

Modelling and simulation of advanced Alkaline Water electrolysis

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Abstract: Hydrogen being the future of green energy, one of the uses of renewable technology is hydrogen production from electrolysis. The water electrolyzer is a critical component of the direct energy interaction between hydrogen production and power supply fluctuations. Finally, the activation potential is higher by 80 % than the ohmic potential, even at the same current density. This research aims to investigate the I-V characteristics and the effects of ohmic and activation potential on the performance of an advanced alkaline water electrolyzer. The fundamental thermodynamic and electrochemical reaction equations were used to model an advanced alkaline electrolyzer and simulate MATLAB. When compared to published models tested against identical sets of experimental data, the model looked perfect.

Keywords: alkaline electrolyzer, I-V characteristics, MATLAB, activation potential, ohmic potential.

1. INTRODUCTION

A simple form of green hydrogen is achieving the most priority because of its significant advantages as an energy carrier, such as high energy density, less emission, and sustainable energy. Hydrogen production. Electrolysis is gaining priority because of its high relative purity, higher fuel cell efficiency, and excellent hydrogen production rates.

Water electrolysis is the process of dissociating the water into hydrogen and oxygen with an external energy supply. An electrolysis unit consists of an anode, cathode and an electrolyte and oxygen ion exchange membrane. Electrolysis of water is not a spontaneous process because the net Gibbs free energy is not negative. It needs an external intervention, and the global reaction can be written as



The reduction half-reactions occur at the cathode, and electrodes flow to this electrode, whereas the half oxidation reactions occur at the electrode called an anode.

2. CLASSIFICATION OF ELECTROLYSIS

Water electrolysis can be classified into four types based on their electrolyte and the operating conditions. They are

- i. Alkaline water electrolysis
- ii. Solid oxide electrolysis
- iii. Microbial electrolysis cell
- iv. PEM electrolysis cell

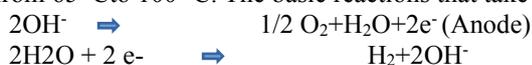
Another classification is based on the gap between the electrodes and the cell separator. They are

- i. The gap cells
- ii. The zero-gap cell
- iii. The PEM cell

2.1 Alkaline Water electrolysis

Troostwijk and diemann first introduce alkaline water electrolysis in 1789. The cell comprises two electrodes separated by a diaphragm to avoid the recombination of oxygen and hydrogen produced.

The diaphragm should have high physical and chemical stability with high Ionic conductivity. An operating temperature is from 65 °C to 100 °C. The basic reactions that take place in alkaline electrolysis are



The advanced alkaline cell uses a zero-gap configuration to reduce the impact of the gas bubbles and the ohmic losses by reducing the space between the electrodes. The primary limitations related to alkaline technology are the corrosive environment, the low current density and the limited production rate of 25 % -100 % due to the diffusion of

gases through the diaphragm at partial load. There are two cell structures of alkaline electrolysis on the market, unipolar and bipolar. In AWE, asbestos diaphragm and nickel electrodes are used.

Alkaline water electrolysis is entirely safe and reliable and can reach up to 47 % to 82 %. The production is in practice limited to 25-100 %, leading to the formation of a flammable gas mixture. The purity levels of oxygen and hydrogen are 99.9 % and 99.7 % without any auxiliary purification unit. In modern AWE cells, the zero-gap configuration is widely used to avoid ohmic resistance and which helps in increasing the process efficiency.

Nernst formula shows a relationship between the equilibrium cell voltage. The partial pressure of the gases and water in the electrolyte.

$$E = E_0 + \frac{RT}{\eta F} \ln\left(\frac{P_{O_2}^{1/2} \cdot P_{H_2}}{\alpha_{H_2O}}\right)$$

It is estimated as 480 €/KW by the EC and national renewable energy laboratory's fuel cells and hydrogen joint undertaking. Significant advances in alkaline water electrolysis are mainly in two directions. The efficiency of the electrolyzer needs to be improved to reduce the operating costs associated with the consumption of electricity. Investment costs are reduced by increasing the operating current densities.

