Control of hydrogen bubble plume during electrolysis of water

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Abstract

Hydrogen bubble plumes are generated from the cathode during electrolysis. The plume formation mechanism contributes to the control of bubble diameters and alignment in solvent. The generation of hydrogen bubbles (HBs) and oxygen bubbles (OBs) from electrodes was observed in tap water and saline using a high-speed microscope. Bubble diameter changes were analysed from the obtained microscopic images, and the growth kinetics of HBs and OBs were compared. The result showed that plume formation was primarily dependent on ion strength of water and not voltage to the electrode. HB diameter change in plume was proportional to the distance from the cathode in tap water. Such correlation between HB diameter and distance from the cathode was not observed in saline. By simultaneous observation of HBs and OBs attached to the electrodes, the increase in HB diameter was faster than that of OB. The kinetic properties in HBs and OBs were proportional to (time)\(^{1/2}\) and (time)\(^{1}\), respectively, suggesting that the diffusion of oversaturated hydrogen gas and pressure difference at OB surfaces were dominant. Based on these results, HB plume formation was determined by the lower gas solubility and mass density of HB than that of OB, as well as controlled by voltage and ionic strength of water.

1. Introduction

Fine bubbles are currently used to cleaning, as an ultrasound contrast reagent and for blood oxygenation [1–7]. Fine bubbles are generated by Venturi effect systems, partial heating method, sonication, microfluidic devices and hydrogen bubble method [1–13]. Bubble growth or shrink kinetics is influenced by generation method and solvent type [14–21]. Bubble gas is important in the application of fine bubbles. For example, fluorocarbon microbubbles are preferably used as an ultrasound contrast reagent [22], whereas oxygen bubbles (OBs) are inevitably used for blood oxygenation [5, 23].

Hydrogen bubbles (HBs) are generated by electrolysis of conductive water including acid and base, by a method called as the hydrogen bubble method. HBs and OBs are generated from the cathode and anode, respectively [12–20]. Simultaneous HB and OB generations using charge-coupled device (CCD) camera were exhibited in KOH solution on proton exchange membrane [12]. Chandran et al. reported the growth rate of HBs in bubble plume during water electrolysis for an hour [13]. Oxygen evolution reaction on perovskite-based electrode was analysed in alkaline media by observing the increase in OB volume using optical microscope and chronocoulometric measurements [14]. Generation kinetics are useful for the control of bubble diameter, a factor that determines their potential applications. The question regarding the generation of HB plumes by electrolysis instead of OBs is still unanswered. We are also considerably interested in the critical physical properties of gas and water in the regulation of bubble plume formation. Microscopic analyses of HB and OB behaviours should provide solutions for these questions.
Here, to solve these questions, we investigated diameter changes of floating and adhering HBs as well as adhering OBs to electrodes using a high-speed camera for 1000 fps. The plume generation of HBs from the tungsten cathode was observed. The influences of bubble diameter changes induced by ion strength as well as dissolved gas neighbouring the electrode were studied to effectively regulate bubble functions that are determined by diameter and gas molecule. This study provides insights into bubble plume generation and bubble diameter kinetics, which might be useful for tracer generation, separation, purification and cleaning.

2. Materials and methods

2.1. Hydrogen bubble methods and preparation of the bubble generating container
HBs and OBs were generated from a tungsten cathode and stainless iron anode with diameters of 0.1 mm and 1 mm, respectively. We used two containers for bubble generation: (1) an acrylic container with a height of 15 cm for side observation (figure 1(A)) and (2) a plastic container by cutting cuvette with a height of 5 mm for observation of generated bubbles neighbouring the electrodes (figure 1(B)). Diameters of the observed bubbles were analysed using Image J (National Institutes of Health, Bethesda, MD, USA) [6].

2.1.1. Observation of HBs
Voltages of 1.8–10.0 V between the two electrodes were applied using a direct current power supply without controlling the current. We observed bubbles generated from the cathode from the side using a high-speed camera (Keyence VW-9000, Osaka, Japan), which was connected with a microscope (Z16APO, Leica Microsystems, Tokyo, Japan) as shown in figure 1(A). Frame rate of the observation was 1000 fps. Using bubble generating container (1), HBs floated from the tungsten wire electrode. We used tap water and saline (0.9 w/w%
sodium chloride, Otsuka Pharmaceutical Co., Ltd, Tokyo, Japan) as solvents for bubble generation. Plume formation was considered as the uniform bubble diameter from areas of the cathode.

