

The compression of hydrogen in an electrochemical cell based on a PE fuel cell design

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Abstract

The compression of gases in conventional compressors is often combined with low efficiency and the contamination of the compressed gases. In this paper, a system is described that uses an electrochemical cell for the compression of hydrogen. This electrochemical hydrogen compressor operates at lower hydrogen flux than mechanical hydrogen compressors. Further development of polymer electrolyte membrane (PEM) fuel cells afford a good prospect of realizing the electrochemical compression on a competitive basis. A specialized gas diffusion layer established the possibility to pressurize the cathode volume up to 54 bar. The ohmic resistance and pressure stability have been rescued by an improved membrane electrode assembly (MEA). A three cell stack on a laboratory scale has been designed. Data of single cell and stack experiments will be discussed in this paper. The advantages of the electrochemical system, apart from the efficiency, are: noiseless operation, purified hydrogen and simplicity of the system cooling. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Research in hydrogen storage technologies has taken place for several decades. But there is still no satisfying solution to overcome the problem of the low volumetric energy density. To store the hydrogen at cryogenic temperatures results in a high volumetric energy density, but the costs for cooling of the hydrogen and the loss of hydrogen by evaporation makes this mode only useful for special applications. As is shown in Fig. 1, a multiplicity of hydrogen sorption materials have been investigated for storage, but no material could achieve high volumetric energy storage density. The storage of hydrogen in chemicals like gasoline, methanol or cyclohexane has the disadvantage of the production step and the reformation into hydrogen. Even though the storage of hydrogen at high pressure in the gas phase results in a high volume, it is still an economically and simple way to store hydrogen. For several applications, like small electrolyzers, it is necessary to compress the hydrogen in low quantities to high pressures. For this low power performance region, mechanical hydrogen compressors are not very efficient. An alternative way to compress hydrogen is the use of an electrochemical hydrogen pump, which is a system well-known for years [1–5]. New material

developments for the polymer electrolyte membrane (PEM) fuel cells make it possible to realize PEM hydrogen compression. High efficiency (>80%) is achievable due to the very low cathode polarization in comparison to the PEMFC. An improved design of PEM-cell to operate with a high pressure difference between the anode side and the cathode side has been developed.

2. Working principle

The working principle of electrochemical hydrogen compressor is shown in Fig. 2. Because of a applied potential difference, hydrogen at pressure p_a is oxidized at the anode to H^+ , transported through the PEM and reduced at the cathode to hydrogen at pressure p_c . If the cathode compartment (V_c) is hermetically sealed, the formation of hydrogen at the cathode results in the increase of the pressure p_c .

3. Experimental set-up

Fig. 3 shows the experimental set-up used for the investigations in this paper. The hydrogen flux is regulated by a flow controller, in general, the utilization of hydrogen was adjusted to 85%. To avoid the dehydration of the membrane the hydrogen stream has been led to the cell via a humidifier.

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Nomenclature

A	electrode area (cm^2)
dc	concentration difference, Δp_{ca}
dm	amount of hydrogen diffused through the membrane
dt	time of diffusion
dx	diffusion distance (membrane thickness) (μm)
D_m	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
E_N	Nernst potential (V)
E_0	standard potential (V)
F	Faraday's constant (96487) (C mol^{-1})
i	electrode area specific current (A cm^{-2})
I	current (A)
OCV	open circuit voltage (V)
p_a	anode pressure (0.1 MPa = 1 bar) (bar)
p_c	cathode pressure (0.1 MPa = 1 bar) (bar)
$p_a^*(t)$	increased anode pressure (bar)
$\Delta p_a(t)$	the pressure difference between cathode and anode $p_c > p_a$ (bar)
Δp_{ca}	the pressure difference between cathode and anode $p_c > p_a$ (bar)
r	electrode area specific resistance (Ωcm^2)
R	gas constant (8.314) ($\text{J mol}^{-1} \text{K}^{-1}$)
R'	resistance (Ω)
T	temperature (K)
T_0	standard temperature (273.14) (K)
U	cell voltage (V)
V_a	anode volume (l mol^{-1})
V_c	cathode volume (l mol^{-1})
V_0	standard molar volume (22.4) (l mol^{-1})
$v_{ac}^{\text{H}^+}$	migration from anode to cathode because of the applied potential difference U (ml min^{-1})
$v_{ca}^{\text{H}_2}$	diffusion from cathode to anode because of the pressure difference Δp_{ca} (ml min^{-1})
x	membrane thickness (μm)
z	number of electron exchange

