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Mathematical modelling and simulation analysis of advanced alkaline electrolyzer system for hydrogen production

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Abstract

As a result of increasing global energy demand, conventional energy sources such as coal, gas and liquefied petrol are being depleted at an alarming rate. An alternative way to overcome this is by applying renewable energy as a backup energy supply. One of the useful renewable energy technology used these days is the production of hydrogen from electrolysis. When combine with solar-PV or wind energy, Production of hydrogen from water electrolysis has the potential to play an important role as an energy carrier for future sustainable development. In alkaline electrolysis the electrochemical reactions possess energy barriers which must be overcome by the reaction species, this energy barrier is called activation energy and results in activation overpotential which are irreversible losses. The purpose for this work is to investigate the I-V characteristics of an advanced alkaline electrolyser. The main parameters such as ohmic overpotential, activation overpotentials (at anode and cathode) affecting the performance of the electrolyser were investigated. For this analysis, the equations related to fundamental thermodynamics and electrochemical reactions are model in MATLAB. In conclusion activation overpotential was observed to be higher by about 80 % compare with ohmic overpotential at the same current density.

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Keywords: Advanced alkaline electrolyzer; Mathematical modeling; Simulation; Renewable hydrogen; Activation overpotential

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1. Introduction

The continuous use of conventional energy sources poses tremendous challenges associated with pollution, greenhouse gas emission and climate change. As a result there is increasing global concern on the need to shift towards sustainable renewable energy system. In this perspective, renewable hydrogen has been recognized as a promising future energy carrier [1]. Hydrogen may be used as fuel in almost every application where fossil fuels are being used today, but without harmful emissions [2]. The Hydrogen may be converted into useful forms of energy more efficiently than fossil fuels. And despite public perception regarding hydrogen, it is as safe as other common fuels [3]. Hydrogen is not an energy source, and it does not occur in nature in its elemental or molecular form. Hydrogen is found most abundantly in water and this requires some amount of energy for the splitting process and because of the laws of thermodynamics, energy required to split water is higher than energy that can be released from produced hydrogen. Because of that, hydrogen is a convenient form of energy carrier just like electricity [4].

Nomenclature

Roman

A	area of electrode, m ²
ΔG	Gibbs free energy, J/mol
F	Faraday constant, 96485 C/mol
Q	volume flow rate, Nm ³ /h
T	temperature, K
V	cell voltage, V
n	number of cells
\dot{n}	production rate, Nm ³ /h
r	ohmic resistance parameter, Ωm^2
s	coefficient for overvoltage on electrodes, V
t	coefficient for overvoltage on electrodes, A-1m ²
z	number of electrons

Subscripts

H ⁺	hydrogen ions
H ₂	hydrogen gas
H ₂ O	water
O ₂	oxygen gas
OH-	hydroxide
aq	aqueous
g	gaseous
l	liquid
rev	reversible
act	activation
ohm	ohmic

Greek

η_F	Faraday efficiency
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Acronyms

DC	Direct current
KOH	potassium hydroxide
NaOH	sodium hydroxide
NaCl	sodium chloride
GUI	Graphical user interface

Traditionally hydrogen has been produced and utilized in industry for over a decade [5] and it can be produced through different sources with different technologies. Although several methods have been and are being developed for production of hydrogen from renewable energy sources, the only state-of-the-art technique is advanced water electrolysis. Water electrolysis is a mature and commercially available technology which is widely being used for hydrogen production capacities ranging from few cm^3/min to thousands m^3/h [6]. Other features associated with Water electrolysis are [7,8]: it has relatively high efficiency (above 70%) with electricity consumptions in order of $4.3 \text{ kWh}/\text{Nm}^3\text{H}_2$. very pure hydrogen can be produced since the gases are physically separated during their evolution at the electrodes, water electrolyzers operate with few moving parts, require little space and maintenance costs are low, production costs are high because they depend on the cost of electricity; however, advantage can be taken of relatively inexpensive off-peak period rates, it has the potential of producing hydrogen essentially free from CO_2 emissions when the required electricity is produced through routes not based on fossil fuels.

