TITLE

Analysis and visualization of water flow impact on hydrogen production efficiency in solid polymer water electrolyzer under high-pressure condition

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ABSTRACT

When a solid polymer water electrolyzer (SPWE) is operated under high-pressure conditions, a large pressure difference occurs between the anode and cathode. This causes crossover of produced gas, especially hydrogen gas, leading to a decrease in the production efficiency of an SPWE. As a countermeasure against gas crossover, water should be supplied into the cathode channel, as well as into the anode channel, because the water flow will facilitate the drainage of hydrogen gas outside of the cell, resulting in decreased crossover and increased efficiency of the SPWE. This countermeasure is evaluated by observing SPWE operation at a pressure of 2 MPa, with a visualization of hydrogen bubbles in the cathode channel. The evaluation revealed that supplying water into the cathode channel increases the efficiency by several percent at 0.33 A/cm^2 . Further, the visualization of the hydrogen bubbles revealed an enhancement in the separation of hydrogen bubbles from the surface of the current supplier. This suggests that additional water flow can increase the hydrogen production efficiency through promoting bubble detachment.

BODY

INTRODUCTION

Hydrogen gas is a candidate energy medium that contributes to a low carbon emission society. Because it is a secondary energy source, efficient production of hydrogen is essential for realizing an energy society based on hydrogen gas. Although a few alternative methods of producing hydrogen gas exist, water electrolysis driven by renewable electricity is expected to become the predominant method [1, 2]. From the viewpoint of energy density, hydrogen gas should be produced at a high pressure, such as 40 MPa. Thus, the complete process of hydrogen production involves the addition of water at atmospheric pressure and producing hydrogen gas at high pressure.

Figure 1. Comparison of high-pressure hydrogen gas production paths, including one with a water electrolyzer. The high-pressure electrolyzer path has advantages in the energy cost of gas compression and drying.

Fig.1 shows two possible paths for producing high-pressure hydrogen gas: the conventional process and a high-pressure electrolysis process [3, 4]. In the conventional process, water is electrolyzed at atmospheric pressure, and the produced hydrogen gas is pressurized using mechanical gas compressors. In the high-pressure electrolysis process, water is first compressed using water pumps, and then electrolysis is performed to directly produce high-pressure hydrogen gas. There is also an alternative approach that involves high-pressure water electrolysis, in which the electrolyzer itself has two roles: electrolyzing water at atmospheric pressure and pressurizing the hydrogen gas within the electrolyzer. A comparison between the conventional process and the high-pressure water electrolysis process suggests that the high-pressure water electrolysis process has advantages in practice [4]. The high-pressure water electrolysis does not require a mechanical gas compressor; the compressor is not acceptable level in terms of efficiency and maintainability. Additionally, because the high-pressure operation decreases the ratio of water vapor in the hydrogen gas, high-pressure water electrolysis can decrease the energy cost required to dry the produced hydrogen gas. Conversely, the conventional process requires a compressor, and requires relatively large quantities of energy to dry the gas. The advantages of high-pressure electrolysis have motivated

companies to demonstrate high-pressure water electrolysis with solid polymer water electrolyzers (SPWEs) [5, 6], in which a solid polymer is used as the electrolyte.

Although the use of SPWEs in high-pressure operation is expected to be an advanced method to directly produce high-pressure hydrogen gas, the production efficiency of SPWEs is expected to decrease. Under high-pressure operation, a large pressure difference occurs between the anode and cathode, and the produced hydrogen gas permeates through the polymer electrolyte membrane from the cathode to the anode, leading to a decrease in the production efficiency of hydrogen gas. In the case of a pressure of 40 MPa and electrolysis current of 1 A/cm^2 , an estimation based on the gas permeability [7] of a Nafion 112 membrane suggests that the amount of permeating hydrogen gas reaches 10% of the theoretical amount of hydrogen production, reducing the production efficiency to 90%. Experimental studies [3] report a hydrogen gas crossover of 23%.

The problem of decreased production efficiency under high-pressure operation can be solved by the convection effect. Additional water is supplied to the channel in the cathode, pushing produced hydrogen gas outside the cell; this effect is expected to decrease the crossover. Although supplying water to the cathode is not generally required, this study intentionally supplied water to the cathode channel. The water flow conveys the hydrogen gas, appearing in the cathode, to outside of the cell. This promoted drainage of hydrogen gas may reduce the crossover, resulting in an increased production efficiency.

