

APPENDIX B
EFFECT OF CURRENT DENSITY, CONCENTRATION AND
DISTANCE BETWEEN ELECTRODES IN NaOH AND NaCl

EFFECT OF CURRENT DENSITY, CONCENTRATION AND DISTANCE BETWEEN ELECTRODES IN NaOH AND NaCl

The electrolytic process consists in water dissociating oxygen and hydrogen by means of continuous electrical current which crosses an electrolyte laid out between two electrodes. Hydrogen can be easily produced by DC electricity via electrolysis and retransferred to electricity by fuel cell plants. However, only 1-4 % of hydrogen is currently produced from the electrolysis of water, which is currently a very expensive process. The efficiency of electrolysis is low as a result of electrical resistance in the circuit and electrolyte causing higher voltage over the cells. In the preceding chapters a large number of mathematical solutions have been presented. This section aims to study the effects of concentration, current density, type of electrolyte and distance between electrodes on the gas production rate and efficiency via empirical method. The authors display the experimental results which it is guides from an analysis of parameter to a systems design and improvement.

B.1 Experimental Apparatus

The water electrolysis is conducted under atmospheric pressure using the pressure switch controller. The pressure switch (P) is connected to measure the gauge pressure of produced hydrogen and oxygen gases. Electrodes are rested on a support, grooved for keeping a fixed or varied distance between electrodes. AC power supply is connected to a bridge rectifier through a step down transformer (5.3 KVA, input: 220/230 V AC). The electrodes are connected with AC to DC converter. Regulated DC power supply working in the range of 10-160 A is used and the current is adjusted in the range of 5 - 60 A. Voltmeter (V) and ammeter (A) are connected in parallel and series respectively to the electrolyzer to measure voltage and current applied to electrolysis process. The gases obtained from the cathode and the anode are collected separately in gas tube and the volume of hydrogen and oxygen produced is measured with hydrogen digital gas mass flow meter and flow meter for oxygen and re-checked by water displacement. Temperature, voltage and current are recorded by the NI-USB6218 (DAQ) as illustrated in figure B.1.