Water electrolysis is considered the only practical method for producing hydrogen from renewable energy sources such as wind energy, hydroelectric power and photovoltaic [9]. This however makes water electrolyser system an integral component of the renewable hydrogen energy systems (RHES), particularly for weak-grid applications [10, 11, 12]. Many recent studies on electrolysis of hydrogen production focus on alkaline electrolysis for instance reports of Hug et al. [13], Ulleberg and Mørner [14], and Ulleberg [15] are very good outstanding examples of the modelling and simulation of RHES including water electrolyzers. The above cases show that the electrolyzer is a crucial component, and its technical challenge is to make it operate smoothly with intermittent power from renewable energy sources. The motivation of this work is to gain insight on the thermal behaviour of advance alkaline electrolyser from mathematical modeling and simulation points of view. The models are based on fundamental thermodynamics and electrochemical relations for investigating the molar flow rate of hydrogen. Also the effects of operating parameters such as current density, temperature, and ohmic losses on hydrogen production have been investigated.

2. Theoretical concept of alkaline electrolysis/Technology

2.1. Alkaline electrolyzer design basics

Alkaline electrolyser is the most widely used technology for water electrolysis. Traditionally, the electrolyte used in the conventional alkaline water electrolyzers has been aqueous solution of water and mostly 20–30 wt % potassium hydroxide (KOH) because of the optimal conductivity and remarkable corrosion resistance of stainless steel in this concentration range [15]. However sodium hydroxide (NaOH) and sodium chloride (NaCl) and other electrolyte have also been used. The liquid electrolyte enables the conduction of ions between the electrodes. Typically the new advanced commercial alkaline electrolyzers are run with current densities in the range of $100\text{--}400 \text{ mA cm}^{-2}$.

An alkaline electrolyzer consists mainly of a cell frame, electrolyte, anode cathode and separating diaphragm. The two main design configurations are unipolar (tank) and bipolar (filter press) [16]. In the unipolar design the electrodes, anodes and cathodes are alternatively suspended with parallel electrical connection of the individual cells (see Fig.1a), while in the bipolar design the individual cells are linked in series electrically and geometrically (see Fig. 1b).

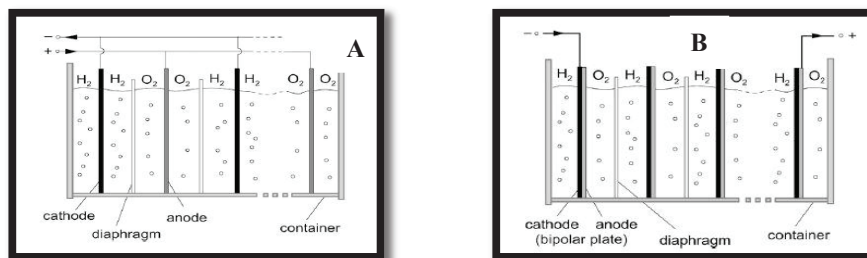


Fig.1. Alkaline Electrolyzer design configurations: (a) Unipolar electrode geometry (b) Bipolar electrode geometry [15].

The advantage of the unipolar design is that it requires relatively few parts, very simple to manufacture and repair. Its disadvantage is that it is operated at lower current densities and temperature. The advantage of the bipolar electrolyzer stacks is that they are more compact than unipolar systems. The advantage of the compactness of the bipolar cell design is that it gives shorter current paths in the electrical wires and electrodes. This reduces the losses due to internal ohmic resistance of the electrolyte, and therefore increases the electrolyzer efficiency. The disadvantage is that it cannot be repaired without servicing the entire stack. The reactions for the alkaline anode and cathode are shown in equations (1) and (2) respectively, showing the hydroxyl (OH⁻) ion transport.



