Journal of Electroanalytical Chemistry 754 (2015) 22–29

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jeac

Hydrogen bubble growth at micro-electrode under magnetic field

Hongbo Liu, Liang-ming Pan *, Haojie Huang, Qijun Qin, Pengfei Li, Jian Wen

Key Laboratory of Ministry of Education of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400044, PR China

ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form 2 June 2015
Accepted 10 June 2015
Available online 16 June 2015

Keywords:
Lorentz force
Micro-MHD
Micro-electrode
Hydrogen bubble
Water electrolysis

ABSTRACT

The effect of magnetic field, with perpendicular to working electrode surface configuration, on the hydrogen bubble evolution at 0.2 mm diameter micro-electrode was investigated in sulfuric acid solution. This paper analyzed the periodical bubble growth and detachment within the current density range of 15.9–57.3 A/cm^2. As the current density increases, the bubble release frequency becomes larger without magnetic field. While the bubble becomes more difficult release, and the larger current density brings smaller release frequency under magnetic field. The further computational fluid dynamics (CFD) analysis found that a pair of lower pressure regions was formed as the rotating flow of fluid around the bubble driven by the Lorentz force. The pressure difference plays the role of stabilizing the bubble at the micro-electrode surface under magnetic field.

1. Introduction

Hydrogen plays an important role in the green energy development to overcome environment problems. Water electrolysis is one of the most economical and efficient routes for high-purity hydrogen production [1]. The gas bubble plays a dual role in such electrochemistry process. On the one hand, hydrogen gas is the desired product; on the other hand, its appearance adds potential drop as the bubble's non-conducting property. Many works have been done about the convective effect on the bubble behavior, the mass transfer and the energy loss that caused by IR-drop due to the bubble layer [2–8].

Bubble management is an important issue in water electrolysis process, and has aroused many attentions in recent years [9,10]. A series of researches have shown that a superposed magnetic field has significant influence on the gas involved electrolysis process [11–14]. The fraction of bubble coverage and the bubble size was reduced under the external magnetic field [11,13]. The efficiency of water electrolysis was enhanced and IR-drop between the working electrodes was reduced by superposition external field [12,14]. All the phenomena are induced by the Lorentz-force-driven convection, i.e. the magnetohydrodynamic (MHD) convection, which introduces an additional convection in the electrolyte [15]. Koza and his co-workers [11,16,17] found that bubble size was decreased and bubble release becomes easier when the macro-electrode is used, regardless of the magnetic field orientation with respect to the gas-evolving electrode. They suggested that the Lorentz force gave rise to a twist-off effect by the azimuthal flow around each bubble, which was defined as the micro-MHD [17], as shown in Fig. 1.

Gas desorption at electrode surface is a typical interfacial mass transfer phenomenon. The bubble growth is controlled by the interfacial phenomena in the three-phase zone where bubble, electrolyte and electrode surface contact each other. The electrons flow from the anode to the cathode where they are consumed by hydrogen ions to form hydrogen gas. As time goes on, the dissolved hydrogen is accumulated near the electrode surface to form the supersaturated layer. Hydrogen is transported by means of diffusion and convection from the electrode surface, one part of dissolved hydrogen is transported to the bulk liquid and the rest is into the gas bubbles [18].

This paper pays attention on the rotating flow around gas bubble induced by the Lorentz force, i.e. the micro-MHD, when the magnetic field is perpendicular to the electrode. The bubble evolution at micro-electrode was observed during their lifetime, and the restrain effect of magnetic field on the bubble release was analyzed via computational fluid dynamics (CFD) method.

2. Experimental

A copper micro-electrode with diameter of 200 μm was used as working micro-electrode in this experimental investigation. It was composed of 99.99% pure wire and was sealed in the electrolysis cell by rosin. The electrode was polished under continuous water flow using #8000 diamond emery papers. Water electrolysis is conducted by a two-electrode cell which consists of a transparent plastic container containing 9.0 mL of aqueous 1.0 M H_2SO_4 solution. The working electrode surface was horizontal facing up to allow free detachment of the bubbles formed on the surface. A magnetic field was superimposed

* Corresponding author. Tel.: +86 23 65102280.
E-mail address: cneng@cqu.edu.cn (L. Pan).

http://dx.doi.org/10.1016/j.jelechem.2015.06.015
1572-6657/

Nomenclature

$\vec{B}$	magnetic field, T
c	dissolved substance concentration, mol/m^3
D	diffusion coefficient, m^2/s
d	bubble diameter, m
$\vec{j}$	current density, A/m^2
k	mass transfer coefficient, m/s
t	time, s
$\vec{V}$	velocity, m/s
Greek letters	
β	growth coefficient
ρ	electrolyte density, kg/m^3
ϕ	potential, V
σ	electrolyte conductivity, S/m

by a set of two large NdFeB permanent-magnets (150 × 150 × 150 mm) in a paralleled up-and-down arrangement that gave a homogenous magnetic field up to 0.9 T over the whole experiment space. The magnetic field was measured through Gauss meter. The electrolysis cell was placed in the middle of magnet gap. With this configuration, the magnetic field was parallel to the electric current far away from the working electrode surface.

