Mechanism of Potential Oscillation during Electrolysis of Water in Acidic Solutions

Terumasa KUGE,a Takanobu NISHIMOTO,b Masayuki KUROHAGI,a Kouji MAEDA,b Shinji YAE,b and Yoshiharu MUKOUYAMAa,*

a Division of Science, College of Science and Engineering, Tokyo Denki University, Hatoyama, Saitama 350-0394, Japan
b Department of Chemical Engineering and Materials Science, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

* Corresponding author: mukoyama@mail.dendai.ac.jp

ABSTRACT
We have previously reported that the hydrogen evolution reaction (HER) in acidic water electrolysis shows a potential oscillation with amplitude of about 1 V. The oscillation, named HER oscillation, is accompanied with a periodic change in the evolution rate of hydrogen bubbles, i.e., hydrogen bubbles evolve more vigorously at low potentials than at high potentials, which has led us to propose a mechanism for HER oscillation (J. Electroanal. Chem., 713, 39 (2014)). In order to obtain a deeper insight into the mechanism of HER oscillation, this present work studies the effect of high pressure (e.g. 0.7 MPa) on the oscillation and current-potential curves. It reveals that any N-shaped negative differential resistance characteristics are not involved in HER oscillation unlike the majority of electrochemical oscillations. It also shows that a solution-stirring effect due to the hydrogen bubble evolution, which causes an enhancement of convection near the electrode surface, plays an essential role in HER oscillation. We thus conclude that the appearance of HER oscillation can be explained by considering that the enhancement occurs only at low potentials at which hydrogen bubbles evolve vigorously.

Keywords : Electrochemical Oscillation, Hydrogen Evolution Reaction, Acidic Water Electrolysis, Hydrogen Bubbles

1. Introduction

Hydrogen evolution reaction (HER), or the electrochemical reduction of H⁺, occurs at the cathode during electrolysis of water (2 H₂O → 2 H₂ + O₂). In the early 20th century, kinetic studies on the HER were conducted by Tafel. Since then, the HER has been extensively studied as reviewed in literature. As for the HER in aqueous electrolytes, a large number of hydrogen bubbles are formed on the electrode surface at potentials much more negative than its onset potential. This often causes disturbances in electrochemical measurements, control, and analysis. Thus, the HER has been mostly studied in a low overpotential region where no bubbles are formed or in an intermediate region where bubbles hardly affect electrochemical measurements.

It is known that when the HER occurs under galvanostatic conditions, hydrogen bubble evolution due to the HER affects the electrode potential. Hydrogen bubble growth and its detachment from the electrode induce potential fluctuations with a range of up to 0.1 V because the active surface area of the electrode decreases as bubbles grow and the area recovers when the bubbles detach from the electrode. When a microelectrode is used as working electrode, the growth of a single bubble and its detachment cause a periodical potential oscillation with a maximum amplitude of 0.6 V. That is, a negative potential shift in the electrode potential coincides with the growth of a bubble and a positive potential jump corresponds to the detachment of a bubble, which has been clearly observed by using a high-speed camera. Additionally, the same type of oscillation appears during oxygen evolution reaction.

We have reported that the HER on Pt and Au in 0.1 M (M = mol/dm³) H₂SO₄ solution is anomalously affected by salts such as Na₂SO₄ and K₂SO₄ at high overpotentials. The reduction current due to the HER becomes low (in absolute value) because the alkali metal ions originated from the salts decrease the transport rate of H⁺ in the solution. Interestingly, a potential oscillation, named HER oscillation, appears under current controlled conditions. The oscillation is different from the reported ones in the literature because it is not caused by bubble growth and detachment.

Electrochemical oscillations, which are attractive phenomena from the viewpoint of dynamic self-organization of molecular systems, have been classified into several categories based on oscillation mechanism. It is established that an N-shaped negative differential resistance (N-NDR) plays crucial roles in the most typical oscillators, namely, N-NDR oscillator and “hidden” N-NDR oscillator. When current (I) – potential (E) curves are measured under potential controlled conditions, N-NDR characteristics are observed depending on the potential scan rate. As for N-NDR oscillator, they are observed at slow scan rates. In contrast, as for HN-NDR oscillator, they are observed at fast rates, i.e., the N-NDR characteristics are hidden at slow scan rates.

