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Experimental evidence of local heterogeneities in a PEM Electrochemical Hydrogen Compressor

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Abstract

Electrochemical hydrogen compressor (EHC) has proven to be a valid solution for the development of Fuel Cell Vehicles and hydrogen refueling stations. Hydrogen pressures up to 1000 bar can be reached by using an EHC. However, low compression efficiencies are obtained at very high pressures, mainly because of difficulties in sealing and hydrogen back diffusion through the polymer electrolyte membrane (PEM). Moreover, the performances of an EHC are affected by local dehydration of the PEM. A segmented cell of active area 30 x 1 cm² and divided into 20 segments of 1.5 cm² was used to investigate the local behavior of an EHC. Such a system allowed measuring the current density along the channel direction and the resistances of each single segment by impedance spectroscopy, making possible the evaluation of the local water transport through the PEM. In fact, heterogeneities in the distribution of the electric resistances were observed, reflecting the unbalanced contribution of the two water transport mechanisms along the PEM, i.e. electro-osmosis and water back diffusion. A pseudo 2D model, which simulates the mass and energy transfer occurring in the EHC, was developed along with the experimental investigation. It was observed that these heterogeneities can significantly alter the efficiency of an EHC. Hence, several parameters affecting the performance of an EHC, such as the humidity of the inlet flow, temperature, PEM thickness, discharge pressure and stoichiometric ratio, were investigated in order to optimize the system and enhance its overall efficiency.

Introduction

Although hydrogen mechanical compressors are used for hydrogen compression worldwide, they are affected by low efficiency as well as by several operating drawbacks, as the embrittlement phenomena produced by hydrogen and the presence of several moving parts [1]. Electrochemical hydrogen compressors (EHC) proved to be a valid alternative, since they allow compressing hydrogen in silent and compact systems, ensuring reaching compression efficiencies higher than 60% [2].

Hydrogen is fed along with water at the anode compartment of the EHC, where hydrogen oxidation occurs while electric energy is applied to the system. High pressure hydrogen is therefore produced at the cathode compartment, where protons reduction takes place. The current density-voltage I - V characteristic curves reveal that the effective voltage applied to an EHC deviates from the Nernst voltage mainly because of the total ohmic resistance of the system, which takes into account: (i) the ionic resistance of the membrane; (ii) the ionic and electronic resistance of the electrodes and (iii) the contacts and cell hardware resistances [3].

Operating heterogeneities can arise while compressing hydrogen in an EHC, i.e. the current density distribution along the gas channel direction can be non-uniform because of the instability of the total resistance of the EHC all over the compressor. Onda et al. [4] found that this behavior is strictly related to the water transport in the EHC.

Water management is a key factor in the EHC operation. Water is mandatory to humidify the polymer electrolyte membrane (PEM), and it is an essential requirement to enhance its protonic conductivity [5]. Low water content can make the PEM protonic conductivity decreasing, thus increasing the ohmic resistance of the EHC. A solution to maintain an adequate PEM humidity is to circulate liquid water in the high pressure side but the cost of a pressure-resistant pump may be prohibitive. So generally, water is supplied as a vapor along with low pressure hydrogen at the anode side. Local heterogeneities in an EHC arise from the unbalanced contribution of the main water transport mechanism across the membrane, i.e. (i) the electro-osmotic drag; (ii) water concentration gradient and (iii) water gradient due to the liquid hydraulic pressure difference [6]. A uniform current density distribution can be thus obtained only when a well-balanced water management is set up.

Along with the issues arising from an unbalanced water management, the EHC is also affected by the hydrogen permeation occurring when high pressure gradients exist along the system. Rohland et al. [7] showed that hydrogen permeation across the membrane increased linearly with the pressure gradient, and an increase of 66% was also observed when increasing the system temperature from 24 to 70°C.

Both the unbalanced water management and hydrogen permeation can affect the efficiency of an EHC. In this study, the effects of the membrane thickness, the humidity of the feed gas, the global current density applied to the system and the hydrogen pressure at the cathode on the distribution of the local current densities were evaluated and discussed, in order to find the operating conditions giving the highest efficiency potentially achievable.

1. Experimental

The distribution of the local current densities was obtained by using a 30 x 1 cm² EHC, which was segmented into 20 identical sections operating at the same voltage and with an active area of 1.5 cm² each. A detailed description of the system is given elsewhere [8,9]. An external power supply having a nominal capacity of 1500 W was used.

