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 10wt% potassium hydroxide (KOH) 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.

Nomenclature

E : voltage between electrodes, V

F : Faraday constant (= 9.65×10^4 , C/mol)

H : height of electrode, m

p : system pressure, Pa

R : universal gas constant, J/mol·K

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T : system temperature, °C or K

u : rising velocity of bubbles, m/s

W : width of electrode, m

x : coordinate, m

Greek symbols

α : void fraction

δ : space between electrodes, m

Φ : current density, A/m^2

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, Winter and Nitsh [1], Sandstede and Wurster [2]), applicable to fuel for vehicle and rocket, chemical use, Ni-H_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 (=1.23V at 1 atm, 25°C), overvoltage on electrodes, and ohmic loss in aqueous solution as shown in Figure 1 (LeRoy et al. [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 (Abe et al. [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 el 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 resistance and current density. Recently, Riegel et al. [9] examined bubble diffusion, convection and transportation between electrodes in detail. These former works ([3], [5] ~[9]) were successful to generally explain the effects of bubbles on water electrolysis efficiency at a rather low current density or a rather large electrode space. It is easily postulated, however, that there is an optimum electrode space under high current densities; i.e. 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.

In this report, therefore, the effect of bubbles between electrodes on efficiency of water electrolysis was studied by conducting water electrolysis of potassium hydroxide (KOH) aqueous solution in various experimental conditions. Especially, the authors’ attention was focused on whether or not there is an optimum condition of hydrogen production in water electrolysis.

2. Experimental Apparatus and Method

The water electrolysis of 10wt% potassium hydroxide (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.

Figure 2 shows outline of the experimental apparatus used. Inside the liquid container (360mm width × 200mm depth × 300mm 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, 10mm, while the width of

electrodes was fixed to 50mm. A separator was set at the middle position between electrodes. The separator sheet tested was either polyflon filter sheet of 0.4mm thickness or without separator. DC power supplier enabled DC current up to 60A and DC voltage up to 6V between electrodes: current density ranged from 0.1 to 0.9 A/cm^2. Hydrogen gas generated was collected to H_2 collector bottle through water, while oxygen gas was released to open air. The temperature of the KOH aqueous solution was controlled to 20, 40, 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 a certain mass flux 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 (=0.5mΩ).

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. Figure 3 illustrates the relation between voltage, E (V), and space between electrodes, δ (mm), at the following condition as an example: height of electrodes, H=100mm, system temperature T=20°C, vertical setting, polyflon separator, and without surface treatment. While current density

was lower (Φ=0.1~0.5A/cm^2), 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 0.6A/cm^2, the voltage increased a little as the space got closer in the small-space region (δ=1~2mm). 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 (Figure 3), the optimum space is 1~2 mm when the current density is over 0.5 A/cm^2.

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 Figure 3.

(1) Height of Electrodes. Figures 4, 5 illustrate the experimental result when the height of electrodes, H, was 50, 10mm, respectively, while the other parameters were the same with those of Figure 3. Comparing Figures 3, 4, and 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 10mm height (Figure 5). This means the existence of optimum space depends on not only the current density but also the height of electrodes.

(2) System Temperature. Figure 6 shows the experimental result when the system temperature, T, was 60°C, while the other parameters were the same with Figure 3. The tendency of experimental results for T=40°C was just between T=20°C and T=60°C. As seen from Figures 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 introduction. The increase of bubble volume is related to both the direct increase of void fraction and the decrease of rising velocity of bubbles which results also in the increase of void fraction. Combining these two antithetical effects, the efficiency is considered to become higher as the temperature gets higher.

(3) With or Without Separator. Figure 7 shows the experimental result without separator while the other parameters were the same with Figure 3. As shown in Figures 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.

(4) Inclination of Electrodes. Figure 8 is the experimental result when the electrodes were set horizontal while the other parameters were the same with Figure 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.

(5) Surface Wettability. Figure 9 shows the experimental result with silicone oil treatment on electrodes while the other parameters were the same with Figure 7. As seen from Figures 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 2mm when the current density is over 0.7 A/cm^2. 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 hasn't been cleared yet, open to further study.

(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 (~1m) 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 flow with very small diameter of bubbles (~0.1mm) 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.