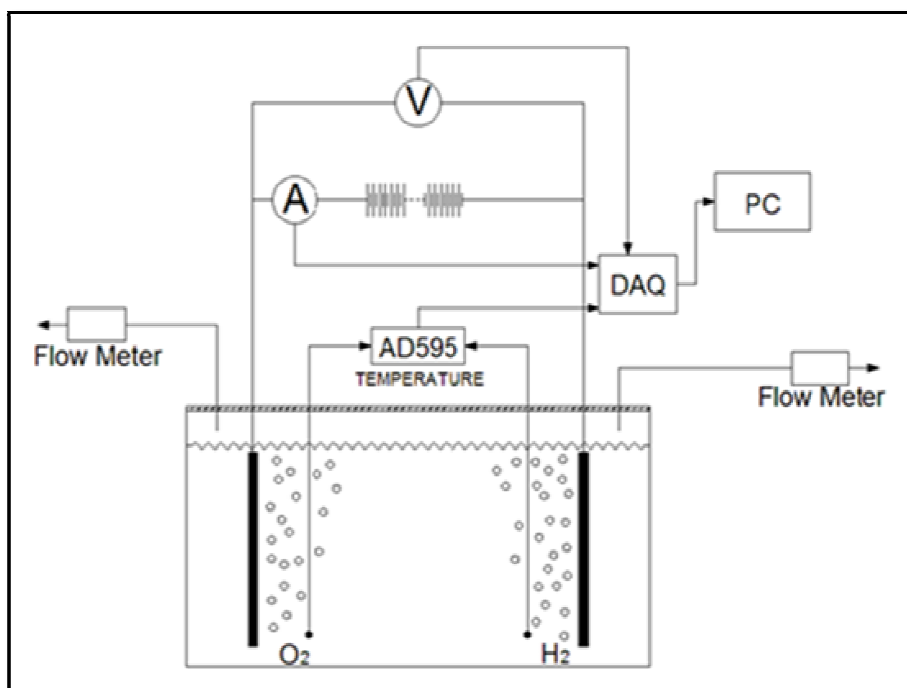


Figure B.1 Diagram of experimental apparatus

B.2 Experimental Setup

This section B.2.1 aims to conduct the correlation study of factors related to the hydrogen production rate by the alkaline electrolysis process using Design of Experiment (DOE) and statistic method. The water electrolysis of NaOH and NaCl aqueous solution is conducted under atmospheric pressure using alloy steel (stainless steel) as electrodes.. Parameters varied are current density, distance between electrodes and solution concentration without a separator as illustrated in figure B.1. Current, distance between electrodes and solution concentration are considered as input data and the hydrogen production rate as an output (Y). The levels adopted for factors are summarized in table B.1.

Table B.1 Levels of the factors

Factor	Number of Level	Value of Level
Concentration	5	0.1, 0.5, 1.0, 1.5, 2.0 (molL^{-1})
Current	5	5, 10, 20, 30, 40 (A)
Type of electrolyte	2	NaOH, NaCl
Distance of electrode	3	55, 100, 145 (mm.)

B.3 Experimental Design

Response surface methodology or RSM is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of a problem in which a response of interest is influenced by several variables and the objective is to optimize this response. The form of the relationship between the response (Y) and the factors (x_i) is given by Eq.B.1 which is called the second-order model. It is used for a polynomial of higher degree (Montgomery, 2001).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j} \beta_{ij} x_i x_j + \varepsilon \quad (\text{B.1})$$

where β_0 is the arithmetic mean value of the responses, β_i corresponds to the factor effects, β_{ii} is the quadratic effects and β_{ij} is the interactions between the various factors. The ε variable stands for the fitting error. Almost all RSM problems use one or both of these models. Of course, it is likely that a polynomial model will be a reasonable approximation of the true functional relationship over the entire space of the independent variables.

B.4 Results and Discussion

The results are consists of the analysis of correlation of parameters, in particular, the significance of the regression model obtained from the experimental data and the effect of direct current, concentration, temperature, flowing electrolyte, materials, frequency and duty cycle influencing on hydrogen production and improvement the electrolysis process the electrolysis process. Which a correlation study of parameters affecting hydrogen production discusses the relationship of concentration, current, distance between electrodes and solution temperature influencing on hydrogen through statistical analysis. Taking the number of factors and levels into account, the full factorial design includes $5 \times 5 \times 3 \times 3 = 225$ experiments for NaOH and NaCl electrolyte.

B.4.1 NaOH Electrolyte

The shorter distance between electrodes resulted in smaller resistance. It was found that distance between electrodes varies with the electrolyte resistance but the results of statistical calculations showed that the significant changes of distance between

electrodes give insignificant values of the hydrogen production rate as shown in figure B.2 with significant level at 0.05. As a consequence, this can be used to improve the design of the electrolyzer and to maintain the electrolyte with the high conductivity. Figure B.2 shows the estimation of regression coefficients, T-score and P-value between the hydrogen production rate, and three important factors, including current density, concentration, distance between electrodes and others. The coefficient of factors taken into consideration is determined by the P-value which is less than the significance level of 0.05. Factors analysis of current density and concentration without the distance between electrodes are shown in figure B.3. Effects of current density and solution concentration on hydrogen production rate are shown in Eq. B.2.

$$Y = 0.1821A + 5.8435B - 0.0804A^2 - 33.0744B^2 + 0.9367AB \quad (\text{B.2})$$

where A is the concentration of the solution (mol l^{-1}), B is the current density (Amm^{-2}), and Y is the hydrogen production rate (Lmin^{-1}).

