A mathematical model for hydrogen evolution in an electrochemical cell and experimental validation

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Abstract

Electrochemical reaction is largely employed in various industrial areas such as hydrogen production, chlorate process, electroplating, metal purification etc. Most of these processes often take place with gas evaluation on the electrodes. Presence of gas phase in the liquid phase makes the problem two-phase flow which is much knowledge available from heat transfer and fluid mechanics studies. The motivation of this study is to investigate hydrogen release in an electrolysis processes from two-phase flow point of view and investigate effect of gas release on the electrolysis process.

Hydrogen evolution, flow field and current density distribution in an electrochemical cell are investigated with a two-phase flow model. The mathematical model involves solutions of transport equations for the variables of each phase with allowance for inter phase transfer of mass and momentum.

An experimental set-up is established to collect data to validate and improve the mathematical model. Void fraction is determined from measurement of resistivity changes in the system due to the presence of bubbles. A good agreement is obtained between numerical results and experimental data.

Keywords: Water Electrolysis, Two-Phase Flow, Void Fraction, Resistivity Measurements

INTRODUCTION

Bubble evolving electrodes have various practical applications such as in electroplating, hydrogen production, chlorine production etc. Bubbles nucleate on the electrodes when the gas concentration exceeds super saturation level and depart from the surface after its size grows over a critical size. Bubbles significantly affect mass transfer, flow field, the conductivity of bulk electrolyte and macroscopic current density distribution which is curial in determination of the reaction rate. A two-phase mathematical model is employed in this study to investigate effect of bubbles on the performance of electrolyzer process.

There are a number of experimental and theoretical studies in the literature investigating various aspects of electrochemical cells. Voght [1] has conducted extensive experiments for gas release behavior in the electrochemical systems. Vogt showed that bubble nucleation and departure are a strong function of current density and several distinct mechanisms can be observed depending the current density. At low current density molecular diffusion dominates on the bubble behavior. At higher current densities, bubbles grow with the gas not only coming from electrochemical reaction also dissolved gas from the surrounding electrolyte.

Reigel et al.[2] experimentally investigated flow regimes, bubble distribution in a vertical gas evolving cell. A reference electrode is used to determine local voltage distribution in the cell and employed Maxwell [3] equation for void fraction calculation. They have shown that at higher density a back-flow form and adversely affect the performance of the system.

Boissanneau and Byrne [4] investigated velocity field in an electrochemical cell with vertical electrodes for chlorine production. Advance measurement system such Laser Doppler Anemometry and particle image velocity meter is employed to determine flow field. They showed that although flow is laminar in terms of Reynolds number range considered. Bubbles cause local turbulence causing velocity fluctuations due to the interactions with continuous phase. Therefore, both laminar and turbulent regimes exist in the system. In a resent experimental Nagai et al.[5] investigated several process parameters such as temperature, height of the electrodes and space between the electrodes on the performance of the cell. They found that smaller space between the electrodes decreases the efficiency of the system.
Gas evolution at electrodes has similarities with boiling at a heating surface. Therefore some useful theories, formulations may be benefited to study details of gas – liquid interaction, mass transfer, bubble – nucleation and break up and flow induced by the large density differences between bubbles and liquid phase in the electrochemical systems. Recently, Vogt et al. [6] analyzed the limits of analogy between boiling and gas evolution at electrodes. They concluded although there are many similarities between two processes, both processes has their own distinct properties and are not analogous. For example while a significant heat transfer takes place from heating surface during boiling, a reactant is transferred from the liquid to the electrode. They found that gas evolution at electrodes is 6 orders of magnitude larger than those of boiling case.

The presence of gas bubbles in the liquid (or electrolyte) makes the problem a two – phase flow problem which many studies are available in the literature. Mainly two models are employed in the literature for bubbly two phase flow where number of bubbles is more than individual tracking. The first model employs separate transport equation for both phases and closure relations for exchange of momentum and mass between both phases. The second model treats both phases as a single phase (ie, a mixture) and only a set of transport equations are solved.

Using Ishii’s drift flux model Ziegler and Evans[7] calculated mass transfer, void fraction distribution and velocity field. Dahlilkild [8] extended the drift flux model to an electro chemical cell where only a single electrode is considered and employed empirical models developed for particle transport in a sheared and sedimenting suspension to describe bubble distribution in the liquid phase. A non uniform current density distribution is estimated along the electrode. The model was successful investigating the details of non-linear boundary condition mainly due to the electrode kinetics.