Other than the typical oscillators, there are five types of oscillators, namely, strictly potentiostatic type, S-shaped NDR type, coupled N-NDR type, capacitance-mediated positive differential resistance (C-PDR) type, and electrochemical reactions and diffusion-convection (ERDC) type. Besides, as described above, there is another one: bubble growth and detachment type.

In our previous paper, we have proposed a mechanism of HER oscillation based on experimental results. The proposed mechanism does not involve any N-NDR characteristics, unlike the majority of electrochemical oscillations. In this work, to further study the mechanism of the oscillation, we show that the oscillation disappears when high pressure (e.g. 0.7 MPa) is applied to electrolysis solution by using a high pressure apparatus, and also reveal that any N-NDR characteristics are not involved in HER oscillation.
oscillation by measuring $I-E$ curves at fast scan rates. Through these studies, we conclude that the appearance of HER oscillation can be explained in the framework of ERDC-based mechanism.

As for the high pressure apparatus, the first experiments of this apparatus at high pressure have been performed for the electrical conductivity of aqueous alcohol electrolyte solutions, and it was found that high pressure may enhance the decreasing the electrical conductivity because of alcoholic permittivity. Moreover, effect of high pressure was examined in charge-discharge cycle of lead-acid battery in the same apparatus, and it was found that high pressure exactly improved any qualities of lead-acid battery. The apparatus was also utilized to apply high pressure on electroless nickel–phosphorous plating bath. Furthermore, as shown in this present work, it enabled us to study the HER in a high overpotential region where hydrogen bubbles evolved vigorously on electrode. We thus believe that the high pressure apparatus is useful also for a deep understanding of gas-evolving electrochemical reactions.

2. Experimental

2.1 Electrochemical measurements

The electrolyte solution was 0.1 M H$_2$SO$_4$, to which Na$_2$SO$_4$ or K$_2$SO$_4$ was added. It was prepared using special grade chemicals (FUJIFILM Wako Pure Chemical Corporation, Japan) and purified water (resistivity: >18 MΩ cm) obtained from a Millipore system. Electrochemical measurements were conducted at room temperature (around 25°C) using two types of three-electrode cells: a beaker-type cell and high-pressure cell.

A Pt sphere of 1.5 mm diameter was used as working electrode (WE). It was prepared by melting a tip of Pt wire and then covering the wire with a Teflon heat-shrink tube (see Fig. 4). Regarding the beaker-type cell, a polycrystalline Pt (99.99%) wire (0.5 mm in diameter) of 4 mm was also used as WE (see Fig. 2). Prior to measurements, the wire was annealed in a hydrogen flame for about 20 seconds to clean its surface. A Pt wire of 10 mm in length was used as counter electrode (CE). A saturated mercury-mercuric sulfate electrode (0.64 V vs. SHE at 25°C), Hg | Hg$_2$SO$_4$ | sat. K$_2$SO$_4$, was used as reference electrode (RE); however, in this paper, the potentials are referred to SHE. Regarding the high-pressure cell, Pt wires (1 mm in diameter) of 19 and 24 mm in length were respectively used as CE and pseudo-RE. Accordingly, the potentials are referred to Pt pseudo-RE.

2.2 Apparatus for high-pressure measurements

A quartz cylinder with two free pistons (top and bottom pistons), contained 4 mL of electrolyte, was used as the high-pressure cell. The Pt electrodes were inserted into the cell through holes in the top piston. To pressurize the electrolyte, the high-pressure apparatus was used as described elsewhere. In short, the cell was placed into a pressure vessel that was filled with water. A high-pressure water pump was connected to the vessel through pressure valves, and thus the pressure of electrolyte solutions inside the cell could be increased up to as high as 400 MPa. However, in this work, the pressure was limited up to 40 MPa.

2.3 Video recording devices

Two types of cameras were used to observe hydrogen bubbles that were formed on WE: a high-speed camera (Shinano Kenshi, PLEXLOGGER) with a recording rate of 250 fps (= frames per second) and a normal-speed camera (30 fps). The former was used for electrochemical measurements at 0.1 MPa and the latter for those at high pressures.

