of the HC was modeled to estimate the maximum output pressure and quantify the role of gas permeability. It turns out that gas permeability of SPE can produce significant limitations in terms of faradic efficiency and output pressure, mainly because of the back-diffusion of molecular hydrogen from the cathodic compartment (high pressure chamber) to the anodic compartment (low pressure chamber). From a physical viewpoint, parasite transport of molecular hydrogen back to the anode through the membrane is caused by two basic processes:

- diffusion of molecular hydrogen across the SPE (from cathode to anode);
- convective transfer of hydrogen dissolved in water linked to protons (electroosmotic flow).

In the HC, both flows have opposite directions. Because of the symmetry of the cell, modeling is a one-dimension problem which can be expressed as:

$$\begin{cases} Q_{HM} = -D_{HM} \frac{dC_H}{dy} + v_c \Gamma_H C_H = \text{const} & 0 < y < h_m \\ y = 0 \quad C_H = C_{ga}(1 - \tau_a) \quad y = h_m \quad C_H = C_{gc}(1 - \tau_c) \end{cases} \quad (1)$$

In transfer equation (1), the different terms have the following meaning :

y is the one-dimension space coordinate and h_m the membrane thickness;

C_{gc} and C_{ga} are gas phase concentrations of hydrogen in cathode and anode compartment;

τ_c, τ_a denote the ratio of saturated water vapor to full pressure for cathode and anode chambers respectively;

v_c is the convective water velocity due to the electro-osmotic flow;

Γ_H is the Henry factor (proportionality factor between concentration of hydrogen in liquid and gas phases (here, $\Gamma_H = 1.67 \cdot 10^{-3}$ mol/mol);

D_{HM} is the hydrogen diffusion coefficient in the SPE at full humidification

$$D_{HM} = 5.65 \cdot 10^{-8} \exp\left(-\frac{2100}{T}\right) m^2 / s \quad (\text{an expression approximating data provided in Ref. [10]).}$$

Convective velocity is obtained from Eq. (2) :

$$v_c = \frac{I_0 n_p}{FC_l} \quad (2)$$

Equation (1) contains two unknown: the hydrogen concentration C_H and the full hydrogen flow through the membrane Q_{HM} . Equation (1) is first order and has two boundary conditions. Using (2), we obtain :

$$\begin{cases} C_H = \frac{C_{gc}(1-\tau_c) \left[\exp\left(\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} y\right) - 1 \right] + C_{ga}(1-\tau_a) \left[\exp\left(\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right) - \exp\left(\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} y\right) \right]}{\exp\left[\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right] - 1} \\ Q_{HM} = -\frac{I_0 n_p \Gamma_H}{FC_l} \frac{C_{gc}(1-\tau_c) - C_{ga}(1-\tau_a) \exp\left[\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right]}{\exp\left[\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right] - 1} \end{cases} \quad (3)$$

At large operating pressure, τ_c (cathodic compartment) is close to zero, and Q_{HM} in equation (3) simplifies into:

$$Q_{HM} = -\frac{I_0 n_p \Gamma_H}{FC_l} \frac{C_{gc} - C_{ga}(1-\tau_a) \exp\left[\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right]}{\exp\left[\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right] - 1} \quad (4)$$

At small current densities, a further simplified expression of Q_{HM} is:

$$\left\{ Q_{HM} \approx -[C_{gc} - C_{ga}(1-\tau_a)] \frac{D_{HM}}{h_m}, \right. \quad (5)$$

From (5), the flow value does not depend on the current density. At high current densities, Q_{HM} can be approximately expressed as follows:

$$Q_{HM} = -[C_{gc} - C_{ga}(1-\tau_a)] \frac{I_0 n_p \Gamma_H}{FC_l}, \quad (6)$$