Typically, experiment is implemented in galvanostatic condition. A fixed current of 1–18 mA corresponding to average current densities of 3.2–57.3 A/cm^2 through working electrode, was set by PARSTAT 4000 potentiostat/galvanostat. A high speed camera was used to record bubble behaviors with speed of 500 fps (frames per second). The bubbles were illuminated by using an 8 W LED light in conjunction with a diffusion plate. Micro-Nikon 60 mm f/2.8D lens was applied to achieve local magnification. The bubble diameters were measured directly on the image after a ruler calibration. The image processing software is Image-Pro. The transient behavior of bubble growth during electrolysis is measured from the grayscale images, and the bubble release frequency is calculated from the potential oscillation. It is set to record after the electrolysis maintains 10 s or more to ensure the electrolysis process stabilization.

3. Numerical Simulation

A simplified model is used to analyze the micro-MHD on the bubble behavior in this section. In fact, the relative scale of bubble and electrode size is changed continuously as the bubble growing in experiment, and the fluid flow is rather complicated. In addition, the bubble nearly covers most area of the electrode surface and the current is conducted to the working electrode surface by the liquid film under the bubble. Here the growing bubble is simplified as a solid sphere located at the electrode with a contact angle under the no-slip boundary condition at the bubble wall [19]. The model and corresponding boundary conditions are shown in Fig. 2. To avoid the influence of the chosen relative scale of bubble and electrode size in this simulation, three cases ($r_b = r_e$, $1.5r_e$, $2r_e$) have tested.

The Ohm's law takes the form $\vec{j} = \sigma\left(-\nabla\phi + \vec{V} \times \vec{B}\right)$ under magnetic field. From the principle of conservation of electric charge $\nabla \cdot \vec{j} = 0$, the electric potential equation is given $\nabla \cdot (\sigma\nabla\phi) = \nabla \cdot \left\{\sigma\left(\vec{V} \times \vec{B}\right)\right\}$. Due to the small magnitude of the microscale velocity in the simulation, the term of $\sigma\left(\vec{V} \times \vec{B}\right)$ can be neglected, and so the potential equation is simplified as:

$$\nabla \cdot (\sigma\nabla\phi) = 0. \tag{1}$$

A standard scalar transport equation is included in Fluent® as shown:

$$\frac{\partial\phi}{\partial t} + \nabla \cdot \left(\vec{V}\phi - \Gamma\nabla\phi\right) = 0 \tag{2}$$

which is used to solve the potential equation. Here both the unsteady and convective terms should be turned off and the diffusion coefficient, Γ, should be replaced by electrolyte conductivity, σ.

Neglect the Joule heating effect, the coupling of electric and magnetic fields is achieved by introducing additional source terms to the fluid momentum equation. The additional momentum source is Lorentz force given by $\vec{F}_L = \vec{j} \times \vec{B}$.

The solution flow around the bubble is governed by the continuity equation and Navier–Stokes (N–S) equation as below:

$$\frac{\partial\rho}{\partial t} + \nabla \cdot \left(\rho\vec{V}\right) = 0 \tag{3}$$

$$\frac{\partial\left(\rho\vec{V}\right)}{\partial t} + \nabla \cdot \left(\rho\vec{V}\vec{V}\right) = -\nabla p + \nabla \cdot \mu\left(\left(\nabla\vec{V} + \nabla\vec{V}^T\right) - \frac{2}{3}\nabla \cdot \vec{V}I\right) + \rho\vec{g} + \vec{F}_L \tag{4}$$

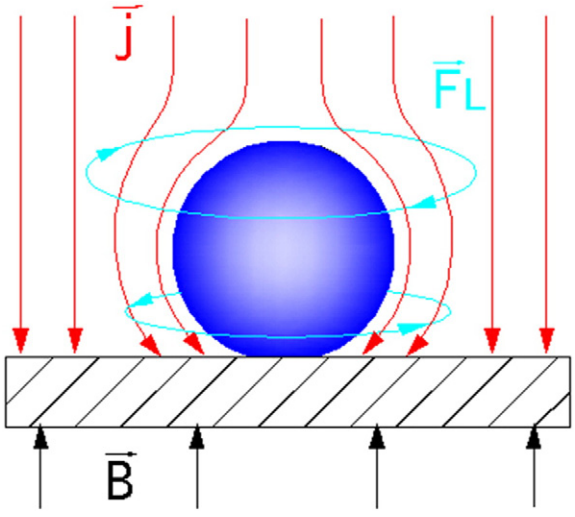

Fig. 1. Schematic diagram of the micro-MHD convection induced by the current distortion around the bubble under homogeneous magnetic field.

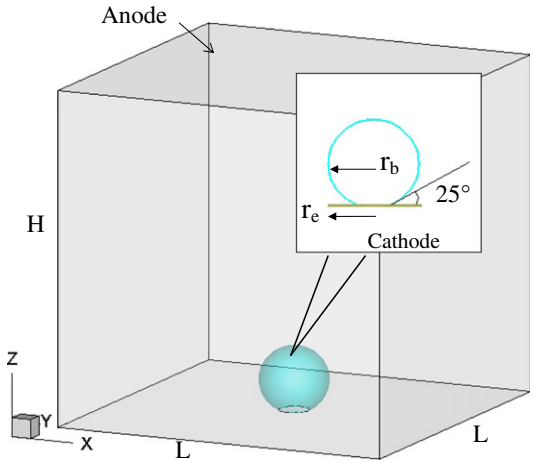

Fig. 2. Calculation model of micro-MHD, the top surface is anode (L × L), and the circle micro cathode (r_e) is a part of the bottom; the bubble radius is r_b, the contact angle is 25°, H = L = $5r_e$.