Figure 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 $\mathrm{H_2O + e^- \rightarrow OH^- + \frac{1}{2}H_2}$ (1)

at anode $\mathrm{\frac{1}{2}H_2O \rightarrow H^+ + \frac{1}{4}O_2 + e^-}$ (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 ~ x + dx, shown in Figure 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 $\frac{3}{4}\frac{RT}{p}\frac{\Phi W}{F}dx$ (m^3/s) (3)

where p: pressure, Pa, R: universal gas constant, J/mol·K, T: temperature, K, F: Faraday constant (= 9.65×10^4 , C/mol), Φ: current density, A/m^2, W: width of electrodes, m.

Therefore, considering that void fraction, α, 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 ~ x + dx, leads to the following equation.

$$u\delta W(\alpha + d\alpha) = u\delta W\alpha + \frac{3}{4}\frac{RT}{p}\frac{\Phi W}{F}dx \tag{4}$$

$$\text{then,} \quad d\alpha = \frac{3}{4}\frac{RT}{p}\frac{\Phi}{Fu\delta}dx \tag{5}$$

where δ denotes the space between electrodes.

Solving Equation (5), the local void fraction, $\alpha=\alpha(x)$, and the average void fraction of whole region between electrodes, α_{av}, can be obtained as follows:

$$\alpha = \frac{3}{4}\frac{RT}{p}\frac{\Phi}{Fu\delta}x \tag{6}$$

$$\alpha_{av} = \frac{1}{H}\int_0^H \alpha\, dx = \frac{3}{8}\frac{RT}{p}\frac{\Phi H}{Fu\delta} \tag{7}$$

Thus, the average void fraction between electrodes can be expressed in Equation (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 Equation (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.

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Figure Captions and Tables

Table 1. Experimental Conditions Tested

Electrodes	Material	Ni-Cr-Fe alloy (Inconel 600)
	Space	δ = 1 ~ 20 mm
	Height	H = 10, 50, 100 mm
	Width	W = 50 mm
	Inclination	vertical or horizontal
	Wettability	lower wettability with silicone or without treatment
Pressure		atmospheric
Temperature		T = 20, 40, 60 °C
Current density		Φ = 0.1 ~ 0.9 A/cm^2
Separator		polyflon filter sheet of 0.5mm thickness or without separator