Figure 2. Convection effect, which enhances to drain hydrogen gas bubbles that appear on the surface of the channel side of the porous current supplier.

Figure 2 explains the convection effect. A hydrogen bubble is formed as a result of a cathode electrochemical reaction in the catalyst layer. This bubble passes through the porous current supplier and reaches the flow channel. The bubble finally drains out when it grows large so that the convection effect (drag force) surpasses the adhesion force between the bubble and the surface of the porous current supplier. The bubble leaves the surface and moves to the channel drain; this behavior is expected to impact and decrease the pressure and staying time of the hydrogen bubble on the catalyst layer. This is because the bubble on the surface of the porous current supplier has connection to that on the catalyst layer through the porous current supplier, as shown in Fig. 2. Moreover, as understood in visualization in a later section, the bubbles emerge in the channel in a discrete manner over the entire channel area, and thus, a high mass flux of hydrogen gas forms in the through-plane direction. From the above, the convection effect owing to the water flow intentionally supplied to the cathode channel enhances drainage of the hydrogen bubble; this enhancement practically results in a decrease in the pressure and staying time of the hydrogen bubble on the catalyst layer in the cathode, leading to less crossover of the produced hydrogen gas and an improvement in the **production efficiency**. In addition, the drag force on the bubble owing to the water convection effect is proportional to the square of the water flow rate. This result also implies that the convection effect improves the **production efficiency** of hydrogen gas.

This study, considering the above background information, evaluates whether water flow in a cathode channel enhances the detachment of hydrogen gas bubbles from a porous electrode, and whether the production efficiency is improved. This evaluation is conducted with an SPWE system, which operates under a pressure of 2 MPaG and also provides visualization of the cathode channel. A glass window built into the separator in the cathode and a high-speed camera help visualize the manner in which the water flow rate changes bubble behavior. Furthermore, the impact of this flow rate is analyzed with a simple force modeling of the bubble. The system measures the flow rate of the produced hydrogen gas, and its production efficiency is examined by comparing the measured hydrogen flow rate with the theoretical one. With this methodology, the impact of water flow rate both on hydrogen gas bubble behavior and on production efficiency is clarified.

EXPERIMENTAL METHOD

Water electrolysis system

Figure 3 shows the system that was designed and introduced. For both the anode and cathode, water is supplied with the pump built into the circulation piping. The circulation in the cathode is composed of a cell, gas/liquid separator, pressure reducing valve, and pump. The hydrogen gas produced by electrolysis is separated from water at the gas/liquid separator, and drains through the back pressure valve. The hydrogen gas boosts the pressure in the cathode, and the back pressure valve controls the pressure up to 2 MPaG. The circulation in the anode, which is operated at atmospheric pressure, is composed of a cell, gas/liquid separator, and pump.

The flow rates of the hydrogen and oxygen gases are measured with a flow meter (differential type, ALICAT, M-50SCCM) that is downstream of the back pressure valve. The SPWE cell used in this study is small, and the flow rates of both hydrogen and oxygen are of the order of 10 NmL/min. Moreover, in some operation conditions, the

flow rate may fluctuate. For these reasons, a differential-type flow meter was chosen, which can respond quickly and quantify the flow rate even if it is small. The precision and responsivity of the flow meter are $\pm 0.16 \text{ NmL/min}$ and 10 ms, respectively. The meter records the flow rate of hydrogen and oxygen every second. The recorded data are averaged, and the averaged value is set to be the flow rate of produced gas for each specific condition.

The flow rate $\dot{V}_{H_2}$ of the produced hydrogen gas thus measured and electrolysis current I can determine the production efficiency of hydrogen gas.

$$\eta_I = \frac{\dot{V}_{H_2} P_0 / (RT_0)}{I / (z_{H_2} F)}$$

The value of z_{H_2} is 2, which is the number of electrons involved in the hydrogen evolution reaction. F and R are the Faraday constant and gas constant. P_0 and T_0 are the standard pressure and temperature used in the flow meter, respectively.