2.2. Mathematical modelling and simulation approach

In order to split the water molecule, electric current (DC) need to passed between two electrodes separated by an aqueous electrolyte with good ionic conductivity [15]. Generally the overall reaction for splitting the water is as follows;



Based on the chemical equation, a minimum electric voltage (reversible voltage) must be applied to both electrodes and this can be determined from Gibbs equation [15,16] .

$$\Delta G = zFV_{\text{rev}} \quad (4)$$

$$V_{\text{rev}} = \Delta G/zF \quad (5)$$

$$V_{\text{rev}} = \frac{237.2 \text{ kJ/Kmole}}{2 \times 96485 \text{ C/mole}} = 1.229 \text{ V} \quad (6)$$

ΔG =Gibbs Energy, z = number of electron, F =Faraday's Constant

In electrolysis, the operating cell voltage or overpotential is the summation of the reversible overvoltage, the activation overvoltage which is the electrode response and also the addition of ohmic overvoltage of electrolyte [17]. In order to make an increment on the electric power to produce hydrogen, both overvoltage and ohmic loss will increase with the raise of current density and then, will raise the value for the cell voltage.

$$V_{\text{cell}} = V_{\text{rev}} + V_{\text{act}} + V_{\text{ohm}} \quad (7)$$

The relation for the correspond equation (7) can be equal to the equation of empirical current-voltage (I-U) or (I-V) model as follows;

$$V_{\text{act}} = s \log \left(\frac{t_1 + \frac{t_2}{T} + \frac{t_3}{T^2}}{A} I + 1 \right) \quad (8)$$

$$V_{\text{ohm}} = \frac{r_1 + r_2 T}{A} I \quad (9)$$

Taking account of temperature dependent for ohmic resistance parameter, r and the overpotential coefficient s and t , as suggested by the Oystein Ulleberg [15], equation (7) can be express as.

$$V = V_{\text{rev}} + s \log \left(\frac{t_1 + \frac{t_2}{T} + \frac{t_3}{T^2}}{A} I + 1 \right) + \frac{r_1 + r_2 T}{A} I \quad (10)$$

Based on Faraday's law, the production of hydrogen is affected by the rate of transfer of electrons at the electrodes where it is corresponding to the electrical current in the external circuit [15]. In contrary, the Faraday efficiency is the ratio of the actual over the theoretical maximum amount of hydrogen produced in the electrolyzer. Besides, the Faraday efficiency is caused by parasitic current losses in which it will increase due to the decreasing in current densities because of the share of electrolyte has also increasing and in return, the electrical resistance will become lower. In the aspect of temperature, whenever the temperature is increasing, the resistance will become lower, the parasitic current losses will gain, and Faraday efficiency is lowered. This can be expressed as follows [15]:

$$\eta_F = \frac{\left(\frac{I}{A}\right)^2}{f_1 + \left(\frac{I}{A}\right)^2} f_2 \quad (11)$$

To determine the total hydrogen production rate in the electrolyzer that consists of several cells connected in series, the equation for the operation is stated as below.

$$\dot{n}H_2 = \eta_F \frac{n_c I}{zF} \quad (12)$$

Moreover, by using stoichiometry, the production rate for water consumption and oxygen also can be determined [21, 25].

$$\dot{n}_{H_2O} = \dot{n}H_2 = 2\dot{n}_{O_2} \quad (13)$$

The volume flow rate of hydrogen can be expressed in unit of Nm³/h [18] as follows:

$$Q = \dot{n}H_2 \times 3600 \times 0.022414 \quad (14)$$

2.3. Simulation background

The data used in the present modelling is shown in Table 1, constant parameters used for simulation calculation taken from Oystein Ulleberg [15].

Table 1. Constant Parameters [15].

CONSTANT PARAMETERS	SYMBOLS	UNITS	VALUE
Reversible Voltage	V_{rev}	V	1.229
Area of Electrode	A	m ²	0.25
Faraday's Constant	F	C/mol	96485
Number of Electrons	z		2
Number of cells	n		1
Coefficient for overvoltage on electrodes	s	V	0.185
Coefficient for overvoltage on electrodes	t_1	A ⁻¹ m ²	1.002
	t_2	A ⁻¹ m ² °C	8.424
	t_3	A ⁻¹ m ² °C	247.3
Parameter related to ohmic resistance of electrolyte	r_1	Ωm ²	8.05e -5
	r_2	Ωm ² °C ⁻¹	-2.5e -7

The simulation codes were developed in MATLAB, the MATLAB user interface gives the over view of the

parameters at a glance and also used to display the result (see Fig. 2)



Fig. 2. A snapshot of the GUI generated by the simulation program in MATLAB environment.