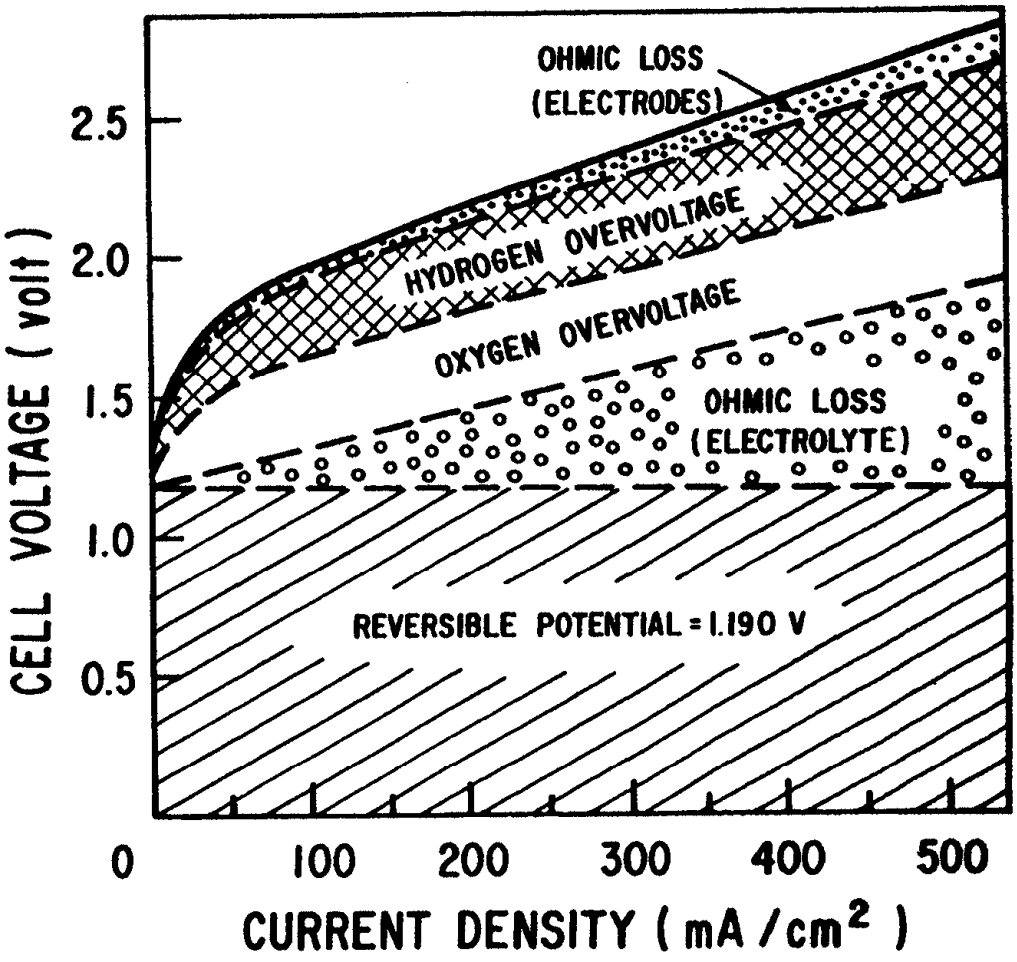
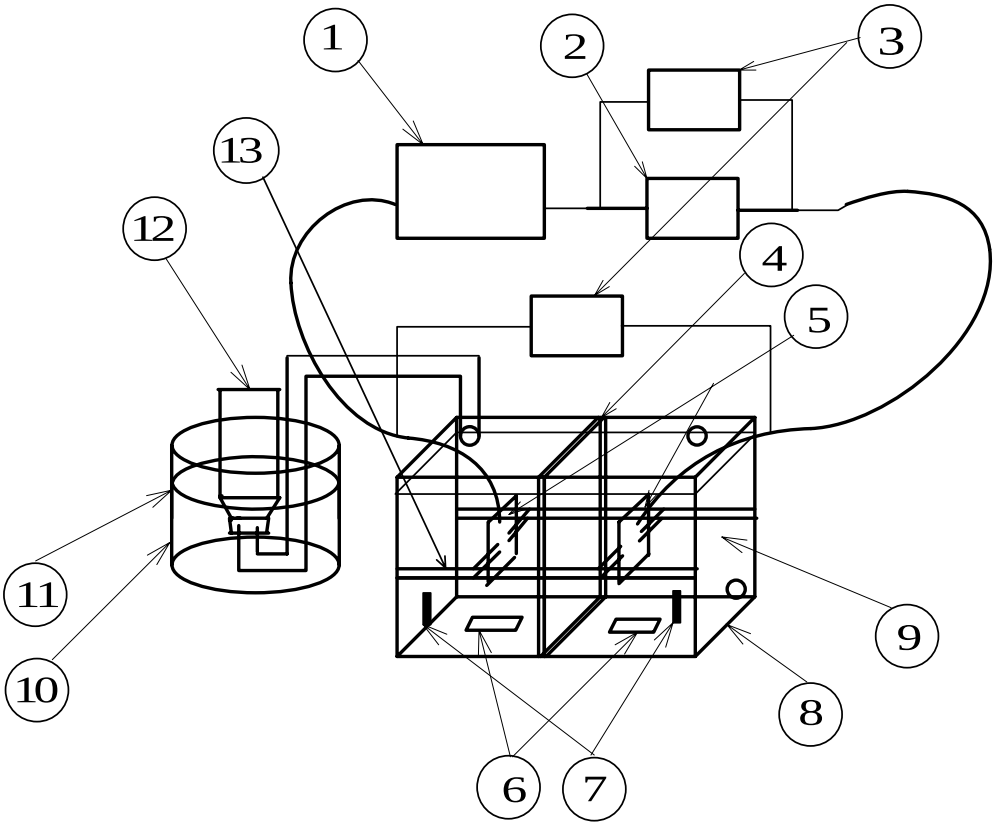


Figure 1 Components of Voltage between Electrodes (LeRoy et al. [3])



1. DC power supplier
2. Standard resistance
3. Voltmeter
4. Separator
5. Electrode
6. Cartridge heater
7. Thermometer
8. Liquid vessel
9. Aqueous solution
10. Water vessel
11. Water
12. H_2 collector
13. Stainless steel rod

