CHAPTER 3 MODELING

This chapter focuses on research methodology and methods for modeling which describe how a mathematical model has been developed. It leads from an analysis of parameters to a model of system design. This chapter is divided into three sections, presenting models of the void fraction, conductivity and resistance. The factors associated with consist of the current density, temperature, diameter of bubble, height of electrode, distance between electrodes, operating time and concentration of ions which are presented in section 3.1. The analysis of modeling is presented in section 3.2 in which a detailed description of the relationship between variables and the factors affecting the void fraction, conductivity and resistance are contained. Finally, the conclusions are discussed in section 3.3.

3.1 Development the Mathematical Models

In this study, the mathematical model consists of two sections: 1) mathematical model of the conductivity and void fraction and 2) mathematical model of ionic resistance. The parameters affecting the change of the electrolyte conductivity consists of the transfer of charge, current flow in an electrolyte, the void fraction mainly focused on mixture of electrolyte and gas bubbles and physical parameters related to the electrolysis process.

3.1.1 Mathematical Model of the Conductivity and Void Fraction

This section presents the assumption and basic equations in the creation and development of the conductivity and void fraction model.

3.1.1.1 Model Assumptions

To calculate the electrolyte conductivity, assumptions are set up as follows:

- The calculation is in one dimension along the electrode height.
- The component of gas phase velocity is calculated by assuming that both hydrogen and oxygen transform into the gas phase and leave the free surface.
- Mass convection is neglected in this calculation.
- Two electrodes are in parallel; therefore, the ions velocity depends on the electric field strength distribution.
- Current density is constant along the electrode height.

- Ohmic resistance is low when compared with the reaction resistance.
- The surface area of the electrode is fixed at 100 cm^2.

3.1.1.2 Model of Conductivity

In the electrolysis process, gas bubble covering the electrode surfaces and ions transferring in the electrolyte are considered as charge transport resistances. The physical model of ohmic resistance is built on the Ohm's law as shown in Eq.3.1.

$$R = \frac{L}{\sigma_B A} \tag{3.1}$$

where R is the resistance of electrolyte, L is the distance between electrodes, A is the surface area of the electrode. The mixture conductivity (σ_B) is determined from the void fraction. It is decreased due to the presence of the gas in the electrolyte. The conductivity can be calculated using Bruggeman correction as expressed in Eq. 3.2.

$$\sigma_B = \sigma_0 (1 - \alpha_{total})^{1.5} \tag{3.2}$$

where σ_0 is the conductivity with no bubbles and α_{total} is the total void fraction.

In addition to the transport of charge, the current flow in an electrolyte is also accompanied by mass transfer. The species mass flux in dilute solution can be calculated using Planck-Nernst law. The conductance of the solution which is the reciprocal of the resistance, is given by Ohm's law. Under electroneutrality state and no current, I = 0 is set and σ_0 can be written as expressed in Eq. 3.3.

$$\sigma_0 = \frac{F^2 |Z_i|^2}{R'T} (C_{i+} D_{i+} + C_{i-} D_{i-}) \tag{3.3}$$

3.1.1.3 Model of Void Fraction

The bubble rise by their terminal speed ϑ_i refers to the bubbles per unit time leaving and entering the control volume as illustrated in figure 3.1. The number of bubbles has a differential equation in the control volume as described in Eq. 3.4.

$$\frac{dN}{dt} = (N_{i-1} - N_i)_i \frac{\vartheta_i}{\Delta y} + \dot{N}_{gen,i} \tag{3.4}$$

The void fraction of hydrogen and oxygen gas is proportional to the current, diameter of bubble, rising velocity of bubble and geometry of electrode. The volume flux of gas bubble between electrodes is related by the ideal gas law ($V_{gen,i} = \frac{n_i R'T}{P}$) and Faraday's law ($n_i = \frac{Q}{z_i F}$) where $Q = It$ and Q is charge (coulomb), I is current (A), t is time (s) and T is temperature (K). $N_{gen,i}$ can be related to the volume of gas $N_{gen,i} = \frac{V_{gen,i}}{V_{unit}}$ and $\dot{N}_{gen,i} = \frac{N_{gen,i}}{t}$. Under steady-state condition, $\frac{dN}{dt} = 0$ is assumed. It is noted that the amount of species i entering the control volume is equal to zero ($N_{i-1} = 0$) and by letting $\Delta y \rightarrow 0$, Eq. 3.4 can be written as expressed in Eq.3.5.

$$(N_{i,i}) = (\frac{\Delta y}{\vartheta_i})(\dot{N}_{gen,i}) \tag{3.5}$$

The species terminal velocity is a function of bubble diameter ($\vartheta_i = \frac{g d_b^2 \Delta\rho}{18\mu_L}$). The void fraction is equal to the volume of bubble per control volume as $\alpha_i = \frac{V_i}{V_{cv}}$.

The void fraction can be expressed by Eq. 3.6.

$$\alpha_i = \frac{\phi R'Ty}{Z_i FPX \vartheta_i} \tag{3.6}$$

Thus, the average void fraction of all species i equals to

$$\alpha_{av,total} = \frac{1}{H}\int_0^H \alpha \; dy = \frac{\phi R'TH}{FPX}\left[\frac{1}{Z_{H_2}\vartheta_{H_2}} + \frac{1}{Z_{O_2}\vartheta_{O_2}}\right] \tag{3.7}$$

Eq. 3.7 enables one to determine analytically the rate of gas bubbles motion with the void fraction.

