A Study of The Loss Characteristic of a High Pressure Electrolyzer System for Hydrogen Production

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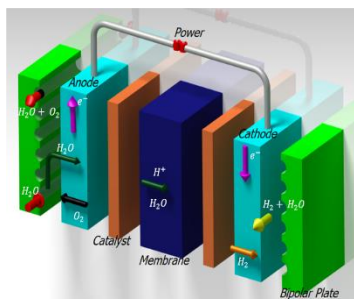
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Graphical abstract

Abstract

The aim of this paper is to analyse loss characteristic of a high-pressure electrolyzer system for hydrogen production. Fundamental thermodynamics and electrochemical relations related to polymer electrolyte membrane (PEM) electrolyzer have been modelled in MATLAB. Simple proton exchange membrane water electrolysis is analysed on the basis of well-known Butler-Volmer kinetic for the electrodes and transport resistance in the polymer-electrolyte. The overpotential at the anode, cathode and overpotential due to ohmic resistance were analysed individually. A sensitivity analysis was carried out to study the effect of exchange current density on Faraday efficiency. At current density of 0.2A/cm^2, a higher efficiency of 87.8 % was observed.

Keywords: High pressure electrolyzer, hydrogen production, overvoltage, faraday efficiency

1.0 INTRODUCTION

Due to increasing global energy demand, the non-renewable energy such as coal, natural gases are depleting at an alarming rate. Thus most sectors are looking for a more reliable energy and sustainable energy sources. In order to improve the quality of human life, further study has to be carried out regarding renewable energy sources [1]. One of such state of the art renewable energy source is hydrogen production through electrolysis. Electrolysis processes accounts for only about 4% of global hydrogen production [2]. In recent studies, there have been extensive studies in literature to investigate the fundamental theoretical concept related to operating costs, increasing energy efficiency and the performance of a proton exchange membrane electrolyzer [3-4]. Other literatures also focus on increasing the electrochemical activity of electrodes and also reduce the total resistance of the electrolytic cell [4]. In previous work Maximilian et al.

[5] did estimate efficiency losses due to the reduced Faraday efficiency caused by crossover, ohmic loss of the membrane and pressurised hydrogen and oxygen evolution of PEM Electrolyzer. In the recent literature published by Dedigama et al. [6], they observed that electrical efficiency of electrolyzer decreases with increasing current density, they also concluded that efficiency of electrolyzer decreases with increasing operating inlet water flowrate and this was confirmed by Zhang et al. [7].

The purpose of this research is to study the loss characteristic of a high-pressure electrolyzer system for hydrogen production. Basic thermodynamic and electrochemical relations related to polymer electrolyte membrane (PEM) electrolyzer have been modelled in MATLAB. Simple proton exchange membrane water electrolysis is analysed on the basis of well-known Butler-Volmer kinetic for the electrodes and transport resistance in the polymer-electrolyte.

2.0 PRINCIPLE OF OPERATION OF (PEM) ELECTROLYZER

A minimum potential of 1.23V (equilibrium voltage or reversible voltage) is applied across the electrochemical cell to induce electrochemical reactions at both electrodes. Water is introduced at the anode (see Fig. 1) and dissociated into oxygen, protons and electrons via the following reaction:

$$Anode : H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \tag{1}$$
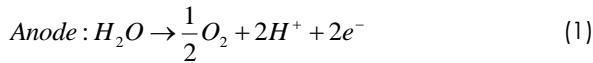
The hydrogen ions are driven through the membrane to the cathode under an electric field where they combine with the electrons arriving from the external circuit to form hydrogen gas:

$$Cathode : 2H^+ + 2e^- \rightarrow H_2 \tag{2}$$
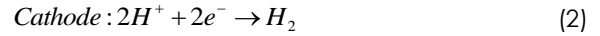
The net reaction for entire cell is