With some exceptions the experiments were done at 25 ± 2 °C, and the hydrogen gas humidifier was kept at the same temperature. For temperature and leakage control the hydrogen compressor has been kept in a thermostated water bath. This was possible because the cell voltage was kept below 0.5 V. The excess hydrogen at the anode and cathode outlets was controlled by gas bubblers. The compressor has been operated galvanostatically by an dc-generator. For the pressure experiments the cathode compartment was hermetically sealed by a tab and the pressure was controlled by an electronic pressure gauge. The principle parts of the single cell are shown in Fig. 4. As in the PEMFC, two end plates hold the cell together. Because of the high applied pressure, these end plates are made of stainless steel. The membrane is sealed against the end plates with a specialized gasket. The flow field at the anode is reinforced to withstand the pressure. The flow field at the cathode involves a dynamic characteristic to keep the contact to the electrode in a good position. The cell is held

together with eight 10 mm bolts. The electrode area is 100 mm × 100 mm (area 100 cm²). In general, a carbon supported platinum- or platinum-ruthenium catalyst, with varying loading, has been used. The commercial membrane electrode assemblies utilized were two types of membranes. One (E-TEK) with the electrode in the gas diffusion layer and this layer hot pressed on the membrane. Because of the thick gas diffusion layer (0.5 mm), this electrode is called thick layer membrane electrode assembly (MEA). The other commercial MEA (GORE) where the electrode is directly applied on the membrane is called thin layer (~50 μm) MEA. At the noncommercial electrodes the catalyst has been sprayed as an ink on the hot polymer membrane. The membranes used were different Nafion[®]-based membranes. Because the electrode layer is (as well) very thin these MEAs are also named thin layer MEA.

4. Results and discussion

The kinetics of the hydrogen electrodes are rapid. A slightly slower kinetics of the reduction at the cathode compared with the oxidation at the anode has been determined (Fig. 5). This can be explained due to slower kinetics of the Volmer–Tafel-mechanism [6] for the reduction. The low overpotential leads to an I/U characteristic mainly caused by IR' -drop. This is shown in Fig. 6. The polarization plot is close to zero and the IR' -drop almost amounts to the cell voltage. The Nernst voltage in this case is zero because the pressure difference is zero.

The total cell voltage of the PEM hydrogen compressor includes the Nernst potential, the polarization voltage and the IR' -drop. The Nernst potential depends on the pressure difference of the cathode and the anode pressure (Δp_{ca}). This equilibrium potential is given by the Nernst Eq. (1). The polarization voltage summarizes the overpotential at the anode (η_a) and at the cathode (η_c) Eq. (2). Therefore, the cell voltage is given by Eq. (3):

$$E_N = E_0 + \frac{RT}{2F} \ln \frac{p_c}{p_a} \quad (1)$$

$$\eta = \eta_a + \eta_c \quad (2)$$

$$U = E_N + \eta_a + \eta_c + IR' \quad (3)$$

The evaluation of these potentials during the pressure increase is shown in Fig. 7. The Nernst potential calculated for the measured pressure increase follows a logarithmic curve. The difference between the Nernst potential and the cell voltage is due to the polarization voltage and the IR' -drop ($IR' + \eta$). Because the polarization voltage is low the difference is mainly the IR' -drop. At low pressures (<25 bar) the difference between cell voltage and Nernst potential is almost constant, but at higher pressures (>25 bar) the difference increases. This effect is caused by contraction and expansion of the materials inside the cell, the result is an increase of the contact resistance and, therefore, the IR' -part.

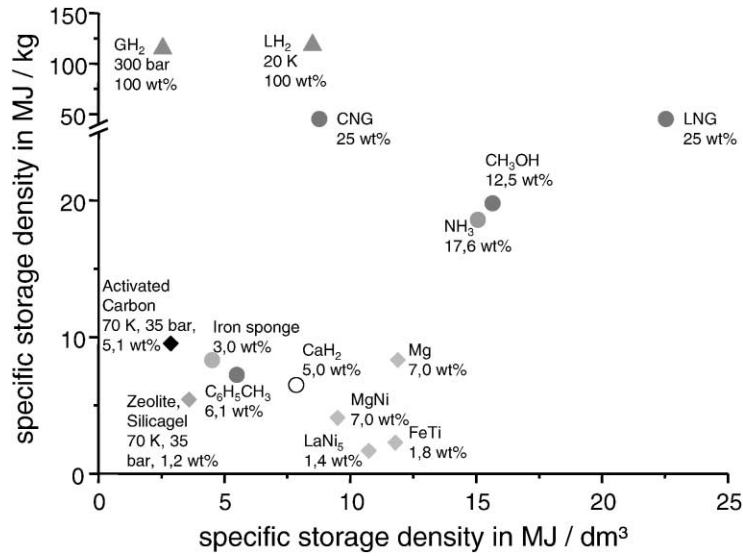


Fig. 1. Specific storage densities of hydrogen storage systems.