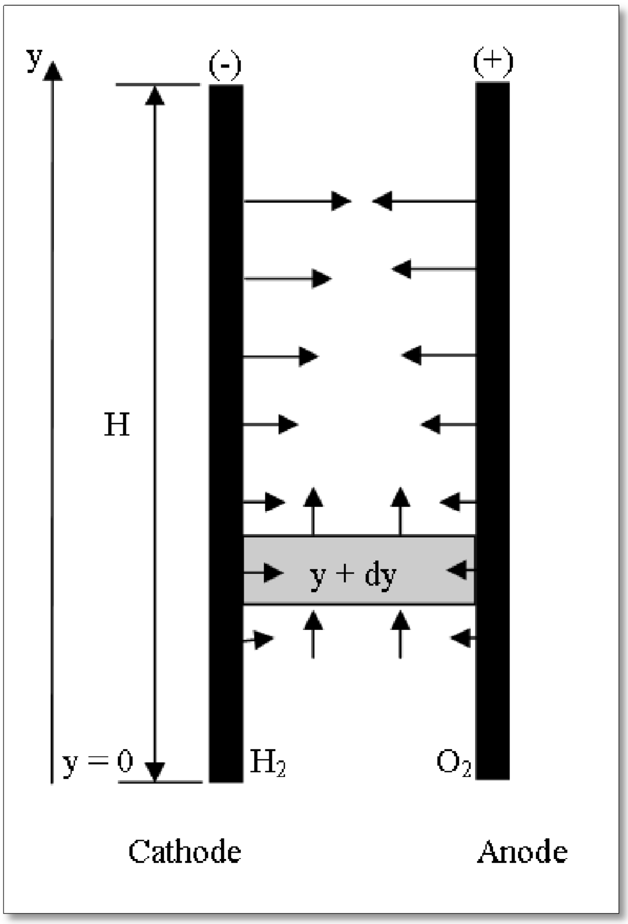

Figure 3.1 Control volume of the electrochemical cell

3.1.2 Mathematical Model of Ionic Resistance

In the electrochemical system, moving charges between electrodes and the electrolyte are two major types of charged species: electrons and ions. In most electrolyzers, due to its larger size, ion charge transport is far more difficult than electron charge transport, thereby resulting in the resistance to charge transport as a voltage loss. Because this voltage loss obeys Ohm's law, it is called an "ohmic", or "IR loss". Ohmic loss consists of resistance of electrodes (R_{elec}) and resistance of ionic (R_{ionic}) (electrolyte). Mathematical model has been developed in order to build the relationship between ionic resistance, distance between electrodes and charging time. Therefore, this section presents the assumption and basic equation in the creation and development of the ionic resistance model.

3.1.2.1 Model Assumptions

Figure 3.1 shows the schematic diagram of the molar conductivity of the electrolyte. The mathematical model of ionic resistance with material balance has been established based on the following assumptions:

- The mass diffusion in y and z directions is neglected.
- The concentration of the diffusing substance depends on the time and the coordination.
- Physical properties are

  $F = 96548 C \bullet mol^{-1}$

  $R = 8.314 J \bullet mol^{-1} K^{-1}$

  $Temperature = 298K$

  $\mu_{K^+} = 7.62 \times 10^{-4} cm \bullet V^{-1} \bullet S^{-1}$

  $\mu_{OH^-} = 2.05 \times 10^{-3} cm \bullet V^{-1} \bullet S^{-1}$

  $Z_{K^+} = Z_{OH^-} = 1$
- The models of mass migration, convection and membrane are neglected.

3.1.2.2 Model of Ionic Resistance

Electrolyte conductivity (σ) which permits the flow of charge is driven by an electric field. The electrolyte's conductivity is influenced by 2 parameters: a number of transport charge and the mobility of electrolyte. Electrolyte conductivity can be defined by Eq.3.8 (O'Hayre, 2009).

$$\sigma_i = (|Z_i| \cdot F) \cdot c_i \cdot u_i \tag{3.8}$$

where Z_i is the charge number, F is the Faraday's constant, c_i is the concentration of species j and u_i is carrier mobility.

For the simple case of a none-conducting electrolyte, the diffusion is dependent on the concentration of the diffusing substance, time and coordinates in the form of partial differential equations as shown in Eqs. 3.9 and 3.10 (Bagotsky, 2006, Bard and Faulkner, 2000, Crank, 1975, Koryta et al., 1993 and Zeng and Zhang, 2010).

$$\frac{\partial C}{\partial t} = D\nabla^2 C \qquad (3.9)$$

where C is the concentration, t is the time and D is the diffusion coefficient.
The concentration is a function of coordinates (x) and time (t). The initial condition is thus

$$x > 0\ ,\ t = 0\ ,\ C = C^0 \qquad (3.10)$$

And the boundary conditions are

$$\begin{aligned} x &= 0\ ,\ t > 0\ ,\ C = 0 \\ x &\to L\ ,\ t = 0\ ,\ C = C^0 \end{aligned} \qquad (3.11)$$

Solution of the differential Eq. 3.9 together with the initial and boundary conditions yields the relationship (Bagotsky, 2006, Bard and Faulkner, 2000, Crank, 1975 and Koryta et al., 1993) as shown in Eq. 3.12.