2.2. Simultaneous observation of HBs and OBs

We set the container (2) in a position so that it did not physically interact with the microscope lens on the upright microscope stage (MULTIZOOM AZ100, Nikon Corporation, Tokyo, Japan). HBs and OBs that were generated from tungsten and stainless electrodes, respectively, were simultaneously recorded from the top as shown in figure 1(B). We used the same high-speed camera as described above. Kinetic data points of HB and OB diameters were curve-fitted using IGOR Pro (WaveMetrics, Inc., Portland, OR, USA).

3. Results and discussion

3.1. Generation of bubble plume from cathode

As shown in figure 2(A), we observed the HB floatation called as bubble plume in tap water after voltage input of 3.4 V for 1 min. When a direct voltage of 1.6 V was applied to saline, HBs were generated randomly and no plume was observed as shown in figure 2(B). Because the conductivities of saline and tap water are 16.0 and 0.2 mS cm\(^{-1}\), respectively, ion strength, i.e. the number of ions that function as charge carriers in water, is possibly associated with the generation of HB plume \([25, 26]\). Figures 3(A) and (B) show the relationship between the distance from the cathode and HB diameter in tap water and saline, respectively. When ion strength, decreases, the resistance between the electrodes increases, resulting in an increase in the number of HBs generated, as shown in figure 2(B). In the case of saline, the number of bubble generation sites increased compared with tap water, and the generated HBs in the plume interacted less frequently with neighbouring bubbles because of non-periodic bubble generation. Size control of HBs and plume conditions were related to solvent, electrode and voltage between electrodes, which is discussed later.

3.2. Correlation between distance from electrode and floatation velocity of HB

Figure 3(C) shows the relationship between distance of HBs from the cathode and HB floatation velocity. Increasing distance of HBs from the cathode increased the floatation velocity. Therefore, floatation was accelerated with the increase in diameter of bubbles neighbouring an electrode. Under plume generating conditions, the coefficient of determination was almost 1, and derived from the uniform bubble diameter and the same bubble buoyancy. Because of the correlation between distance from cathode and bubble diameter, almost the same floatation velocity of the generated bubble was found in saline. Therefore, uniform bubble diameter from the cathode is necessary for continuous plume generation of HBs.
3.3. Effects of salt concentration in tap water

Figure 4 shows the relationship between HB plume structure and conductivity of solvents using mixture of tap water and saline possessing different conductivities. Solvent conductivities of the mixture were measured and calculated by the linear combination of conductivities of tap water and saline. We considered plume formation as the generated bubbles having the same bubble diameter from the same area of the cathode. By increasing the solvent conductivity, frequent bubble fusion neighbouring the cathode was found in data points 'plume with bubble fusion'. Bubble number and non-uniformity of HB diameter were observed in the points 'No plume' in solvents having conductivities larger than 4 mS cm\(^{-1}\). Plume formation was primarily dependent on solvent conductivity rather than electrode voltage.

3.4. Diameter change kinetics of HB and OB

Figure 5 shows cropped microscopic images of HBs and OBs adhering to cathode and anode, respectively, from a recorded video. By comparison, the increase of HB diameter was larger than that of OBs. Figures 6(A) and (B) show kinetic properties of bubble diameter variations of three HBs and three OBs, respectively, at 3 V of applied voltage. The HB diameter at the starting point of the diameter evaluation was approximately 60 \(\mu\)m. When the HB diameter increased to 100–200 \(\mu\)m, these bubbles were detached from the cathode.

Different bubble generation mechanisms have been considered to explain the growth kinetics of HB and OB diameters [27–31]. The concentration of gas in the liquid is governed by diffusion (Fick’s second law), as shown in equation (1) [28]. Details of its formulation are shown in references [31, 32].

\[
\frac{dc}{dt} = D \left( \frac{2}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right)
\]  

The gas is saturated at the bubble’s surface \(r = R\). We defined the saturated gas concentration as \(c_s\). An oversaturated gas concentration of initial condition in solvent is considered as \(c(r = \infty, t = 0) = c_L (c_L > c_s)\).
Considering these boundary conditions, equation (1) can be solved to produce equation (2), where $\rho$ is the solvent density.

$$\frac{dR(t)}{dt} = \frac{D(C_L - C_s)}{\rho} \left( \frac{1}{R(t)} + \frac{1}{\sqrt{\pi Dt}} \right)$$