Estimated Regression Coefficients for Rate(L/min)						
Term	Coef	SE Coef	T	P		
Constant	-0.1209	0.03267	-3.700	0.000		Line1
Current density	5.9404	0.39758	14.941	0.000		Line2
Dis	0.0011	0.00059	1.819	0.070		Line3
Conc	0.1782	0.02004	8.888	0.000		Line4
Current density*Current density	-33.0744	2.44226	-13.543	0.000		Line5
Dis*Dis	-0.0000	0.00000	-0.214	0.831		Line6
Conc*Conc	-0.0004	0.00721	-11.149	0.000		Line7
Current density*Dis	-0.0010	0.00192	-0.506	0.614		Line8
Current density*Conc	0.9367	0.10360	9.041	0.000		Line9
Dis*Conc	0.0000	0.00011	0.364	0.716		Line10
S = 0.04024 R-Sq = 90.5% R-Sq(adj) = 90.1%						

Figure B.2 The result of Response Surface Regression: Rate (Lmin^{-1}) versus Current density (Amm^{-2}), Distance (mm) and Concentration (mol l^{-1})

Estimated Regression Coefficients for Rate(L/min)						
Term	Coef	SE Coef	T	P		
Constant	-0.0204	0.01658	-1.233	0.219		Line1
Current density	5.8435	0.45789	12.762	0.000		Line2
Concentration	0.1821	0.02224	8.188	0.000		Line3
Current density*Current density	-33.0744	3.20986	-10.304	0.000		Line4
Concentration*Concentration	-0.0804	0.00948	-8.483	0.000		Line5
Current density*Concentration	0.9367	0.13616	6.879	0.000		Line6

S = 0.05289 R-Sq = 83.3% R-Sq(adj) = 82.9%

Figure B.3 The result of Response Surface Regression: Rate (Lmin⁻¹) versus Current density (Amm⁻²) and Concentration (molL⁻¹)

The model of Eq. B.2 is suitable for calculating the optimal hydrogen production rate of NaOH solution and the coefficient R^2 and adj- R^2 equal to 83.3% and 82.9%, respectively. Eq. B.2 is a correlation among the main factors and interaction factors that affect the hydrogen production rate. Therefore, Eq. B.2 is reliable when the current density and the solution concentration are in the considered range from 0.015 to 0.12 Amm⁻² and 0.1 to 2.0 molL⁻¹, respectively.

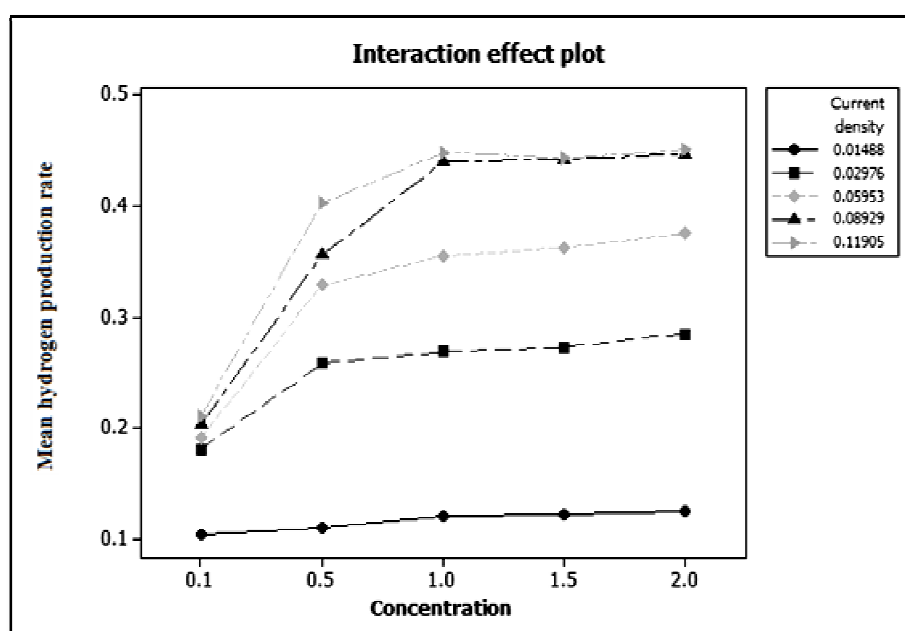


Figure B.4 The mean hydrogen production rate on the y axis by varying the concentration on the x axis