Figure 2 Outline of Experimental Apparatus

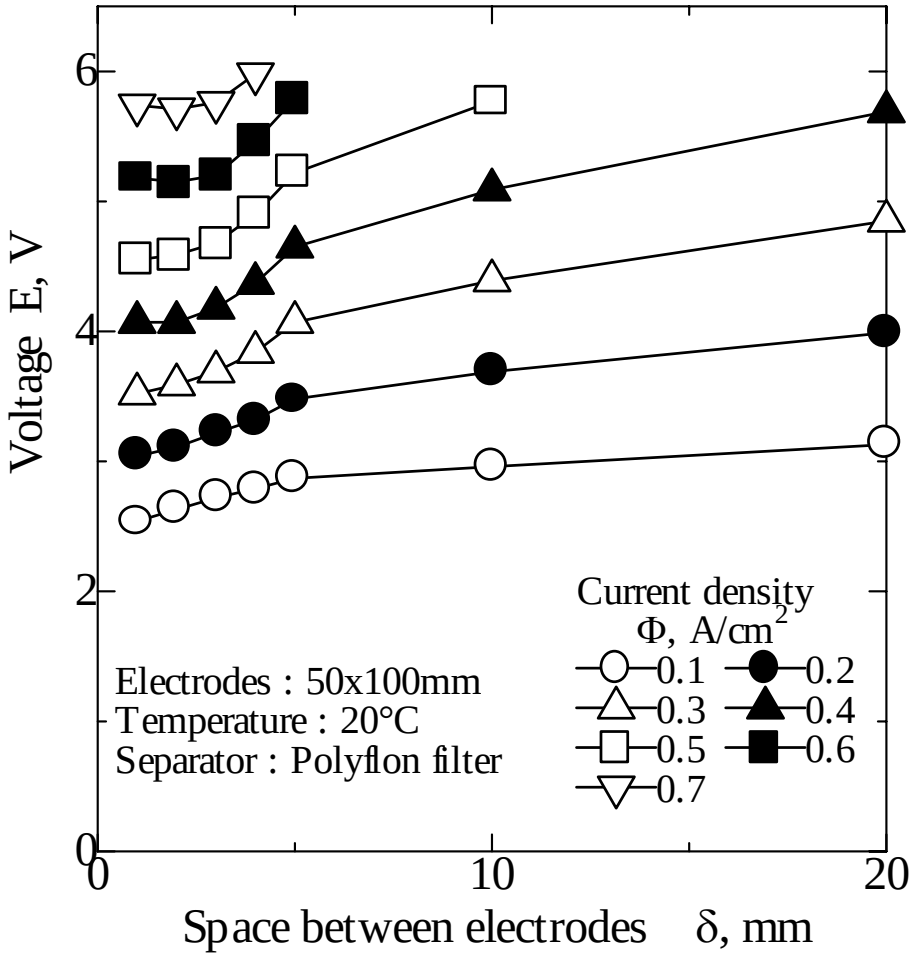


Figure 3 Effects of Current Density and Space between Electrodes on Efficiency

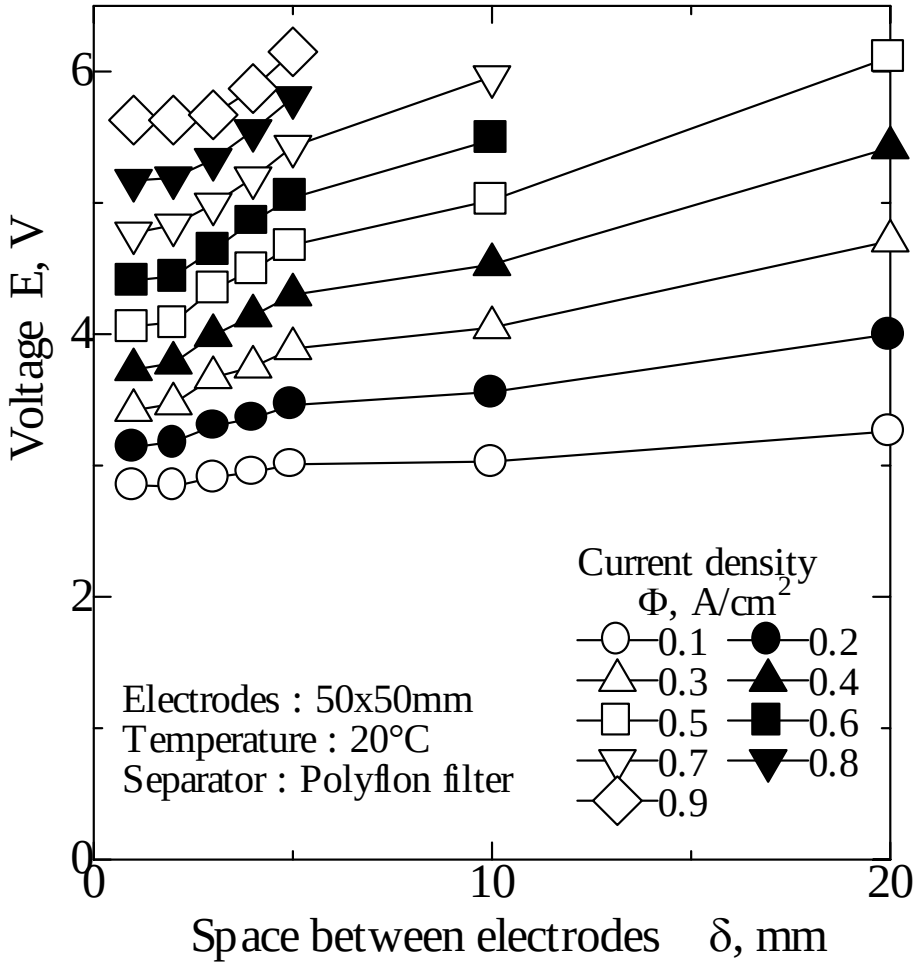