1. Integrating the electrodes and the diaphragm as a single element to achieve zero-gap configuration to harness the ohmic losses and experience higher current densities.
2. Development of new advanced materials to be used as the diaphragm, electrocatalytic materials reduce the previous ones made of asbestos.
3. Increasing the performance and enhancing structural integrity by the high-temperature alkaline water electrolysis up to 150 °C.

2.2 Proton Exchange Membrane Electrolysis

The unit cell is relatively compact and is enclosed by two terminal titanium endplates. MEA is placed at the centre in the core cell component, where the water splitting takes place. Hydrogen and oxygen produced by the reactions are collected at the mixtures are pumped to separators for gravimetric separation.

PEM water electrolyzers have great load flexibility and have the capacity to provide grid balancing services. It is possible to achieve 10 A/cm² a maximum current density, and 99.99 % purity can be obtained. The energy required to split water in a PEM electrolyzer ranges from 3.9 -4 Kwh/Nm³ at 1 A/cm². The point to be noted is that operating pressure in PEM stacks up to tons of bars, facilitating the decrease in energy consumption. An increase in pressure, temperature, and water flow rate may hinder the mass transfer losses and decrease current density. The range of interest for mobility applications in European countries is to reduce the cost of the electrolytic hydrogen down to the 5 €/KW. The significant challenge that needs to be looked at is decreasing the cost of platinum group metals. There are two ways of doing it. They were

- i. The reduction of PEM loadings
- ii. Their replacement by alternative materials

The vital energy required for the production of hydrogen depends on the hydrogenated compounds supplied to the cell. Anodic depolarization can be accomplished by switching to hydrogen compounds. It might be better to choose in-organic hydrogen compounds than organic ones to avoid toxic emissions.

2.3 Solid Oxide Electrolysis

It is highly appreciable and attractive to decompose water into hydrogen and oxygen at elevated temperatures in the range of 800-1000 °C. Even the energy requirements are less because of the high temperature and drawbacks that limit its commercialization. Mainly start-up and shut-down procedure and faster degradation of the cell components and a relatively rapid degradation and corrosion management is more challenging, and lifespans of the electrolyzers were reduced. The oxygen produced at the anode side at such elevated temperatures is very corrosive, and it can rapidly degrade the cell components. Air dilution is the solution, but this adds additional energy costs and complexity to the operation. The significant and additional future of interest is that both half-cell reactions are reversible. Since SOECs and SOFCs cells have similar designs, the integration of SOEC and SOFC facilitates more efficiency. The energy demand for water splitting is lower and in the vapour phase than in the liquid phase.

From the material viewpoint, oxygen ion-conducting ceramics are used as solid membranes. Electrodes are placed opposite sides of the ceramic membrane, and the following of water vapour and the collection of gases is organized by using cell separators with flow fields also called interconnects. SOECs has the will to operate reversibly and is used as regenerative FC/ electrolyzer systems. With this, we can conclude that it is possible to electrolyze CO₂. If both CO₂

and steam are sent to the cathode, co-electrolysis occurs, resulting in syn-gas formation. SOFC technology could produce oxygen in long-distance human missions like mars or other planets or the moon.

2.4 Microbial Water Electrolysis

Electro-hydro genesis can produce hydrogen gas in microbial electrolysis cells (MECS) at greater yields than fermentation and greater energy efficiencies than water electrolysis. A membrane is needed to suppress the product gas consumption. Even without a membrane and zero cell-gap configuration, Electrohydrogenesis is a recently developed electrolysis technique that facilitates hydrogen production from biodegradable waste using modified microbial fuel cells. The hydrogen production rates are almost twice that of the membrane. These results demonstrate that high hydrogen recovery and production rates are possible in a single chamber in MEC without a membrane, thus leading to reliable and simple designs with less cost.

In an MFC, the microorganisms called exoelectrogens oxidize the organic matter and transfer electrons to an anode. However, the hydrogen produced at cathode is contaminated by other gases produced at the anode, like carbon dioxide, even when a membrane is used. The membranes do not prohibit the diffusion of hydrogen back to the anode surface. Membranes hinder the proton diffusion between the electrodes and create a substantial pH gradient across the electrodes, resulting in a potential loss over the electrodes. A hypothesis exists that the MEC performance would not change much, even in the absence of a membrane. Due to the voltage losses, the actual overpotentials required to make it spontaneous are more significant than the theoretical value.