For the interaction factors affecting the hydrogen production rate, the results are shown in figures B.4 and B.5. It has been found that the interaction of co-factors effect contributes to the process of increasing gas quantities. Figure B.4 shows the mean

hydrogen production rate on the y axis by varying the concentration on the x axis. It has been observed that the higher current density and concentration result in a raise of hydrogen production rate. A variation of concentration affects the hydrogen production rate significantly in the range lower than 1.0 molL^{-1} . In addition, figure B.5 illustrates the optimum of hydrogen production rate and demonstrates the contour of response surface of hydrogen production rate where the level of the factors or the area in contour which is the amount of hydrogen production rate that occurs when the current density and concentration are fixed.

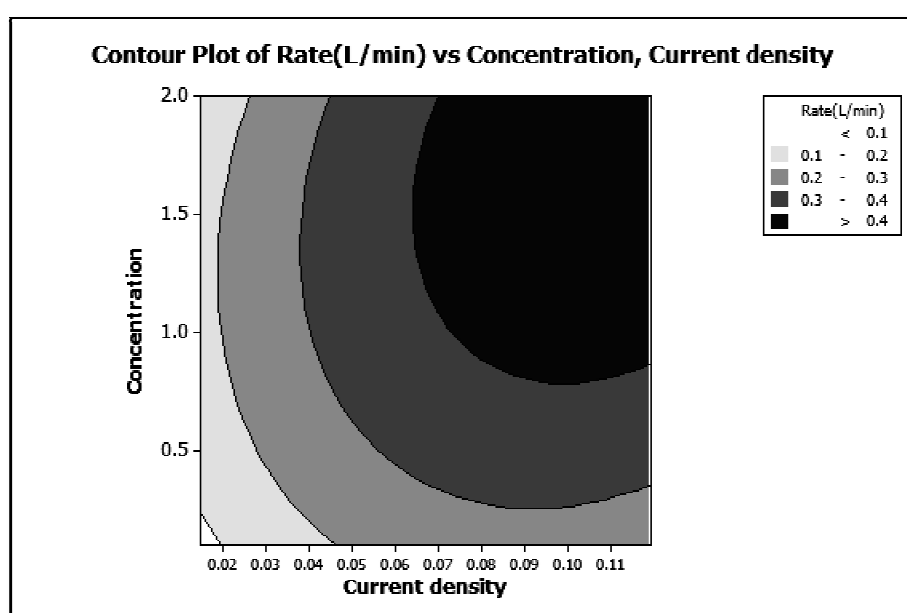


Figure B.5 The contour of a response surface of hydrogen production rate (Lmin^{-1})

B.4.2 NaCl Electrolyte

The results of statistical calculations showed that the significant changes of distance between electrodes give insignificant values of the hydrogen production rate similar to the results of NaOH and as shown in figure B.6 with significant level at 0.05.

Estimated Regression Coefficients for Rate(L/min)					
Term	Coef	SE Coef	T	P	
Constant	-0.0834	0.03139	-2.659	0.008	Line1
Current density	2.7670	0.38201	7.243	0.000	Line2
Distance	0.0011	0.00057	1.918	0.056	Line3
Concentration	0.1408	0.01926	7.310	0.000	Line4
Current density*Current density	-22.7581	2.34658	-9.698	0.000	Line5
Distance*Distance	-0.0000	0.00000	-1.218	0.224	Line6
Concentration*Concentration	-0.0866	0.00693	-12.502	0.000	Line7
Current density*Distance	0.0040	0.00184	2.166	0.031	Line8
Current density*Concentration	1.6646	0.09954	16.723	0.000	Line9
Distance*Concentration	0.0004	0.00010	4.300	0.000	Line10

S = 0.03867 R-Sq = 91.6% R-Sq(adj) = 91.3%

Figure B.6 The result of Response Surface Regression: Rate (Lmin^{-1}) versus Current density (Amm^{-2}), Distance (mm) and Concentration (moll^{-1})

Figure B.6 shows the estimation of regression coefficients, T-score and P-value between the hydrogen production rate, and three important factors, including current density, concentration, distance between electrodes and others. The coefficient of factors taken into consideration is determined by the P-value which is less than the significance level of 0.05. Factors analysis of current density and concentration without the distance between electrodes are shown in figure B.7.