Figure 3. Solid polymer water electrolyzer system. Operational pressure is 2 MPaG. Bubbles of hydrogen gas are visualized through the window in the cathode.

A high-speed camera (Keyence 9000) is placed above the window built into the cathode separator, as shown in Fig. 3, and this camera helps evaluate the impact of the water flow on the detachment of hydrogen gas bubbles from the porous electrode. The diameter of a hydrogen gas bubble is of the order of 100 μm . The bubble motion velocity, which is assumed to be the same as the water flow velocity in the cathode channel, is approximately 0.5 m/s. The bubbles at this size and velocity are captured under the photographing speed of 6000 fps with a lens having a deep focal depth (Keyence VH-Z25). An angled light illuminating the window, which is introduced with an optical fiber, improves the contrast of the bubble image.

Cell specifications

Table 1 lists the specifications of the water electrolysis cell. In the through-plane direction, the cell consists of a cathode separator, cathode channel plate, cathode current supplier, membrane electrode assembly (MEA), anode current supplier, anode channel plate, and anode separator. The cathode and anode channel plate are made from SUS316L with gold plating for the cathode, and titanium with platinum plating for the anode. The cathode and anode channel plate have a serpentine-shaped channel, where the width, height, and pitch between channels are 1, 5, and 2 mm respectively. The cathode and anode current supplier are SUS sintered compact and titanium sintered compact with platinum plating. The platinum plating decreases the contact resistance on the titanium surface.

Nafion324 membrane is used as the polymer electrolyte membrane (PEM). The PEM is loaded by a differential pressure of at most 2 MPa between cathode and anode, because the pressure is boosted in the cathode in this study. The differential pressure causes a large tensile stress on the PEM. In addition, the PEM is subjected to cycles of humidified and dried conditions. The PEM is humidified during operation, and is dried in a purge process after the operation. The PEM is predicted to expand and shrink, causing mechanical fracture. Thus, the Nafion324 membrane is introduced, which is reinforced with Teflon fiber and is comparatively highly dimensionally stable. A

MEA is fabricated on the Nafion324 membrane with electroless plating [8]. Iridium and platinum is plated for the anode, and platinum for the cathode. The electrode area, which should have the same area as the electroless plating, is 3 cm^2 .

Table 1.Cell Specifications.

Component	Specification
MEA	
	PEM Nafion 324
	Cathode/Anode catalyst layer Pt/C / PtIr
Channel plate	
	Anode material Pt-plating on Ti
	Cathode material Au-plating on SUS316L
	Channel width × height × length 1 mm × 5 mm × 52 mm
	Channel pattern Serpentine type
Current supplier	
	Anode Ti-sintered compact with Pt-plating
	Thickness:0.3 mm
	fiber diameter: 20 μm
	Porosity: 0.7(400 g/m ²)
	Pt thickness: 1 μm
	Cathode SUS316L sintered compact
	Thickness: 0.3 mm
	fiber diameter: 35 μm
	Porosity: 0.75(600 g/m ²)
Separator	

Operation condition

As mentioned above, the pressure in the cathode is 2 MPaG and that in the anode is atmospheric pressure. In general, there are two types of high-pressure SPWEs: The first has high pressure only in the cathode [2] similar to the SPWE employed in this study, and the second is balanced, i.e., it has high pressure in both the cathode and anode [3]. The former has an advantage in simplicity. However, because of the high differential pressure, there is a requirement of some support for the PEM. The latter has an advantage in being without differential pressure. It also has the side-benefit of the production of high-pressure oxygen gas (which is valuable for space applications). However, the latter type and requires a rather complex system, and there is a safety issue because of the high-pressure oxygen gas. This study examines the impact of water flow on the crossover and production efficiency of hydrogen gas. An SPWE with pressurizing only in the cathode meets the objective of this study.