$$C(x,t) = C^0 \mathrm{erf}\left[\frac{x}{2D^{\frac{1}{2}}t^{\frac{1}{2}}}\right] \qquad (3.12)$$

where the error function y is defined by Eq. 3.13 and C(x,t) is the concentration of species at distance x at time t (Crank, 1975, Koryta et al., 1993).

$$\mathrm{erf}\,[y] = \frac{2}{\sqrt{\pi}}\int_{o}^{y} e^{-z^2}\,dz \qquad (3.13)$$

The diffusion coefficient (D) in Eqs. 3.9 and 3.12 is linked to the mobility of species j by the Einstein-Smoluchowski equation as shown in Eq. 3.14 (Bard and Faulkner, 2000).

$$D_j = \frac{u_j RT}{|Z_j| F} \tag{3.14}$$

where u_j is the mobility of species j, R is gas constant, T is the temperature.

The resistance of ionic solution can be modeled as a function of distance and time by deriving Eqs. 3.1 and 3.8 – 3.14 and expressed in Eq. 3.15.

$$R_{ionic,j}(x,t) = \frac{L}{A \times (|Z_i| F) u_i C_i(x,t)} \tag{3.15}$$

where

$$C_i(x,t) = C^0 - \frac{C^0 x^2 (\sqrt{\frac{x^2}{D}} \sqrt{D} \times \mathrm{erf}(\frac{1}{2} \frac{x}{\sqrt{T}\sqrt{D}}) - x}{\sqrt{\frac{x^6}{D^3}} D^{3/2}} \tag{3.16}$$

3.2 Results and Discussion

This section shows the effect of current density, temperature bubble diameter, height of electrode, distance between electrodes, operating time and concentration of ions on conductivity and resistance, respectively. Finally, the result of the model is also investigated with experiments.

3.2.1 The Conductivity Model and Void Fraction Model

Figure 3.2 shows the relationship between the solution temperature and the electrolyte conductivity. Generally, the higher solution temperature causes the increase of bubble volume and the decrease of reversible potential. In the meanwhile, the rise of bubble volume is related to both the direct enhance of void fraction and the reduction of driven force of ions in electric filed which results in the increase of void fraction. With the increase of void fraction, the conductivity of the electrolyte can be reduced since the path of charged ion is occupied by gas volume. Thus, the increasing of bubble volume leads to the moderation of the conductivity of the electrolyte. In addition, the raise of solution temperature also affects the decline of voltage of the system, resulting in a reduction of ionic conductivity. When considering the effect of current density, it can be found that the electrolyte conductivity of the higher current density is lower than the electrolyte conductivity of the lower current density since, at the higher current density, more amount of bubbles are occurred by the chemical reaction according to Faraday's law.

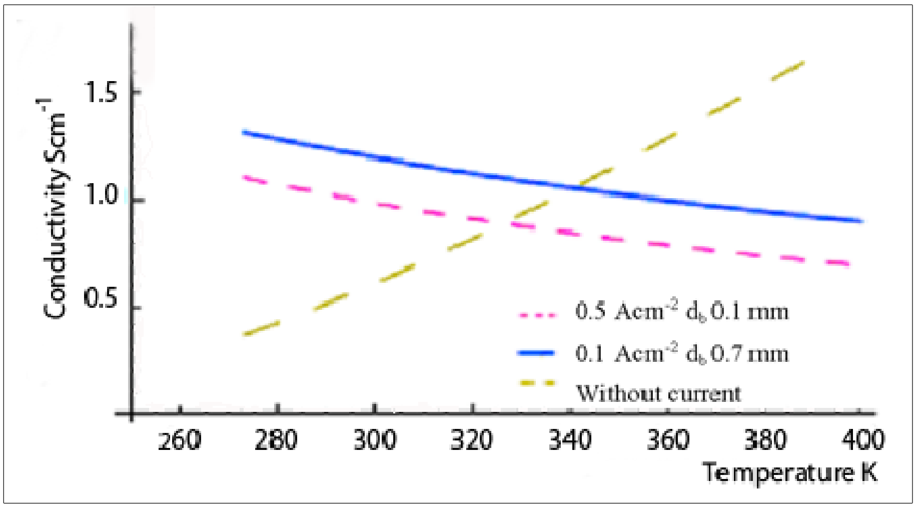

Figure 3.2 The relationship between the solution temperature and the electrolyte conductivity

In the case without current applied (Gilliam et al., 2007), the electrolyte conductivity is accrued with an increase of solution temperature since the bubbles are not presented in the electrolyte. Consequently, the ions in the electrolyte can move more conveniently at the higher kinetic energy with an increase of solution temperature.