Estimated Regression Coefficients for Rate(L/min)					
Term	Coef	SE Coef	T	P	
Constant	-0.0122	0.01830	-0.664	0.507	Line1
Current density	3.1657	0.50543	6.263	0.000	Line2
Concentration	0.1852	0.02455	7.544	0.000	Line3
Current density*Current density	-22.7581	3.54315	-6.423	0.000	Line4
Concentration*Concentration	-0.0866	0.01046	-8.280	0.000	Line5
Current density*Concentration	1.6646	0.15030	11.076	0.000	Line6

S = 0.05838 R-Sq = 80.6% R-Sq(adj) = 80.2%

Figure B.7 The result of Response Surface Regression: Rate (Lmin^{-1}) versus Current density (Amm^{-2}) and Concentration (moll^{-1})

Correlation of current density and solution concentration on hydrogen production rate are shown in Eq. B.3.

$$Y = 0.1852A + 3.1657B - 0.0866A^2 - 22.7581B^2 + 1.6646AB \quad (\text{B.3})$$

where A is the concentration of the solution (moll^{-1}), B is the current density (Amm^{-2}), and Y is the hydrogen production rate (Lmin^{-1}).

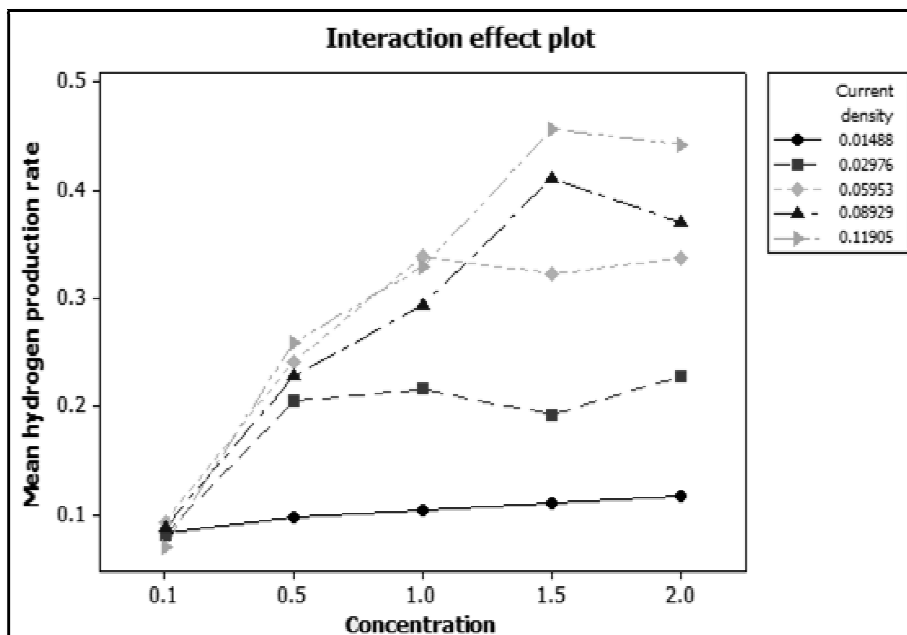


Figure B.8 The mean hydrogen production rate on the y axis by varying the concentration on the x axis