The conclusions from the following facts are

- 1) As there is no formation of oxygen at the anode, there is no need to keep the membrane to separate the product gas without being mixed.
- 2) Although Exoelectrogens consume the hydrogen gas, we reasoned that if hydrogen gas production rates were sufficiently high, then the low solubility of the Hydrogen gas in water would allow higher recoveries.
- 3) Lack of membrane in a MEC would not adversely affect current densities, and based on reports, MFCS with cation, anion or ultrafiltration membrane would not adversely affect current densities.
- 4) Even if some hydrogen gas was lost, the reduced cost of the system due to the lack of membrane might reduce the overall system cost and simply reactor architecture.

In order to increase the current density, some recent design futures have been introduced, like using graphite brush electrodes, Ammonia treatment on the anodes and zero gap-cell configuration and varying the solution conductivity to improve performance.

3. MODELING AND SIMULATION IN ALKALINE WATER ELECTROLYSIS

3.1 Theoretical concept of alkaline electrolysis/technology

All the electrochemical reactions possess activation energy barriers which the reactants must overcome. This activation energy induces an irreversible activation overpotential. The output of the electrolyzer was modelled using the basic thermodynamic and electrochemical reaction equations and is simulated in MATLAB.

In the unipolar design, the oppositely charged electrodes are alternatively arranged with parallel connection, while in bipolar design, the individual cells are linked in series electrically and geometrically. However, it is impossible to maintain high current density and temperature, but it is easy to manufacture and repair. Bipolar designs have more compactness than unipolar because they give shorter current paths that help avoid internal ohmic resistance. The repair and maintenance of the bipolar electrolyzer are complicated.

3.2 Mathematical modelling and simulation approach

A minimum reversible voltage calculated from the Gibbs free energy required to split water molecules is $V_{rev}=1.229$ V. The operating cell voltage is the sum of the reversible overvoltage, the activation and ohmic overvoltage of the electrolyte. An increase in the electric power to produce hydrogen results in an increment in the operating cell voltage.

$$V_{cell} = V_{ohm} + V_{act} + V_{ohm}$$

The relation of the corresponding equation can be equal to the empirical current-voltage equation.

$$V_{act} = \text{sln}\left(\frac{t_1 + \frac{t_2}{T} + \frac{t_3}{T}}{A} I + 1\right)$$

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

Substituting V_{act} and V_{ohm} in V_{cell} , we get

$$V_{cell} = V_{ohm} + V_{act} = \ln\left(\frac{t_1 + \frac{t_2}{T} + \frac{t_3}{T}}{A} I + 1\right) + V_{ohm} = \frac{r_1 + r_2 T}{A} I$$

In temperature prospect, the resistance will become lower; hence the parasitic current losses gain. As a result, faraday efficiency decreases. It can be mathematically represented as

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

The hydrogen production rate in the electrolyzer is given by

$$n \cdot H_2 = \eta_f \frac{n_c I}{ZF}$$

And From stoichiometry

$$n \cdot H_2 O = n \cdot H_2 = 2n \cdot O_2$$

The volumetric flow rate of hydrogen is

$$Q \cdot = n \cdot H_2 \cdot 3600 \cdot 0.022414$$

3.3 Simulation Background

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

Table 1. Constant parameters

Constant Parameters	Symbols	Units	Value
Reversible Voltage	V_{rev}	V	1.229
Area of the electrode	A	m ²	0.25
Faraday's constant	F	C/mol	96485
Number of electrons	z		2
Number of cells	n		1
The coefficient for overvoltage on electrodes	s	V	0.185
Coefficient for overvoltage on electrodes	t_1	A ⁻¹ m ²	1.002
		A ⁻¹ m ² °C	8.424
t_2		A ⁻¹ m ² °C	247.3

t ₃			
Parameters related to ohmic resistance of the electrolyte	r1	Ωm^2	8.05e-5
	r2	$\Omega\text{m}^2\text{C}^{-1}$	-2.5e-7

