



Electrochemical model of electro-flotation



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ABSTRACT

The relationship between the electrolysis voltage and the other variables (such as inter-electrode spacing, electric conductivity, current density, pH, bubble void fraction etc.) of an electro-flotation (EF) process using a Ti based anode is analyzed. The Nernst equation, Tafel equation, Fick's model, and Ohm's law are applied to determine the Nernst potential, activation overpotential, concentration overpotential and ohmic overpotential respectively. The simulation results are compared with experimental data of the present study as well as with data obtained from the literature. The good agreement of the comparison indicates that the models derived can be used to calculate the total electrolysis voltage required for an EF cell under different operating conditions. The effect of void fraction between electrodes on the electrolysis voltage of EF is experimentally investigated. The Bubble volumetric fraction between the electrodes was estimated to be 25%–35%, which significantly increases the cell resistance and hence overall cell potential.

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1. Introduction

Electro-flotation (EF) is an electrochemical technology that is effective in separation of solids and liquids, such as fine slimes of low grade ores, domestic and industrial waste water, by means of hydrogen and oxygen gas bubbles generated from water electrolysis. Bande et al. [1] identified three principal advantages of EF. First, dispersed gas bubbles formed from electrolysis are finer and more uniform compared to air bubbles in conventional flotation system. Second, the size and density of electrolytic bubbles can be controlled by varying current density in the flotation medium, thereby increasing the probabilities of bubble-particle collision. Third, a specific separation application can be designed via the selection of appropriate electrode surface and solution conditions to obtain optimum results. Therefore, its applications to the recovery of fine minerals, oil from oil/water emulsions and treatment of industrial wastewaters have become a topic of recent research (e.g. [14,22,27,1]). Muller [20] stated that for the 21st century EF would be the key electrochemically based technology.

The operating cost is one of the primary concerns for the performance of an EF system. Operating cost depends on the power consumption that is strongly reliant on the electrolysis voltage and current. The electric power of an EF cell can be obtained by multiplying the cell voltage with current. For a higher current, which is more likely applied for electro flotation, any small raise of the

cell voltage can cause a severe rise in the power demand. Therefore, the prediction of electrolysis voltage under desired operating conditions is very important for industrial applications. Although EF has been practiced since 1900s [10], a comprehensive electrochemical model to simulate electrolysis voltage in an EF cell has not been reported in the literature. A simple model involving terms of activation overpotential, concentration overpotential and ohmic overpotential of the solution resistance was proposed by several researchers (e.g. [25]). However, the prediction of the unknown terms needs to be addressed more specifically, such as the activation overpotential and the concentration overpotential. Moreover, the bubble effect on the overall electrical resistance in an EF cell needs to be considered. In this study, a simplified analytical model has been derived for the estimation of electrolysis voltage of an EF cell based on Nernst equation, Tafel equation, Fick's model, and Ohm's law, considering both the activation overpotential and concentration overpotential. The effect of bubbles in an EF cell is also considered in the theoretical model, which is an enhancement to previous studies (e.g. [5]).

The objectives of this study is to derive the theoretical models regarding the electrolysis voltage required in an EF process and to verify the simulation results by comparing with experimental data from both this study as well as data obtained from the literature.

2. Electrochemical model

When an electrolyte solution is brought between two electrodes with opposite electric charges, a direct current (dc) is passing through from the positive pole (anode) to the negative pole (cath-

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ode), and an electric field is established. As a result of electrolysis reactions, hydrogen and oxygen gases are formed and liberated at cathode and anode, respectively, in the form of gas bubbles.

The oxygen evolution reaction at the anode is [23]



The hydrogen evolution reaction at the cathode is [23]



The overall electrolysis reaction is expressed as



The operating current in an EF cell must exceed the equilibrium potential difference, anode overpotential, cathode overpotential, and ohmic overpotential of the solution in order to maintain electrochemical reactions [25], as shown in Eq. (4).

$$E_{\text{cell}} = E_{\text{eq}} + \eta_{\text{a,a}} + \eta_{\text{a,c}} + \eta_{\text{a,p}} + |\eta_{\text{c,a}}| + |\eta_{\text{c,c}}| + \eta_{\text{ohm}} \quad (4)$$

where E_{cell} is the electrolysis voltage (V); E_{eq} is the equilibrium potential difference for water split (V); $\eta_{\text{a,a}}$ is the anode activation overpotential (V), $\eta_{\text{a,c}}$ is the anode concentration overpotential (V), $\eta_{\text{a,p}}$ is the anode passive overpotential (V), $\eta_{\text{c,a}}$ is the cathode activation overpotential (V) and $\eta_{\text{c,c}}$ is the cathode concentration overpotential (V) and η_{ohm} is the ohmic overpotential (V). For a new electrode system, the passive overpotential is negligible i.e. $\eta_{\text{a,p}} = 0$. The typical voltage components in an EF cell are shown Fig. 1.

2.1. Equilibrium voltage

The equilibrium voltage of an EF cell can be expressed by the Nernst equation:

At anode:

$$E_A = E^0_A + \frac{RT}{nF} \ln \left\{ \frac{[P_{\text{O}_2}][\text{H}^+]^4}{[\text{H}_2\text{O}]} \right\} \quad (5)$$

At cathode:

$$E_C = E^0_C + \frac{RT}{nF} \ln \left\{ \frac{[\text{H}^+]^2}{P_{\text{H}_2}} \right\} \quad (6)$$

where E^0_A and E^0_C are the equilibrium potentials of anode and cathode, respectively, under standard conditions ($T = 298 \text{ K}$, $P = 1 \text{ atm}$ and $[\text{H}^+] = 1 \text{ M}$ (i.e. at pH 0)), $R = 8.314 \text{ J/K mol}$, is the ideal gas law constant, T is the absolute temperature, n is the amount of electrons involved in the reaction (at anode $n = 4$ and at cathode $n = 2$) and F is the Faraday constant ($96,485 \text{ C/mol}$).