Five parallel gas channels 30 cm long, 0.1 cm wide and 0.5 cm deep were milled in the support plates at both the anode and the cathode compartments. Hydrogen was previously humidified by bubbling it through water, then it was fed into the anode side through the gas channels and its flow was adjusted by using mass flow controllers. Unreacted hydrogen was collected at the anode outlet and its humidity was measured by a probe Vaisala HUMICAP[®] HMT330 thermostated at 75°C. At the cathode, the inlet was closed and a condenser unit was placed at the outlet to remove excess water from the high pressure hydrogen flow. The hydrogen discharge pressure was adjusted by using a pressure regulator Brooks[®] SLA5820s. The EHC was thermally controlled by a water circulating system mounted on the anode and cathode plates, thus generating a homogeneous temperature profile along the channel. All the gas lines were thermostated at 75°C to prevent water condensation and purged with nitrogen before each measurement.

Commercial membrane electrodes assembly (MEA) from Ion Power were used, made from Nafion 117 or Nafion XL membranes (thickness 175 µm and 25 µm, respectively) with Pt/C catalyst. On the anode side, a gold-coated titanium porous transfer layer (PTL) was used (thickness 1 mm, pores size 3 µm), whereas two Sigracet gas diffusion layers (thickness 240 µm each) were used on the cathode size.

2. Modelling

Water transport across the PEM membrane can occur via three mechanisms: (i) the electro-osmosis, in the form of water molecules dragged by the protons due to electrostatic attraction, from the anode to the cathode; (ii) water diffusion, as a consequence of the water concentration gradient, from the cathode to the anode; (iii) water gradient due to the liquid hydraulic pressure difference, from the cathode to the anode too. The water molar flux [mol s⁻¹ cm⁻²] across the membrane can be thus evaluated by using the following equation:

$$\dot{N}_{H_2O}^{memb} = \zeta \frac{i(y)}{F} - D_{H_2O}^{memb} \frac{\rho_{dry}}{EW} \frac{d\lambda(y)}{dx} - K_p \frac{\rho_l}{\mu_l} \frac{dP_l}{dx} \quad (1)$$

According to Eq. (1), $\dot{N}_{H_2O}^{memb}$ is supposed to be positive when directed from the anode to the cathode. Electro-osmosis depends on the electro-osmotic drag coefficient, ζ [-], and the local current density $i(y)$ [A cm⁻²], where y is the spatial coordinate referring to the along the gas channels direction. F is the Faraday's constant [C mol⁻¹]. Water concentration gradient across the membrane depends on both the local water content of the membrane, $\lambda(y)$ [-], and the effective water diffusion coefficient, $D_{H_2O}^{memb}$ [cm² s⁻¹]. ρ_{dry} is the dry membrane density [0.002 kg cm⁻³] and EW is the membrane equivalent weight [1.1 kg mol⁻¹]. Finally, the water gradient due to the hydraulic pressure depends on the pressure difference between the cathode and the anode, the membrane permeability K_p [cm²], the viscosity of the liquid water μ_l [Pa s] and its molar density ρ_l [mol cm⁻³].

Both $i(y)$ and $\lambda(y)$ change along the gas channel direction because of hydrogen and water transport across the membrane, according to the following equations:

$$\frac{d\dot{N}_{H_2O}(y)}{dy} = p \dot{N}_{H_2O}^{memb} \quad (2)$$

$$\frac{d\dot{n}_{H_2}(y)}{dy} = -p \left[\frac{i(y)}{2F} - \dot{N}_{H_2,perm} \right] \quad (3)$$

where \dot{n}_{H_2O} [mol s⁻¹] and \dot{n}_{H_2} [mol s⁻¹] are the water and hydrogen flow rate along the gas channels, respectively, p is the width of the active area [cm] and $\dot{N}_{H_2,perm}$ [mol cm⁻² s⁻¹] is the hydrogen molar flux permeating across the membrane, which depends on the pressure difference between the cathode and the anode as well. A decrease or an increase of \dot{n}_{H_2O} and \dot{n}_{H_2} along the channel direction can take place, due to the simultaneous water and hydrogen transport across the membrane.

Heat transfer is negligible in an EHC, since isothermal compression takes place in this system [12]. The balance of charges is given by the following Eq. (4):

$$E = E_{Nernst} + E_{over} + \frac{x_m}{\sigma(\lambda(y))} i(y) \quad (4)$$

where E [V] is the effective voltage applied to the cell, E_{Nernst} [V] is the Nernst potential (the reversible potential for an ideal gas), E_{over} [V] includes both the overpotential at the anode and the cathode, x_m [cm] is the membrane thickness and σ is its protonic conductivity [S cm⁻¹], shows that $i(y)$ directly depends on $\lambda(y)$, which has influence on the protonic conductivity of the membrane. Thus, the variation of the local current density along the gas channels direction can be interpreted through the change in the local water content of the membrane.