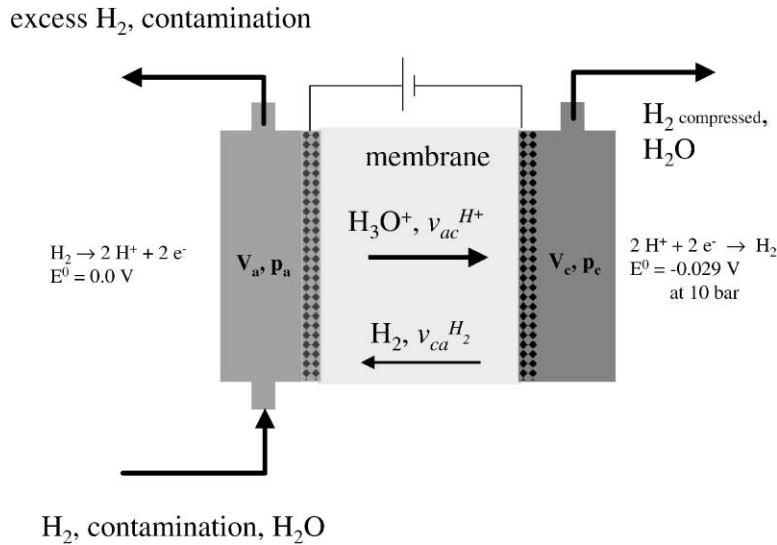


Fig. 2. Principle of the electrochemical hydrogen compressor.

A main problem of a high pressure difference over a polymer membrane is the hydrogen permeation through the membrane. This permeation limits the maximal achievable pressure. If this permeation is too high it will reduce the efficiency and will defeat the possibility to realize a hydrogen compressor in a PEM cell. For this reason a focus has been put on diffusion studies by different membranes.

5. Measuring of the diffusion coefficient

According to the first Fick's law (stationary) the relation between gas diffusion rate (dm/dt) and membrane thickness (x) is given by the diffusion coefficient (D_m):

$$\frac{dm}{dt} = -D_m A \frac{dc}{dx} \quad (4)$$

During the operation of the hydrogen compressor the protons are transported by migration, caused by an external potential difference through the membrane from the anode to the cathode with the rate $v_{ac}^{H^+}$. Because of the increasing hydrogen pressure at the cathode also a diffusion of hydrogen molecules through the membrane from the cathode to the anode with the rate $v_{ca}^{H_2}$ takes place (back diffusion). In order to determine this value, the following experiment was carried out. At OCV and $p_c > p_a$ the hydrogen diffusion from the cathode to the anode ($v_{ca}^{H_2}$) will increase the pressure at the anode because of the additional hydrogen. This additional value is called $\Delta p_a(t)$. Therefore, the total anode pressure $p_a^*(t)$ is determined by:

$$p_a^*(t) = p_a + \Delta p_a(t) \quad (5)$$

If the anode is open to the atmosphere the pressure excess results in a gas flow out of the anode outlet. This gas flow can