The equilibrium potential difference between the anode and the cathode is

$$E_{\text{eq}} = E_A - E_C \quad (7)$$

Thus,

$$E_{\text{eq}} = \left[E^0_A + \frac{RT}{nF} \ln \left\{ \frac{[P_{\text{O}_2}][\text{H}^+]^4}{[\text{H}_2\text{O}]} \right\} \right] - \left[E^0_C + \frac{RT}{nF} \ln \left\{ \frac{[\text{H}^+]^2}{P_{\text{H}_2}} \right\} \right] \quad (8)$$

2.2. Activation overpotential

The activation overpotential is related to the electrode kinetics at the reaction site, which represents the overpotential incurred due to the activation energy necessary for charge transfer [18]. The anode activation overpotential (η_a) and cathode activation overpotential (η_c) can be estimated by applying the Tafel Equation as follows [6]:

$$\eta_{\text{a,a}} = a_a + b_a \ln j \quad (9)$$

$$\eta_{\text{c,a}} = a_c + b_c \ln j \quad (10)$$

where, j is the current density (A/m^2), a_a and a_c are the constant of Tafel equation at the anode and cathode respectively, and b_a and b_c are Tafel slope of Tafel equation at anode and cathode, respectively.

2.3. Concentration overpotential

The concentration overpotential is caused by the resistance to the transport of reactant species approaching the reaction site, and the transport of product species leaving the reaction site [18]. In the present study, the equations of concentration overpotential in an EF system are derived based on a previous study of Chen et al. [6]. In an electrochemical reaction, the mass transport, J_m includes diffusion ($-D_m \frac{\delta C_m(x)}{\delta x}$), convection ($C_m(x) v(x)$) and electric migration ($t_m j$), and can be calculated based on Nernst–Planck equation [6]:

$$J_m(x) = -D_m \frac{\delta C_m(x)}{\delta x} + C_m(x) v(x) + t_m j \quad (11)$$

where $J_m(x)$ is the net flux of a species m , D_m is the diffusion coefficient of species m , m^2/s , $C_m(x)$ is the concentration of species m at distance x , (mol/L), $v(x)$ is the convective velocity of water flow in the current direction at distance x , m/s , t_m is the transport number of species m and j is the current density (A/m^2).

Within the diffusion layer adjacent to the electrode surface, non-reactive ions coming from electrolyte (e.g. Na^+ or SO_4^-) and other sources (such as water or wastewater) produce a gradient of concentration and thus cause diffusion current [6]. However, the current from those non-reactive ions are equal but opposite to the migration current at steady state [6]. Therefore, the net transport and the net current from those non-reactive ions are considered to be zero [6]. Fig. 2 illustrates the concentration variation of reactive ions H^+ and OH^- near the anode and cathode. As the concentration of H^+ near the anode is relatively high, the total current in the anode diffusion layer is composed primarily of the migration and diffusion of H^+ . On the other hand, as the concentration of OH^- near the cathode is much higher than that of H^+ , the current comes predominantly from the diffusion and migration of OH^- . Near the electrode surface, the convective flux term ($C_m(x) v(x)$) can be ignored [25]. Moreover, at a high electrical conductivity, t_{H^+} and t_{OH^-} approach zero [6]. Therefore Eq. (11) becomes Eq. (12), which is widely known as the Fick's model:

$$J_m(x) = -D_m \frac{\delta C_m(x)}{\delta x} \quad (12)$$

2.3.1. Concentration overpotential at anode

Under the assumption that the H^+ concentration varies linearly across the whole diffusion layer at anode,

$$\frac{\delta C}{\delta x} = \frac{[C_{\text{H}^+}|_{x=0}] - [C_{\text{H}^+}]}{\delta_a} \quad (13)$$

where, $C_{\text{H}^+}|_{x=0}$ is the concentration of H^+ at the anode surface, C_{H^+} is the bulk concentration of H^+ , and δ_a is the diffusion layer thickness at the anode. At the anode Eq. (12) becomes

$$J_{\text{H}^+} = \frac{D_{\text{H}^+} [[C_{\text{H}^+}|_{x=0}] - [C_{\text{H}^+}]]}{\delta_a} \quad (14)$$

where J_{H^+} is the flux of $[\text{H}^+]$ ($\text{mol/m}^2 \text{ s}^{-1}$), D_{H^+} is the diffusion coefficient of the $[\text{H}^+]$ (m^2/s). Hence the current density, j , as a function of mass transport flux at the anode can be expressed as [6]:

$$j = z.F.J_{\text{H}^+} = \frac{z.F.D_{\text{H}^+} [[C_{\text{H}^+}|_{x=0}] - [C_{\text{H}^+}]]}{\delta_a} \quad (15)$$

where, z is the number of electron in the half reaction.

Usually, at anode, $[C_{\text{H}^+}|_{x=0}] \gg [C_{\text{H}^+}]$; hence Eq. (15) becomes:

$$j = \frac{z.F.D_{\text{H}^+} [C_{\text{H}^+}|_{x=0}]}{\delta_a} \quad (16)$$

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