High Speed Video Observation of Gas Bubble Evolution Phenomena Accompanying Water Electrolysis on Transparent Electrode under Quasi-Microgravity

Megumi OHNO¹, Go SAKUMA¹, Hisayoshi MATSUSHIMA² and Yasuhiro FUKUNAKA¹

¹Kyoto University, Kyoto, Japan, fukunaka@pe.energy.kyoto-u.ac.jp
²Kiel University, Kiel, Germany

Abstract
Galvanostatic water electrolysis was conducted in 2 wt. % KOH solution for 5 s under terrestrial and quasi-μ-G condition. These conditions were realized by using two types of cell arrangement: (1) the vertical arrangement and (2) the downward facing horizontal electrode arrangement over the counter electrode, respectively. The latter arrangement can be regarded as a quasi-μ-G condition because the natural convection induced by generating gas bubbles is macroscopically excluded. The gas bubble formation of O₂ or H₂ was in-situ observed by using high speed camera. Sputter-deposited Pt film on transparent FTO glass was used as the working electrode to record backside images of evolving bubbles. O₂ gas bubbles were less hydrophilic than H₂ and tended to coalesce with each other to grow in larger size. They stayed much longer on electrode surface than H₂. The attachment of bubbles decreased the effective reaction area to result in energy loss for O₂ gas evolution. Quasi-μ-G experiment made it possible to measure the larger contact angle of O₂ than H₂, but difficult to realize H₂ froth layer formation. Thus, the measured results in the downward facing electrode arrangement were partially coincident with those in microgravity experiment conducted in a drop tower. It suggests that careful and appropriate experimental design with downward facing electrode may sometimes reduce the expenses and time necessary for the scientific research in the international space station.

1. Introduction
Water electrolysis under μ-G may be challenged or optimized from three reasons¹⁻⁵. First, it leads to optimum condition of water electrolysis in space. Solar-powered water electrolysis generates H₂ and O₂, and fuel cell is operated. This is the main energy conversion system in the international space station. That is, water electrolysis is a key technology in the operation of the space station. Although water electrolysis is essential also for the life support system in space, μ-G environment is not suitable to operate these devices. The buoyancy force, which quickly removes gas bubbles from the electrode surface in the normal gravity environment, does not work under μ-G. Special design must be considered to overcome this demerit.

Second, μ-G condition helps to design strategy for the industrial electrolysis cell. To drive an electrochemical reaction, a cell voltage, \( V \), is required. \( V \) consists of four factors as expressed by

\[
V = E + \eta_A + \eta_C + IR
\]  

where \( E \) stands for the equilibrium voltage, \( \eta_A \) for the anodic overpotential, \( \eta_C \) for the cathodic overpotential and \( IR \) for the IR drop in electrolyte solution. Generally speaking, \( \eta_C \) is not significant in the case of water electrolysis. Many researchers have been struggling to develop lower \( \eta_A \) electrode, because it is considered that the technology level to reduce IR drop has been already saturated. However, we would like to emphasize there may be still a possibility to decrease IR drop from the viewpoint of interfacial chemistry. As water electrolysis proceeds, gas bubbles cover the electrode surface or dissolve into electrolyte. Presence of bubbles on electrodes or in electrolyte increases IR drop to result in poor electrolysis efficiency. In order to analyze this subject, the gas bubble evolution process (nucleation, growth and coalescence), the coverage or dissolution of bubbles and the release from the electrode surface must be quantitatively analyzed.

All electrochemical phenomena among gas bubble, electrolyte and electrode occur at three-phase interface, where they contact each other, and the analysis of this zone is quite complicated because of macroscopic natural convection induced by released gas bubbles. The complex fluid movement makes it difficult to analyze micro-convection derived from gas bubble formation and growth⁶. This micro-convection dominates the ionic mass transfer rate and then has a great influence on bubble release from the electrode surface. Thus, a deeper understanding of the electrochemical interfacial phenomena in three-phase interface region is straightforwardly directed to a rational design strategy for the industrial electrolytic process. That is, it is a key issue to quantitatively understand the ionic mass transfer rate accompanying micro- and macro-convection due to gas evolution for the industrial electrochemical process. Microgravity
experiments thus provide an ideal environment to examine the effect of micro-convection on the electrochemical reaction in three-phase interface in the absence of buoyancy. The results will become useful not only for water electrolysis but also for every type of industrial electrolysis generating gas bubbles.

Thirdly, we have already reported that μ-G environment in a drop shaft provides the interesting gas bubble evolution behavior especially in alkaline solution\(^1\)\(^{-3}\)). It may be essentially related to the surface tension driven flow near three-phase interface. μ-G environment is therefore worthwhile to be utilized as a unique experimental technique for the fundamental investigation of gaseous electrode phenomena.

Based on above standpoints, we have carried out water electrolysis in a drop shaft for several times and calculated bubble coverage by electrochemical method. Some uncertainties have still remained on the transition phenomena from bubble nucleation to the growth process. In this study, a transparent FTO glass electrode was applied to directly observe three-phase interface under terrestrial quasi-μ-G condition. Downward facing electrode arrangement can be utilized as an appropriate electrochemical device to examine the gas evolution behavior quantitatively through the backside of effective electrode surface\(^2\)\(^{-9}\)).

