Existence of optimum space between electrodes on hydrogen production by water electrolysis

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Abstract

The effect of bubbles between electrodes on efficiency of hydrogen production by water electrolysis was experimentally investigated. The water electrolysis of 10 wt% potassium hydroxide aqueous solution was conducted under atmospheric pressure using Ni–Cr–Fe alloy as electrodes. In order to examine void fraction between electrodes, the following parameters were controlled: current density, with or without separator, system temperature, space, height, inclination angle and surface wettability of electrodes. The efficiency of water electrolysis was qualitatively evaluated by the voltage drop value at a certain current density. The experimental results showed that increase of void fraction between electrodes by decreasing the electrode space brought about decrease of the electrolysis efficiency; i.e. there is an optimum condition of water electrolysis at a certain current density. In addition, a physical model of void fraction between electrodes was presented, which was found to represent a part of the qualitative tendency of experimental results. © 2002 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Hydrogen energy; Water electrolysis; Bubble; Void fraction

1. Introduction

Water electrolysis is a very important technology for a large scale of hydrogen production. Hydrogen energy is expected to be useful as secondary energy in the near future (for example, [1,2]), applicable to fuel for vehicle and rocket, chemical use, Ni–H\textsubscript{2} electric cell, thermal engine using hydrogen storage alloys, direct combustion for heat, and so on. In addition, hydrogen energy can be used to build up dispersive energy system together with electric power by using water electrolysis and fuel cell. In such an energy system, water electrolysis will become a key technology, and high performance of water electrolysis should be achieved.

The voltage needed to realize water electrolysis consists largely of reversible potential (=1.23 V at 1 atm, 25°C), overvoltage on electrodes, and ohmic loss in aqueous solution as shown in Fig. 1 [3]. On purpose to realize good efficiency of water electrolysis, many researches have been conducted so far, mainly focused on decrease of reversible potential and overvoltage by realizing water electrolysis under high temperature and pressure or developing new electrode materials [4]. However, little attention has been paid to ohmic loss in aqueous solution from hydrodynamic and two-phase flow point of view. LeRoy et al. [3] pointed out that the increase of volume fraction of hydrogen or oxygen bubbles between electrodes, i.e. increase of void fraction, would cause the increase of electric resistance in aqueous solution, resulting in efficiency decrease of water electrolysis. Funk and Thorpe [5] presented an analytical model of void fraction and current density distributions between electrodes, from view point of two phase flow. Hine and Sugimoto [6] obtained detailed information on void fraction, rising velocity and diameter distributions of bubbles. Bongenaar-Schlenter et al. [7] measured void fraction and current density distributions, and proposed a “bubble diffusion model” for ohmic resistance between electrodes. Janssen and Visser [8] also measured void fraction, ohmic
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>voltage between electrodes, V</td>
<td>V</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant (=9.65 $\times$ 10$^4$, C/mol)</td>
<td></td>
</tr>
<tr>
<td>$H$</td>
<td>height of electrode, m</td>
<td>m</td>
</tr>
<tr>
<td>$P$</td>
<td>system pressure, Pa</td>
<td>Pa</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant, J/mol K</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>system temperature, °C or K</td>
<td></td>
</tr>
<tr>
<td>$u$</td>
<td>rising velocity of bubbles, m/s</td>
<td>m/s</td>
</tr>
<tr>
<td>$W$</td>
<td>width of electrode, m</td>
<td>m</td>
</tr>
<tr>
<td>$x$</td>
<td>coordinate, m</td>
<td>m</td>
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</tbody>
</table>

Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>void fraction</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>space between electrodes, m</td>
<td>m</td>
</tr>
<tr>
<td>$\phi$</td>
<td>current density, A/m$^2$</td>
<td></td>
</tr>
</tbody>
</table>

2. Experimental apparatus and method

The water electrolysis of 10 wt% KOH aqueous solution was conducted under atmospheric pressure using Ni–Cr–Fe alloy (Inconel 600) as electrodes. In order to vary void fraction between electrodes, parameters as follows were controlled: current density, with or without separator, system temperature, and space, height, inclination angle, surface wettability of electrodes. As easily postulated from hydrodynamic and two-phase flow point of view, the increase of void fraction would occur by following conditions; increasing current density, with separator, higher temperature, narrower space, larger height, horizontal setting of electrodes, and higher wettability.