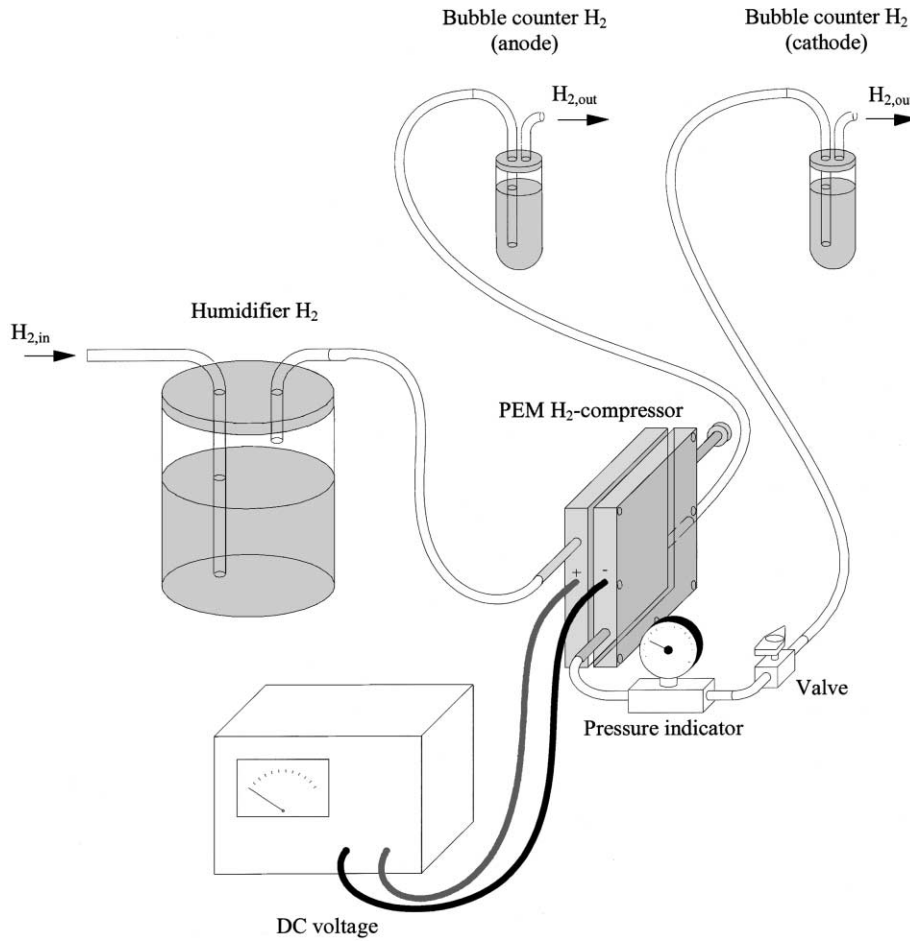
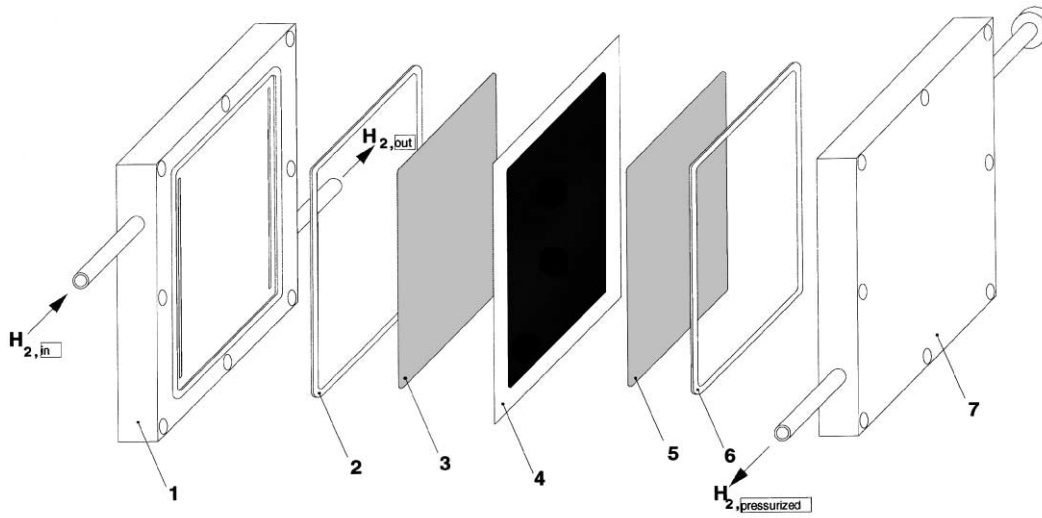


Fig. 3. Experimental set-up for the electrochemical hydrogen compressor.



- (1) anode endplate
- (2) anode seal
- (3) flow field with gas diffusion layer anode
- (4) membrane electrode assembly
- (5) flow field with gas diffusion layer cathode
- (6) cathode seal
- (7) cathode endplate

Fig. 4. Single cell of the electrochemical hydrogen compressor.

