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Numerical Modeling the Effect of Operating Variables on Faraday Efficiency in PEM Electrolyzer

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Abstract

In PEM water electrolysis, extensive mixing of the product gases due to gas crossover could produce explosive conditions and also at low current densities this leads to efficiency losses due to reduced Faraday efficiency. In this study, the effect of different temperatures, pressures and membrane thicknesses on the performance of a PEM electrolyzer have been carried out. The effect of membrane thickness on voltage was not apparent at lower current density but it increases from current density of 0.2A/cm². It was also observed that temperature has no effect on the Faraday efficiency. On the other hand, Faraday efficiency increases as the current density increase. Also Faraday efficiency decreases with decrease in membrane thickness At 0.2 A/cm² current density and membrane thickness of 150 μm.

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Keywords: PEM electrolyzer; hydrogen production; polarization curve; Faraday efficiency

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1. Introduction

The global dependence on fossil fuel, such as coal and natural gas for the world energy demand, has generated a lot of concern among researchers and primary energy consumers such as energy industry. In order to solve this problem, more research attention is being turn towards renewable and sustainable clean energy production. Different technologies are available in the market today for the production of clean energy; one of such widely used technology is electrolysis of water.

Renewable hydrogen is an excellent energy carrier that can be produced through wide variety of technologies namely, coal gasification, hydrocarbon reformation and electrolysis of water [1-4]. Currently, electrolysis represents only about 4% of world hydrogen production, this is attributed to its high cost [5].

Traditionally, alkaline based electrolysis has been commercially available for more than a century [6], but due to its poor hydrogen production rate, higher and lower efficiency, it has been replaced by polymer electrolyte membrane PEM electrolyzer[7]. PEM electrolyzer is a more promising technology due to its operation at high current density, and generates high and differential pressure, gas purity. Even though PEM electrolyzer is expected to be an advanced technique to produce hydrogen at high pressure, only a few researchers have reported the effect of pressure on gas purities and efficiency of PEM electrolyzer [7, 8]. Recently, Schalenbach et al. [8] developed a model and simulated gases cross-over for a pressurized PEME. The model based on Fick's Law correlated diffusion to the respective flux densities of oxygen and hydrogen across the membrane of thickness. Tijani et. al [9] did study the effect of exchanges in current density on Faraday efficiency of a PEM electrolyzer. In this study we estimate the effects of different temperature and membrane thickness on Faraday efficiency in PEM electrolyzer at different pressure.

Nomenclature

ΔH	Enthalpy change
ΔG	Gibbs free energy
T	Temperature
ΔS	Entropy change
n	Stoichiometric coefficient of electron
F	Faraday constant,
E	Voltage
i	Current density
η	Efficiency
V	Overvoltage
α	Transfer coefficient
d	Membrane thickness
ϕ	Gas crossover flux density
p	Partial pressure
S	Solubility
ξ	Drag coefficient
Δc	Concentration difference
Δp	Partial pressure difference
ε	Permeability constant
A	Partial pressure enhancement factor

SUBSCRIPTS

rev	Reversible voltage
tn	Thermaneutral voltage
$A0$	Anode exchange current density
$C0$	Cathode exchange current density
a	Activation anode
c	Activation cathode

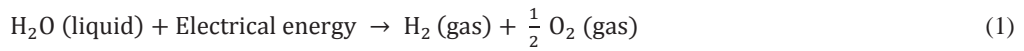
s	Interfacial resistance
m	Membrane
O_2	Oxygen
H_2	Hydrogen

SUPERSCRIPTS

cat	Cathode
an	Anode
en	Total

2. Operation principle of PEM electrolyzer

PEM electrolyzer uses the electrolysis principle to dissociate water molecule into hydrogen and oxygen by applying a high current through two electrodes separated by an electrolyte. Water is supplied into the anode side, there the water flow through the bipolar plate [10-12]. Figure 1 shows the schematic of the components in the PEM electrolyzer and the flow of water, oxygen, hydrogen ion, electron and hydrogen in the reaction. The electrochemical reactions can be expressed as:



The reaction at the two electrodes, anode and cathode can be expressed as following:

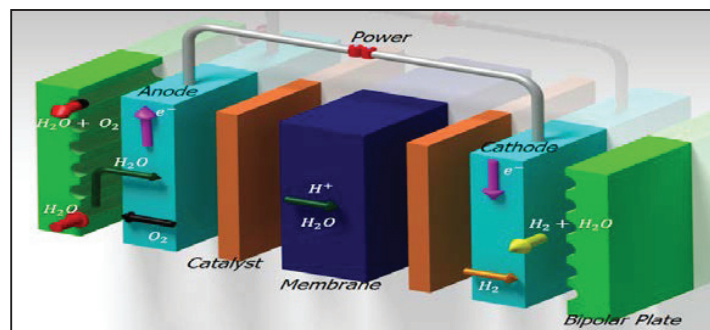


Fig. 1. Schematic diagram of PEM electrolyzer [9]

2.1. Thermodynamic models of PEM electrolyzer

Thermodynamically, for the electrochemical decomposition of water, the heat energy and the voltage corresponding to Gibb's free energy, denoted as reversible voltage [9]:

$$V_{rev} = \frac{\Delta G}{nF} \quad (4)$$

The value of F is 96485.3 C/mol. Therefore the standard condition for the reversible voltage is equals to 1.23V. It is necessary to calculate the theoretical energy demand for electrolytic hydrogen production. The total energy demand for PEM electrolyzer can be calculated as [9]:

$$\Delta H = \Delta G + T\Delta S \quad (5)$$

where ΔG is the electrical energy demand (change in Gibb's free energy) and $T\Delta S$ is the thermal energy demand (J/mol H_2). The total energy demand is the theoretical energy required for H_2O electrolysis without any losses [10-12]. The voltage correlated to the enthalpy (assuming that no energy is provided in the form of heat) is referred to the thermoneutral voltage [9]. The equation of the thermoneutral voltages expressed by

$$V_{tn} = \frac{\Delta H}{nF} \quad (6)$$

At the standard conditions, the value of the thermoneutral voltages is 1.48V. As widely known the real cell voltage in an electrolytic cell is higher than the ideal open-circuit voltage and can be expressed as [9].

$$V_o = V_{rev} + \eta_{act} + \eta_{ohmic} + \eta_{diff} \quad (7)$$

2.2. Activation overvoltage

For each of the electrodes the current density at the electrolyte interface can be calculated by Butler-Volmer equation [10-12]

$$i = i_o \left[\exp\left(\frac{\alpha_1 F}{RT} \eta_{act}\right) - \exp\left(-\frac{\alpha_2 F}{RT} \eta_{act}\right) \right] \quad (8)$$

Assuming $\alpha_1 = \alpha_2$, equation (8) can be easily inverted, yielding

$$\eta_{act} = \frac{RT}{\alpha F} \operatorname{arcsinh}\left(\frac{i}{2i_o}\right) \quad (9)$$

This equation can applied for both anode and cathode where $\alpha_{an} = 0.5$ and $\alpha_{cat} = 0.5$

2.3. Diffusion Overvoltage

Resistance is present when flowing through the electrode, and this resistance increases with increasing flow. Some energy is lost during operation and this is the cause of diffusion overvoltage. The diffusion overvoltage can be estimated with the Nernst equation where the '0' condition is a working condition taken as reference [9]:

$$\eta_{diff} = V_1 - V_0 = \left(E^0 + \frac{RT}{zF} \ln C_1\right) - \left(E^0 + \frac{RT}{zF} \ln C_0\right) = \frac{RT}{zF} \ln \frac{C_1}{C_0} \quad (10)$$

This equation can be applied both for the anode and the cathode, yielding where $C_{O_2,me}$ and $C_{H_2,me}$ indicate, respectively, the oxygen and hydrogen concentration at the membrane-electrode interface [9]

$$\eta_{diff,an} = \frac{RT_{an}}{4F} \ln \frac{C_{O_2,me}}{C_{O_2,me,0}} \quad (11)$$

$$\eta_{diff,cat} = \frac{RT_{cat}}{2F} \ln \frac{C_{H_2,me}}{C_{H_2,me,0}} \quad (12)$$

2.4. Ohmic overvoltage

The Ohmic overvoltage across each cell can be expressed as [13]:

$$\eta_{\text{ohm}} = R_{\text{cell}}I \quad (13)$$

where R_{cell} is the Ohmic resistance of each cell inside the stack and I is the stack current [3]. The voltage drop due to the membrane can be separated from that due to electrodes and plates as follows [3]

$$\eta_{\text{ohm}} = R_{\text{cell}}I = (R_{\text{eq,an}} + R_{\text{mem}} + R_{\text{(eq,cat)}})I = R_{\text{mem}}I + (R_{\text{eq,an}} + R_{\text{eq,cat}})I = \eta_{\text{ohm,m}} + \eta_{\text{ohm,e}} \quad (14)$$