Table 2 illustrate the parameters used to evaluate Faraday efficiency at different temperatures, these data were taken from the HYSOLAR test and research facility [15].

Table 2. Faraday Efficiency Parameter [15].

PARAMETERS	Units			
Temperatures	°C	40	60	80
f1	$\text{mA}^2\text{cm}^{-4}$	150	200	250
f2	0...1	0.990	0.985	0.980

3. Result and discussion

3.1. Polarization Curve

Simulation studies were carried at different temperatures. Fig. 3a 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. Besides, as temperature increases the cell voltage decrease due to the decrease in ohmic resistance which leads to lower operating cost. As shown in the Fig. 3a, the highest operating cell voltage occur at 40°C, while the lowest occurred at 80°C with the cell voltage of 2.395 V and 2.359 V respectively.

In alkaline electrolysis, activation losses occur because the cell needs energy to initiate reactions at the electrodes. This produces a voltage drop in both electrodes of the cell. In this work different overvoltages are identified and compared in the matlab model (see Fig. 3b-c). In Fig.3b the curves represent the comparative relationship between activation overpotentials as a function of current density. The steep slope of the initial portion of Fig.3b is an indication of the activation polarization. As the current density increases, the slope of the curve becomes less steep. This is a result of the activation polarization becoming less significant due to the increase in other polarization phenomena such as ohmic effects. It can also be observed in Fig.3b that the changes in temperature have no significant effect on activation overpotentials. Fig. 3c shows a linear relation between ohmic and current density ie at higher current density the interfacial resistance of the electronic components increases and this causes increase in ohmic overvoltage. Also the effect of temperature at low current density is insignificant, at higher current densities and varying operating temperatures, the characteristics of the ohmic overpotential shows a

diverging behaviour. In conclusion activation overpotential is observed to be higher compare with ohmic overpotential at the same current densities. For example at 300 current density and at 40°C, activation overpotentials is about 1.12 V whiles ohmic overvoltage is observed to be 0.022V (see Fig 3c). Fig.3d shows the relationship between Faraday's efficiency and current density, at low current density the efficiency increases sharply from 0.7 to 0.96.