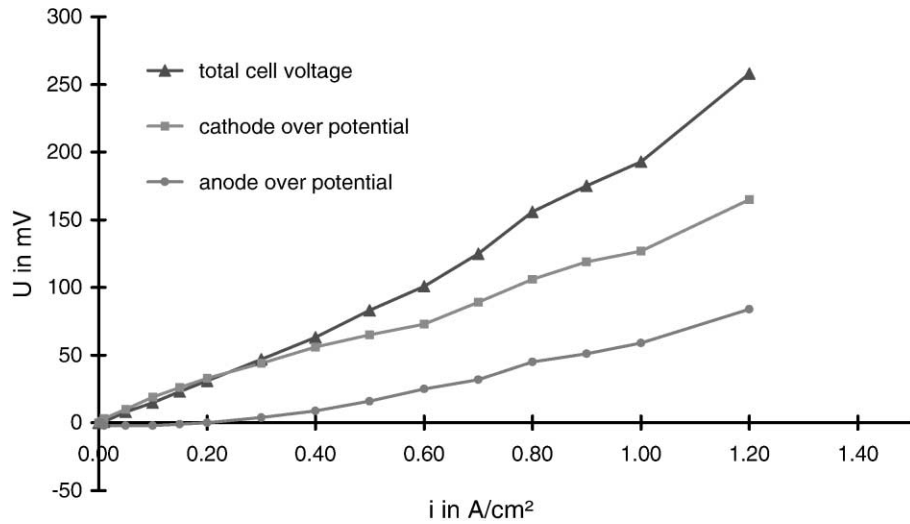


Fig. 5. Polarization of thin layer electrodes on Nafion[®]: at 70 °C; Δp , 0 bar; A, 25 cm²; r , 0.13 Ω cm⁻²; hydrogen stoichiometry, 1.25; anode catalyst loading, 167 μ g Pt cm⁻²; cathode catalyst loading, 171 μ g Pt cm⁻².

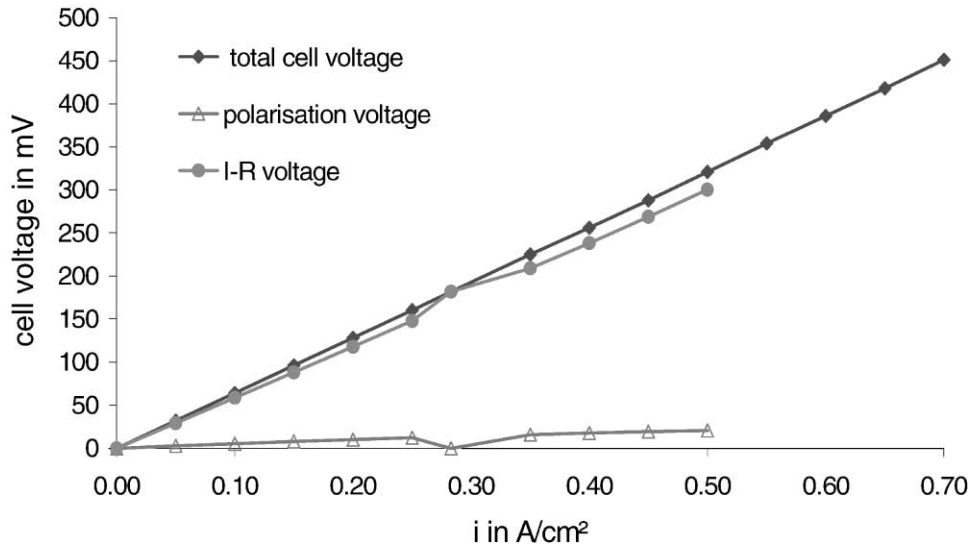


Fig. 6. I/U -characteristic of the MEA GORE 6000: Δp , 0 bar.

be detected by gas bubbles. In order to avoid the gas flow at the outlet, the diffusion flow $v_{ca}^{H_2}$ results in $\Delta p_a(t)$, has to be compensated by the reduction of $p_a^*(t)$. This can be done by the electrochemical pumping of hydrogen from the anode to the cathode via protons $v_{ac}^{H^+}$. The electrical compensation current i_{ac} is described by the Faraday's law.

$$v_{ac}^{H^+} = \frac{i_{ac}}{zF} \frac{V_0 T}{T_0} \quad (6)$$

If the compensation current, applied by an external source, equalizes the back diffusion current no gas bubbles will occur at the outlet. If the applied current is too low, gas bubbles still occur. If the applied current is too high, hydrogen from the tubing will be sucked into the anode compartment. For this reason the electrical compensation current i_{ac} is measured and characterizes the back diffusion.

The diffusion coefficients for different membranes are listed in Table 1. The data measured here are in the same order of magnitude as the results of Ogumi et al. [7].