Finally, the efficiency of an EHC can be defined as follows:

$$\eta = \frac{E_{Nernst}}{E} \cdot \frac{I - I_{loss}}{I} \quad (5)$$

where E [V] and I [A cm⁻²] are the effective voltage and global current density of the EHC and I_{loss} [A cm⁻²] is the equivalent current density corresponding to the hydrogen permeation flux across the membrane, previously introduced.

3. Results and discussion

Effect of membrane thickness

In order to investigate the presence of local heterogeneities in the current density along an EHC, we first investigated the existence of an eventual limiting current density by using two different membranes: Nafion 117, 175 µm thick, and Nafion XL, 25 µm thick. Figure 1 shows the polarization curves for both the cases:

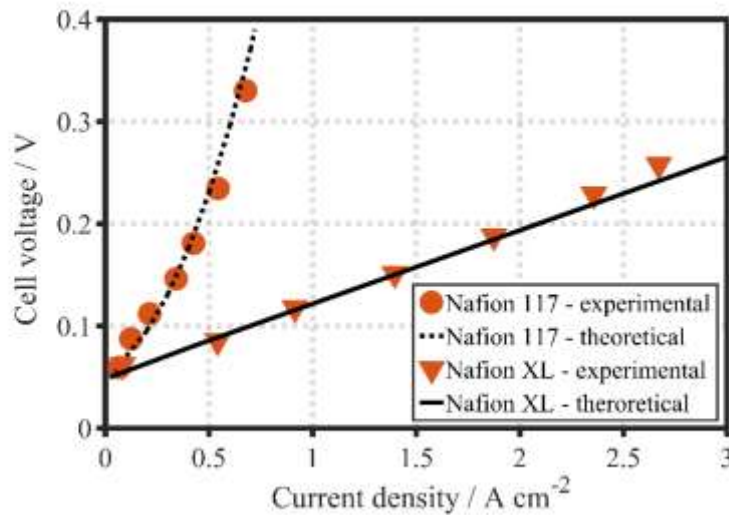


Figure 1 – Measured and calculated polarization curves when using Nafion 117 and Nafion XL membranes ($T = 60^\circ\text{C}$, $RH_{chan,in} = 90\%$, $P_c = 40 \text{ bar}$, $P_a = 1 \text{ bar}$, $S_{H_2} = 1.2$).

For theoretical calculations, $\zeta = 0.9$, $\lambda(x=x_m) = 14$, $E_{Nernst} = 0.053 \text{ V}$, $E_{over} = 0 \text{ V}$.

$D_{H_2O}^{memb}$ and σ were evaluated by using the expressions from [10] and [5], respectively

Figure 1 shows that the cell voltages sharply increased with the global current density reaching an asymptotic value around 0.7 A cm^{-2} when using Nafion 117. This behavior is probably due to the significant increase in the total resistance of the EHC at high current density, due to the membrane dehydration according to Eq. (4). On the other hand, high current density can be applied to the EHC when using Nafion XL, for which the polarization curve is quite linear. Even if hydrogen permeation through the membrane is not at all negligible when using a thin membrane (45.31 mA cm^{-2} for Nafion XL and 5.22 mA cm^{-2} for Nafion 117, both at $T = 60^\circ\text{C}$ and $P_c = 40 \text{ bar}$), high efficiency can be reached by using Nafion XL because of the significantly lower voltage resulting from an applied current density. When applying 0.33 A cm^{-2} to the EHC, 0.06 V were measured when using Nafion XL whereas 0.137 V (2.3 times higher) were measured when using Nafion 117. The advantage is clearly on the side of thin membranes; thus this study was focused on measurements carried on an EHC having Nafion XL membrane.

Effect of humidity

One way for humidifying the EHC membrane, thus enhancing its proton conductivity, consists in feeding water vapor along with hydrogen on the anode side. Nevertheless, water transport across the PTL and the membrane can make water content along the gas channels decreasing or increasing. Figure 2 shows the local current density distribution in the gas channels direction for different relative humidity of the hydrogen flow fed to the EHC ($RH_{chan,in}$). The global current density was fixed at 1 A cm^{-2} .

