EFFECT OF TEMPERATURE ON PERFORMANCE OF ADVANCED ALKALINE ELECTROLYZER

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ABSTRACT: *Water electrolysis is one of the most widely used techniques for hydrogen production whereas alkaline electrolyzer is the most commercially available technology in industry. Conventionally, the industrial electrolyzers normally produce around 70 % efficiency. This low efficiency is due to high power dissipation in electrolysis process. In an ideal water electrolysis, the cell voltage is equal to the minimum reversible voltage which is 1.23 V for chemical reaction to take place in electrolysis process. However, this cell voltage is much higher in industrial electrolysis cells. This excess voltage is caused by the over voltage potential which increases the electrical impedance of an electrolysis cell causing a fraction of the applied energy to be wasted as heat while allowing the electric current passes through it. This paper aims to study the effect of temperature towards the I-U curve, over-voltage potentials, hydrogen flow rate and energy efficiency of an advanced alkaline electrolyzer. The simulation model is carried out at five different temperature levels varying between $20\,^0C$ and $100\,^0C$. All related equations to the electrochemical reaction are modelled and simulated in MATLAB/Simulink. The results have shown that the temperature does not have an effect on the hydrogen flow rate but instead have a significant effect on the I-U curve, over voltage potentials and energy efficiency.*

Keywords: Advanced alkaline Electrolyzer, Mathematical modelling, Activation voltage, Ohmic voltage, Energy efficiency

1. INTRODUCTION

Hydrogen is the most abundant chemical element in the world and it can be found in water molecule, petroleum, natural gas, coal and bio-mass. Nevertheless, hydrogen does not exist by itself where it needs to be extracted from those fuel stock through chemical process. The major advantage of this hydrogen is its property of high mass energy density for an energy carrier used for the storage of intermittent renewable energy (RE) sources such as solar and wind energy [1-3]. There are many ways to produce hydrogen and one of the most recent method is by water electrolysis process. This method is capable of producing hydrogen ranging from few cm^3/min to thousand m^3/h [2]. In general, water electrolysis uses

4.3 kWh/Nm^3H_2 of power to produce hydrogen [4, 5]. The hydrogen gas produced from this method is very pure (H_2 purity of 99.998 %) since the gases are physically separated at the electrodes. However, the production cost is very high since it is depends on electricity [2].

The alkaline electrolysis, PEM (Proton Exchange Membrane) electrolysis and Solid Oxide Electrolysis (SOE) are the main technologies for the electrolysis device. They are commercially available and have been used widely in industry [6]. There are many attempts made to study the effects of temperature on the alkaline electrolysis [1, 7-11]. It has been found that with the increasing of temperature, the required cell voltage for the electrolysis is reduced hence improved the efficiency of the electrolyzer.

The objective of this paper is to study the thermal behavior of an advanced alkaline electrolyzer from mathematical modeling and simulation points of view. The models are based on the fundamental thermodynamics and electrochemical relations for investigating the effect of temperature towards I-U curve, over-voltage potential hydrogen flow rate and the energy efficiency.

2. ALKALINE ELECTROLYSIS CONCEPT

DC current is applied between two electrodes (Anode and Cathode) in order to split the water molecule into hydrogen and oxygen as shown in Figure 1. These two electrodes are separated by an aqueous electrolyte with good ionic conductivity [1]. In alkaline electrolyzer, the electrolyte is usually aqueous potassium hydroxide (KOH). This chemical compound will increase the conductivity level of the electrolyte since pure water has a less conductivity.
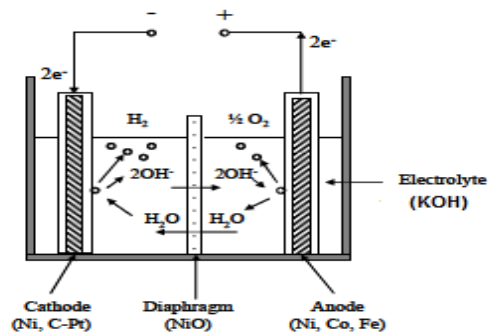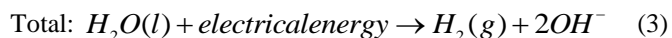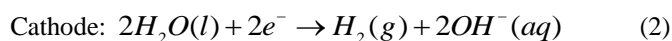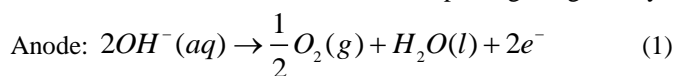