The model of Eq.B.3 is suitable for calculating the optimal hydrogen production rate of NaCl solution and the coefficient R^2 and adj- R^2 equal to 80.6% and 80.2%, respectively. Eq. B.3 is a correlation among the main factors and interaction factors that affect the hydrogen production rate. Therefore, Eq. B.3 is reliable when the current density and the solution concentration are in the considered range from 0.015 to 0.12 Amm-2 and 0.1 to 2.0 molL-1, respectively. For the interaction factors affecting the hydrogen production rate, the results are shown in figures B.8 and B.9. Figure B.8 illustrates the mean hydrogen production rate on the y axis by varying the concentration on the x axis. It has been found that the higher current density and concentration result in an increasing hydrogen production rate. A variation of concentration affects the hydrogen production rate significantly in the range lower than 1.0 molL-1. In addition, figure B.9 demonstrates the optimum of hydrogen production rate, the level of the factors or the area in contour which is the hydrogen production rate that occurs when the current density and concentration are fixed. The optimum of hydrogen production rate is more than 0.4 Lmin-1 at current density more than 0.09 Amm-2 and the solution temperature more than 1.5 molL-1, approximately.

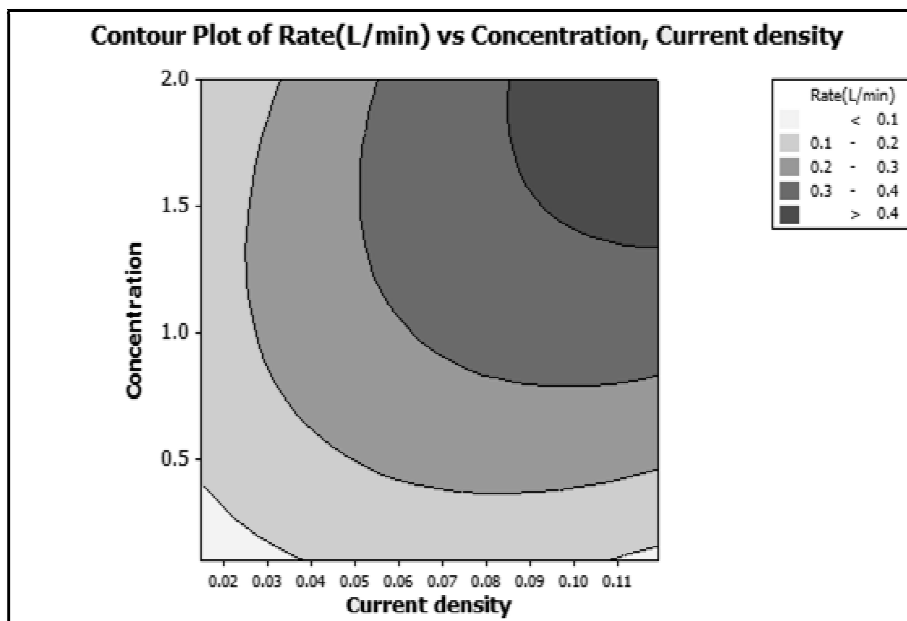


Figure B.9 The contour of a response surface of hydrogen production rate (Lmin^{-1})

In figure B.10, the mean hydrogen production rate on y axis is plotted against the concentration on x axis. It has been found that the change of NaOH concentration affects the incidence of hydrogen as well as that of NaCl. The hydrogen production rate increases gradually and approaches to a constant value at the higher concentration due to saturation of the solution. The hydrogen production rate develops gradually and approaches to a constant value at the higher concentration due to saturation of the solution.