2. Experiments

Three-phase interfacial phenomena through a transparent electrode surface were in-situ observed at a speed of 1000 frames a second with a high speed video camera (Phantom V7.0). Electrolytic cell is schematically illustrated in Fig. 1. Two types of cell arrangement, the horizontal and vertical one, were employed. With the vertical arrangement, natural convection is induced to drive gas bubbles upwards (terrestrial environment). On the other hand, gas bubbles nucleated on the downward-facing horizontal electrode tend to progressively grow in size. Therefore, the horizontal arrangement may simulate a quasi-μ-G environment as frequently described\(^10\)). Light source was placed at the opposite side to high speed camera and two convex lenses were located between light source and electrolytic cell to produce parallel beam of light. In the horizontal arrangement, two prisms were symmetrically set above and below the electrolytic cell to vertically bend light beam. FTO glass was sputtered with Pt. It was supplied as the working electrode (W. E.) and a 4-mm-square area of W. E. was exposed to the electrolyte, 2 wt. % KOH solution. Two sheets of Pt plate were employed as the counter electrode (C. E.) and Pt wire was as the conventional reference electrode (R. E.). 150 mA cm\(^{-2}\) galvanostatic electrolysis was carried out for 5 s.

![Fig. 1 Schematic diagram of electrolytic cell. The (a) horizontal and (b) vertical arrangement.](image1)

3. Results and Discussion

Contact angle —— Fig. 2(a) is a high speed camera image of O\(_2\) gas bubble evolution in the horizontal arrangement. Black circles represent the shadows of bubbles. Contact areas are successfully observed as shown by dashed line in the horizontal arrangement. In the vertical arrangement, relatively

![Fig. 2 (a) High speed camera images in the horizontal arrangement. Contact area is observed as shown by dashed line, (b) Schematic image of bubble coverage at three-phase interface and (c) \(\sin\theta\) of O\(_2\) and H\(_2\).](image2)
large sized gas bubbles started to crawl or roll up on electrode surface by buoyancy force. It results in “receding” and “advancing” contact angle. It makes the shape of contact area complex, upside-down teardrop. Therefore, only horizontal arrangement is used for the analysis of three-phase interface images.

As illustrated in Fig. 2(b), contact angle, $\theta$, is calculated by

$$\sin \theta = \frac{a}{d}$$

(2)

where $d$ is bubble’s, and $a$ is contact area’s diameter. Fig. 2(c) represents $\sin \theta$ of both gases. Once the gas bubble volume exceeds a certain value, the effect of buoyancy cannot be neglected and the spherical shape of gas bubble may be deformed. In the present case, the diameter of bubble is less than 500 \( \mu \)m. Then, the distortion effect due to buoyancy is rather small. Fig. 2(c) demonstrates that $\theta$ for H$_2$ was a little smaller than that of O$_2$. This result suggests that H$_2$ bubble is more hydrophilic than O$_2$. It corresponds to our previous experimental results in microgravity environment$^{11}$, but the difference is rather smaller than expected.

**Bubble behavior** —— In the vertical arrangement, buoyancy force lifts up bubbles to introduce the upward moving behavior significantly different between O$_2$ and H$_2$. O$_2$ bubbles tended to cling on the electrode surface until bubble nucleus diameter grew large enough. On the other hand, H$_2$ readily rose up even while growing. Fig. 3(a) is images taken at 1.200, 1.800 and 4.800 s after starting electrolysis in the vertical arrangement. It indicates that effective electrode area became smaller on the O$_2$ evolving electrode, while the surface coverage of H$_2$ bubbles seemed to be saturated. The transient variation of bubble coverage is plotted in Fig. 3(b). The coverage was defined as the total area of bubble’s shadow divided by electrode area in the photograph. Bubble shadow was assumed to be equal to contact area. O$_2$ bubble coverage continued to increase and this result coincides well to the impression from high speed camera images. The coverage of H$_2$ increased at the beginning followed by a decrease around 2 s. At that time, several larger H$_2$ gas bubbles left from the electrode surface all together at once. Such a kind of H$_2$ gas bubble detachment behavior has been already reported$^{11}$. The average bubble coverage of O$_2$ and H$_2$ during 5 s electrolysis was well correspondent to following equation;

$$\Theta = 0.023j^{0.3}$$

(2)

where Balzer and Vogt$^{12}$ summarized the reported data in the empirical equation between coverage, $\Theta$, and current density, $j$.

In addition to the upward moving behavior, two types of gases showed a different mode of coalescence. O$_2$ bubbles readily coalesced as soon as two bubbles touched. However, H$_2$ bubbles seldom coalesced even when two H$_2$ bubbles collided with each other as demonstrated in Fig. 4. This figure shows the images of H$_2$ evolving electrode taken every 0.040 s from 1.320 s after the start of electrolysis. Bubble A (a white dashed circle) and B (gray dotted) are now focused. Bubble A rises and collides to another bubble, B (at 1.360 s), while they do not coalesce (at 1.420 s) and bubble A passes away by bubble B (at 1.460 s). A much smaller probability for H$_2$ gas bubbles to coalesce than that for O$_2$ bubble agrees well with our results in a drop shaft experiment in KOH solution$^{1, 2}$. In JAMIC drop tower, O$_2$ bubbles coalesced to form larger bubbles on Pt electrode surface, while H$_2$ froth layer thickness composed of finer H$_2$ bubble ensemble.
dramatically grew without coalescence. Nevertheless, H₂ bubble froth layer has not been confirmed in the present arrangement.