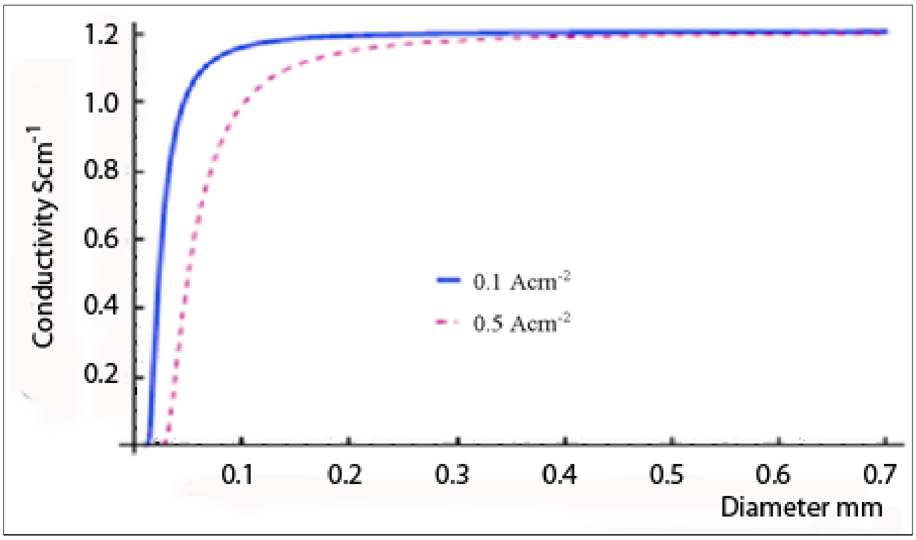

Figure 3.3 The relationship between the bubble size and the conductivity of the electrolyte

Figure 3.3 shows the relationship between the bubble size and the conductivity of the electrolyte at the pressure of 1 atm, solution temperature of 298 K and distance between electrodes of 20 cm. It has been found that the gas bubble in the range of 0.2 – 0.7 mm in diameter does not affect the conductivity of the electrolyte. However, for smaller bubbles, the diameter of bubble is related to the bubble rising speed. The smaller bubbles would move at slower velocity than the larger ones due to higher frictional force between the liquid and gas phases. Therefore, very small bubbles could cause a change in conductivity than those larger ones. From figure 3.3, it can also be seen that, when the current density is increased, the influence of diameter becomes more distinct. It can be implied that the conductivity drop due to gas evolution can be compensated by increasing the diameter of the bubbles. Sarkar et al. (2010) also discussed that the current density hardly has influence on the detachment diameter.

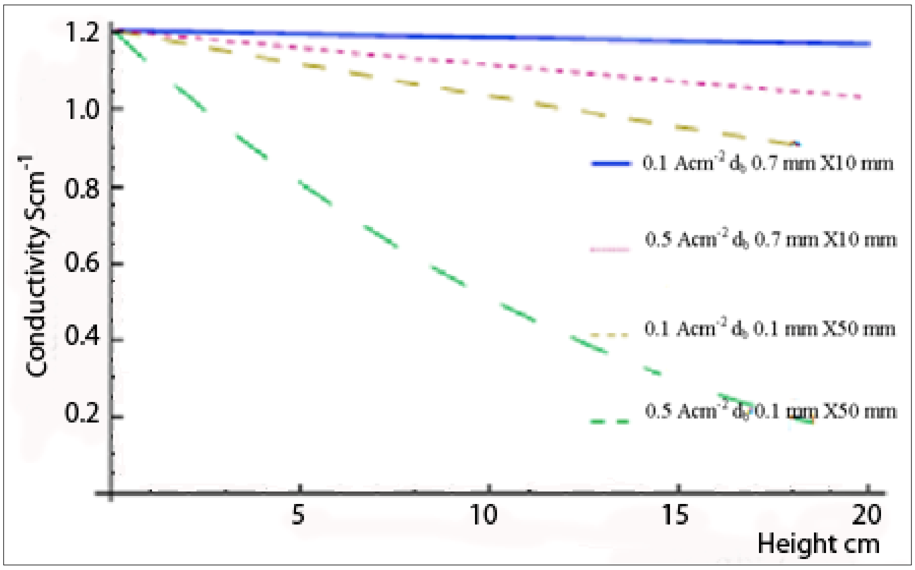

Figure 3.4 The relationship between the height of the electrodes and the conductivity of the electrolyte

Figure 3.4 shows the relationship between the height of the electrodes and the conductivity of the electrolyte. The surface area of the anode is fixed at 100 cm^2 and only the height of the electrode is varied as well as that of the cathode. It can be estimated that electrolyte conductivity at lower current density is higher than that of the higher current density at all range of current density because less gases are evolved in the electrolyte. In addition, when the electrode height is lengthened, the electrolyte conductivity is lessened due to gas bubbles evolve at the electrodes become inhomogeneously polarized as a result of the uneven gas phase distribution along the electrode. This is because the accumulation of gas bubbles is occurred on the electrode and, therefore, blocks the flow of electrical current.

3.2.2 Ionic Resistance Model

The model is employed to study the distribution of the concentration and conductivity of solution for ionic resistance in an alkaline water electrolysis. Figures 3.5 and 3.6 illustrate the distribution of ion concentration of K^+ and OH^- at electrode surface, respectively. At electrodes surface where x = 0 cm., the solvent concentration is zero and, afterwards, it is increased with the distance. Having compared figure 3.5 and figure 3.6, it has been found that at the same time the value of the solution concentration is not equal due to the fact that the ion diffusion coefficient value is based on the mobility of ion (u_j) as expressed in Eq.3.14.