Figure 4 Effects of Height of Electrodes on Efficiency (H=50mm)

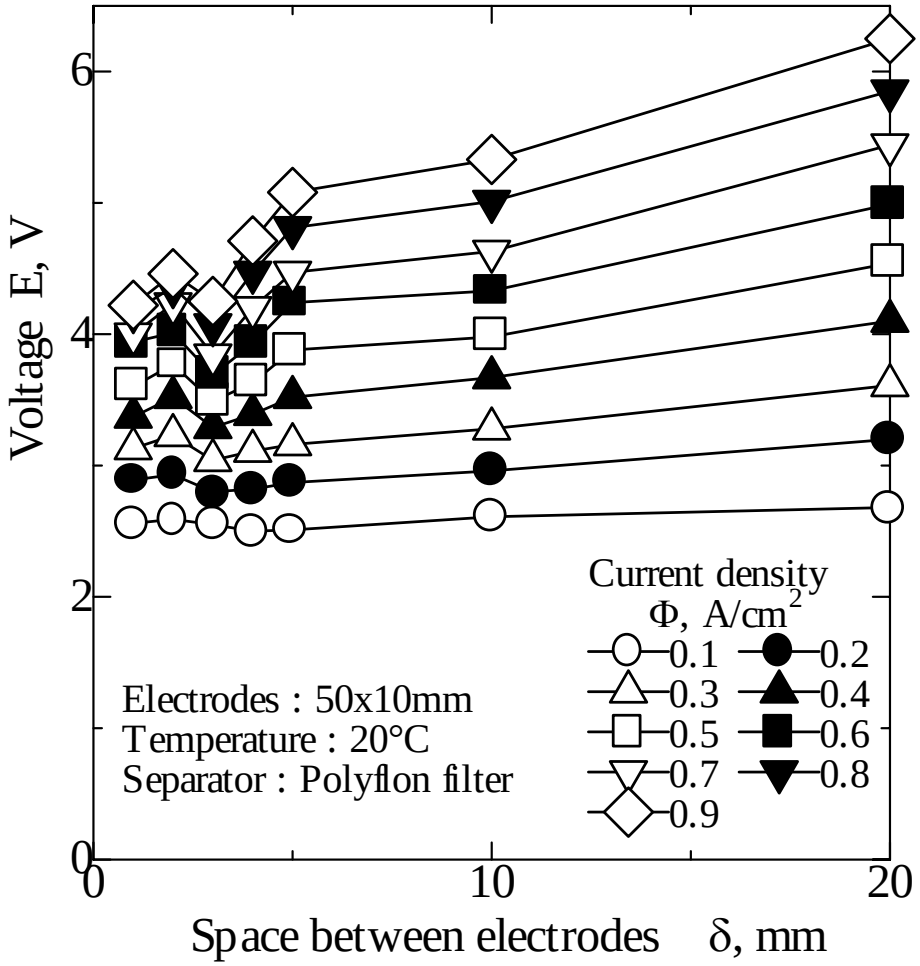


Figure 5 Effects of Height of Electrodes on Efficiency (H=10mm)