In that case, the value of hydrogen flow does not depend on diffusion but only on convective velocity. The total flow of hydrogen Q_Σ through the membrane is obtained by summing both (diffusion and electro-osmosis) contributions, yielding :

$$Q_\Sigma = \frac{I_0}{2F} \left\{ 1 - \frac{2n_p \Gamma_H}{C_l} \frac{C_{gc} - C_{ga}(1-\tau_a) \exp\left[\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right]}{\exp\left[\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right] - 1} \right\} \quad (7)$$

In a first approximation, assuming that hydrogen behaves like an ideal gas, its density can be obtained the law of ideal gases :

$$P_a = C_{ga} RT \quad P_c = C_{gc} RT \quad (8)$$

From equation (7), it appears that for certain value of pressure P_c , the full hydrogen flow through the membrane is zero. The maximal pressure value is obtained for $Q_\Sigma=0$ and this can be written as :

$$P_{c\max} = RT \frac{C_l}{2n_p \Gamma_H} \left[\exp\left(\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right) - 1 \right] + (P_a - P_s) \exp\left(\frac{I_0 n_p \Gamma_H}{FC_l D_{HM}} h_m\right) \quad (9)$$

Maximum output pressures of the HC, calculated by taking into consideration hydrogen back-diffusion, are plotted in figures 3 and 4, as a function of current density and membrane thickness, for two different operating temperatures (50 and 90°C). From these results, it appears that very high pressures can be reached with single PEM-HC cells, even at relatively low current densities.

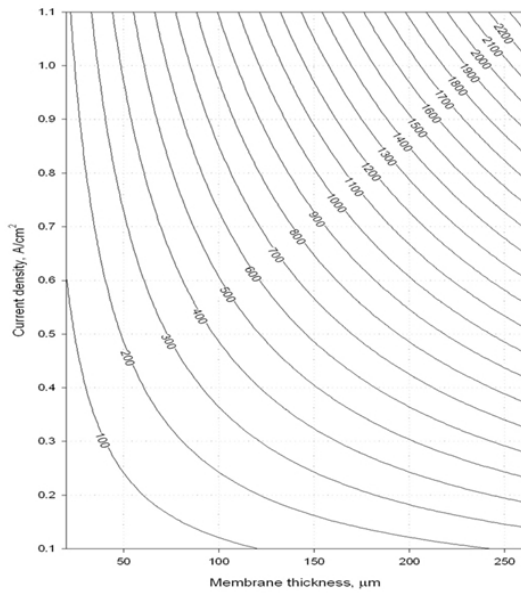


Figure 3. Calculated maximum output pressure as a function of current density and membrane thickness.
 $T = 50^{\circ}\text{C}$ and input pressure = 1 bar.

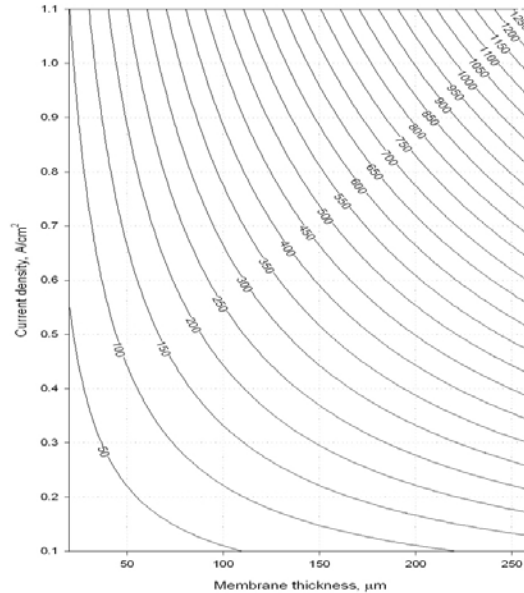


Figure 4. Calculated maximum output pressure as a function of current density and membrane thickness.
 $T = 90^{\circ}\text{C}$ and input pressure = 1 bar.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Experimental results reported in this communication were obtained to validate predictions from the model. As can be seen from figures 3, 4 and 5, higher output pressures are obtained at lower temperatures. This is explained by the fact that membrane gas permeability decreases with temperature. However, permeation kinetics increases with temperature and this is positive to reduce the cost of electric power associated with H_2 compression. The role of various experimental parameters (mainly water vapor partial pressure and current density) was evaluated and an optimum temperature value of 70°C was determined for both the cell and the anode gas flow humidification unit. At atmospheric pressure, cell voltages of 0.16 and 0.39 V was measured for current densities of respectively 0.5 and 1.3 A/cm^2 (figure 5). No kinetic limitation was observed up to 1.3 A/cm^2 .