Fig. 2 shows outline of the experimental apparatus used. Inside the liquid container (360 mm width $\times$ 200 mm depth $\times$ 300 mm height) made of vinyl chloride, the electrodes were completely immersed and fixed in parallel with a certain space. The height of electrodes was chosen to one of 100, 50, 10 mm, while the width of electrodes was fixed to 50 mm. A separator was set at the middle position between electrodes. The separator sheet tested was either polytetrafluoroethylene filter sheet of 0.4 mm thickness or without separator. DC power supplier enabled DC current up to 60 A and DC voltage up to 6 V between electrodes: current density there is an optimum condition of hydrogen production in water electrolysis.
Table 1
Experimental conditions tested

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Material</th>
<th>Ni–Cr–Fe alloy (Inconel 600)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Space</td>
<td>$\delta = 1–20$ mm</td>
</tr>
<tr>
<td></td>
<td>Height</td>
<td>$H = 10, 50, 100$ mm</td>
</tr>
<tr>
<td></td>
<td>Width</td>
<td>$W = 50$ mm</td>
</tr>
<tr>
<td></td>
<td>Inclination</td>
<td>Vertical or horizontal</td>
</tr>
<tr>
<td></td>
<td>Wettability</td>
<td>Lower wettability with silicone or without treatment</td>
</tr>
</tbody>
</table>

| Pressure   |                        | Atmospheric                 |
| Temperature| $T = 20, 40, 60$ °C    |                             |
| Current density | $\Phi = 0.1–0.9$ A/cm² |                             |
| Separator  | Polyflon filter sheet of 0.5 mm thickness or without separator |

ranged from 0.1 to 0.9 A/cm². Hydrogen gas generated was collected to H₂ collector bottle through water, while oxygen gas was released to open air. The temperature of the KOH aqueous solution was controlled to 20°C, 40°C, or 60°C by cartridge heaters. The inclination angle of electrodes was either vertical or horizontal. Rotation of the whole liquid container enabled horizontal setting of electrodes. The surface of electrodes was polished after several experiments to keep same overvoltage on electrodes. The surface wettability was tested to either lower surface wettability with silicone oil treatment or without treatment.

The efficiency of hydrogen production by water electrolysis was qualitatively evaluated and compared by the voltage value at a certain current density. Since the amount of hydrogen gas is proportional to electric current, the voltage value becomes good index to represent electric power necessary to produce certain mass of hydrogen when compared among data of the same current density. The voltage between electrodes was measured by voltmeter, while the DC current was estimated by measuring voltage drop of standard resistance ($\approx 0.5$ mΩ).

The experimental conditions are summarized in Table 1.

3. Results and discussion

3.1. Effects of current density and space between electrodes on efficiency of water electrolysis

In this section, the effects of current density and space between electrodes on efficiency of water electrolysis are discussed. As stated in the previous chapter, the voltage qualitatively represents electric power necessary to produce certain mass flux of hydrogen. In other words, lower voltage means higher efficiency of water electrolysis.

The experimental results show that current density and space between electrodes have significant effects on the efficiency of water electrolysis. Fig. 3 illustrates the relation between voltage, $E(V')$, and space between electrodes, $\delta$ (mm), at the following condition as an example: height of electrodes, $H = 100$ mm, system temperature $T = 20$ °C, vertical setting, polyflon separator, and without surface treatment. While current density was lower ($\Phi = 0.1–0.5$ A/cm²), the voltage decreased as the space became smaller. It is postulated from this tendency that the electric resistance between electrodes basically becomes smaller as the space gets closer while void fraction is rather small. However, when current density was rather high, beyond 0.6 A/cm², the voltage increased a little as the space got closer in the small-space region ($\delta = 1–2$ mm). These results can be explained as follows; when the current density is rather high and the space is rather small, the void fraction between electrodes gets rather large resulting in increasing electric resistance between electrodes, and then decreasing the efficiency of water electrolysis. It is presumed, therefore, that there is an optimum space as to the efficiency of water electrolysis and the optimum space depends on current density and other experimental conditions. In this case (Fig. 3), the optimum space is 1–2 mm when the current density is over 0.5 A/cm².
3.2. Effects of the other parameters on efficiency of water electrolysis