The water flow rate in the cathode, which is the key operation parameter, is adjusted so that the volumetric ratio of hydrogen gas to water is approximately 5% to 10%. The volumetric flow rate of produced hydrogen gas under a standard state of 20°C and 1 atm is 7.6 NmL/min at the representative electrolysis current of 1 A (0.33 A/cm²) in this study. The water flow rate in cathode is regulated to 150, 120, and 80 mL/min. Thus, the volumetric ratio of hydrogen gas to water is 5.1% to 9.5%. The volume of hydrogen gas decreases by 1/20 under the 2 MPa condition, and the volumetric ratio becomes 0.026% to 0.48%. The superficial velocity of water, regulated with the channel cross section, is 0.27 m/s to 0.5 m/s. In terms of the Reynolds number, the velocity can be specified in 443 to 830. The velocity of the hydrogen gas ranges from 0.13 m/s (0.1 MPa) to 0.006 m/s (2.0 MPa). These superficial velocities suggest that flow region of water and hydrogen gas mixture is “Bubbly” in the gas/liquid two-phase flow

map [9]. The water flow rate in the anode is fixed to be 80 mL/min. The utilization ratio of water in anode is 70 ppm, which implies that a large amount of water is supplied compared to the water that is electrolyzed.

Before water electrolysis, the function of the each component of the SPWE system is carefully checked. In particular, the gas seal at the piping and cell is proved for a precise evaluation of production efficiency. A gastight test under 2 MPaG of hydrogen gas, provided by a hydrogen gas cylinder with a regulator valve, is performed after assembling the cell and mounting it on the SPWE system. The pressure loss due to small leakage appeared to be less than 0.01 MPa for 5 min, corresponding to a leakage rate of 0.056 NmL/min. For comparison, the theoretical production rate of hydrogen gas is 7.6 NmL/min in the representative case of electrolysis current of 1 A. Thus, the impact of the gas leakage to the production efficiency is approximately 0.7%, and can be ignored in this study. All experiments (water electrolysis) were conducted in room temperature; the thermocouples in the anode and cathode separator indicated the temperature to be between 18°C and 25 °C.

Figure 4. Force balance modeling of hydrogen bubble that detaches from the electrode (porous current supplier) into the channel. Horizontal and vertical force balance can be obtained from this modeling.

FORCE BALANCE MODELING

Bubble diameter

A force balance model on the bubble, as shown in Fig. 4, is used for analyzing the detachment behavior of bubbles obtained with the visualization. It also helps understand the relationship between the water flow rate and the amount of hydrogen gas crossover, more precisely between the water flow velocity and hydrogen production efficiency. This model can estimate the bubble diameter when the bubble detaches from the porous electrode (porous current supplier). During water electrolysis operation, the hydrogen gas bubble is attached to the electrode by surface tension F_A . The horizontal and vertical components of surface tension can be described as follows [10].

$$F_A^H = \sigma d \frac{\pi}{2} \left[\frac{\sin(\Delta\theta - \theta) - \sin(\theta + \Delta\theta)}{2\Delta\theta - \pi} + \frac{\sin(\Delta\theta - \theta) - \sin(\theta + \Delta\theta)}{2\Delta\theta + \pi} \right] \quad (1)$$

$$F_A^V = \sigma \pi d \sin\theta \quad (2)$$

where σ is the surface tension, d is the diameter of bubble, θ is the contact angle shown in Fig. 4, and $\Delta\theta$ is the change in the angle when the bubble is detached.

Additionally, a drag force caused by the water flow (convection effect) acts on the bubble in the horizontal direction, and a buoyancy force acts in the vertical direction.

$$F_D^H = \frac{1}{2} \rho_l U^2 C_D S \quad (3)$$

$$F_B^V = \frac{\pi}{6} d^3 (\rho_l - \rho_g) g_0 \quad (4)$$

Here, ρ_l is the density of water, U is the velocity of water, and C_D is drag coefficient. S is a representative area over which the drag force acts, $S = \pi \left(\frac{d}{2}\right)^2$. ρ_g is the density of hydrogen gas, and g_0 is the gravitational acceleration.