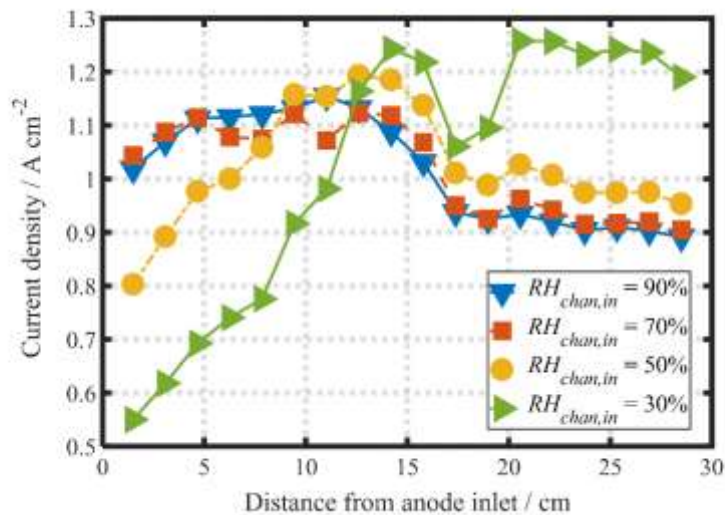


Figure 2 – Local current density distribution along the gas channels direction for different $RH_{chan,in}$ (Nafion XL, $T = 60^\circ\text{C}$, $P_c = 40 \text{ bar}$, $P_a = 1 \text{ bar}$, $I = 1 \text{ A cm}^{-2}$, $S_{H_2} = 1.2$)

An almost constant local current density distribution (variation around 0.2 A cm^{-2}) was obtained when $RH_{chan,in}$ was high ($RH_{chan,in} = 70\% - 90\%$). According to Eq. (4), this behavior is due to the fact that the protonic conductivity of the membrane, i.e. the water content of the membrane, was almost constant all over the gas channels direction at this conditions. This gave a net and stable water flow across the membrane, since the electro-osmotic drag, the water diffusion due to the concentration gradient and that due to the hydraulic pressure difference were well balanced all over the EHC.

On the other hand, unstable local current density distributions (variations higher than 0.7 A cm^{-2}) were obtained for low $RH_{chan,in}$ ($RH_{chan,in} = 30\% - 50\%$). At these conditions, the local current density significantly increased in the first centimeters of the cell, especially in the case of $RH_{chan,in} = 30\%$. This behavior evidently reflects an unstable water flow across the membrane. In fact, a net water flow directed from the cathode to the anode took place from the inlet up to the middle of the cell, since the water diffusion was more important than the electro-osmotic drag therein. Thus, this operating mode “consumed” water at the cathode and gave rise to unstable performances. Liquid water may be supplied on the high-pressure side in order to prevent the cathode dehydration thus balancing the water transport across the membrane when low humidity hydrogen is fed to the EHC. However, this solution would clearly make the system more complex because it requires pumping water at high pressures.

Effect of the applied current density

According to Eq. (1) and (4), the entity of the global current density supplied to the EHC can directly affect the water flow across the membrane and with this, the water content of the membrane. Figure 3 shows the distribution of the local current density along the gas channels when applying different global current densities to the EHC and when feeding hydrogen at $RH_{chan,in} = 90\%$.

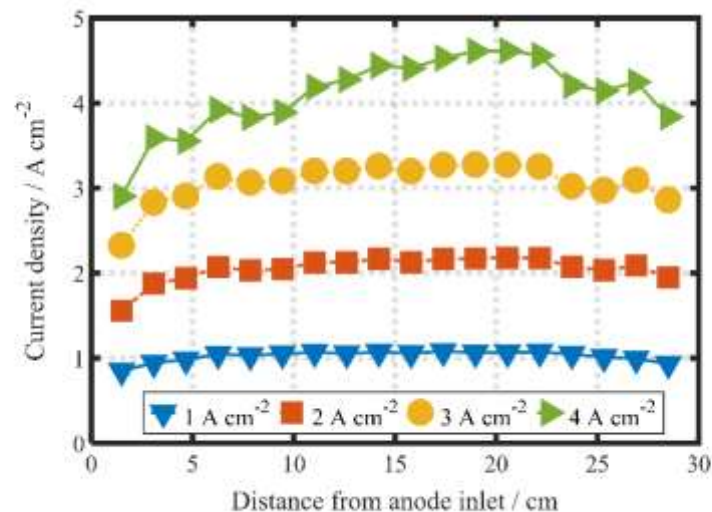


Figure 3 – Local current density distribution along the gas channels direction for different applied current densities (Nafion XL, $T = 60^{\circ}\text{C}$, $P_c = 40 \text{ bar}$, $P_a = 1 \text{ bar}$, $RH_{chan,in} = 90\%$, $S_{H_2} = 1.2$)

When a relatively low current density was applied to the EHC ($I = 1 - 2 \text{ A cm}^{-2}$) the local density distribution was quite constant along the gas channel direction, meaning that the water flux across the membrane towards the cathode side and that in the opposite direction were well-balanced all over the EHC.