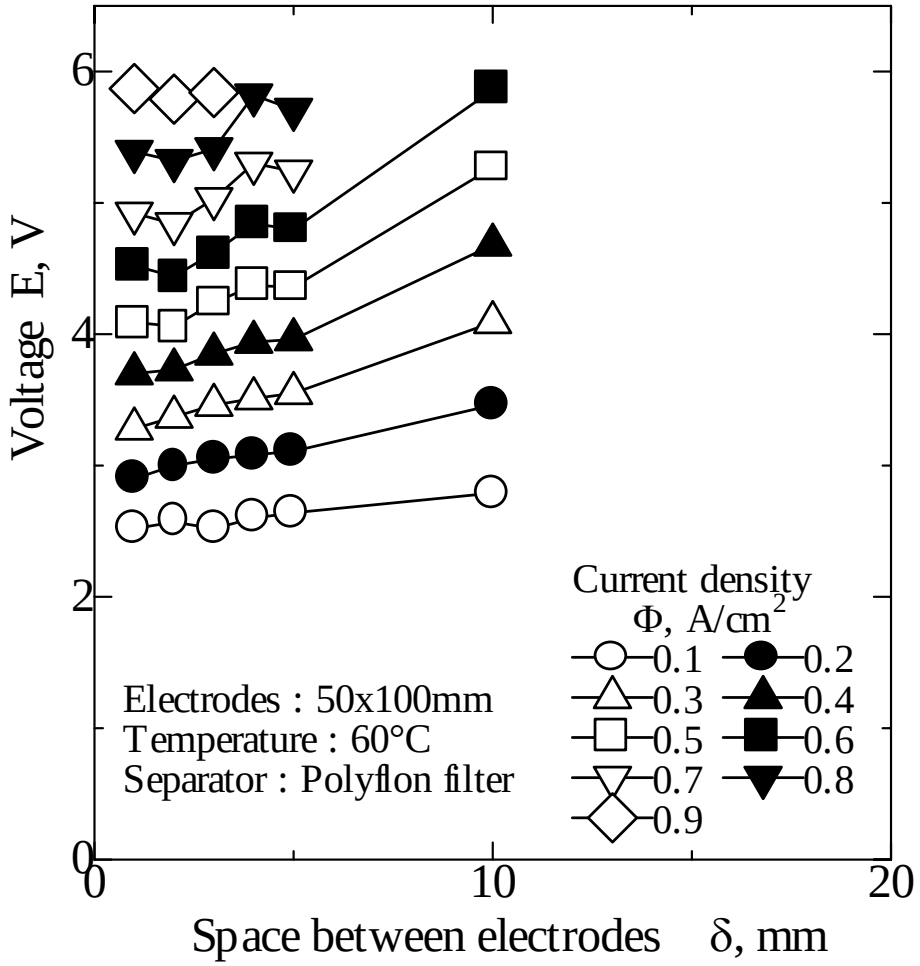


Figure 6 Effects of System Temperature on Efficiency (T=60°C)