Figure 1: Internal structure of an alkaline electrolyzer [3]

Hydrogen is formed at the cathode (- terminal) while at the anode (+ terminal) oxygen is formed. The reaction at anode, cathode and the total reaction for water splitting are given by

Anode: $2OH^-(aq) \rightarrow \frac{1}{2}O_2(g) + H_2O(l) + 2e^-$ (1)

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ (2)

Total: $H_2O(l) + electrical energy \rightarrow H_2(g) + 2OH^-$ (3)

The diaphragm is used to prevent the recombination of hydrogen and oxygen and should have low electric resistance. A minimum electric voltage is required at the two electrodes in order to break down the bond between the hydrogen and

oxygen in (3). This minimum voltage is known as reversible voltage U_{rev}.

3. MODEL DESCRIPTION AND METHODOLOGY

3.1 Thermodynamic model

The electrical and thermal energy in water electrolysis are firstly converted into chemical energy. Then, this chemical energy will be stored in hydrogen. The relationship between the Gibbs free energy, enthalpy and entropy is given by (4) [12].

$$\Delta G = \Delta H - T\Delta S$$
(4)

Where ΔG is the change in the Gibbs energy (electrical energy), ΔH is change in enthalpy of formation of water (energy required for reaction describe in 1), T is temperature and ΔS is the change in entropy (thermal energy). For an electrochemical process operating at constant pressure and temperature (T = 25 °C and, p = 1 bar), the electrical work done known as reversible voltage U_{rev} is equal to the free energy change as expressed by

$$U_{rev} = \frac{\Delta G}{zF}$$
(5)

This U_{rev} is the lowest required voltage for the electrolysis to occur and also known as the equilibrium cell voltage, or the electromotive force. However, the thermo-neutral cell voltage U_{tn} is the actual minimum voltage applied to the electrolysis cell. This is because as the electrolyte temperature increases, the ideal voltage required to pull water molecules apart decreases. The effect of temperature on the cell voltage is illustrated in Figure 2.
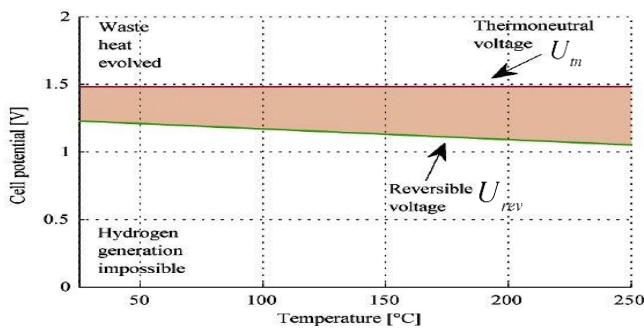

Figure 2: Cell potential for ideal electrolytic hydrogen production [12]

From Figure 2, it can be seen that if the cell potential is under U_{rev}, hydrogen generation is impossible. An efficient process of water electrolysis can be achieved in the red shaded area whereby, water splitting would take place by absorbing heat from the environment. If the cell potential is above the U_{tn},

waste heat is produced (exothermic) in which will increase the cell loses.

The U_{tn} can be determined from the total amount of energy needed in water electrolysis which is equivalent to the change in enthalpy ΔH. From (4), ΔH includes the thermal irreversibility $T\Delta S$, which for a reversible process is equal to the heat demand. Then, the U_{tn} is expressed by

$$U_{tn} = \frac{\Delta H}{zF}$$
(6)

Where in standard operating condition,

ΔG = Gibbs energy = 237 kJ/mol,
ΔH = Change in enthalpy = 286 kJ/mol
z = number of electron = H_2= 2,
F = Faraday constant = 96485 C/mole

Therefore, by substituting these parameter values into (5) and (6), this gives U_{rev} = 1.229 V and U_{tn} = 1.482 V. However, these value will change with temperature and pressure. Here, the effect of temperature has more significant influence on the U_{rev} compared to U_{tn}. This can be seen from Figure 2 where U_{rev} decreases slightly with increasing of temperature while U_{tn} remains constant.

3.2 Electrochemical model

In an ideal water electrolysis, the cell voltage is equal to U_{rev}. However, this cell potential is much higher than U_{rev} in industry. This is due to the irreversible process in over voltage potential that lowers the efficiency of the cell [13]. The sources of over-voltage potential are listed as follows [14]:

- Ohmic loss of electrolyte.
- Overvoltage associated with oxygen and hydrogen.
- The ohmic loss caused by electric resistance of electrodes and circuitry.