Under the condition that the bubble remains stationary on the electrode, the horizontal component of the surface tension balances with the drag force, and the vertical component balances with the buoyancy force.

$$F_A^H = F_D^H \quad (5)$$

$$F_A^V = F_B^V \quad (6)$$

Eq. (5) with the Eqs. (1) and (3) estimates the bubble diameter determined by the force balance between the drag force and horizontal component of the surface tension.

$$d = d_D = \frac{4\sigma}{\rho_l U^2 C_D} \left[\frac{\sin(\Delta\theta - \theta) - \sin(\theta + \Delta\theta)}{2\Delta\theta - \pi} + \frac{\sin(\Delta\theta - \theta) - \sin(\theta + \Delta\theta)}{2\Delta\theta + \pi} \right] \quad (7)$$

The physical properties shown in this equation are listed as follows. The water density at 20°C and 0.1 MPa is $\rho_l = 998.2 \text{ kg/m}^3$ [3, 11]. The surface tension between hydrogen gas and water is $\sigma = 7.198 \times 10^{-2} \text{ N/m}$ [12]. A representative water flow velocity is $U = 0.27 \text{ m/s}$ (in the case of 80 cc/min). The static contact angle measured by the falling drop method is $\theta = 120^\circ$, and the contact angle hysteresis is assumed to be $\Delta\theta = 5^\circ$. The drag coefficient is also assumed to be $C_D = 1$. Substituting these properties results in $d_D = 250 \text{ }\mu\text{m}$. Thus, the manipulations on the horizontal force balance reveal the physical situation that a hydrogen bubble on the electrode detaches due to the drag force given by the water flow in the channel, when the bubble diameter reaches several hundred micrometers.

Alternatively, Eq. (6) with Eqs. (2) and (4) yield a different diameter for bubble detachment that is determined by the vertical force balance between the buoyancy force and vertical component of the surface tension.

$$d = d_B = \left[\frac{6\sigma \sin \theta}{(\rho_l - \rho_g)g_0} \right]^{\frac{1}{2}} \quad (8)$$

Substituting the properties into this equation gives $d_B = 6180 \text{ }\mu\text{m}$. Thus, it is understood that the hydrogen bubble detaches from the electrode into the water channel due to the buoyancy force when the diameter reaches several thousand micrometers.

Thus, the estimations for the system in this study result in $d_D \ll d_B$, implying that the drag force by water flow in the channel is superior to the buoyancy force. Namely, the drag force by water flow, the convection effect, causes the hydrogen bubble to detach into the channel when the diameter of the bubble becomes several hundred micrometers. Moreover, as Eq. (7) suggests, a higher water flow rate decreases the diameter in proportion to the inverse square of the flow rate, and increases the frequency of bubble detachments, leading to the suppression of hydrogen gas crossover and to the improvement of production efficiency.

The impact of pressure on the surface tension and densities involved in Eq. (7) should be considered. Although these properties have pressure dependence, they change only a small amount, less than 1% [8, 9] within the pressure range in this study (from atmospheric pressure up to 2.0 MPaG). Thus, changing operation pressure does not change the detachment diameter.

Detachment frequency

The hydrogen bubble repeatedly forms and detaches on the porous electrode. The frequency of this behavior can be determined with the assumption that the bubble leaves the electrode when the diameter reaches d_D shown above. Based on this assumption, we can estimate the frequency through calculating the hydrogen gas molar number n_{H_2} within the bubble volume V_{H_2} denoted with d_D , and the specific time when the amount of hydrogen gas reaches the molar number n_{H_2} .

The equation of state for ideal gas gives the molar number n_{H_2} within the volume V_{H_2} .

$$n_{H_2} = \frac{V_{H_2} P_{Cat hode}}{RT} = \frac{\frac{\pi d_D^3}{6} P_{Cat hode}}{RT} \quad (9)$$

where R is gas constant and T is temperature. $P_{Cathode}$ is the operation pressure at the cathode. It is assumed that the partial pressure of hydrogen gas in the bubble is the same with the operation pressure. The low temperature operation (i.e., room temperature) of this study is consistent with this assumption.

The time t to achieve this molar number n_{H_2} can be directly estimated by the Faraday law.

$$n_{H_2} = \frac{It}{z_{H_2}F} \quad (10)$$

where I is load current and F is Faraday constant. z_{H_2} implies two electrons contribute to the cathode cell reaction.

Considering that the reciprocal of t is the frequency of bubble detachment, Eqs. (9) and (10) give the frequency of f .

$$f = \frac{1}{t} = \frac{6}{\pi} \frac{RTI}{d_D^3 P_{Cathode} z_{H_2} F} \quad (11)$$

This suggests that a lower pressure increases the frequency. Eliminating d_D in this equation with Eq. (7) yields,

$$f = \frac{1}{t} = \frac{3}{32\pi} \frac{\rho_l^3 U^6 C_D^3 RTI}{\sigma^3 P_{Cathode} z_{H_2} F} \left[\frac{2\Delta\theta - \pi}{\sin(\Delta\theta - \theta) - \sin(\theta + \Delta\theta)} + \frac{2\Delta\theta + \pi}{\sin(\Delta\theta - \theta) - \sin(\theta + \Delta\theta)} \right]^3 \quad (12)$$

The frequency is thus indicated to depend strongly on the flow velocity U .