In this section, the effects of the other parameters on the efficiency of water electrolysis are discussed one after another: (1) height of electrodes, (2) system temperature, (3) with or without separator, (4) inclination of electrodes, and (5) surface wettability. The experimental results here are shown as the relation between voltage and space between electrodes, as in Fig. 3.

3.2.1. Height of electrodes

Fig. 4 and 5 illustrate the experimental result when the height of electrodes, $H$, was 50, 10 mm, respectively, while the other parameters were the same with those of Fig. 3. Comparing Figs. 3–5, it is found out that the higher efficiency of water electrolysis arises in the smaller height of electrodes when current density is rather large. This result can be explained as follows; the average void fraction between electrodes of larger height is bigger than that of smaller height if the mass flux of gas is uniform on both electrodes, because hydrogen and oxygen bubbles densely pack at the upper part between electrodes.

It is also worth noticing that there is no clear optimum space in the result of 10 mm height (Fig. 5). This means the existence of optimum space depends on not only the current density but also the height of electrodes.

3.2.2. System temperature

Fig. 6 shows the experimental result when the system temperature, $T$, was 60°C, while the other parameters were the same with Fig. 3. The tendency of experimental results for $T = 40^\circ$ C was just between $T = 20^\circ$ C and 60°C. As seen from Figs. 3 and 6, the electrolysis efficiency become higher as the system temperature gets higher, especially in the region of smaller space between electrodes. This result can be interpreted as follows; the higher system temperature causes the increase of bubble volume and the decrease of reversible potential as stated in Section 1. The increase of bubble volume is related to both the direct increase of void fraction and the decrease of rising velocity of bubbles.
3.2.3. With or without separator

Fig. 7 shows the experimental result without separator while the other parameters were the same with Fig. 3. As shown in Figs. 3 and 7, the electrolysis efficiency without separator is higher than that of with separator. The existence of separator obstructs rising movement of bubbles to cause the increase of void fraction and at the same time increases electric resistance between electrodes, thus resulting in the decrease of efficiency. It must be noted that the thickness and material of separator may have effects on efficiency, which was not examined in this experiment.

3.2.4. Inclination of electrodes

Fig. 8 is the experimental result when the electrodes were set horizontal while the other parameters were the same with Fig. 7. As easily expected, the electrolysis efficiency of horizontal setting is lower than that of the vertical one when the current density is rather high. In this case, the exhaust of generated bubbles from between electrodes is restrained at horizontal setting, which causes the decrease of void fraction.

3.2.5. Surface wettability

Fig. 9 shows the experimental result with silicone oil treatment on electrodes while the other parameters were the same with Fig. 7. As seen from Figs. 7 and 9, the electrolysis efficiency with silicone oil treatment becomes higher than that of without surface treatment. In this case, the optimum electrode space is about 2 mm when the current density is over 0.7 A/cm². The silicone oil treatment makes the surface of lower wettability, which may cause larger size of bubbles to increase rising velocity of bubbles. On the other hand, the silicone oil treatment may changes the overvoltage of electrodes, which was not estimated in this experiment. Therefore, the effect of surface wettability on electrolysis efficiency has not been cleared yet, open to further study.
3.2.6. Summary of this section

As summary of this section, the effects of several parameters on efficiency of water electrolysis discussed above can be qualitatively explained by void fraction between electrodes in addition to the effects of current density and space between electrodes.