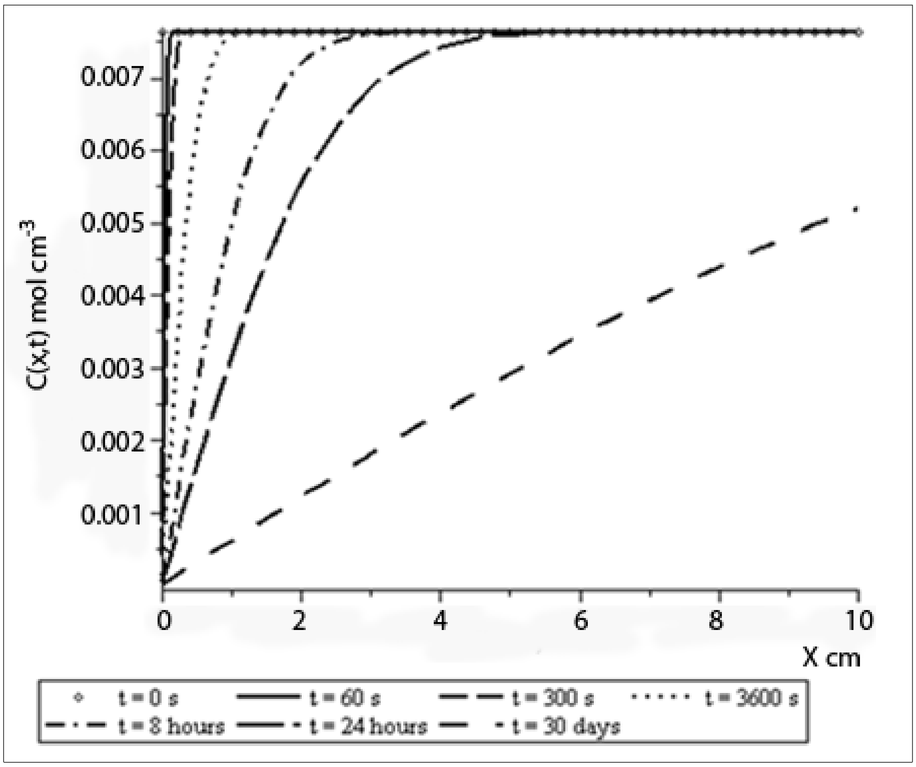

Figure 3.5 Concentration of K^+ at surface electrode

From figures 3.5 and 3.6, when operating with the longer period of time, the concentration gradient will be taken placed in the solution. The concentration layer thickness will vary depending on time of use. Initially, the concentration value of K^+ is the same as that of OH^- in the reaction. However,under a given period of time, it is found that the concentration of K^+ is greater than the concertration of OH^-, meaning that the concentration gradient layer thickess of K^+ is less than that of OH^-.

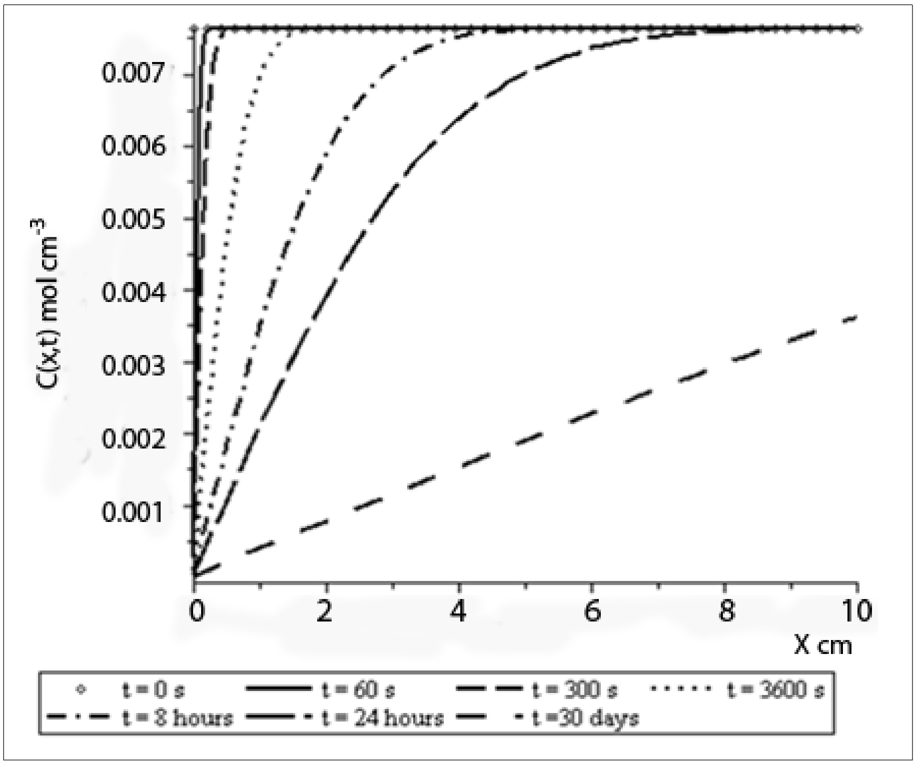

Figure 3.6 Concentration of OH^-

The relationship between conductivity and distance as expressed in Eq.3.8 can be plotted in figures 3.7 and 3.8. Figure 3.7 depicts the conductivity of K^+ and OH^-. The conductivity of OH^- (1.51 Ωcm^{-1}) is higher than the conductivity of K^+ (0.56 Ωcm^{-1}). This is due to the influence of the higher mobility of OH^- resulting in the higher concentration as expressed in figures 3.5 and 3.6, respectively.