Although there are numerous mathematical modeling studies in the literature only limited studies consider liquid and bubbles as a separate phases and effects of bubble dynamics on flow, current distribution and efficiency of gas evolution. Mat et al [9,10] developed a mathematical model based on a two-fluid model which both liquid and gas phases are considered as separate fluids and transport equations are solved for both phases. Mat et al [9,10] applied this model to forced and natural convection systems, however model has not been validated with experimental data. The purpose of this study is to establish an experimental set up to collect data and compare with results of mathematical model. Specifically two-phase region and gas evolution determined with an image processing route and void fraction is determined with resistivity measurement.

2. Mathematical Model

The schematic sketch of electrochemical system considered is given in Figure 1. System consists of two electrodes namely cathode and anode which are located on right and left wall of the cavity respectively and an electrolyte which is a dilute solution of KOH. KOH dissociate into K⁺ and OH⁻ ions and hydrogen gas evolves at the cathode while oxygen gas forms at the anode according to following electro-chemical reactions:

**At the cathode**

\[ 4H_2O + 4e^- \rightarrow 2H_2(gas) + 4OH^- \]  \hspace{1cm} (1)

**At the anode**

\[ 4OH^- \rightarrow O_2(gas) + 4e^- + 2H_2O \]  \hspace{1cm} (2)

We assume a uniform gas production over the electrodes, but decrease in gas production rate due the presence of bubbles is accounted by increasing the resistivity of electrolyte. The hydrogen and oxygen gas are allowed to leave the cell from top of the cavity. The flow in the system is generated due to the density difference between the liquid and gaseous phase. To represent the flow behavior and mass transfer in the system a two phase mixture of liquid and gas is considered. Gas evolution is assumed to occur at steady state. The phases are assumed to share space in proportion to their existence probabilities such that their volume fractions sums to unity in the flow field, thus;

\[ \alpha_L + \alpha_G = 1 \]  \hspace{1cm} (3)

where \( \alpha_L \) and \( \alpha_G \) are the volume fraction of liquid and gas respectively. The zone averaged quantities are obtained through solution of separate transport equations for each phase.
Within this framework the governing equations for two phase flow can be expressed in Cartesian coordinate as follows:

**Mass Conservation**

\[
\frac{\partial}{\partial y} \left( \rho_i a_i v_i \right) + \frac{\partial}{\partial z} \left( \rho_i a_i w_i \right) = M_{\text{int}}
\]  

(4)

where subscripts, i and j represent the phases and take the value of L,G in this problem. Subscripts L and G refer to liquid and gas phases, respectively, in this and subsequent formulations. The term on the right of the equation represents mass diffusion between two phases at electrolyte-gas interface.

**y- Momentum**

\[
\frac{\partial}{\partial y} \left( \rho_i a_i v_i^2 \right) + \frac{\partial}{\partial z} \left( \rho_i a_i v_i w_i \right) = -a_i \frac{\partial p}{\partial y} + F_i (v_i - v_j) + \frac{\partial}{\partial y} \left( a_i \mu_i \frac{\partial v_i}{\partial y} \right) + \frac{\partial}{\partial z} \left( a_i \mu_i \frac{\partial v_i}{\partial z} \right)
\]  

(5)

**z- Momentum**

\[
\frac{\partial}{\partial y} \left( \rho_i a_i v_i w_i \right) + \frac{\partial}{\partial z} \left( \rho_i a_i w_i^2 \right) = -a_i \frac{\partial p}{\partial z} + F_i (w_j - w_i) + \frac{\partial}{\partial y} \left( a_i \mu_i \frac{\partial w_i}{\partial y} \right) + \frac{\partial}{\partial z} \left( a_i \mu_i \frac{\partial w_i}{\partial z} \right) + F_f
\]  

(6)

\( F_f \) in both momentum equations is interface friction term and represents momentum exchange between the phases per unit volume and \( F_b = \rho g \) is the buoyancy force where \( g \) being the gravity vector.

**Auxiliary Equations**

Interphase friction term, \( F_f \) in momentum equations can be expressed as:

\[
F_f = 0.75 \frac{c_d}{d_b} \rho_i a_i \frac{\alpha_L \alpha_G}{\mu_i} |u_i|
\]  

(7)
where \( u_r \) is the slip velocity vector between two phases, \( d_b \) is the bubble diameter and \( c_d \) is the drag coefficient. There are extensive works on the drag coefficient in the literature. The “Dirty water” model of Kuo and Wallis [11] is employed here. In this model:

\[
c_d = \begin{cases} 
6.3/Re_b^{0.385} & Re_b > 100, \ We \leq 8 \\
2.67 & Re_b > 100, \ We > 8 \\
We/3.0 & Re_b > 2065.1/We^{2.6}
\end{cases}
\]  

(8)

where \( Re_b \) is the Reynolds number based on the gas bubble diameter, 

\[
Re_b = \frac{\rho_l \ |u_r| \ d_b}{\mu_l}
\]

(9) 

and \( We \) is the Weber number defined as:

\[
We = \frac{\rho_l \ |u_r|^2 \ d_b}{\gamma}
\]

(10) 

where \( \gamma \) is the interfacial tension between the phases.  
It is seen that the bubble diameter \( d_b \) is an important parameter determining interphase friction between two phases.  