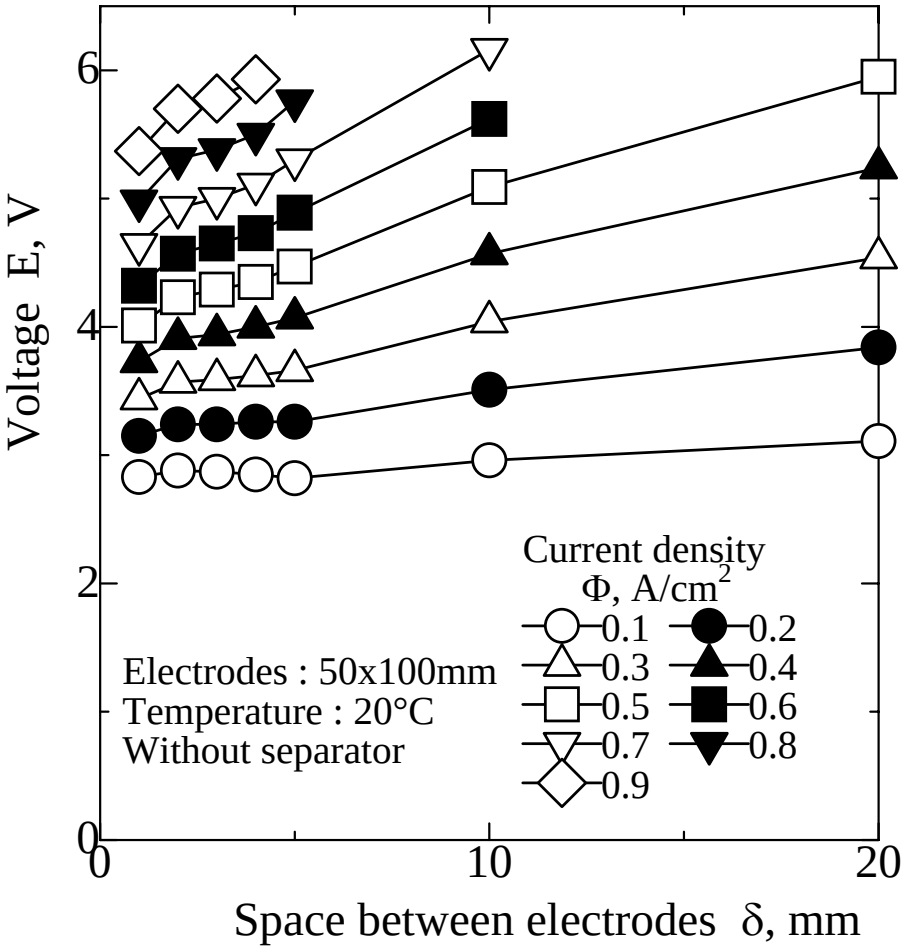


Figure 7 Effects of With or Without Separator

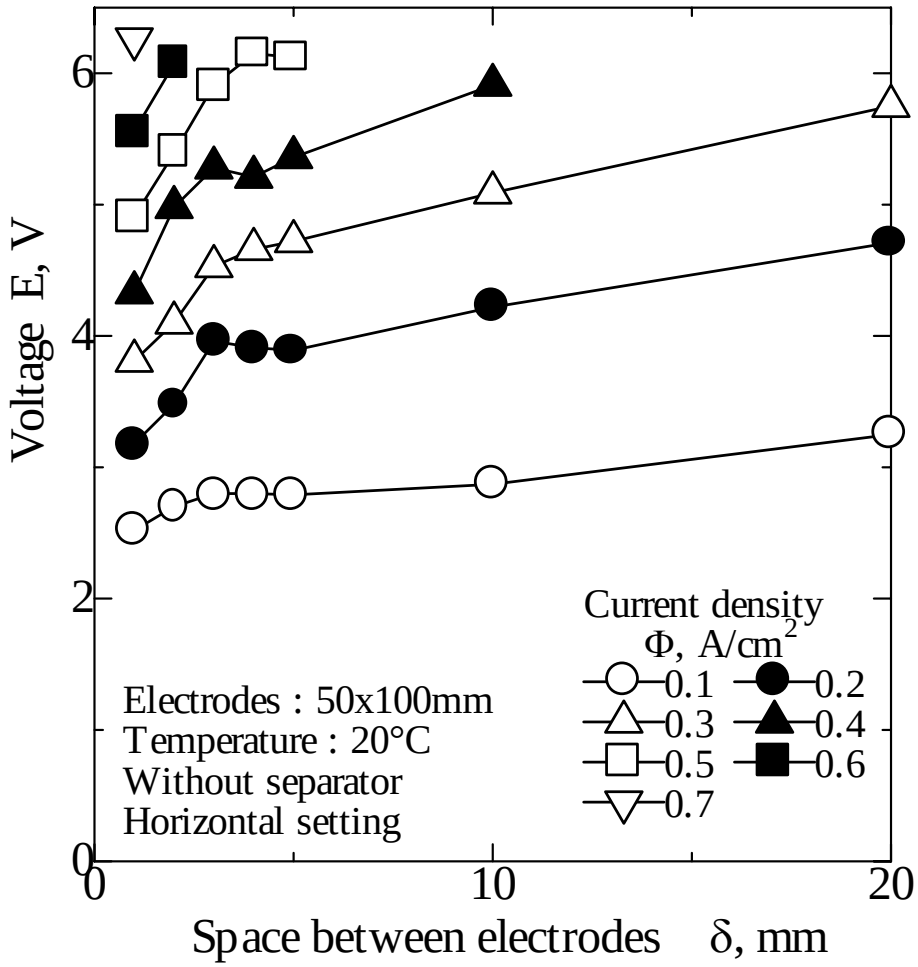


Figure 8 Effects of Inclination of Electrodes