Fig. 8 reveals a correspondence between membrane thickness and diffusion rate. The x error bars are graphed because

Table 1
Thickness and diffusion coefficient of different MEAs

MEAs	Membrane thickness (μ m)	Diffusion coefficient (10^{-7} cm ² s ⁻¹)
W.L. GORE MEA 6000 (thin layer)	40	1.85
ETEK MEA Nafion 105 (thick layer)	120	2.44
ZSW MEA Nafion 115 (thin layer)	120	2.56
ETEK MEA Nafion 117 (thick layer)	200	2.10

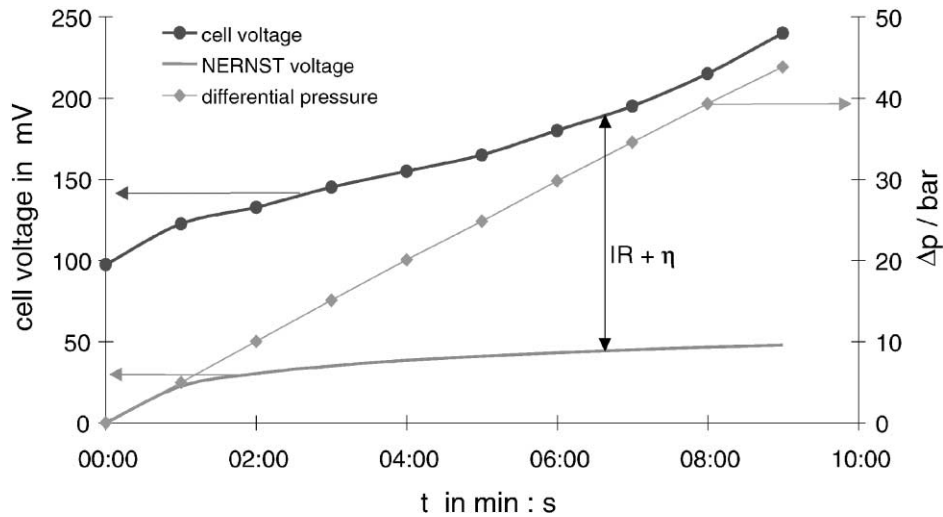


Fig. 7. Proportioning of the cell voltage: V , 13 ml; I , 0.20 A cm^{-2} ; r , $0.42 \Omega \text{ cm}^{-2}$.

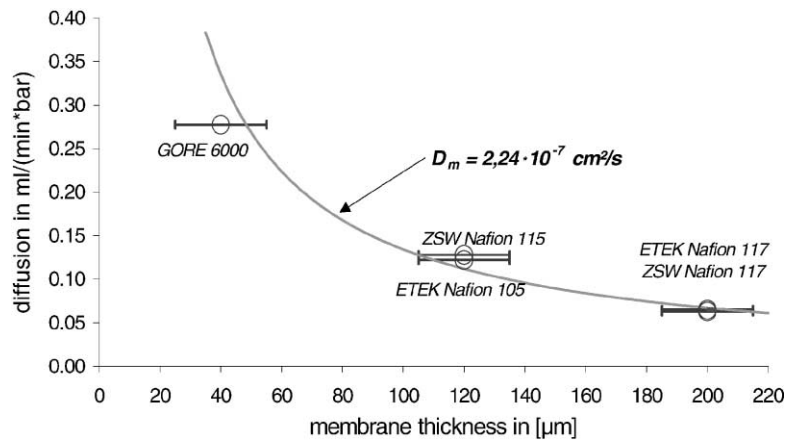


Fig. 8. Hydrogen diffusion through the PEM (back diffusion).

the MEA thickness varies with their status of hydration. The graphed line is the calculated diffusion rate dependent on MEA thickness with the average diffusion coefficient ($D_m = 2.24 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) of all measured MEAs. The

purpose is to show the reference to Fick's law but it is understood that the averaging of diffusion coefficients of thin and thick layer MEAs and MEAs of the different structures is not exactly correct. This study gives evidence

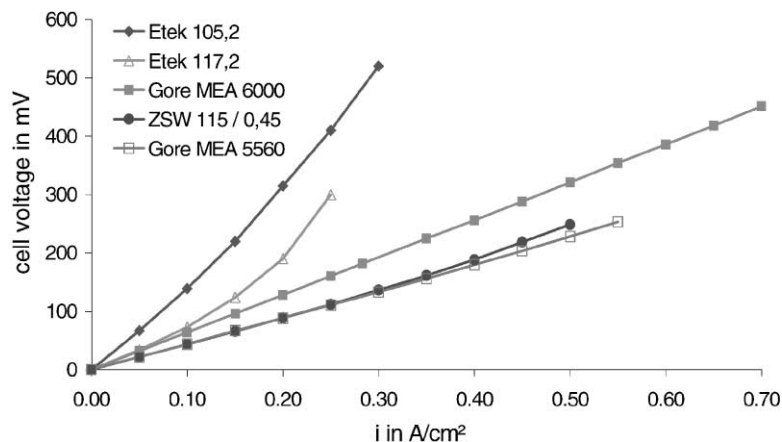


Fig. 9. I/U -characteristic of different MEAs: Δp , 0 bar.