The electrolysis cell potential is the summation of the U_{rev} and the additional over-voltage potential contributed by the sources above. The total electrolysis cell potential is expressed by

$$U_{cell} = U_{rev} + U_{act} + U_{ohm}$$
(7)

Where U_{act} is the activation overvoltage and U_{ohm} the over-voltage caused by the ohmic losses. Equation (7) can be modeled using empirical current-voltage (I-U) relationships.

3.2.1 Activation Over-voltage

The U_{act} occurs due to the electrochemical kinetics of the anode and cathode during simultaneous half-reactions. The U_{act} can be expressed as

$$U_{act} = s \log \left(\frac{t}{A} I + 1 \right)$$

(8)

However, equation (8) is only valid for a given temperature. Since the over-voltage is mainly temperature dependence, it can be modified into more detailed I-U model as given by (9).

$$U_{act} = s \log \left(\frac{t_1 + \frac{t_2}{T} + \frac{t_3}{T^2}}{A} I + 1 \right)$$

(9)

Where s, t_1, t_2, t_3 are the coefficient over-voltage on electrodes, I is the current density, T is the temperature of the cell and A is the electrode area respectively [2].

3.2.2 Ohmic Over-voltage

The ohmic over-voltage U_{ohm} corresponds to the ohmic losses within the cell. These losses are related to wastage of electrical energy in the form of heat formation and are proportional to the electric current that flows through the cell. The most dominant are the ionic losses caused by electrolyte. The U_{ohm} can be represented as

$$U_{ohm} = \frac{r}{A} I$$

(10)

Same goes to U_{act}, where equation (10) is only valid for a given temperature. It is also a temperature dependent which can be remodeled as

$$U_{ohm} = \frac{r_1 + r_2 T}{A} I$$

(11)

Where r_1 and r_2 are the ohmic resistance of electrolyte parameter [1, 2].

3.2.3 Faraday Efficiency

Faraday efficiency or current efficiency is defined as the ratio between the actual and theoretical maximum amount of hydrogen produced in the electrolyzer. This faraday efficiency is caused by parasitic current losses along the gas ducts. The parasitic current loss is contrary to current density where, an increase in parasitic current will decrease the current density. This is due to an increase share of electrolyte will lower the electrical resistance. The temperature has a significant impact on faraday efficiency since an increase in temperature leads to a lower resistance, hence more parasitic current losses and lower the efficiency. An empirical expression of faraday efficiency for a given temperature is expressed by

$$nF = \frac{\left(\frac{I}{A} \right)^2}{f_1 + \left(\frac{I}{A} \right)^2} f_2$$

(12)

Where f_1 and f_2 are the temperature-dependent parameters.

3.2.4 Hydrogen Production Rate

According to the Faraday's law, the rate of transfer of electrons at the electrodes influences the production rate of hydrogen caused by the external circuit electrical current. In addition, the number of cells connected in series also influence the amount of hydrogen rate production. The hydrogen rate production can be expressed as

$$\dot{n} H_2 = nF \frac{nI}{zF}$$

(13)

Where nF is faraday efficiency, n is number of cell connected in series, z is number of electron ($H_2 = 2$) and F is faraday constant.

3.2.5 Energy Efficiency

Energy efficiency is the ratio between thermo-neutral voltage and cell potential. This energy efficiency indicates how efficient the water electrolysis process is. High efficiency indicates that most of energy is used for the decomposition of water into hydrogen and oxygen whereas low efficiency indicates that some of the energy are lost as heat. The generation of heat in water electrolysis is caused by the electrical inefficiencies. The energy efficiency can be expressed as

$$n_e = \frac{U_{tn}}{U_{cell}}$$

(14)

Where U_{tn} is the thermo-neutral voltage and U_{cell} is the cell voltage.

An increase in hydrogen production will increase the current density as well as the cell potential, which consequently decrease the energy efficiency. However, energy efficiency will increase with the increasing of the temperature. This is because less cell potential is required to achieve the same current density for different temperature [1].

4. SIMULATIONS & RESULTS

The simulation is done using MATLAB/Simulink to investigate the effect of temperature towards I-U curve, over-voltage potential, flow rate of hydrogen and energy efficiency of alkaline water electrolysis. The data used for the simulation is shown in Appendix Table I & II.