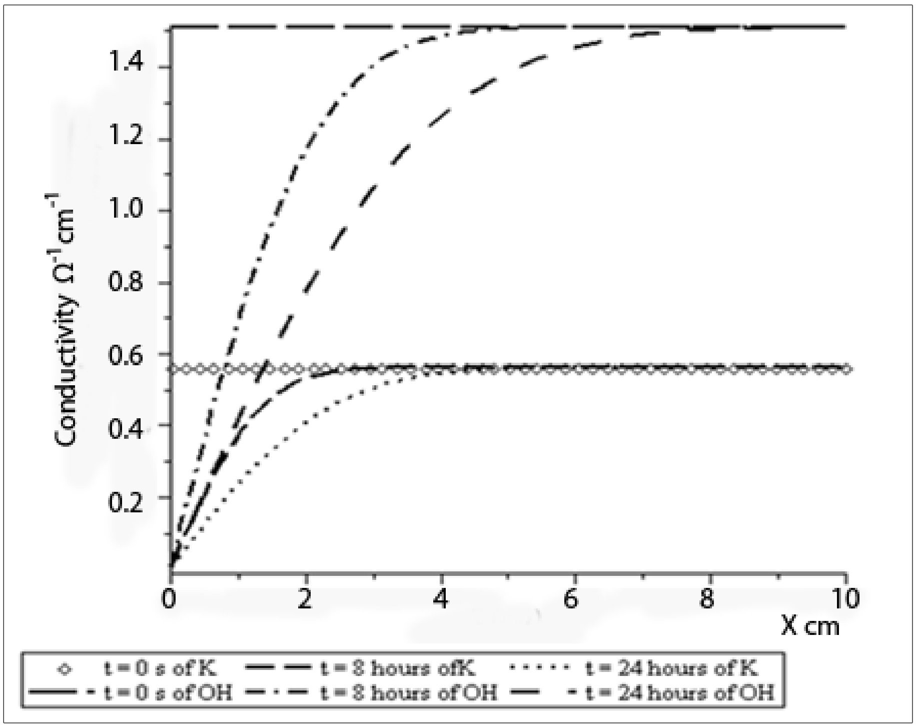

Figure 3.7 Conductivity of K^+ and OH^-

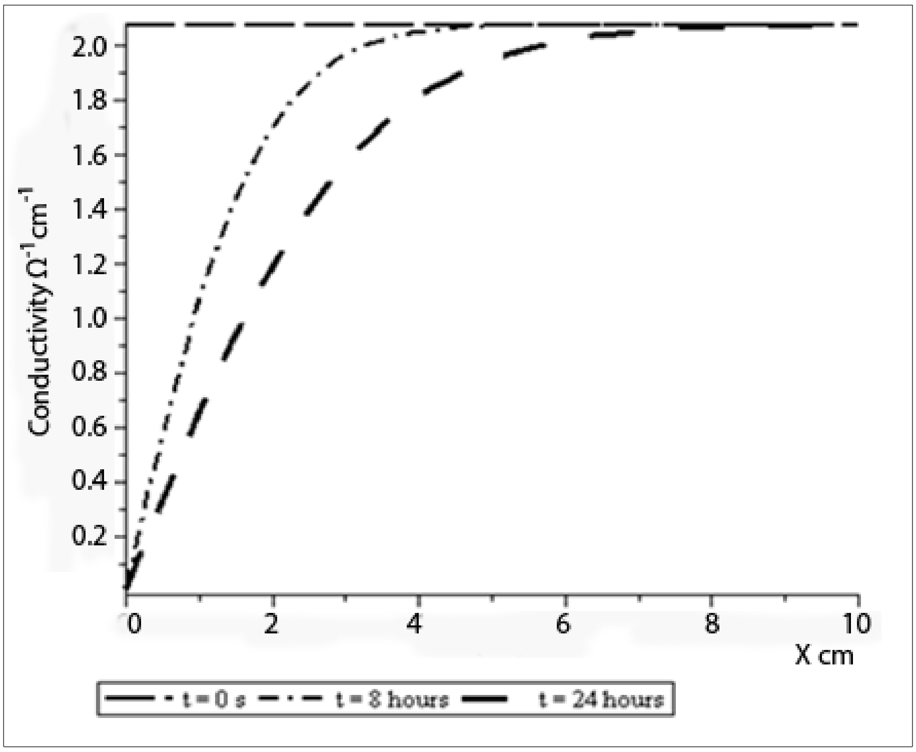

Figure 3.8 Conductivity of KOH solution

Figure 3.8 represents the total value of the electrolyte conductivity of the two ion species (K^+ and OH^-). Electrical conductivity values in the solution at starting time (t =

0) is equal to 2.07 Ωcm^{-1}. Up until 8 hours, electrical conductivity of solution at electrode surface (distance (X) = 0 cm.) is equal to zero. An increase of the distance from the electrode surface raises the solution conductivity abruptly until it reaches 2.07 Ωcm^{-1} at 5 cm. Subsequently, the conductivity is equal to an initial value at 2.07 Ωcm^{-1}. For the time up to 24 hours, electrical conductivity behaves similarly and will enter steady state when the distance is 9 cm approximately.