The difference between H₂ and O₂ gas bubble behavior may be attributed to the difference in wettability. “O₂ cling to Pt electrode” suggests that O₂ bubble has more affinity to the Pt electrode surface, though the effect of possible formation of thin oxide layer surface must be taken into account. The smaller coalescence probability of H₂ bubble may be related to its hydrophilic character.

Potential transient —— Fig. 5 shows the potential transient in both cell arrangements. Quasi-μ-G condition introduces larger increase of potential. The horizontal arrangement compels generating bubbles to stay on downward-facing electrode surface and effective electrode surface area thus become smaller. This may cause the increase of potential under galvanostatic electrolysis. On the other hand, potential of H₂ evolution is substantially constant in the vertical arrangement. As observed from high speed camera images, natural convection forces H₂ bubble to leave from cathode surface to result in constant electrode surface area. However, O₂ potential continues to increase with time. The fact must be kept in mind that O₂ bubbles adhered to the electrode surface and surface coverage gradually ascends even under natural convection flow. Attached O₂ bubbles strongly affect IR drop. It is necessary to correlate the surface coverage with O₂ evolution overpotential to improve the energy efficiency for industrial water electrolysis.

Significance of quasi-microgravity experiment with downward facing horizontal electrode —— With the downward facing horizontal electrode, gas bubbles stay on the discrete nucleation site until bubble coalescence (quasi-μ-G). At the earlier time of bubble evolution (~ about 4.000 s from the start of electrolysis), growth phenomena of each bubble could be observed to allow the estimation of contact angle. As electrolysis progressed, bubble coalescence started at many sites and larger bubbles grew. Consequently, only a few bubbles of large size were noticed in a video frame. Especially after about 4.000 s, one larger bubble (over 1 mm in diameter) occupied almost whole view. These larger bubbles hide newly generated bubbles. That is, bubbles evolved under the larger bubbles could not be clearly observed. Thus, quasi-μ-G in this cell arrangement is convenient to monitor bubble growth process only in

Fig. 4. High speed camera images of H₂ rise in the vertical arrangement taken every 0.040 s from 1.320 s after starting electrolysis.

Fig. 5. Potential transient in the (a) horizontal and (b) vertical cell arrangement. Gray and black line indicates the anode (O₂ evolution) and cathode (H₂ evolution).
the initial stage. Additionally, because this experiment was conducted under terrestrial condition, the effect of buoyancy force was inevitable, which pushed up bubbles toward W. E. and promoted their coalescence. Unfortunately H₂ forth layer appearing in KOH solution under $1 \times 10^{-5}$ G could not be obtained at this experiment. There is another possibility of the absence of froth layer. Upward force to electrode increases the contact area of gas bubbles in the supersaturated zone to enhance the mass transfer rate of dissolved H₂ into the gas bubble. It surely decreases the degree of supersaturation of dissolved gas near W. E. in a quasi-μ-G environment.

The diameter of single gas bubbles in the horizontal arrangement at 2.400 s was measured. O₂ and H₂ gas bubbles had 263 ± 124 and 226 ± 288 μm in diameter, respectively. It is interesting that the mean diameter of H₂ is smaller than O₂, whereas H₂ gas evolves twice the amount of O₂ and that H₂ shows the wide variance of size distribution. These phenomena may be caused by the difference of coalescence mechanism. O₂ readily coalesced as long as two bubbles touched each other. On the other hand, H₂ bubbles coalesced easily only when deformed larger bubble pushes up smaller one between itself and electrode. In this process, larger bubble tends to grow much larger though smaller one distant from larger remains smaller, hence the bubble diameter variance becomes larger.

As mentioned above, the horizontal electrode arrangement has some benefits to demonstrate the effect of gravitational level to bubble evolution behavior of O₂ and H₂. The detail observation becomes possible by combining the transparent electrode with high speed camera. The level of gravitational strength is not good enough in a quasi-μ-G experiment. From this viewpoint, we are planning to carry out the parabolic flight experiments in France in October, 2008. However, even the microgravity level realized in parabolic flight is not so high enough in comparison with a drop shaft facility. Nevertheless, any facility must be fully utilized to reasonably design a better space experiment, carefully confirming the experimental limitations involved in each technique.

**Summary**

The present results should be further analyzed to utilize the better experimental design in the industrial electrochemical reactor, especially from the aspect of electrode wettability. High speed video observation of gas bubble generation phenomena on transparent horizontal electrode facing downward may help our understanding of electrochemically gas bubble nucleation and growth phenomena. Parabolic flight experimental results obtained in last December with DAS may further support the sound strategy of our research projects.

**References**