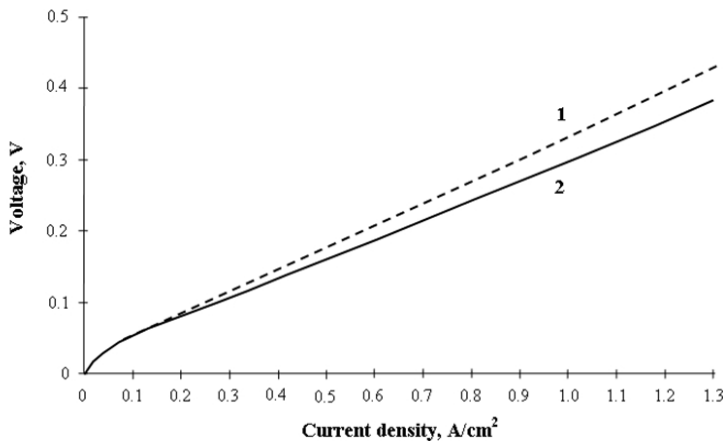


Figure 5. Experimental current-voltage relationship of a HC with optimized MEA at $T_{\text{cell}} = T_{\text{hum}} = 60^{\circ}\text{C}$ (curve 1) and 69°C (curve 2).
 Active area = 7 cm^2 .
 Input H_2 pressure = 1 bar.
 Output H_2 pressure = 1 bar.

Similar experiments have been performed up to 28 bar (figure 6) with no significant kinetic differences. However, it was found difficult to maintain stationary performances over several hours of operation, mainly due to water management issues.

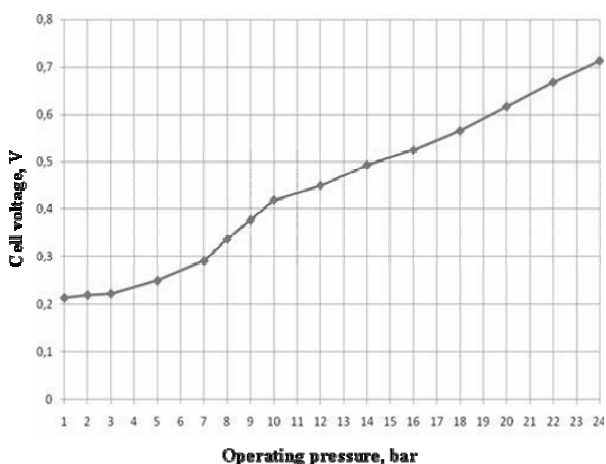


Figure 6. Stationary cell voltages measured vs. output pressure at constant current density of 0.18 A/cm². Active area = 28.26 cm².

4. CONCLUSIONS

The maximum output pressure of a PEM hydrogen electrochemical compressor has been calculated as a function of membrane thickness, current density and operating temperature. Taking into account hydrogen back-diffusion due to the pressure gradient, numerical analysis has shown that for a conventional PEM cell (membrane thickness of 180 microns) a maximum output pressure of 400 bar (at 90°C and 0.5 A/cm²) can be reached. It is shown that the most significant experimental parameters to consider for designing and operating a hydrogen compressor are current density, operating temperature and membrane thickness. Experiments have shown that there is no significant kinetic limitation for current densities up to 1.3 A/cm² and pressure up to 28 bar. This experimental work is currently pursued to reach operating pressures up to 150 bars.

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