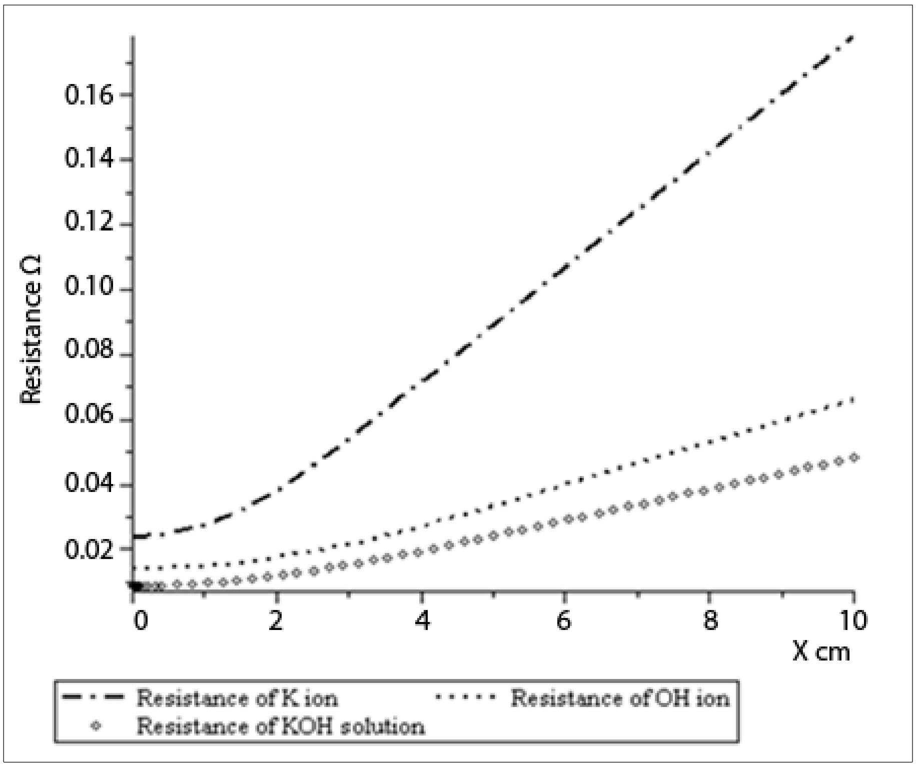

Figure 3.9 Ionic resistances over time up to 8 hours

From Eq. 3.1, the surface area is 100 cm^2, length (L) is in the range 0 to 10 cm, the temperature is 298 K and the conductivity of solution is derived from Eq.3.8. The relationship between the electrolyte resistance and the distance between electrode surface is shown in figure 3.9. It can be inferred that the resistance of solution of K^+ is higher than that of solution of OH^-. When the two ion species combine together, the total resistance is decreased since the two ions help to transmit current. It is also found that the relationship between the resistance and the distance is non-linear in the range of 0-3 cm because the solution concentration closed to the electrode surface forms the concentration gradient. Apart from 0-3 cm, between 3-10 cm, the linear relationship is found due to a constant solution concentration. As a result, the resistance depends on the length or distance between of electrodes.

3.2.3 Modeling Validation

This section aims to validate the electrolyte conductivity and empirical models and to compare them with the experimental results. The numerical model gives a relation to the equations of the physical property, while the empirical model is presented with the aim of confirming the numerical results. The water electrolysis of 20% KOH aqueous solution is conducted under atmospheric pressure using alloy steel as electrodes without a separator as illustrated in figure 3.10. Parameters varied are current, and solution temperature as shown in table 3.1. Since it is difficult to directly determine the value of local electrolyte conductivity and void fraction from on-time experiment, the void fraction is compared with the data obtained from gas flow rate measurement. The flow rate multiplied by time is equal to the amount of gas produced as explained by Eq.3.17.

$$\alpha_{Gas} = \frac{GasFlowRate \times Time}{(GasFlowRate \times Time) + V_L} \tag{3.17}$$

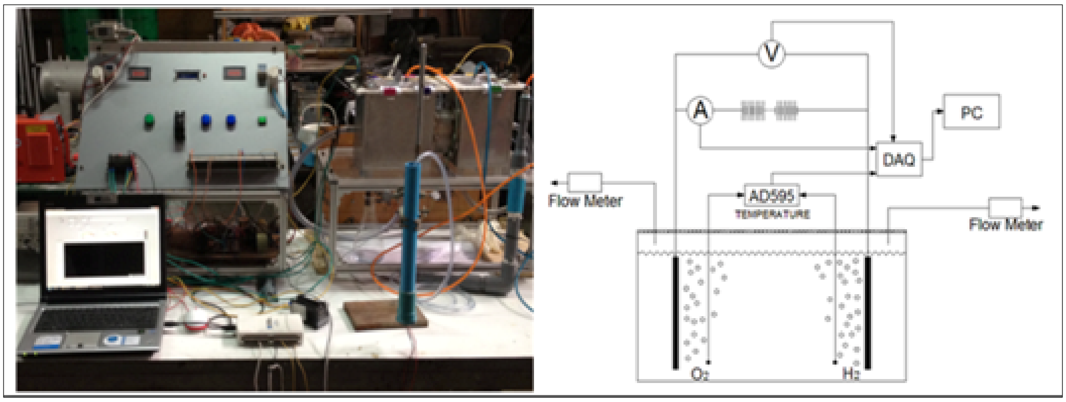

Figure 3.10 Diagram of experimental apparatus

The response *Y* is dependent on k, for $X_1, X_2, \ldots, X_k$. The relationship between these variables is characterized by a mathematical model called a regression model which presents the results of an experiment. The fitting regression model develops an empirical model relating the amount of current and the electrolyte temperature. The levels adopted for factors are summarized in table 3.1. Regression model 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 a response of interest is then optimized. The form of the relationship between the response (*Y*) and the factors (X_i) is given by Eq. 3.18.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \varepsilon \tag{3.18}$$

where β_0 is the arithmetic mean value of the responses, β_i corresponds to the factor effects, and ε stands for the fitting error. In this study, current and solution temperature are considered as input data and the void fraction as an output (*Y*). It is likely that a model will be a reasonable approximation of the true functional relationship over the entire space of the independent variables.