4.1 I-U Curve

An increase in current density will increase the cell voltage as shown in Figure 3. This is due to the nature of electrolysis where, water molecules break into hydrogen and oxygen ion only at higher cell voltage. However, an increase in temperature will decrease the required cell voltage to achieve the same current density. It can be seen from Figure 3 that the

highest cell voltage occurs at 20 ⁰C whilst the lowest cell voltage occurs at 100 ⁰C.
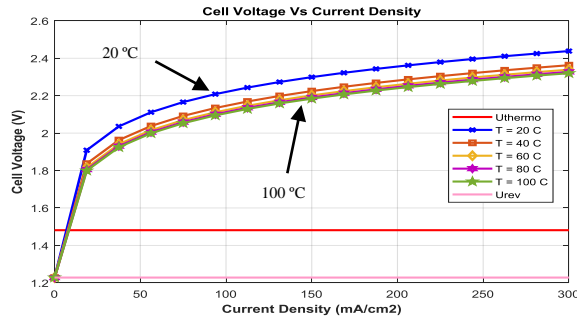

Figure 3: I-U curve

4.2 Overvoltage Potentials

In this simulation, the activation and ohmic over-voltages are observed and compared. In alkaline electrolysis, reactions at the electrodes will only start when there is an energy (activation losses) supplied to it. This energy produces a voltage drop in both electrodes. From the observation in Figure 4a, there is a steep slope for the activation voltage from 0 to 50 mA which indicates the activation of polarization. Beyond 50 mA, the slope of the current becomes less steep since activation polarization has less influence due to ohmic effect. This ohmic effect occurs in the electrode cell causing a voltage drop. From Figure 4b, the ohmic voltage increases linearly with current density. The ohmic effect will produce gas bubbles covering the surface of the electrodes. This will reduce the conductivity of the electrode leading to the increase in ohmic resistance in electrolysis bath and also other components resistance in the alkaline electrolysis. It is also observed that when temperature increases, both over-voltage potentials decrease. For example, at current density equals to 300 mA, the highest activation and ohmic voltages occur at T =20 ⁰C whilst the lowest occurs at T = 100 ⁰C. This is due to less energy required to start the reaction at the electrodes and also the shrinkage of gas bubbles at higher temperature.
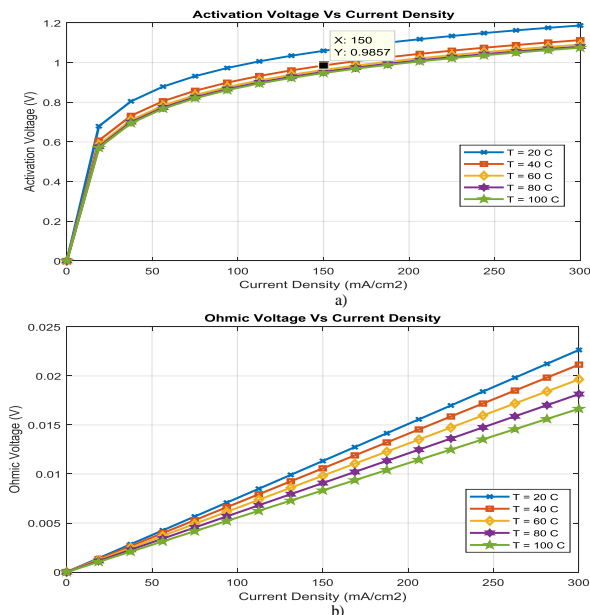

Figure 4: a) Activation voltage; b) Ohmic voltage

4.3 Faraday's efficiency

The relationship between Faraday's efficiency and current density is shown in Figure 5. The Faraday's efficiency increases sharply from 0.5 to 0.96 at low current density. This is because parasitic current decreases when current density increases. However, the increase in temperature will decrease faraday efficiency with respect to current density. This is because more parasitic current flows when electrical resistance becomes smaller.
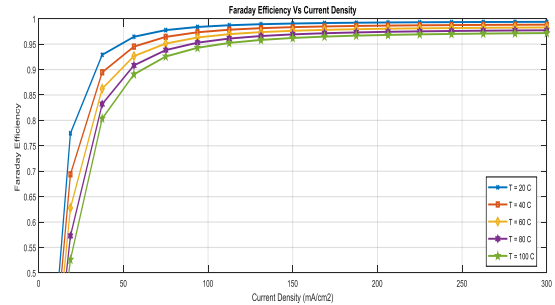

Figure 5: Faraday efficiency

4.4 Flow rate of hydrogen and Energy Efficiency

The effect of temperature towards the hydrogen flow rate and energy efficiency are observed as shown in Figure 6a and 6b. The increase in temperature has no influence towards the flow rates of hydrogen. It can be seen that the hydrogen flow rate increases when current density increases. The hydrogen flow rate is proportional to the current density where, it mainly depends on the injected current This current will increase the chemical reaction of electrolysis process.