Taking the conclusions of Eqs. (7) and (11) together, it is expected that a higher water flow velocity (or rate) will decrease the diameter of bubble at detachment from the porous electrode, and increase the frequency, leading to lower crossover and an improvement of the production efficiency. The cathode pressure is expected to have no effect on the bubble diameter, but is inversely proportional to the frequency. These understandings based on the simple force balance modeling and its analysis allow a quantitative discussion of the production efficiency and bubble visualization that are shown in the following sections.

RESULTS AND DISCUSSION

Production efficiency

Figure 5 shows the production efficiency of hydrogen gas produced under the cathode pressure conditions of 0.3, 0.65, and 2 MPaG. The production efficiency decreases with an increase in pressure. It is considered that the higher pressure in cathode corresponds to a larger differential pressure between the cathode and anode, resulting in more crossover and a smaller production efficiency of hydrogen gas. In agreement with this consideration, Fig. 5 indicates that increasing the pressure from 0.3 to 2 MPaG results in increasing the crossover by several percent (decreasing the production efficiency by several percent). Assuming that the permeability of the Nafion324 membrane is same as that of the Nafion117 membrane⁴, estimation under a differential pressure of 2 MPa and current density of 0.33 A/cm² gives the same amount of hydrogen crossover. Other researchers [13, 14] also suggest approximately the same amount of hydrogen gas crossover. These agreements provide some verification of the measurement.

Figure 5. Hydrogen production efficiency with and without the water flow in the cathode. The production efficiency with water flow is higher than that without it. Operation at a higher pressure operation decreases the efficiency. The efficiency shown here is normalized by the largest value, which was obtained under the 0.3 MPaG and 120 cc/min condition.

Figure 5 indicates a convection effect as expected. The production efficiency with water flow is higher than that without the water flow (0 cc/min). The convection effect caused by the water flow in the cathode promotes the detachment of a hydrogen gas bubble from the electrode, leading to an increase in the production efficiency.

Although the experimental results demonstrated the convection effect where the production efficiency is higher for the case with water flow, the results indicated variations in the dependence of the water flow rate on production efficiency. For instance, the data under 2 MPaG do not show a clear impact of the flow rate, although the production efficiency in the case with water supply is higher than that in the case with no water supply. This study regulated the water flow rate with the pump shown in Fig. 3. Nevertheless, the flow rate monitored by a flow meter was unstable, especially under the higher pressure and smaller flow rate conditions. This limited control of the flow rate is believed to obscure the dependence of the water flow rate on the production efficiency.

Visualization results

Figure 6 shows photographs of a hydrogen gas bubble that appeared on the surface of the porous current supplier within the cathode channel. Although bubbles may intermittently appear in any place on the surface, their appearance is limited to the edge between the current supplier and channel sidewall. The bubble appeared at the edge, grows, detaches within a couple of milliseconds, and flows downstream in the channel. Moreover, this

successive bubble behavior happens in a repetitive manner at the same points. It is noted that, in addition to the characteristic of bubble behavior, bubbles emerge in a discrete manner over the entire channel area. This tendency implies that a high mass flux of hydrogen gas in the through-plane direction forms, and the tendency may enhance the crossover.

The reason for the bubble formation at the edge is thought to be that electrolysis current concentrates in the place below the rib. Although the porous current supplier positioned between MEA and separator is expected to distribute the applied current homogeneously, some factors such as contact resistance may cause the current to concentrate below the rib. Therefore, hydrogen gas was produced below the rib and appeared as bubbles at the edge between the channel sidewall and current supplier.