$$H_2O_{(liq.)} \rightarrow H_{2(g)} + \frac{1}{2}O_{2(g)}, \Delta H^{\circ}_{25} = 285.84kJ \tag{3}$$
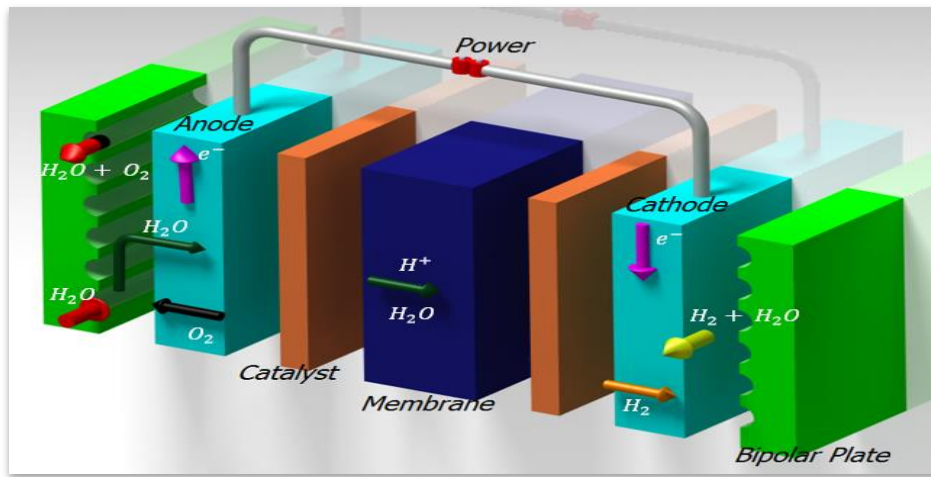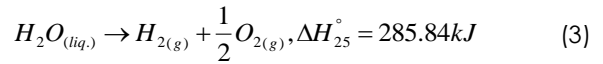

Figure 1 Schematic description of PEM electrolyzer cell

3.0 THERMODYNAMIC MODELS

Thermodynamically, for the electrochemical decomposition of water, the heat energy and the voltage corresponding to Gibb's free energy can be expressed in terms of reversible voltage [10].

$$V_{rev} = \frac{\Delta G}{nF} \tag{4}$$

The total energy demand for PEM electrolysis can be calculated as:

$$\Delta H = \Delta G + T\Delta S \tag{5}$$

Where ΔG is the electrical energy demand (change in Gibb's free energy) and $T\Delta S$ is the thermal energy demand (J/mol H2). At standard conditions, the value of the thermoneutral voltages is 1.48V.

$$V_{tn} = \frac{\Delta G + T\Delta S}{nF} \tag{6}$$

As widely known the real cell voltage in an electrolytic cell is higher than the ideal open-circuit voltage and can be expressed as:

$$V_o = V_{rev} + n_{act} + n_{ohmic} + n_{diff} \tag{7}$$

Where V_{rev} is reversible voltage, η_{act} is activation overpotental at both anode and cathode, η_{ohm} is ohmic overvoltage and η_{diff} is diffusion overvoltage.

4.0 POWER DENSITY

The required power density can be determined by Eq. (10) [1].

$$P = V_o i + \left[\frac{RT}{\alpha F} \arcsin h \left(\frac{i_a}{2i_a o} \right) \right] i \tag{8}$$

$$+ \left[\frac{RT}{\alpha F} \arcsin h \left(\frac{i_C}{2i_C o} \right) \right] i^2 + \left[\frac{L_M}{\sigma_M} \right] i + R_i i^2$$

5.0 HYDROGEN PRODUCTION

The rate of hydrogen production is derived in a way similar to hydrogen usage in the PEM fuel as follows [1].

$$H_{2,production} = \frac{i}{2F}$$

Table 1 shows the constant used to calculate the loss characteristics and the variable parameters used are shown in Table 2 and 3.