(2)

The first and second terms on the right side represent steady and transient states, respectively. Under oversaturated conditions, only the transient state applies and the first term can be ignored to represent fast kinetics of bubble radius changes to produce equation (3).

$$\frac{dR(t)}{dt} = \frac{c_L - c_s}{\rho} \sqrt{\frac{D}{\pi t}}$$

(3)

The solution of equation (3) yields equation (4), where $2R(t)$ and $D$ are the diameter of the observed bubbles and the diffusion coefficient of hydrogen gas, respectively.

$$2R(t) = 4\beta \sqrt{Dt} + 2R(0)$$

(4)

The growth kinetics of the HB diameters can be explained using a function of $(\text{time})^{1/2}$ such as in equation (5), which represents gas transfer through the interface by the diffusion of hydrogen molecules in the solvent [16, 20].

$$2R(t) = k \sqrt{t} + l$$

(5)

The data points in figure 6(A) were curve-fitted to equation (5), which enabled us to calculate values for $k$ and $l$ of equation (5). The average calculated kinetic parameter ($k$) of the three traces in figure 6(A) was $(4.0 \pm 0.1) \times 10^{-5}$ ms$^{-1/2}$. The oversaturation parameter $\beta$ was calculated to $0.15 \pm 0.005$ by $\beta = k/(4\sqrt{D})$. These values are similar to those reported previously in water electrolysis experiments (0.22–0.63) [13]. In the case of our experiments, the HB growth is related with the supersaturation of hydrogen gas in solvent.

OB diameters at the starting point of the diameter evaluation were 50–300 μm. Diameter increase in OBs was fitted using a linear function. This linear kinetic model suggests that bubble growth is driven by the difference in pressures inside and outside the bubbles, which was calculated from the equation of continuity for incompressible fluid with spherical symmetry and the Navier–Stokes equation for incompressive Newtonian
fluid, known as the ‘Rayleigh equation’ [16, 30, 32]. When we ignore effects of surface tension and solvent kinematic viscosity, the equation is equation (6) [30, 33].

\[
\frac{P_r(t) - P_\infty(t)}{\rho} = R \frac{d^2R}{dt^2} + \frac{3}{2} \left( \frac{dR}{dt} \right)^2
\]  

(6)

\(P_r(t)\) and \(P_\infty(t)\) represent pressures at the bubble surface and at infinity, respectively. Because the radius increase kinetics was proportional to time, \(\frac{dR}{dt} = 0\) and \(\frac{dR}{dt} = A/2\) can be considered in this case. Parameter \(A\) includes the difference in pressures (equation (7)) [30, 33]. \(R(t)\) can be described as equation (8). Parameter \(B\) is a constant for initial diameter at the measurement.

\[
A = 2 \left\{ \frac{2(P_r(t) - P_\infty(t))}{3 \rho} \right\}^{1/2}
\]  

(7)

\[
2R(t) = At + B
\]  

(8)

The average constant of proportionality (\(A\)) of three OBs was \((2.8 \pm 0.2) \times 10^{-6} \text{ m s}^{-1}\). When HB diameter kinetic traces were fitted using the linear model, the \(A\) value was 4.1 times smaller than that of HBs at \((1.14 \pm 0.04) \times 10^{-5} \text{ m s}^{-1}\). Therefore, the rate of diameter increase of HBs neighbouring the cathode was larger than that of OBs around the anode.

3.4.1. Comparison of kinetic models of bubble diameter change

Table 1 depicts characteristics of hydrogen and oxygen gases. The relationship between physical properties of hydrogen gas and plume formation was discussed. Bunsen’s solubility coefficients of hydrogen and oxygen are 0.018 and 0.031, respectively [34, 35]. Diffusion coefficients of hydrogen and oxygen gas in water (25 °C) are \(4.5 \times 10^{-9}\) and \(2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}\), respectively [36]. The lower solubility and higher diffusion coefficients of HBs affect both diameter increase and plume generation.
The faster increase of HB diameter than that in OB is discussed here. Gas concentration of hydrogen under oversaturation conditions would be less than that of oxygen during water electrolysis as previously mentioned \[37\]. The increasing speed of HB diameter was larger than that of OB at the onset of the diameter observations because of a higher oversaturation of HB than OB in the solvent. Hydrogen gas in solvent would be transported into HBs due to less solubility. Because the mass density of hydrogen is approximately 1/16 of that of oxygen gas, HBs were easier to be detached from the cathode by buoyancy of HBs having smaller diameter than that of OB \[38\]. Therefore, the observed bubble diameter increasing kinetics and these characteristics suggest that hydrogen concentration in the solvent was oversaturated for bubble generation and that dissolved oxygen gas