B.4.3 Different of Electrolyte

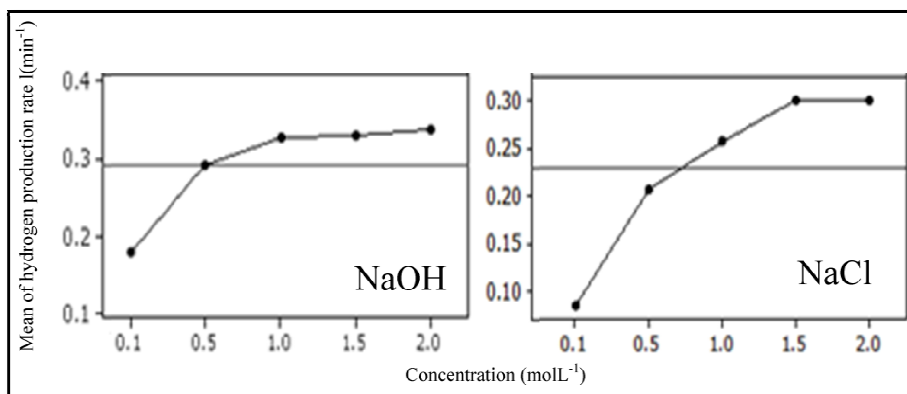


Figure B.10 Effect of concentration on hydrogen production rate

The amount of gas happened in the two types of electrolyte when the same current density and the concentration, it is found that the volume of gas has different. Hydrogen production rate of NaOH electrolyte is the higher than NaCl electrolyte because the ions conductivity of the solution have the ability to move to different. The conductivity of OH^- is higher than the conductivity of Cl^- , as mentioned in previous chapter. For Eqs. B.2 and B.3, it can be used to determine the relationship between the current density, concentration and hydrogen production rate in NaOH and NaCl, respectively. According to the experimental results, At the maximum hydrogen production rate, the efficiency of the system is 15.35% when 2.0 molL^{-1} NaOH solutions is used with the input electricity of 40 Amp and the distance between the electrodes is 145 mm. This is the best case of hydrogen production. The efficiency is calculated from $\eta = \text{HV} / (\text{Power input})$ where HV (Heating Value) is 121.0 MJkg^{-1} , volume of gas is 100 mL, density of gas at atmospheric is 0.0899 kg m^{-3} , voltage is 14.6 Volt and the time is 12.13 seconds. So HV is $(121.0 \times 10^3 \text{ (kJkg}^{-1})) \times (0.0001 \text{ (m}^3)) \times (0.0899 \text{ (kgm}^{-3}))$ which is equal to 1087.79 J, and the power input is $40 \text{ (Amp)} \times 14.6 \text{ (V)} \times 12.13 \text{ (s)}$ which is equal to 7083.92 kJ. For the worse case of hydrogen production, the efficiency of the system is 23.88%.

The optimization of hydrogen production rate is 0.4753 Lmin^{-1} at current density of 0.1124 Amm^{-2} and concentration of 1.7730 molL^{-1} which has been established based on the initial conditions where

current density = 0.01488 Amm^{-2} , concentration = 0.1 molL^{-1} and distance = 55mm.

The boundary conditions are

current density = 0.01488 Amm^{-2} , concentration = 0.1 molL^{-1} and distance = 55mm. and

current density = 0.11905 Amm^{-2} , concentration = 2.0 molL^{-1} and distance = 145mm.

It is noted that the distance between electrodes is fixed since it does not affect the hydrogen production rate as aforementioned.

B.5 Summary

The experimental design technique is used in this work to determine the correlation among relative factors through statistical methods. The correlation between hydrogen production rate and other factors: concentration, current density and distance between electrodes. The results unveil that the hydrogen production rate depends on three

parameters, which are the concentration, current density and distance between electrodes, respectively. Among several factors, it is found that the most important factor is the current density since a higher current density discharges a larger amount of electrons. These electrons take part in electrochemical reactions; thereby enhancing the amount of hydrogen production. In addition, the concentration is also important as it allows the convenient passage for ions and electrons.

When using NaOH, the color and appearance of the electrolyte before and after the reaction remains the same, but, for NaCl solution, large amount of sediments has been found in the solution as displayed in figure B.11. This is the result of a reaction between NaCl and the stainless steel 304 containing chromium.