Table 2. Faraday efficiency parameters

Parameters	Units			
Temperatures	$^{\circ}\text{C}$	40	60	80
f1	$\text{mA}^2\text{cm}^{-4}$	150	200	250
f2		0.990	0.985	0.980

4. RESULTS

4.1 Polarization curve

The figure interprets and concludes that the required cell voltage is increased with a rise in the current density. The above statement shows that more water molecules dissociate into hydrogen and oxygen only at higher current densities at higher voltages. The operating cost of electrolyzer decreases with an increase in temperature, which lowers ohmic resistance. The higher cell voltage is at 40 $^{\circ}\text{C}$ and the least at 80 $^{\circ}\text{C}$.

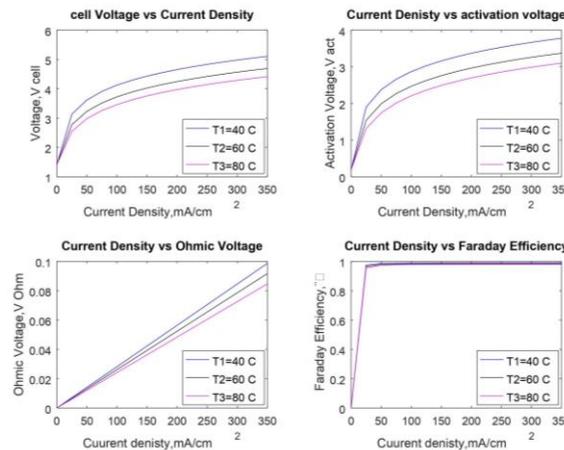


Fig.4. Polarization Curve, (a) I-V curve ; (b) Activation over potential contribution ;(c) Ohmic losses contribution; (d) Faraday efficiency

The steep slope in Fig.4.2 indicates activation polarization which is induced due to voltage drop between the electrodes. A voltage drop is found due to the consumption of the energy in initiating the reaction. As the current density increases, the slope of the curve becomes less steep. However, activation potential is considered negligible when compared to the significant changes in the ohmic potential.

Fig.4c shows a linear relationship between ohmic and current density; at higher current density, the electronic components' interfacial resistance increases, which causes an 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 over potential shows a diverging behaviour. In conclusion, activation potential is higher than ohmic overpotential at the same current densities.

Fig.4d 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 5 depicts that there is no variation in hydrogen production rate with temperature.

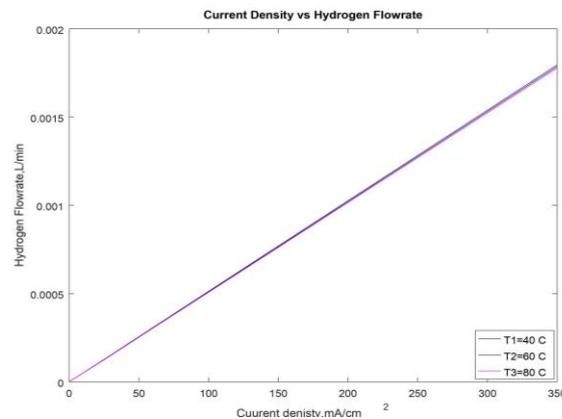


Fig.5: Hydrogen production as a function of measured electric current

The simulation result indicates that there are no remarkable changes in hydrogen flow rate at different temperatures. As the current supply to the electrolyzer increases, the dissociation reaction of breaking the water molecules bond is rapidly increased. The current density is responsible for initiating the disassociation reaction at a higher current density, producing a higher hydrogen flow rate.

5. CONCLUSION

A mathematical model for an advanced alkaline electrolyzer has been developed based on thermodynamics and empirical electrochemical relationships. The model dictates that the electrochemical part of the model accurately predicts the cell voltage, Hydrogen production and efficiencies. The modelling outcomes of this system were performed using MATLAB. The proposed model can predict the performance of the stand-alone power system. In conclusion, activation over potentials are higher than ohmic over potentials at the same current densities.

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