Table 1: Constant parameter

	Parameter	Value	References
α_a, α_c	Anode & Cathode charge transfer coefficient	0.5	[10]
η_a, η_c	Stoichiometric coefficient	4,2	[8]
A	Electrode surface area (cm²)	80	
R_{ele}	Electric resistance (Ω)	0.000035	[9]
t_{mem} / φ	Membrane thickness (μm)	178	[9]
λ	Water humidification factor	25	[11]

Table 2: Variable Input Parameter

| Parameter	Range Selection		
Current density, (A/cm²)	0.1 : 0.1 : 2.0		
Exchange Current Density at Anode, (A/cm²)	1×10^{-9}	1×10^{-10}	1×10^{-12}
Exchange Current Density at Cathode, (A/cm²)	1×10^{-3}	1×10^{-4}	1×10^{-4}

Table 3: Model Parameter

Parameters	Values A/cm²	Type of electrodes
$i_{o\,an}$, Pt	10^{-12}–10^{-9}	Platinum electrode catalyst
$i_{o\,an}$, Pt-Ir	10^{-7}	Platinum Iridium electrode catalyst
$i_{o\,an}$, Pt	10^{-4}–10^{-3}	Platinum electrode catalyst

5.0 RESULTS AND DISCUSSION

Figure 2a and 2b shows the effect of the exchange current density on the polarization of the operating voltage. As shown in Fig. 2a, the exchange current density at the cathode was kept constant whiles that of the anode was varied and the opposite concept was conducted for Figure 2b. It can be observed from both Figs. 2a and 2b that as the exchange current density increase, the cell voltage decreases but the cathode reaction is faster compared with anode reaction, and that is why the voltage requirement for the electrode activity and kinetic reaction at anode is much higher compared with the cathode.
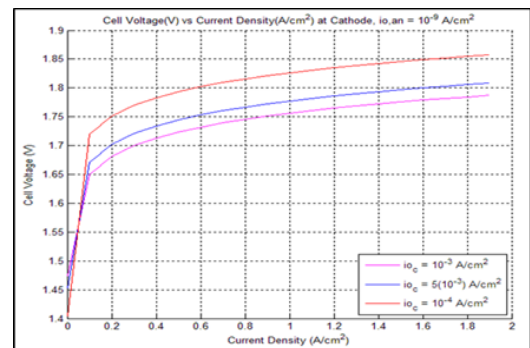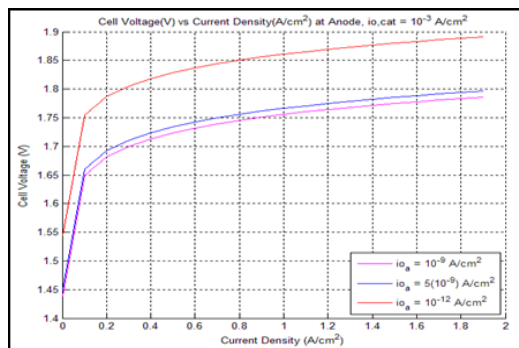
Figure 2 Effect of (a) anode and (b) cathode exchange current density on polarisation

Figure 3a shows that, the anode with Pt electrode attains the highest overpotential of about 2.6 V and it increases as the current density increase. The anode overpotential was however reduced to 2.0 V when Pt-IrO electrode was used. The cathode overpotential was observed to be smaller than that of the anode because of the fast kinetic reaction at the surface of the electrode.
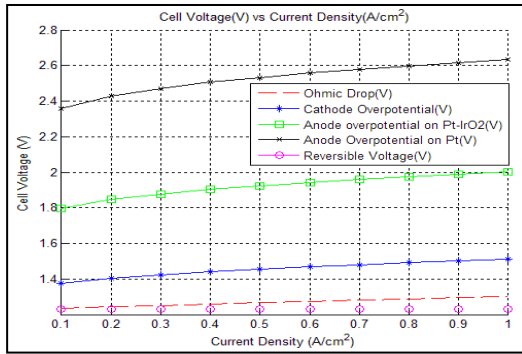
Figure 3b shows the power density versus current density. As we can see, the power supply is directly proportional to the current density. The lowest power supply is 1.2W/cm^2 and the highest is 2.6 W/cm^2 for 1 A/cm^2 at 80°C. It was observed that there is always a minimum power input for water electrolysis because that power comes from the Gibbs free energy change reaction.
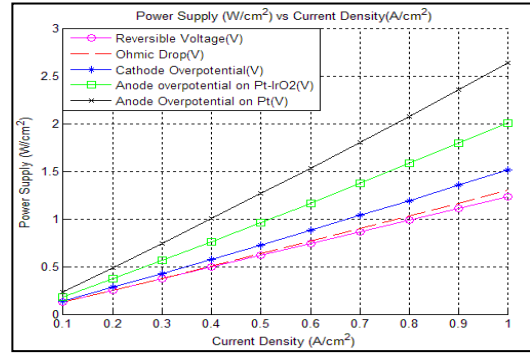