2.5. Molar flowrate

The molar flow of water consumed in anode and the mass balance of oxygen and hydrogen produced in anode and cathode respectively can be written as [13]:

$$\dot{n}_{\text{H}_2} = \frac{n_c I}{2F} \eta_F \quad (15)$$

$$\dot{n}_{\text{O}_2} = \frac{n_c I}{4F} \eta_F \quad (16)$$

$$\dot{n}_{\text{H}_2\text{O}} = 1.25 \frac{n_c I}{2F} \eta_F \quad (17)$$

Where n_c is the number of cell stack, F is the Faraday's constant, I is the current across the cell electrodes and η_F is Faraday's efficiency. Faraday's efficiency is defined as the relation between real hydrogen flow-rate and its theoretical value. Generally, the Faraday's efficiency for PEM electrolyzer is assumed to be 99% or more. The number of cell stack (n_c) in this case is 1 since this research only deal with single stack PEM electrolyzer. Hence, the equation (15-17) can be simplified to:

$$\dot{n}_{\text{H}_2} = \frac{I}{2F} \quad (18)$$

$$\dot{n}_{\text{O}_2} = \frac{I}{4F} \quad (19)$$

$$\dot{n}_{\text{H}_2\text{O}} = \frac{I}{2F} \quad (20)$$

2.6. Faraday Efficiency

Faraday Efficiency can be calculated by using the following equation [8]:

$$\eta_F = \frac{Q_{\text{id}}}{Q_{\text{re}}} \quad (21)$$

Where Q_{id} is the ideal charge for the production of a given amount of hydrogen and Q_{re} represents the required charge. The Faraday efficiency can also be expressed as function of the flux densities across the membrane and production rates of the gases [8]:

$$\eta_F = 1 - \frac{\phi_{\text{H}_2}^{\text{en}}}{i} - 2 \frac{\phi_{\text{O}_2}^{\text{en}}}{i} \quad (22)$$

The total of hydrogen and oxygen diffusion can be calculated from

$$\phi_{H_2}^{en} = \epsilon \frac{d_{H_2}^{cat}}{d} + \epsilon \frac{dp_{H_2}^{cat} - p_{O_2}^{an}}{d} - \frac{i}{F} \xi \frac{p_{H_2}^{cat} S_{H_2}}{c(H_2O)} \tag{23}$$

$$\phi_{O_2}^{en} = \epsilon \frac{d_{O_2}^{an}}{d} + \frac{i}{F} \xi \frac{p_{O_2}^{an} S_{O_2}}{c(H_2O)} \tag{24}$$

2.7. Voltage Efficiency

$$\eta_v = \frac{E_{rev}}{E} \tag{25}$$

3. Results and discussion

In this study a sensitivity analysis is conducted by means of polarization curve in order to evaluate the performance of the parameters of the PEM electrolyzer and operating conditions. Figure 2(a) shows the polarization curve of different membrane thicknesses at balanced pressure and Figure 2(b) shows the polarization curves at different membrane thicknesses and unbalanced pressure. Simulation studies were carried out at different pressures and membrane thicknesses. Both Figures show that apparently pressure has no effect on polarization curve. On the other hand for a fix membrane thickness, Figure 2 (a & b) shows that as the current density increased, the cell voltage is increased. The reason is that, at higher current density more water molecules dissociate into hydrogen ion and oxygen and this process occurs only at higher voltage. The effect of membrane thickness on voltage is not apparent for lower current density but increases from current density of 0.2A/cm2. This is because the membrane thickness of the membrane electrode assembly (MEA) has an effect on the ohmic resistance. The thicker membrane has the highest ohmic resistance which eventually leads to higher voltage requirement to overcome the ohmic resistance and the thinner membrane has the smallest voltage. It can also be concluded that the proton resistance of the proton-conducting membrane contributes the most of the total ohmic resistance. This phenomenon was also reported in the literature [14].