3.3. Modeling of void fraction between electrodes

The physical modeling of void fraction between electrodes is discussed in this section. In most of industrial water electrolyzers, the size of electrodes is much larger (∼1 m) than that tested in this report and the system is operated at higher temperature (∼100°C), larger current density and beyond atmospheric pressure. Therefore, in order to obtain useful information from the experimental results, we need a precise physical modeling of bubble diameter, rising velocity of bubbles, void fraction and current density, which can be developed from several models presented so far [5,7,8]. However, two-phase flow simulation for bubble with very small diameter of bubbles (∼0.1 mm) or high void fraction (over 0.3) is said to be almost impossible at the moment, which means that we cannot obtain a precise expression among bubble diameter distribution, rising velocity of bubbles and void fraction. Therefore, a simplified physical model on the void fraction between electrodes was considered in vertical setting of electrodes for discussing experimental results.

Fig. 10 shows the coordinates for modeling average void fraction between electrodes. As water electrolysis is in progress, the following reactions occur at both electrodes.

at cathode:

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + \frac{1}{2} \text{H}_2 \quad (1) \]

at anode:

\[ \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{H}^+ + \frac{1}{4} \text{O}_2 + \text{e}^- \quad (2) \]

Since the mass flux of hydrogen and oxygen gas is proportional to current density, the volume flux of hydrogen and oxygen gas generated from the region, \( x \sim x + dx \), shown in Fig. 10 can be represented as follows.

at cathode:

\[ \frac{1}{2} \frac{RT}{p} \frac{\Phi W}{F} dx, \]

at anode:

\[ \frac{1}{4} \frac{RT}{p} \frac{\Phi W}{F} dx, \]

then, total:

\[ \frac{3}{4} \frac{RT}{p} \frac{\Phi W}{F} dx \quad (m^3/s), \]

(3)

where \( p \) is the pressure, Pa, \( R \) the universal gas constant, \( J/mol \text{ K} \), \( T \) the temperature, \( K \), \( F \) the Faraday constant \((=9.65 \times 10^4, \text{ C/mol})\), \( \Phi \) the current density, \( A/m^2 \), and \( W \) the width of electrodes, m.

Therefore, considering that void fraction, \( \varepsilon \), is the function of position, \( x \), and assuming the rising velocity of all bubbles is constant, \( u \), m/s, the bubble volume balance between electrodes in the region, \( x \sim x + dx \), leads to the following equation:

\[ u \delta W (x + dx) = u \delta W x + \frac{3}{4} \frac{RT}{p} \frac{\Phi W}{F} dx, \quad (4) \]

then,

\[ dx = \frac{3}{4} \frac{RT}{p} \frac{\Phi}{Fu\delta} x, \quad (5) \]

where \( \delta \) denotes the space between electrodes.

Solving Eq. (5), the local void fraction, \( \varepsilon = \varepsilon(x) \), and the average void fraction of whole region between electrodes, \( \varepsilon_{av} \), can be obtained as follows:

\[ \varepsilon = \frac{3}{4} \frac{RT}{p} \frac{\Phi}{Fu\delta} x, \quad (6) \]

\[ \varepsilon_{av} = \frac{1}{H} \int_0^H \varepsilon dx = \frac{3}{8} \frac{RT}{p} \frac{\Phi H}{Fu\delta} \quad (7) \]

Thus, the average void fraction between electrodes can be expressed in Eq. (7) by the experimental parameters except the rising velocity of bubbles, \( u \).
The rising velocity of bubbles is considered to have close relationship with bubble diameter, liquid viscosity, and the number density of bubbles. Although, these terms were not estimated in this experiment, the rising velocity of bubbles may be related to the existence of separator, system temperature, current density, surface wettability and inclination angle of electrodes. Therefore, it can be said that Eq. (7) explains a part of qualitative tendency of the experimental results discussed in the previous section. Namely, the increase of void fraction would occur by following conditions; increasing current density, with separator, higher temperature, narrower space, larger height, horizontal setting of electrodes, and higher wettability.

4. Conclusion

The optimum condition on hydrogen production by water electrolysis was found to exist from the experimental result that the decrease of electrolysis efficiency occurs by the increase of void fraction between electrodes along with variation of the experimental parameters such as space, height of electrodes, current density, and so on. In addition, a physical model of void fraction between electrodes was presented, which was found to represent a part of the qualitative tendency of experimental results.

References