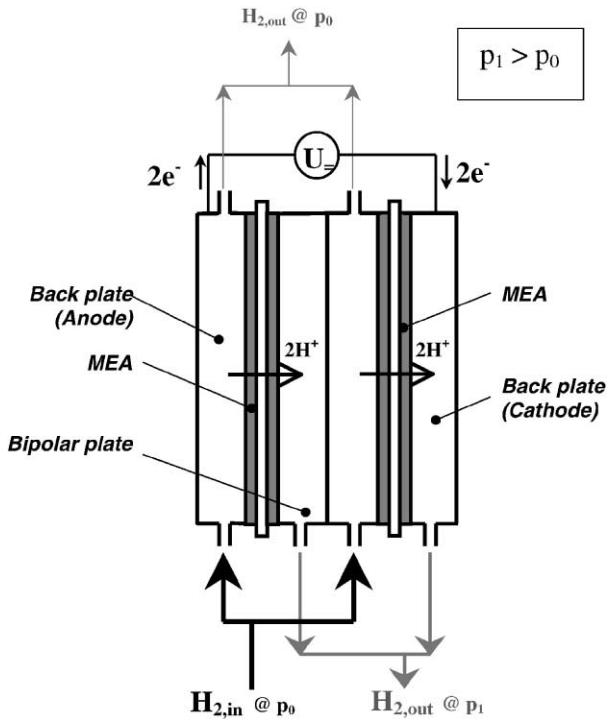


Fig. 10. Principle of stacking the electrochemical hydrogen compressor with external gas manifold.

that it is not possible to avoid the back diffusion, but it is obvious that an acceptable back diffusion rate can be defined. This definition will set the theoretical pressure maximum that can be achieved with a certain membrane. On the other hand, it was found that at membranes where the ionomer is adhesively bound in a net structure the ionomer will be pressed out of the structure at a certain pressure. For ionomers polymerized as a membrane the structure was stable up to the pressures reached in this investigations (about 50 bar). The average diffusion coefficient which has been found can be translated in to a back diffusion rate of less than $67 \mu\text{l h}^{-1} \text{bar}^{-1} \text{cm}^{-1}$ at room temperature. This should be acceptable for most practical systems.

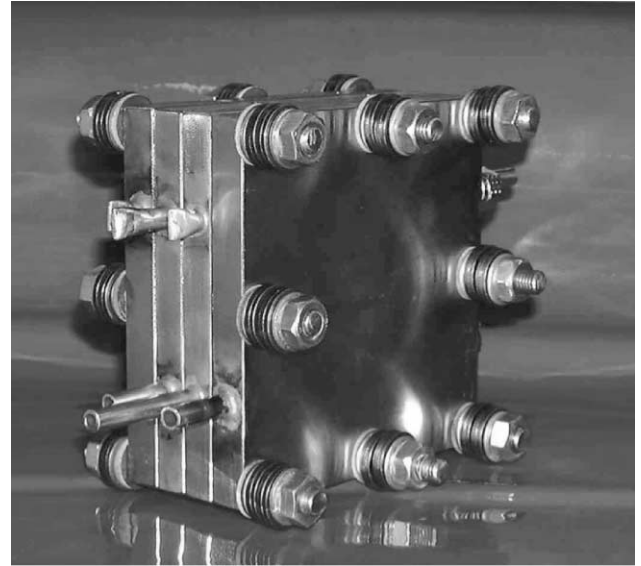


Fig. 11. Triple cell of the electrochemical hydrogen compressor.

Fig. 9 shows the I/U -characteristic of different MEAs. Using mechanically stable thick layer MEAs from E-TEK, the pressure was not limited by the MEA. But the thick layer showed transportation problems and a fairly high IR' -drop. The thin layer GORE MEAs show a low IR' -drop. Furthermore, no transport problem is evident. However, the MEAs were not stable at high pressure as was described before. The thin layer MEA made for this application at ZSW is based on Nafion[®] 115 and shows good performance regarding IR' -drop and pressure stability.