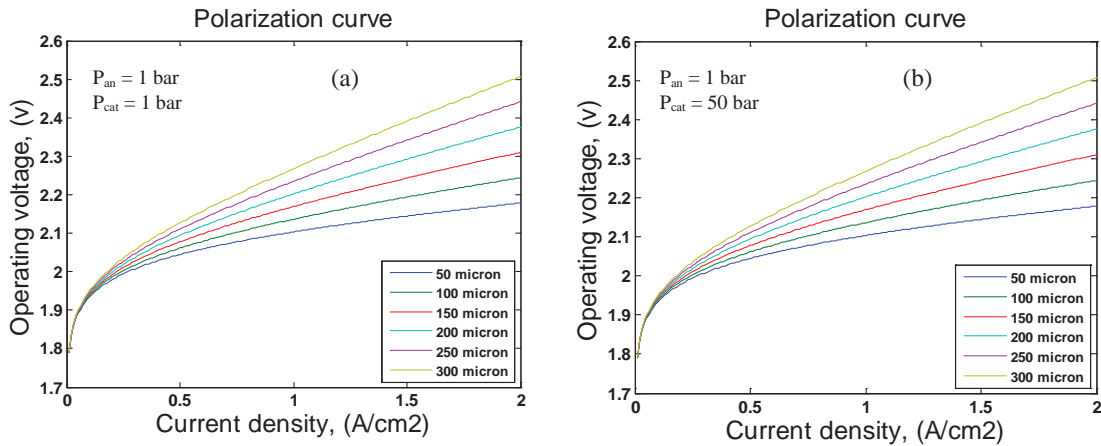


Figure 2: Effects of different pressure and membrane thickness on the operating voltage of PEM electrolyzer a) Balance pressure 1 bar. b) Anode pressure 1 bar and cathode pressure 50 bar.

Figure 3 (a & b) shows the simulation result for the Faraday efficiency of the electrolyzer at unbalanced anode and cathode pressure and at different temperatures. It was observed that temperature has no effect on the Faraday efficiency. On the other hand both Figures show that the Faraday efficiency increases as the current density increase. As shown in Figure 3a, the Faraday efficiency increases sharply up to 0.4 A/cm² before starting to increase slowly. At 0.8 A/cm², for membrane thickness of 150 μm, the simulation result based on Figure 3a shows a Faraday efficiency of 0.943. Again it can be infer from Figure 3 (a & b) that membrane thickness has a significant impact on Faraday efficiency.

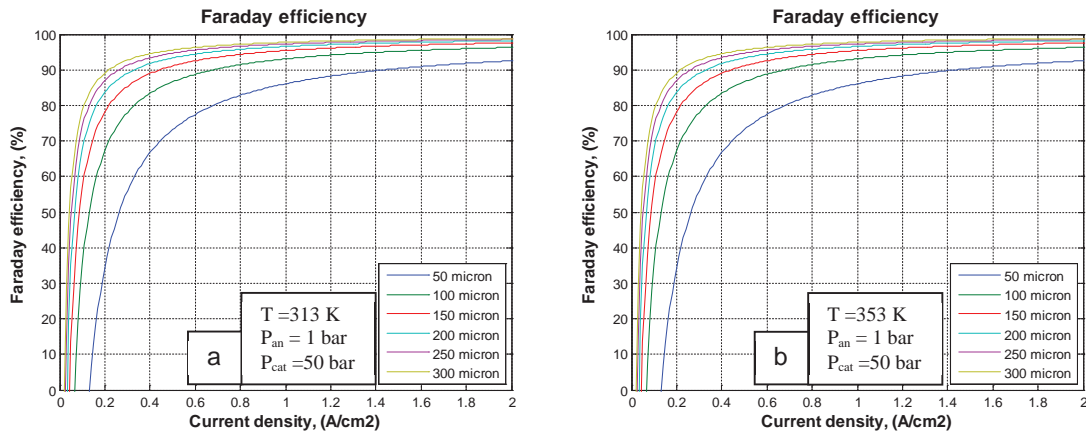


Figure 3: Effects of different temperature and membrane thickness on Faraday efficiency in PEM electrolyzer at different pressure

Figure 4 (a & b) shows the simulation result for the Faraday efficiency of the electrolyzer at balanced anode and cathode pressure and at different temperatures. It was observed that temperature has no effect on the Faraday efficiency. On the other hand both Figures show that the Faraday efficiency increases as the current density increase. Also Faraday efficiency decreases with decrease in membrane thickness, this is because at high unbalanced pressure some of the hydrogen, that is produced at the cathode is forced back to the anode a phenomenon known as gas cross over, this eventually reduces Faraday efficiency. At 0.2 A/cm² current density and membrane thickness of 150 μm, the simulation result based on Figure 3a shows a Faraday efficiency of 0.996.