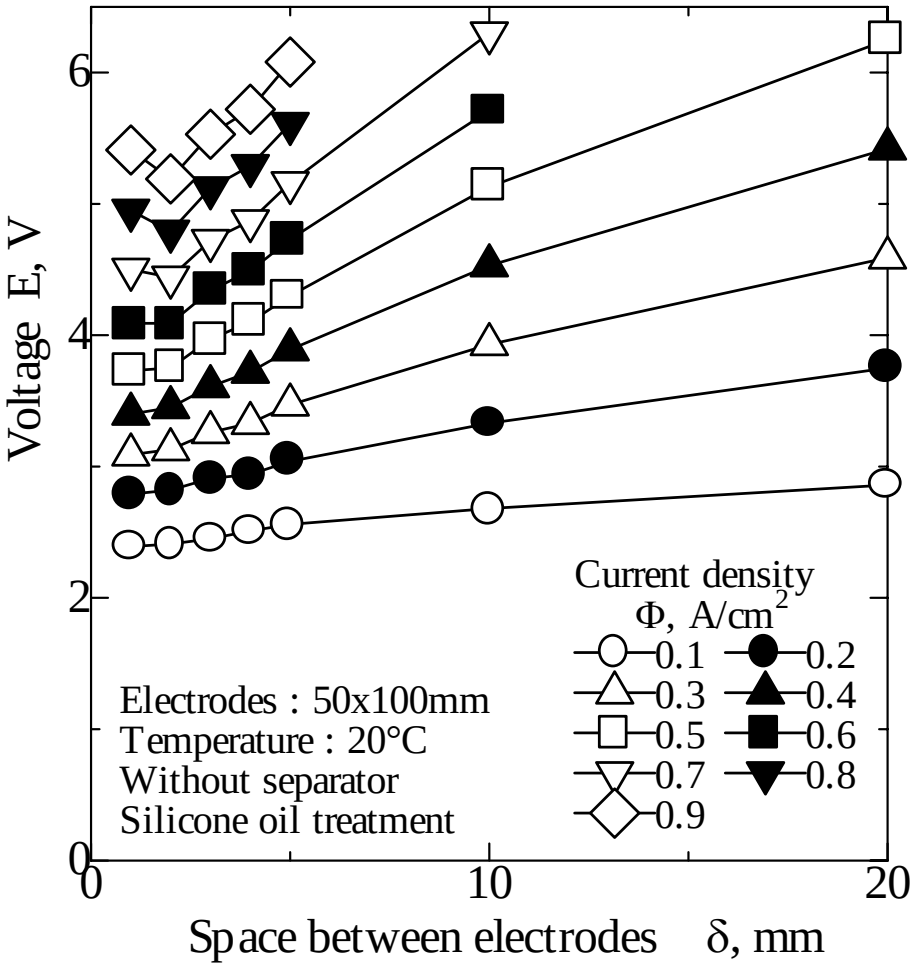


Figure 9 Effects of Surface Wettability

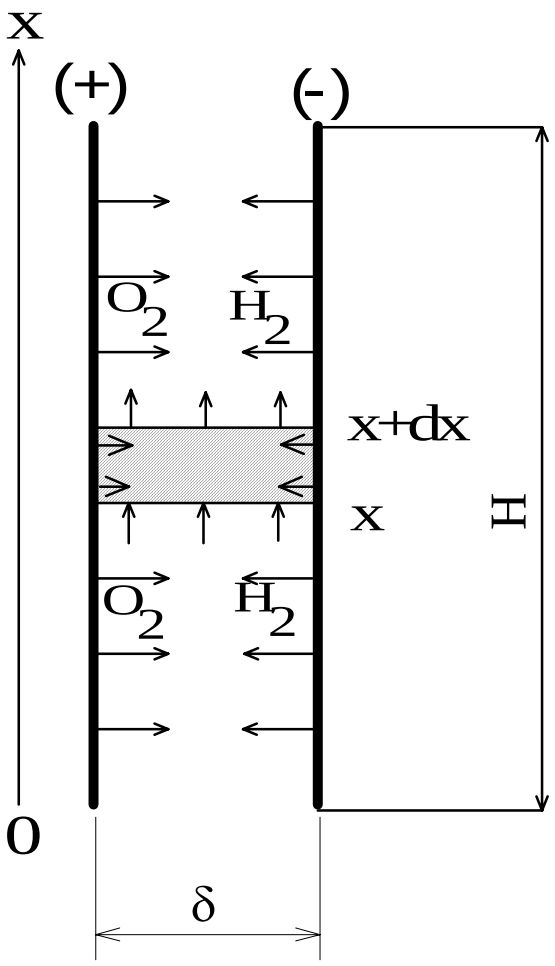


Figure10 Coordinates in Modeling of Void Fraction between Electrodes