(a) 0.0 ms, generation

(b) 0.2 ms, growth

(c) 0.5 ms, detachment

(d) 6.8 ms, moving

(e) 17.2 ms, moving to outlet

Figure 6. Behavior of a hydrogen gas bubble appearing on the surface of the porous current supplier in the cathode. The convection effect, obtained by intentionally supplying water to the cathode channel, promotes the detachment of a hydrogen bubble from the surface of the porous current supplier into the channel.

Relationship between detachment diameter and production efficiency

Figure 7 shows the bubble diameter obtained from the visualization. The bubble was visualized for the each pressure and flow rate condition, and the bubble diameter was determined by averaging the diameters of approximately 30 bubbles under the high-pressure condition and 300 bubbles under the low-pressure condition. The diameters under the 0.65 MPaG condition indicate that the smaller diameter appears in the higher flow rate case of 150 cc/min, suggesting that the convection effect functioned to enhance the detachment of bubble. This tendency agrees with the impact of the flow rate on the production efficiency on Fig. 5.

Figure 7. Bubble diameter when the bubble detaches from the current supplier. The data plotted are average values obtained by observing 30–300 bubbles.

The relationship between the diameter and flow rate can be discussed with Eq. (7) derived from the force balance modeling on a bubble. The increase in the water flow rate from 80 to 150 cc/min corresponds to the increase in its velocity by $15/8$ times, suggesting that the bubble diameter is multiplied by $(15/8)^2=0.28$. Thus, this increase in the flow rate causes the diameter to reduce to less than half. However, the visualization results did not show this large change in diameter. An unstable water flow rate, as mentioned above, seems to cause this difference in the effect of the flow rate between the visualization result and the analysis based on the force balance modeling.

Conversely, for the effect of pressure on the detachment diameter, there is agreement between the visualization result and the prediction by the force balance modeling (Eq. (5) and (7)). The surface tension σ and water density ρ_l vary as a function of pressure, but the effect of pressure is less than 1% in the range from 0.3 to 2.0 MPaG [8, 9]. Thus, Eq. (7) indicates that the detachment diameter is not dependent on the pressure. The visualization result in Fig. 7 also has a similar tendency, suggesting an agreement between the visualization and the prediction by the modeling.

Figure 8. Frequency with which bubbles detach from the surface of the current supplier.

Relationship between detachment frequency and production efficiency

Figure 8 shows the detachment frequency obtained from the visualization. The frequencies in the higher flow rate cases at 120 and 150 cc/min are higher than the frequency in the lower flow rate case of 80 cc/min. This tendency of detachment frequency also supports the existence of the convection effect, having a consistently high production efficiency at a higher flow rate, as shown in Fig. 5.

Eq. (12) is used to understand the detachment frequency, driven by the force balance modeling. The impact of pressure on the detachment frequency is consistent between Eq. (12) and the visualization. The equation suggests that the detachment frequency is inversely proportional to the pressure, namely that higher pressure decreases the detachment frequency. Here, the dependence of the pressure on surface tension and water density in Eq. (12) can be ignored. The visualized detachment frequency, shown in Fig. 8, also indicates the inverse proportionality with the pressure. As explained in the previous section of the modeling, a certain volume is required for bubble detachment to occur, such that the drag force by the convection of water is equal to the adhesion force by surface tension. A higher pressure, if imposed, requires a larger molar number of hydrogen gas to fill the volume of the bubble, resulting in a longer time to reach the volume. This is the mechanism where the detachment frequency is inversely proportional to the pressure.

SUMMARY

This study designed and constructed a solid polymer water electrolysis system that can visualize the channel in cathode and can be operated at a pressure of up to 2 MPaG in the cathode. This system evaluated the convection effect by water flow in cathode channel, with the following conclusions:

(1) The **production efficiency** increased by a maximum of 5% with the water flow, compared to the case without the flow.

(2) Water flow decreased the diameter of hydrogen gas bubbles by 10% or less. It also increased the detachment frequency of the bubbles by approximately 10% to 20%. These effects of the flow on the bubble behavior support the convection effect, causing higher **production efficiency** at a higher flow rate.

(3) The hydrogen gas bubble appears at the edge between channel sidewall and porous current supplier, and grows and detaches within several milliseconds. This behavior is reproduced at the same place in repetitive manner.

(4) The pressure in cathode does not change the diameter of a hydrogen bubble when it detaches from the supplier, but does reduce the detachment frequency in an inversely proportional manner.

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