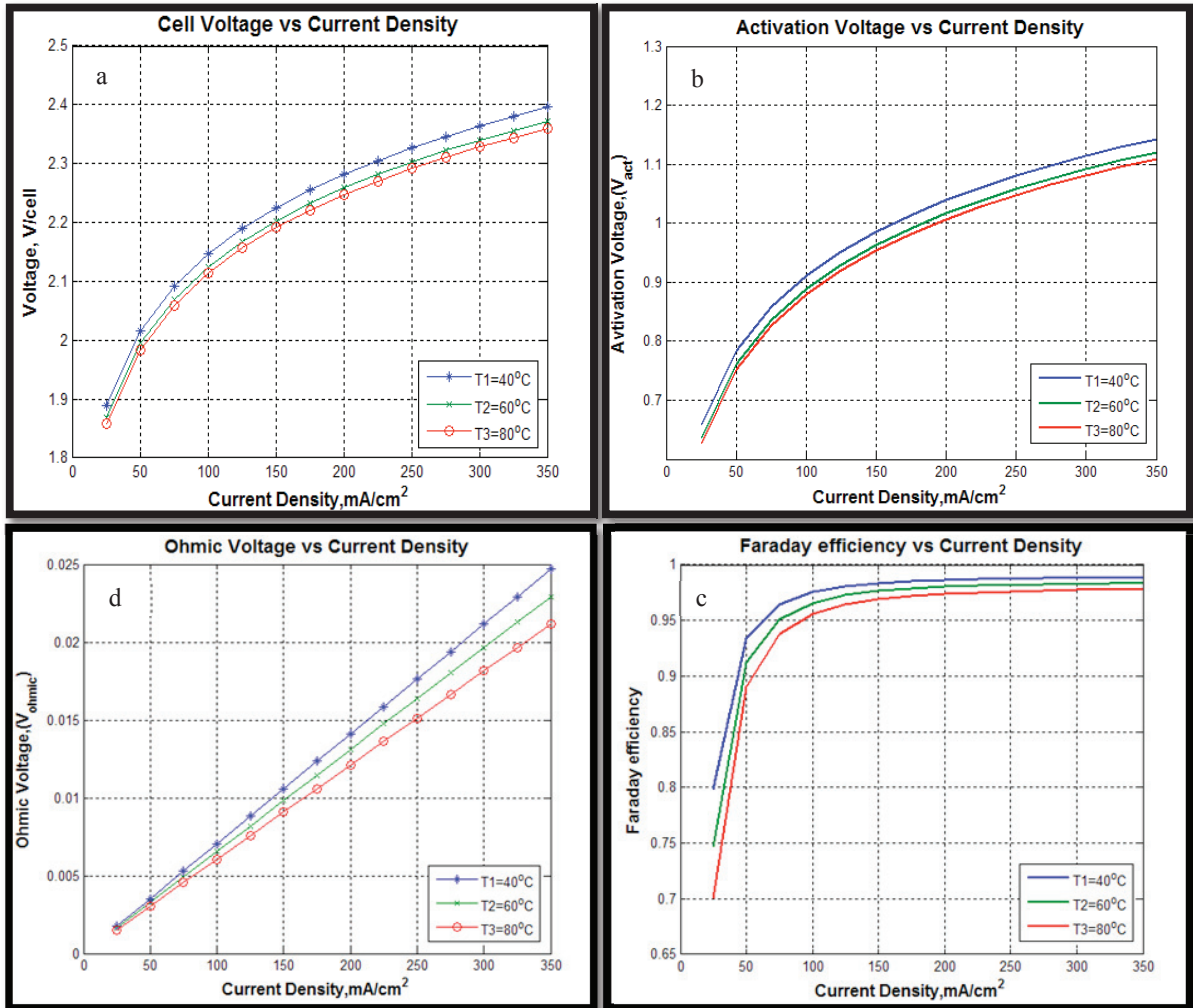


Fig. 3. Polarization curve, (a) I-V curve; (b) activation overpotentials contribution; (c) ohmic losses contribution; (d) Faraday efficiency.

Fig. 4 shows the hydrogen flow rate observed at different temperatures. There is no significance change in hydrogen flow rates at these temperatures. The trends for all the temperature remain the same that is when the current increases, the hydrogen flow rate would also increase. As the current supply to the electrolyser increasing, the dissociation reaction of breaking the water molecules bond is rapidly increased. The current density is responsible for initiating the dissociation reaction that is at higher current density, a higher hydrogen flow rate is produce. The result of the simulation as shown in Fig. 4 indicates that there is no significant change in hydrogen flow rate at different temperatures. Conclusively, the optimum operating condition of the electrolyser system is taking to be at 80°C because this state corresponds to a minimum power consumption of the electrolyser.

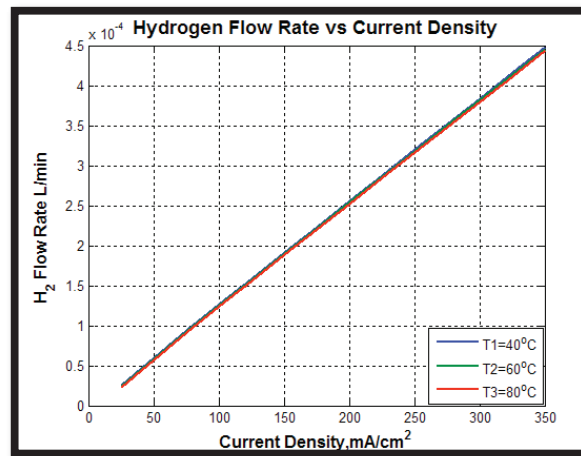


Fig. 4. H₂-production as a function of measured electrical current.

CONCLUSION

A mathematical model for an advanced alkaline electrolyzer has been developed based on a combination fundamental thermodynamics and empirical electrochemical relationships. The model shows that the electrochemical part of the model accurately predicts the cell voltage, hydrogen production, and efficiencies. The results show that several improved electrolyzer-operating strategies can be identified with the developed system simulation model. The modelling outcomes of this system were performed using MATLAB code. The proposed model can predict the performance of a stand-alone power system. In conclusion activation overpotential is observed to be higher compare with ohmic overpotential at the same current densities.

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