CHEMICAL ENGINEERING TRANSACTIONS
VOL. 57, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis

ISBN 978-88-95608- 48-8; **ISSN** 2283-9216
DOI: 10.3303/CET1757270

Analysis of Unbalanced Pressure PEM Electrolyzer for High Pressure Hydrogen Production

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Proton exchange membrane (PEM) electrolyzer is a promising technology and likely to be an important hydrogen generator. The ability to produce high purity hydrogen and deliver it at relatively high pressure is an important advantage of the PEM electrolyzer technology. In this work, the high pressure PEM electrolyzer without the need for external compression is studied. The simulation of the electrolyzer is performed based on an electrochemical model with consideration of hydrogen permeation. The effect of cathode pressure and membrane thickness on electrolyzer performance is studied. The explosion limit of a hydrogen-oxygen mixture in the anode is also taken into consideration. The electrochemical compression shows advantage in term of delivering hydrogen at high pressure with having less effect on performance and low power requirement. The increase of cathode pressure slightly affects the electrolyzer performance. The high pressure operation at the cathode and the use of thin membranes cause hydrogen crossover from the cathode to anode, especially at high current density operation.

1. Introduction

The hydrogen production from a water electrolysis has several advantages in terms of high purity, simple process, no pollution and availability of sources (Herraiz-Cardona, 2013). Industrial water electrolysis cells have been established for one hundred years (Leroy, 1983). There are four types of electrolyzers available: alkaline, acid, polymer electrolyte membrane and high temperature solid oxide electrolyzers. Proton exchange membrane (PEM) or solid polymer electrolyte (SPE) electrolysis is a promising technology and is likely to be an important hydrogen generator in a hydrogen economy. The ability to produce high purity and high pressure hydrogen is a significant advantage of the PEM electrolyzer technology (Santarelli et al., 2009). In contrast to alkaline electrolyzers, caustic alkaline or acidic fluid electrolyte is not necessary for PEM electrolyzers. The electrolyte for PEM electrolyzers is a polymer membrane. The most commonly used membrane is Nafion with a thickness of less than 0.2 mm (Ursua et al., 2012). In addition, PEM electrolysis has additional advantages over alkaline electrolysis such as lower parasitic energy losses and higher purity hydrogen output. Compared to the alkaline electrolyte, PEM can be operated at higher current densities due to the higher conductivity of the electrolyte (Marangio et al., 2009). The electrodes of PEM electrolyzer typically consist of noble metals, e.g., platinum or iridium. The following reactions take place in a PEM electrolysis cell:

Anode: $H_2O \dashrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$ (1)

Please cite this article as: Saebea D., Patcharavorachot Y., Hacker V., Assabumrungrat S., Arpornwichanop A., Authayanun S., 2017, Analysis of unbalanced pressure pem electrolyzer for high pressure hydrogen production, Chemical Engineering Transactions, 57, 1615-1620
DOI: 10.3303/CET1757270

Cathode: $2H^+ + 2e^- \dashrightarrow H_2$ (2)

At the anode, water is oxidized to produce oxygen, electrons and protons. Protons transport across the membrane to the cathode and react with electron to produce hydrogen (Eqs(1) and (2)). PEM electrolyzers are commercially available for low scale production applications. The hydrogen purity is typically above 99.99 vol.% (in some cases up to 99.999 vol.%) without the need of an auxiliary purification equipment (Bhandari et al., 2014). Moreover, low gaseous permeability of the polymeric membranes lowers the risk of flammable mixtures formation. PEM electrolyzers operate at a temperature of around 80 °C and a pressure of up to 15 bar. Typically, PEM electrolyzers have production capacities of 0.06–30 Nm^3H_2/hr. Specific energy demand is typically in the range of 6–8 kWh/Nm^3 H_2 and their efficiencies are in the range of 67–82% (Bhandari et al., 2014).

A solid electrolyte allows for a compact system design with strong/resistant structural properties, which high operational pressures (equal or differential across the electrolyte) are achievable (Medina and Santarelli, 2010). Some commercial models have claimed to reach pressures up to 350 bar (Ayers et al., 2010). System with high pressure operation (Grigoriev et al., 2010) of an electrolyzer (sometimes called electrochemical compression), requires less energy to compress and store hydrogen. High pressure PEM electrolyzers to deliver hydrogen at pressures of 1.4 MPa and 35 MPa were developed by Proton Energy Systems and Mitsubishi, respectively (Barbir, 2005; Witschonke, 2014). In addition, high pressure oxygen production from water electrolysis cell stack has also been developed and it can generate oxygen at pressures over 20 MPa (Roy et al., 2011).