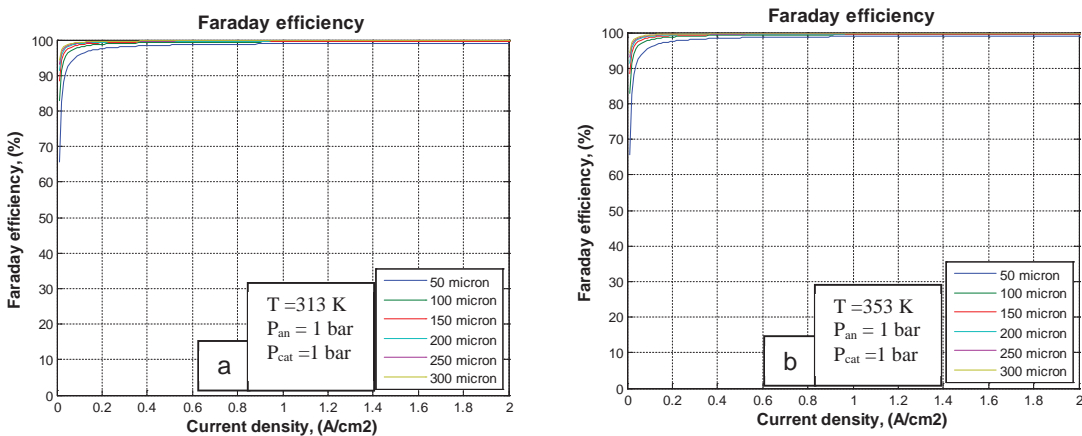


Figure 4: Effects of different temperature and membrane thickness on Faraday efficiency in PEM electrolyzer at balance pressure

It can be observe from Figure 5 (a & b) that at higher and balance pressure the Faraday efficiency decreases more rapidly with decrease in membrane thickness. This is due to the fact that at lower membrane thickness the flux densities of hydrogen across the membrane and production rates of the gases of hydrogen is reduced and this reduces the overall Faraday efficiency.

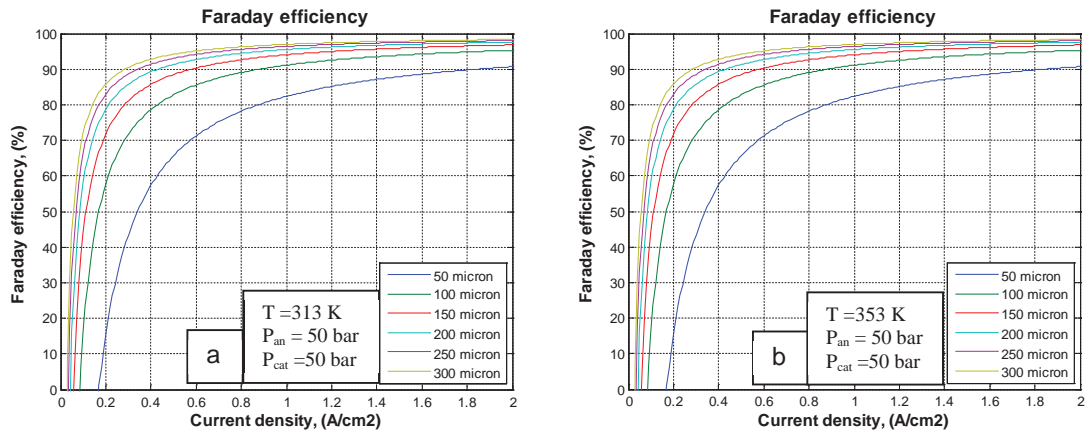


Figure 5: Effects of different temperature and membrane thickness on Faraday efficiency in PEM electrolyzer at different pressure

4. Conclusion

The results from this study suggest that the PEM electrolyzer with balance pressure of 1 bar setting has the best efficiency compared to the other pressure settings. However, the scope of the cell efficiency in this study does not include the energy required to power a compressor, which is required for PEM electrolyzer with cathode chamber operates at atmospheric pressure. The real efficiency of the PEM electrolyzer with the balance 1 bar should be lower than the value shown in this simulation after considering the energy consumed by the compressor. The PEM electrolyzer with cathode chamber operates at high pressure however, should not include the energy required to power a compressor. In order to properly compare which of the pressure settings have the best efficiency, it is recommended that the next study should include the energy required for a compressor in the calculation of efficiency.

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