The species mass flux in dilute solution can be calculated using Planck-Nernst law expressed as:

\[
N_i = C_i U - D_i \nabla C_i - \frac{Z_i F D Z}{RT} C_i \nabla \phi
\]

(11)

where \( C_i \), \( D_i \), \( Z_i \) are concentration diffusivity and charge number of species \( i \) respectively. \( \phi \) represent the electric potential. \( U \) is the velocity vector for the solvent. The first, second and third terms represent the convective, diffusive and migration contribution of mass flux respectively. 

The current density \( i \) in the electrolyte can be calculated by employing the Faraday’s law;

\[
i = F \left(Z_1 N_1 + Z_2 N_2\right)
\]

(12)

The current conservation can be expressed as;

\[
\frac{\partial i}{\partial y} + \frac{\partial i}{\partial z} = 0
\]

(13)

and similarly ionic species conservation can also be given as

\[
\frac{\partial N_i}{\partial y} + \frac{\partial N_i}{\partial z} = 0
\]

(14)

the electroneutrality condition for binary electrolyte can be expressed as;

\[
Z_1 C_1 + Z_2 C_2 = 0
\]

(15)

The electrical conductivity of the electrolyte is defined as;

\[
\sigma_0 = \sum_{i=1}^{N} \frac{Z_i^2 F^2 D_i}{RT} C_i
\]

(16)
The electrical conductivity will decrease due to the presence of the gas in the system. The effective conductivity is calculated using Bruggeman correction

$$\sigma = \sigma_0 (1 - \alpha)^{3/2}$$  \hspace{1cm} (17)

Similarly, diffusion coefficients for each ionic species are also modified as

$$D_i = D_{i,0} (1 - \alpha)^{3/2}$$  \hspace{1cm} (18)

the subindice “o” represent the values in pure electrolyte.

Boundary Conditions

A no–slip condition is applied on electrode surfaces (i.e. vertical walls) for the liquid phase and tangential velocity for the gas phases which are expressed mathematically as:

$$w_L = w_a = 0 \quad v_L = 0 \quad \text{at} \quad y=0 \text{ and } y=L, \quad 0 \leq z \leq H \quad (19)$$

The normal component of gas phase velocity is calculated assuming all hydrogen and oxygen released transform into the gaseous phase and employing Faraday’s law. Thus normal velocity component at the cathode (hydrogen producing electrode);

$$v_a = \frac{1}{2} \frac{RT}{\alpha P_{H_2}} = \frac{1}{4} \frac{RT}{P}$$ \hspace{1cm} (20)

where $T, R, P, F$ are temperature (assumed to be constant in this study), universal gas constant, pressure of gaseous phase and Faraday constant respectively. The multiplication of normal velocity with electrode surface area gives volumetric production hydrogen gas.

Similarly the normal component of gas velocity at the anode side is calculated as:

$$v_a = \frac{1}{4} \frac{RT}{P}$$ \hspace{1cm} (21)

Factors 2 and 4 in Equations 20 and 21 represent the number of electrons taking place in the electrochemical reaction at the electrode surfaces.

There is two ions which are positive [K$^+$] and negative [OH$^-$] ions exist in the system. Since the positive ions does not involve in the electrochemical reaction at the electrode surfaces then for positive ions at two vertical walls.

The current density $i(z)$ calculated as;

$$i_z = -i^o (1 - \alpha) \exp \left( - \frac{F}{2RT} \eta \right)$$  \hspace{1cm} (22)

where $i^o$ is the exchange current density $(1-\alpha)$ represent the reduction of active electrode area due to bubbles on the electrode surface $\eta$ is the over potential calculated as;

$$\eta = \phi$$  \hspace{1cm} (23)

The gas is assumed to leave the free surface at rate it reaches the surface therefore the axial gradient of the volume fraction of the gaseous phase vanishes at the top surface. In addition, a fixed pressure condition is imposed such that the velocities are calculated from the need to satisfy mass conservation at the computational cell adjacent to the surface.

Numerical Method

The coupled governing partial differential equations are solved with an iterative and finite domain solution procedure embodied in PHOENICS [12] computational code. The governing equations are integrated over a control volume which flow domain is divided and following algebraic equation is obtained.
In which a’s represent convection and diffusion coefficient and subscripts W, E, S, N represent west, east, south and north of node P. $I_\phi$ represent the volumetric fluid interaction coefficient. The multi-phase system of equations will be solved by the inter-phase Slip Algorithm (IPSA) [12], involving the use of Partial Elimination Algorithm (PEA) to accelerate convergence of the volume fraction and scalar equations. PHOENICS program solves a general transport equation with convective and diffusive terms and allows incorporation of source terms, additional equations, boundary condition by appropriate coding suitable to main logic of the program. The electrochemical reactions, species conservation, electric potential equations and source terms are added to main program in this study.