Typically, there are two main technology developments for high pressure electrolysis. The former is to keep the whole electrolyzer stack in a pressure vessel, and the feeding water is pumped to the same pressure of the produced hydrogen (Janssen et al., 2004). The latter is emerging in new applications (Cropley, 2005; Degiorgis et al., 2007), at the present in very small sizes, with an unbalanced pressure across the cell (anode near ambient pressure, whereas the cathode side is maintained at the hydrogen delivery pressure). PEM electrolyzer can produce high purity-hydrogen and deliver it at a relatively high pressure but the high pressure operation at the cathode causes hydrogen crossover from the cathode to anode and thus deteriorates the cell performance. However, the study of unbalance pressure PEM electrolyzer is still limit and the effect of membrane thickness on cell performance at high pressure operation should be considered. In this work, the PEM electrolyzer system to produce high pressure hydrogen with consideration of hydrogen permeation is theoretically investigated. The electrochemical and hydrogen crossover models are coded by Matlab. The effect of cathode pressure and membrane thickness on electrolyzer performance is presented when the explosion limit of a hydrogen-oxygen mixture in the anode is also taken into consideration.

2. PEM electrolyzer model

The electrochemical model of a high pressure PEM electrolyzer is used to investigate its performance and efficiency. The unbalanced pressure between the anode (2 bar) and cathode (10-100 bar) are applied to produce high hydrogen pressure and the effect of a hydrogen permeation is taken into account. In the electrochemical model, the cell voltage can be calculated by adding the open circuit voltage, the maximum voltage, by various losses (i.e., activation, concentration and ohmic losses) as shown in Eq(3).

$$V = E + \eta_{ac} + \eta_d + \eta_{ohm} \tag{3}$$

The open circuit voltage can be calculated by the fraction of proton back-permeation to total proton permeation (k) and Gibb's free energy (G) as shown in Eqs(4)-(8). The hydrogen permeation is shown in Eq(7) (Kim et al., 2013).

$$E = -(1-k)\frac{\Delta G}{2F} \tag{4}$$

$$\Delta G = \Delta G^\circ + RT_m \ln \frac{p_{H,c} p_{O,a}^{1/2}}{p_{W,a}} \tag{5}$$

$$k = \frac{\gamma_a \dot{n}_{H,per}}{\dot{n}_H + \gamma_a \dot{n}_{H,per}} \tag{6}$$

$$\dot{n}_{H,per} = \frac{D_H}{H_H} \frac{p_{H,c} - p_{H,a}}{h_m} \tag{7}$$

$$\dot{n}_H = \frac{i}{2F} - \gamma_a \dot{n}_{H,per} \tag{8}$$

The activation loss and ohmic loss are shown as follows:

$$\eta_{ac} = \frac{RT_a}{\alpha_a F}\text{arcsinh}\frac{i}{2i_{0,a}} + \frac{RT_c}{\alpha_c F}\text{arcsinh}\frac{i}{2i_{0,c}} \tag{9}$$

$$\eta_{ohm} = ir_e + h_{mem}\frac{i}{\sigma_{mem}} \tag{10}$$

$$\sigma_{mem} = (0.005139\gamma_{mem} - 0.00326)\exp\left[1268\left(\frac{1}{303} - \frac{1}{T_m}\right)\right] \tag{11}$$

In addition, the concentration loss can be calculated from Fick's law as shown in Table 1.

Table 1: *Concentration loss model*

Parameters	Equations
Concentration loss	$\eta_d = \frac{RT_a}{4F}\ln\frac{C_{a,O}}{C_{0,O,a}} + \frac{RT_c}{2F}\ln\frac{C_{c,H}}{C_{0,H,c}}$
O_2 concentration at catalyst surface	$C_{0,O,a} = C_{O_2,ch} + \frac{\delta_{e,an}}{D_{eff,an}}\dot{n}_{O_2}$
	$C_{O_2,ch} = \frac{\dot{n}_{O_2}}{\dot{n}_{O_2} + \dot{n}_{H_2O,an}} \cdot \frac{P_{an}}{RT_{an}}$
H_2 concentration at catalyst surface	$C_{0,H,c} = C_{H_2,ch} + \frac{\delta_{e,cat}}{D_{eff,cat}}\dot{n}_{H_2}$
	$C_{H_2,ch} = \frac{\dot{n}_{H_2}}{\dot{n}_{H_2} + \dot{n}_{H_2O,cat}} \cdot \frac{P_{cat}}{RT_{cat}}$

It is noted that details of the model describing the voltage losses used in this study can be found in Marangio et al. (2009). The simulation model of high pressure PEM electrolyzer is solved by Matlab.