Figure 3 (a) Overpotentials (loss characteristics) and (b) power consumption of a single cell

A sensitivity analysis was carried out to study the effect of exchange current density on the power requirement of the electrolyzer. It was observed that as the exchange current density for anode and cathode electrodes increase, the Faraday efficiency also increased. Three different sets of efficiency were

analysed as shown in Figure 4a. All the three efficiencies were observed to decrease linearly with current density. At current density of 0.2A/cm^2, a higher efficiency of 87.8 % was observed whiles the lowest efficiency is 79.0 %.
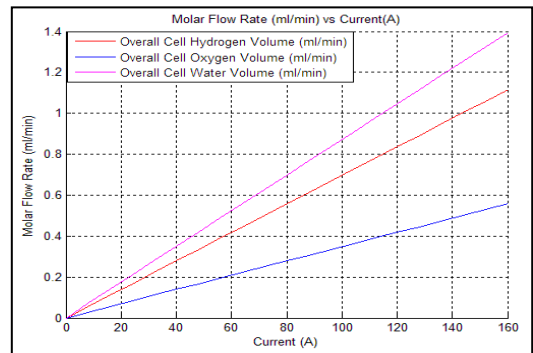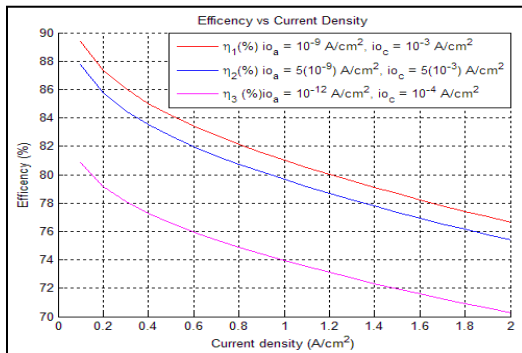

Figure 4 (a) on System efficiency vs. current density (b) Hydrogen volume flowrate

The current supply to the cell is proportional to the hydrogen production. Figure 4b shows the relations between current and hydrogen flow rate. It can be observed that as current increases, the hydrogen flowrate also increases. The simulation result shows a maximum of the hydrogen flowrate at 1.4ml/min at 160A. The individual resistance of the electrolyzer unit calculated based on parameters given in Table 2 is shown in Figure 5. At low current densities of about 0.1A/cm^2, the resistance at the anode was observed to be higher, all other resistance such as the membrane resistance were moderately low compare with the resistance at the anode.

6.0 SUMMARY

In this paper, the mathematical model for solid-polymer electrolyte membrane has been presented based on a combination of fundamental thermodynamic and electrochemical relationship. Different operating conditions such as exchange current density, and current density have been analysed for optimised hydrogen production. It can be concluded from this paper that, the high anode overpotential imposes a limitation on the electro-kinetics dissociation of water and that is the cause of voltage requirement for the electrolysis process.
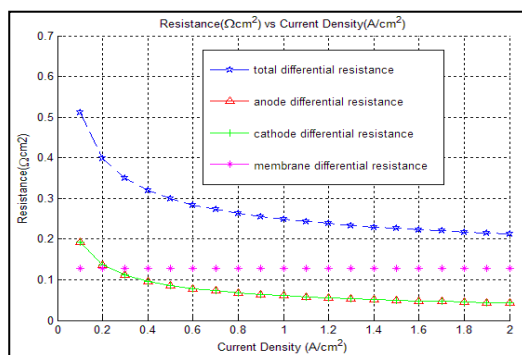
Figure 5: Effect of individual resistance on the performance of the electrolyzer.

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