**Figure 6.** Bubble diameter change kinetics of (A) hydrogen and (B) oxygen bubbles.

**Table 1.** Comparison of coefficients between hydrogen and oxygen.

|                        | Hydrogen       | Oxygen        | Ratio | References |
|------------------------|----------------|---------------|-------|------------|
| The solubility coefficient of Bunsen at 20 °C | $1.8 \times 10^{-2}$ | $3.1 \times 10^{-2}$ | 0.58  | \[33, 34\] |
| Diffusion coefficient (m²/s) | $4.5 \times 10^{-9}$ | $2.1 \times 10^{-9}$ | 2.14  | \[35\]     |
| Saturation concentration at 20 °C (g/m³) | $1.6 \times 10^{-5}$ | $4.4 \times 10^{-5}$ | 0.036 | \[36\]     |
| Mass density (g/m³) | $9.0 \times 10^{-5}$ | $1.4 \times 10^{-3}$ | 0.063 | \[37\]     |
concentration would not change. The excess oversaturation of hydrogen gas in saline results in non-plume HB
generations from various sites of the cathode, and the control of gas concentration in solvent is important for
bubble plume generation. Based on these results, we consider that the most critical physical property of HB
plume generation would be lower solubility to the gas and lower mass density.

4. Conclusion

Summary of the insights from this study are described as below.

- In hydrogen bubble method, bubble plume generation was dependent on the ion strength of the solvent.
- Bubble diameter change was derived from the diffusion of dissolved gas. In water electrolysis, the bubble
diameter increased after bubble generation for both hydrogen and oxygen because of oversaturation of
the gas.
- The bubble diameter of HBs was smaller than that of OBs. The diameter change would depend on low
solubility of hydrogen gas to water and 
  floatation velocity of the bubbles.
- Bubble diameter and plume control in hydrogen bubble method were associated with solvent ion strength.
  Bubble fusion neighbouring electrode should be prevented to decrease the bubble diameter.
- The solubility of hydrogen gas to the solvent is the most critical property for bubble plume generation, because
the gas solubility induces oversaturation of the gas and a faster diameter increase than that of OB. The faster
diameter increase and detachment of HB from the cathode would be important for plume generation related
with lower solubility and mass density.
- These insights regarding HB plume formation can be used for evaluation of fluid flow by particle image
  velocimetry in water and pipe cleaning in microfluidic channels.

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Appendix

Formulation of equation (A5) from equation (A1) was based on [28].

\[
\frac{dc}{dt} = D \left( \frac{2}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2} \right) \tag{A1}
\]

Gas concentration gradient at the surface of bubble \((r = R)\) was shown as equation (A2) from equation (A1)
based on the references [20, 28, 29]. Boundary conditions of concentrations are \(c(r = R, t = 0) = c_s\) and
\((r = \infty, t = 0) = c_L (c_L > c_s)\).

\[
\left( \frac{\partial c}{\partial r} \right)_{r=R} = (C_L - C_s) \left( \frac{1}{R(t)} + \frac{1}{\sqrt{\pi Dt}} \right) \tag{A2}
\]

Fick’s first law of diffusion shows equation (A2), and gas flux \(J\) was proportional to gas density \(\rho\) and radius
increasing rate \(\frac{\partial R(t)}{\partial t}\) (equation (A2) right term). Equation (A3) can be converted to equation (A4).

\[
J = D \left( \frac{\partial c}{\partial r} \right)_{r=R} = \rho \frac{\partial R(t)}{\partial t} \tag{A3}
\]

\[
\left( \frac{\partial c}{\partial r} \right)_{r=R} = \frac{\rho}{D} \frac{\partial R(t)}{\partial t} \tag{A4}
\]

By combination of (A2) and (A4), the radius increase kinetics was shown as equation (A5).

\[
\frac{dR(t)}{dt} = D (C_L - C_s) \left( \frac{1}{R(t)} + \frac{1}{\sqrt{\pi Dt}} \right) \tag{A5}
\]
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