3. Results and discussion

The performance of high temperature PEM electrolyzer is studied under the cathode pressure varying from 10 to 100 bar. The effect of cathode pressure on the voltage and current density relationship is shown in Figure 1.

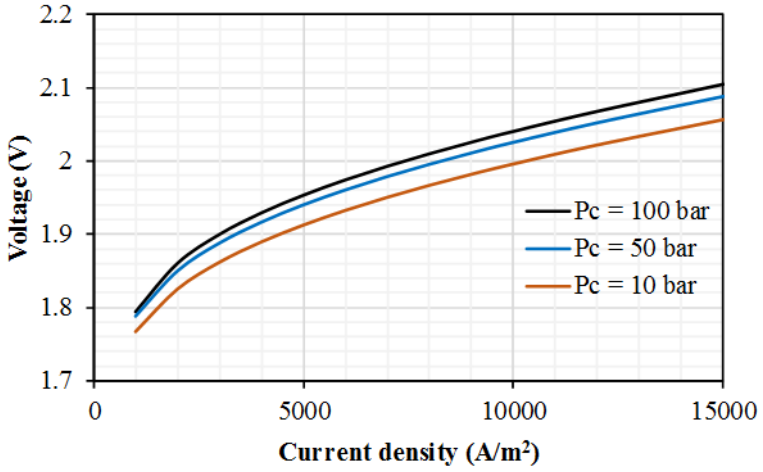

Figure 1: Voltage and current density relationship of high pressure PEM electrolyzer at different cathode pressures

It is observed that the voltage slightly increases with increasing cathode pressure. This results in a higher power demand when hydrogen is produced at high pressure. In addition, the hydrogen concentration at the anode and hydrogen permeated flux caused by the hydrogen crossover phenomena is shown in Figure 2. It is found that an increase in cathode pressure results in the increase of both the hydrogen concentration and hydrogen concentration flux at the anode. This is because a high pressure difference between the cathode and anode promotes the hydrogen permeation from the high pressure to low pressure side (the anode pressure is specified at 2 bar). The hydrogen permeated flux increases with the increasing current density because the high amount of hydrogen is produced at high current densities and this results in high concentration gradient between the cathode and the anode. Although high hydrogen is permeated to the anode at high current density, more oxygen is also produced at high current density. Therefore, high hydrogen concentration at the anode is observed at low current density up to 6000 A/m^2 and the operation at high current density has slightly effect on hydrogen permeation as shown in Figure 2. However, the hydrogen fraction in the anode mixture stream consisting of oxygen and hydrogen is below the explosion limit at all of the studied operational cathode pressures.

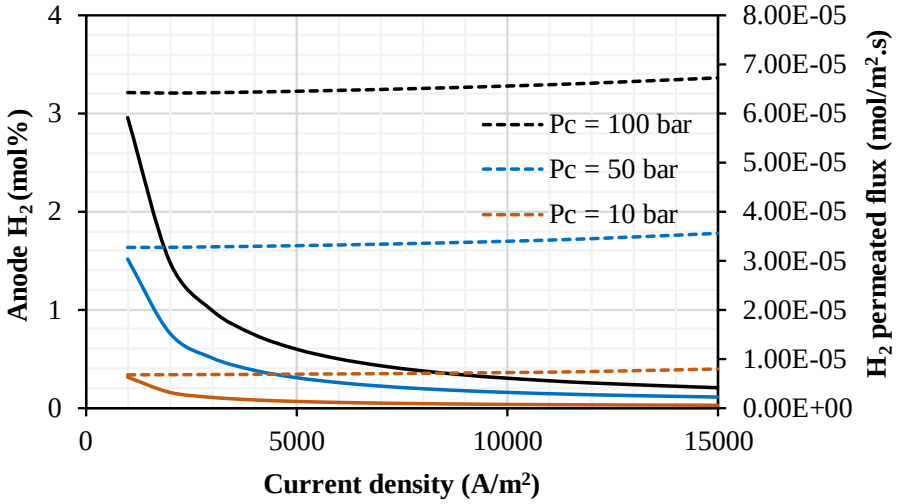

Figure 2: Effect of current density and pressure on anode hydrogen concentration (solid line) and hydrogen permeated flux (dash line) in the high pressure PEM electrolyzer.