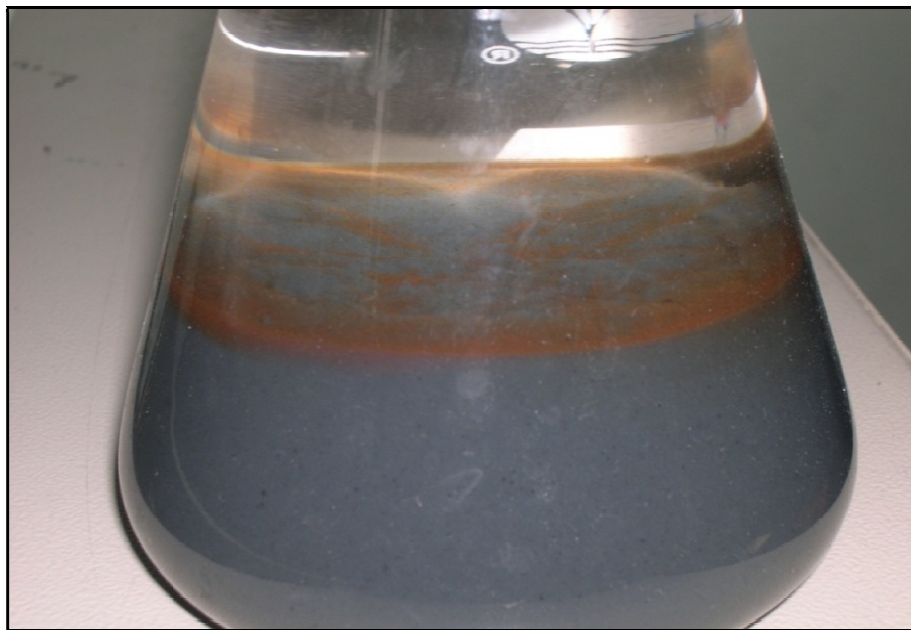


Figure B.11 Sediments in NaCl electrolyte

The electrode surface in NaOH electrolyte solution looks glossy but, for those in NaCl electrolyte solution, it can be observed that the anode trace of corrosion is occur red along the edges and the perimeter (outside) as shown in figure B.12. The cathode has not been changed insignificantly from the beginning of the experiment as appeared in figures B.13 and B.14 which shows the electrodes after the experiment.

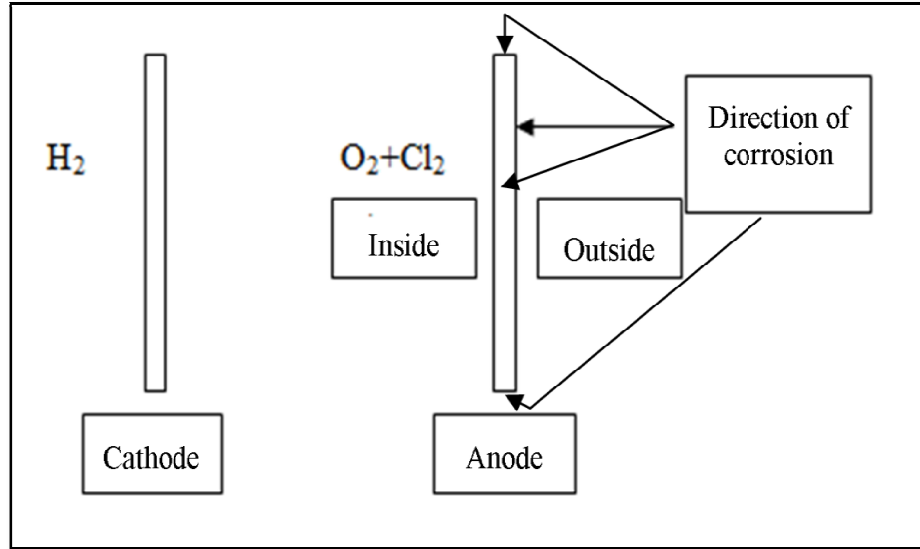


Figure B.12 Direction of corrosion on the anode side



Figure B.13 Outside of Anode



Figure B.14 Inside of Anode