On the other hand, in the case of a high applied current density, as for $I = 4 \text{ A cm}^{-2}$, the results were quite different. The local current density increased from the EHC inlet to the 2/3 of it, and decreased afterwards in the last 10 centimeters. Evidently, water flux across the membrane was not stable at all. This conclusion was also confirmed by the RH measured at the anode outlet, RH_{out} . Whereas RH_{out} was almost equal to $RH_{chan,in}$ in the case of low I ($RH_{chan,in} \sim 92\%$), a slight dehydration was instead observed when 4 A cm^{-2} was applied to the cell, i.e. $RH_{out} \sim 85\%$. We can suppose that these effects derive from the non-isothermal character of the transfers for high current densities.

The self-evident advantage in applying a high current density to the EHC is found in the higher compactness and lower cost of the system. Nevertheless, the obtained efficiency will be lower. According to Eq. (5), the EHC efficiency is around 39% at $I = 1 \text{ A cm}^{-2}$, whereas it is equal to 15% at $I = 4 \text{ A cm}^{-2}$. Thus, a trade-off is necessary when evaluating the performance of an EHC system.

Effect of the cathode pressure

Figure 4 shows the local current density distribution over an EHC obtained for different hydrogen discharge pressures. A global current density of 2 A cm^{-2} was applied to the EHC.

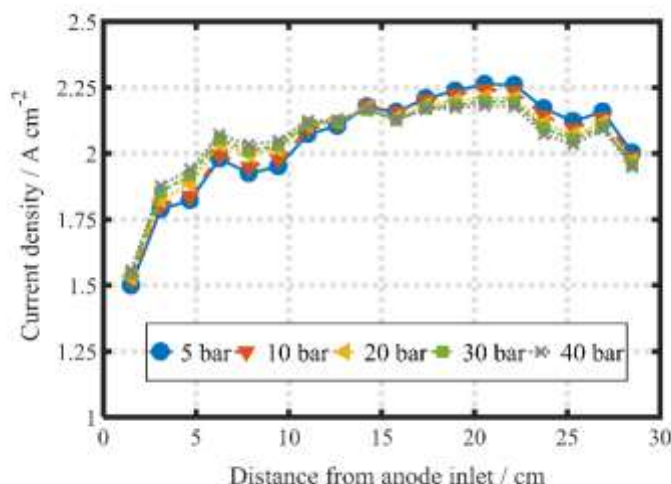


Figure 4 - Local current density distribution along the gas channels direction for different hydrogen discharge pressures (Nafion XL, $T = 60^{\circ}\text{C}$, $I = 2 \text{ A cm}^{-2}$, $P_a = 1 \text{ bar}$, $RH_{chan,in} = 90\%$, $S_{H_2} = 1.2$)

Slight differences in the local current density distribution over the EHC were observed by increasing progressively the hydrogen discharge pressure, P_c . As the values of the local current density increased in the first centimeters of the EHC when using higher P_c , which means that the water flux due to the concentration gradient increases with P_c - as predicted by Eq. (1) -, we can conclude that water management is slightly improved thanks to operating at higher discharged pressures.

4. Conclusion

In this study, we investigated the effect of several parameters on the operation of an EHC through the analysis of the local current density distribution. We found that the current density was not always kept constant over the EHC, which makes operating heterogeneities arising.

A thin membrane gave better performances than a thicker one for pressures lower than 40 bar. In fact, the increase of hydrogen permeation was negligible when compared to the decrease of the working voltage.

As water needs to be fed along with hydrogen to the EHC in order to make the membrane being hydrated, thus enhancing its protonic conductivity, the effect of the relative humidity in the hydrogen flow fed to the EHC was investigated. We found that a stable water flux across the membrane was achieved when high relative humidity was used. On the other hand, more complex and counter-productive operating conditions were obtained at low relative humidity.

The higher the current density applied to the EHC the higher the amount of high pressure hydrogen produced. Nevertheless, unstable water flux across the membrane was observed when high current density was applied to the EHC. This effect is probably related to non-isothermal conditions. Finally, we found that water management is improved when the discharge pressure is increased.

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