Table 3.1 Experimental conditions

Factor	Number of Level	Value of Level
Current	3	30, 40, 50 (A)
Solution temperature	4	313, 323, 333, 343 (K)
Pressure		Atmospheric
Electrodes	Material	alloy steel
	Distance between electrodes	X = 20 cm.
	Height	H = 10 cm.
	Width	W = 10 cm.
Electrolyte	KOH	20% wt

The results are divided in two parts: the first part consists of the analysis of experimental data, in particular, the significance of the regression model obtained from the experimental data and the second part focuses on the mathematical model. Table 3.2 shows the estimation of regression coefficients, T-score and P-value between the void fraction and two factors, including the current and solution temperature. The linear regression of the measured data shows the best fitting. Factor analysis of the current and solution temperature is shown in Eq. 3.19.

$$\text{Void fraction} = -0.00146 + 0.00011048\,A + 0.00003404B \qquad (3.19)$$

where A is the current (A.) and B is the solution temperature (K).

Table 3.2 Regression model of void fraction

Terms	Coefficients	T-score	P-value
Constant	- 0.00146	-5.30	0.000
Current	0.00011048	22.98	0.000
Solution temperature	0.00003404	9.7	0.000
	S= 0.000235506	R-Sq = 95.0%	R-Sq(adj) = 94.7%

Note P-value <0.05 is significant.

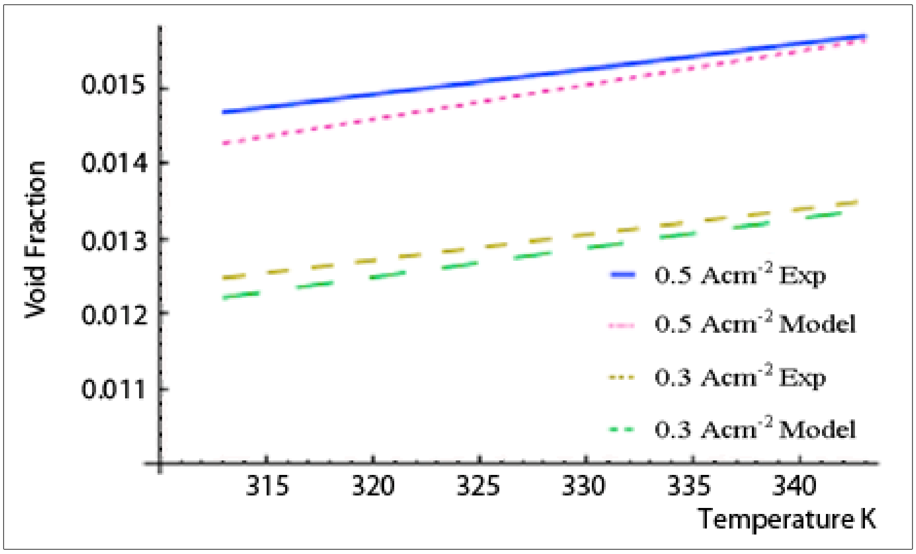

Figure 3.11 Comparisons between experimental and modeling results

Figure 3.11 presents the experimental results of void fraction obtained from the gas flow rate measurement method compared with the mathematical results. It can be seen that void fraction is increased linearly with an increase of solution temperature due to the rise of solution temperature affecting the reaction rate of the electrolysis process. The experimental data show a good fit over the complete solution temperature range with a relative difference of 2.16% at 313 K and 0.85% at 343 K of 0.3 A/cm^2. At 0.5 A/cm^2, a relative difference of 2.87% can be found at 313 K and 0.39% at 343 K. It is clearly seen that the mathematical model is capable of predicting void fraction in the electrolysis cell.

3.3 Summary

A mathematical model of the electrolyte conductivity between two electrodes has been developed based on a combination of electrolyte conductivity, void fraction and velocity of bubble rising in a liquid. The mathematical results show that the drop of the electrical conductivity is caused by an increase of solution temperature and the height of electrode. On the other hand, an increase of bubble diameter results in an increase of conductivity. The electrolyte conductivity has effects on the performance of an alkaline water electrolyzer.

Model of ionic resistance has analyzed and evaluated the behavior of a solution resistance with mass diffusion of concentration depending on time and distance between electrodes in an alkaline electrolyzer at room temperature, without migration and convection. It is found that the solution resistance is raised up as time and the distance between electrodes are increased. This results in an increase of ohmic loss at the electrolyte.

For validation, the Design of Experiment technique along with statistical method is used to develop the empirical model to investigate the correlation between void fraction, current and solution temperature. Subsequently, the mathematical results are compared with the experimental results where the void fraction obtained from the model agrees well with those obtained from the experimental results.