As for the energy efficiency, the temperature does have a significant effect. It can be seen in Figure 6b where, as when the temperature increases, the energy efficiency also increases. The highest energy efficiency occurs at T = 100 ⁰C while the lowest energy efficiency at T = 20 ⁰C. At the temperature equals to 20 ⁰C, the energy efficiency is low due to initial heating during start-up. This initial heating will require more energy to be consumed in water electrolysis process where the energy is wasted as heat. It is clearly shown that the optimum temperature for this simulation analysis is at the temperature of 100 ⁰C since the alkaline electrolysis can produce high hydrogen production rate with minimum power consumption.
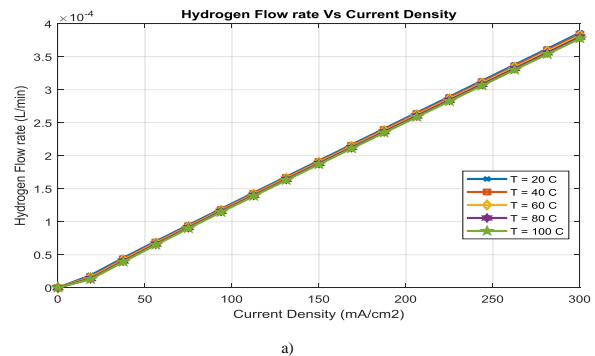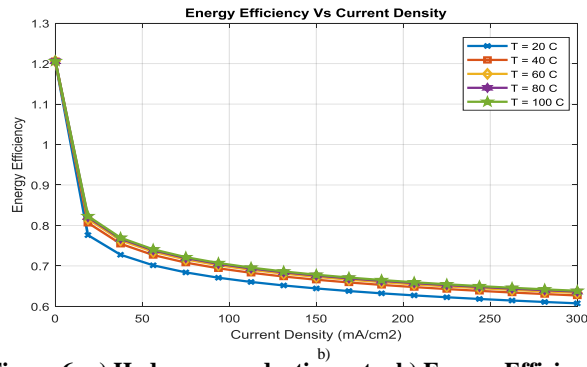
Figure 6: a) Hydrogen production rate; b) Energy Efficiency

5.   CONCLUSION

The effect of temperature towards the I-U curve, over-voltage potentials, hydrogen flow rate and energy efficiency of an advanced alkaline electrolysis have been observed and analyzed. The simulation is carried out using MATLAB/Simulink with temperature varying from 20 ºC to 100 ºC. The result shows that the temperature does not have a significant effect on the hydrogen flow rate where when current increases and so does hydrogen flow rate. However, temperature does have effect on the I-U curve, over-voltage potentials and energy efficiency. It is observed that at high temperature less cell voltage is required because the over-voltage potentials, activation and ohmic voltages contributed to the overall cell voltage are reduced. In fact, energy efficiency at high temperature is much higher compared to low temperature. This is because the overall cell voltage is much closer to the actual minimum voltage (thermo-neutral voltage)..

APPENDIX

The data used for the modelling of the alkaline water electrolysis in MATLAB/Simulink is shown in Table I. The constant parameters used for simulation is taken from [1, 2].

Table I Constant Parameter[2]

Constant Parameters	Symbols	Unit	Value
Reversible Voltage	U_{rev}	V	1.229
Area of Electrode	A	m^2	0.25
Farady Constant	F	C/mol	96485
No of Electrons	z		2
No of cells	n		1
Coefficient for overvoltages on electrodes	s	V	0.185
Coefficient for overvoltages on electrodes	t1	$A^{-1}m^2$	1.002
	t2	$A^{-1}m^2{}^{o}C$	8.424
	t3	$A^{-1}m^2{}^{o}C$	247.3
Parameter related to ohmic resistamce of electrolyte	r1	Ωm^2	8.05e-5
	r2	$\Omega m^2{}^{o}C^{-1}$	-2.5e-7

Table II. Faraday Efficiency Parameter [1]

Parameters				Units
Temperature	20	40	60	ºC
f1	100	150	200	mA^2cm^{-4}
f2	0.995	0.990	0.985	0…1

Parameters		Units
Temperature	80	100	ºC
f1	250	300	mA^2cm^{-4}
f2	0.980	0.975	0…1

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