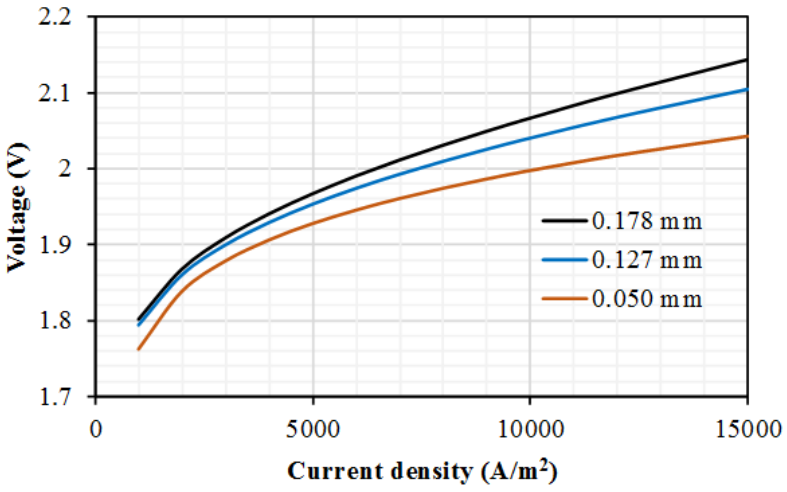

Figure 3: Voltage and current density relationship of the high pressure PEM electrolyzer at different membrane thickness.

Furthermore, the effect of membrane thickness of 50, 127 and 178 μm for Nafion 112, Nafion 115 and Nafion 117, respectively, on the performance of high pressure PEM electrolyzer is investigated and the simulation results are shown in Figure 3. From the results, it is found that thinner membranes provide higher performance at high pressure operation. The use of thick membrane result in the increase of ohmic loss and thus the high

voltage operation is observed. However, the membrane thickness also affects the hydrogen permeation from the cathode to anode. The effect of membrane thickness on hydrogen fraction on anode stream and hydrogen permeated flux at high cathode pressure (100 bar) is shown in Figure 4. The opposite trend is observed when the results are compared with effect of membrane thickness on electrolyzer performance in Figure 3. It is found that the use of thick membrane has the positive effect on the reduction of hydrogen crossover. Hydrogen easily permeates from the cathode to anode when thin membrane is applied. In addition, the hydrogen fraction in the anode stream is over the explosion limit at membrane thickness of 50 μm with low-current density operation but the hydrogen is below the explosion limit (5.7% at 100 bar) at all studied current density when the membrane thickness of 127 and 178 μm is used.

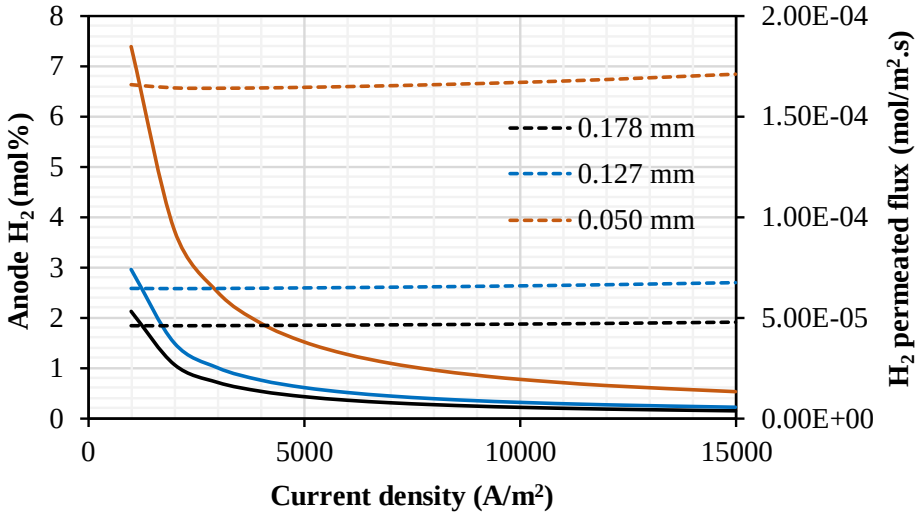

Figure 4: Effect of current density and membrane thickness on anode hydrogen concentration (solid line) and hydrogen permeated flux (dash line) in the high pressure PEM electrolyzer.

4. Conclusions

The simulation of a high pressure PEM electrolyzer without the need for external compression based on electrochemical model is studied for clean hydrogen production. High pressure operation of the PEM electrolyzer brings the advantage of delivering hydrogen at a high pressure with the acceptable hydrogen permeation. The concentration of hydrogen at the anode increases with increasing pressure at the cathode and reducing membrane thickness and current density. Compared to thinner membrane, the use of thick membrane provides lower performance. However, the high hydrogen permeation is promoted with the use of thin membrane and high cathode pressure operation.

Acknowledgments

Support from Srinakharinwirot University, Thailand research fund (DPG5880003) and the Ernst Mach-Grants-ASEA-UNINET is gratefully acknowledged.

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