A grid independent result is obtained with 30x80 grid system y, z directions respectively.

3. Experimental Apparatus and Method

Experimental system built for both flow visualisation and void fraction measurements is shown in Figure 2. The system consists of a plexiglass vertical channel (15mmx20mmx300mm) with pure nickel electrodes, a video-microscope which is attached to CCD camera for flow visualisation and direct observation of bubble nucleation and bubble distribution, a peristaltic pump used for electrolyte flow and impose required Reynolds number, a cold light source, a DC power source, a high resolution digital avometer and a system for resistance measurements. The flow visualization experiments are performed before resistance measurements not to disturb flow and microscope vision.

The two phase flow at the vicinity of hydrogen and oxygen electrodes are magnified with a stereo microscope and recorded to a PC using a high speed CCD system. Two phase flow characteristics then analyzed with an image processing software. Since it is difficult to obtain void fraction distribution at the vicinity of the electrodes from the images, an apparatus build and attached to the lexiglas pipe. The apparatus which is based on the resistivity measurement has ten 0.25mm nickel wires placed 1mm apart. The resistance between the wires are measured without applying first electricity (no bubble case) and by changing concentration, velocity, and applied current. The local void distribution is calculated by using the Maxwell formulation given as;

$$\frac{R_{EI}}{R_{0,EI}} = \frac{1 + \alpha/2}{1 - \alpha}$$

where $\alpha$ is the void fraction $R_{EI}$ and $R_{0,EI}$ are measured electric resistance with and without bubbles respectively.

Figure 2. Schematic of experimental set-up.
4. Results

The structure of two phase region is illustrated in Figure 3a-b. These figures are obtained from video recording of experiments after an image processing. Figure 3a present a picture of two phase flow region and Figure 3b contains corresponding image contour which showing void fraction distribution and boundary of two phase region. Recording and subsequent image analysis is performed only for vicinity of cathode (hydrogen electrode). It is seen that two phase region is confined at the vicinity of electrode. The thickness of the two phase region increases along the electrode due to accumulation of hydrogen bubbles. An irregular shape toward to top of the electrode is mainly local turbulence (although flow is not turbulent in terms of Reynolds number, in this case). The predicted two phase structure for the same conditions is shown in Figure 4c. It is seen that mathematical model capture basic structure of the two phase flow region. Since turbulence (or chaotic flow) is not accounted in the mathematical model, a smoother two phase boundary is obtained.

Since it is difficult directly determine and compare the value of local void fraction from image processing, the estimated void distribution is compared with the data obtained from resistivity measurements.

Figure 4 compares measured lateral void fraction profile obtained resistivity measurement method with numerical data. It is seen that void fraction higher at vicinity of electrode and decrease exponentially in lateral direction. It is also seen that mathematical model capable of predicting void fraction profile in the system. Small discrepancies between numerical and experimental results may be attributed to the measurements errors and inherent assumptions in the mathematical model (mainly laminar flow assumption).

Figure 5 shows the effect of flow rate on hydrogen evolution and compares predicted void fraction profile with data obtained from resistivity measurement. It is seen that the gas evolution increases with increasing flow rate while the applied current is kept constant. This may be explained lower residence time of bubbles on the electrodes with higher flow rate. Figure shows that numerical results reasonable agree with experimental data. It is seen that mathematical model slightly underestimates measured data. This is may be attributed local turbulence which is not accounted in the mathematical model. The local turbulence locally enhance dispersion and mixing and thus gas evolution.

![Figure 3](image3.png)

Figure 3. (a) Image of two phase region from video recordings (b) measured, (c) calculated void fraction distribution.
Figure 4. Numerical and experimental results (i=1000 A/m$^2$).

Figure 5. Effect of flow rate on hydrogen evolution (i=1000 A/m$^2$).
5. Conclusions

A mathematical model is adapted and improved to study hydrogen evolution in an electrochemical cell. The model is based on two phase flow which solves transport equation for both liquid and gaseous phases. An experimental setup is developed to measure local void fraction, validate and improve mathematical model. The general characteristics of gas evolution and two phase region are determined by image processing of video-microscope recordings. The local void fraction is measured with a system based on electrical resistivity changes with the presence of bubble in the system.

The hydrogen gas concentration increases along the vertical electrode in the electrochemical system considered. A wavy structure is observed at the two phase boundary because of the local turbulence or chaotic mixing. The predicted void fraction reasonably agrees with the experimental data obtained from resistivity measurement.

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6. References