To reach practical flow rates it is necessary to enlarge the cell area. This is possible by increasing the MEA area by stacking the cells, a design typically used in fuel cells. Using the described ZSW Nafion[®] 115 membranes a cell stack similar to a PEMFC stack has been designed. To provide access to single cells an external gas manifold has been used. A draft of a two cell unit is shown in Fig. 10. The pressure increase in the cathode volume and the cell voltage versus

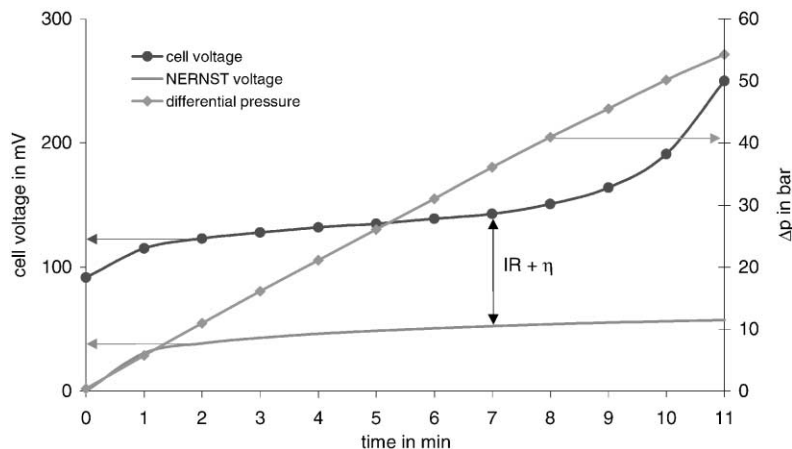


Fig. 12. Proportioning of the cell voltage of a triple cell unit: cell area, 300 cm^2 ; I , 0.20 A/cm^2 ; r , $0.15 \Omega \text{ cm}^2$.

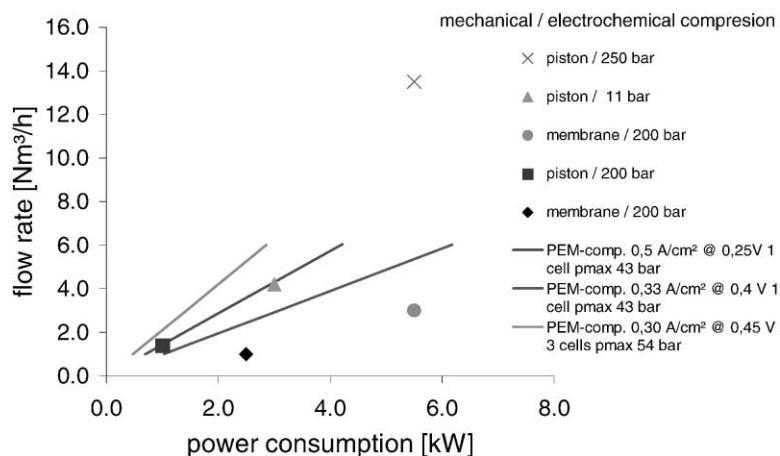


Fig. 13. Comparison of mechanical and electrochemical compressors.

time of a three cell unit (Fig. 11) is plotted in Fig. 12. As was outlined before, but is more obvious here, beginning at 35 bar the internal cell components are contracted with increasing pressure, for this reason the internal resistance increases. The maximal pressure difference achieved with this unit was about 54 bar.

To compare the data determined in this work with commercially available hydrogen compressors the single and triple cell data are numerically scaled up to a unit with several kilowatt and compared with mechanical compressors. Fig. 13 shows for the electrochemical hydrogen compressors a higher efficiency in the low power range.

6. Conclusions

In this work it was shown that it is possible to realize a very efficient PEM-based electrochemical hydrogen compressor for pressures up to 54 bar. With an improved sealing construction and cell design it might be possible to reach pressures above 100 bar. Except for back diffusion, these research data do not give any evidence of a pressure limitation caused by the electrochemical working principle of the system. Because of the logarithmic behavior of the Nernst voltage it is an efficiency enhancement to increase the possible differential pressure. It has been shown that it is possible to increase the hydrogen flux for a practical system by stacking the cells. For this reason even large units are possible. The materials cost reduction achievable through PEMFC serial production will also reduce the materials

costs for the PEM hydrogen compressor. Apart from the efficiency the selective permeability for hydrogen is another advantage of the system. Only clean (except water vapor) hydrogen appears at the cathode.

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