3. Results and Discussion

3.1 Effects of alkali metal ions on HER

For later discussion, let us summarize the effect of alkali metal ions such as Na$^+$ and K$^+$ on the HER, which has been reported in earlier works. Figure 1 shows $I-E$ curves for a Pt wire electrode in 0.1 M H$_2$SO$_4$ and 0.1 M H$_2$SO$_4$ + 0.05 M Na$_2$SO$_4$, measured under potential and current controlled conditions using the beaker-type cell at an atmospheric pressure of 0.1 MPa. The reduction of H$^+$(2 H$^+ + 2e^- \rightarrow H_2$) started to occur at ca. 0.1 V. In the absence of Na$_2$SO$_4$, the reduction current almost linearly increased (in absolute value) with decreasing potential under potential controlled conditions (panel a).

In the presence of Na$_2$SO$_4$, the alkali metal ions, which were originated from the salt, diminished electromigration of H$^+$. In general, there are three forms of mass transport: diffusion, convection, and electromigration. Hence, in a high overpotential region, $E < ca. -0.7$, the current was limited by diffusive and convective transport of H$^+$, and thus, the $I-E$ curves showed the state where the current was almost constant even if the electrode potential decreased. In the potential region below the constant-current state, $E < ca. -1.7 V$, the reduction of H$_2$O molecule (2 H$_2$O + 2e$^- \rightarrow H_2 + 2OH^-$) occurred and thus the reduction current increased again with the decreasing potential.

It should be noted that the current in the constant-current region was dependent on the scan direction. In other words, a hysteresis behavior was observed in the constant-current region: the current was lower (in absolute value) in the negative-going scan than in the positive-going scan. In the presence of Na$_2$SO$_4$, the potential oscillation with amplitude of about 1 V, which we called HER oscillation, appeared under current controlled conditions in the potential range of the constant-current state (panel b).

Figure 2 includes a waveform of HER oscillation observed for a Pt wire electrode in 0.1 M H$_2$SO$_4$ + 0.05 M K$_2$SO$_4$ and snapshots of the electrode. The amount of hydrogen bubbles oscillated synchronously with the oscillating potential: the bubbles evolved
more vigorously at low potentials where the water reduction occurred (marks C and D) than at high potentials where the \( \text{H}^+ \) reduction occurred (marks A and B). Note that the addition of \( \text{K}_2\text{SO}_4 \) had almost the same effect on the HER as \( \text{Na}_2\text{SO}_4 \).\(^{13}\) This synchronous behavior led us to think that the bubble evolution played essential roles for HER oscillation.\(^{14}\) The other point was that the electrode potential decreased when almost no bubbles were formed at the electrode and it increased while bubbles evolved vigorously, from which we concluded that HER oscillation was not caused by bubble growth and detachment.\(^{14}\)

Importantly, the oscillation disappeared, i.e., the electrode potential stayed at a high potential where the \( \text{H}^+ \) reduction occurred, when the electrolyte solution was continuously stirred by a magnetic stirrer, and it reappeared a few seconds after the stirring of the solution was stopped. The reason for the disappearance will be discussed in a later section.

3.2 Effect of pressure on HER oscillation

In order to confirm the role of bubble evolution, we studied the effect of pressure on the oscillation. Figure 3 shows \( I-E \) curves for a Pt sphere electrode in 0.1 M \( \text{H}_2\text{SO}_4 + 0.05 \text{ M} \text{Na}_2\text{SO}_4 \), measured under current controlled conditions using the high-pressure cell. When the pressure was 0.1 MPa, the oscillation appeared at around \(-15 \text{ mA}\) (panels a1 and a2). When the pressure was 0.3 MPa or higher, the oscillation became more unlikely to occur with the increasing pressure: it almost disappeared at 0.5 MPa (panels c1 and c2) and was never observed at 0.7 MPa (panels d1 and d2). These
results, whose reproducibility was confirmed by repeatedly performing the same experiment, led to a conclusion that the bubble evolution induces the oscillation.

According to Boyle’s law, if the temperature of a gas is held constant, the volume of the gas is inversely proportional to its pressure. On the other hand, regardless of pressure, the rate of hydrogen production was determined by electrolytic current. Thus, at a given applied current, the total volume of hydrogen bubbles decreased as the pressure increased. This is why the oscillation became more unlikely to occur with the increasing pressure.

Incidentally, the onset potential of the HER ($E_{\text{onset}}$) fluctuated from $-0.1$ V (at 0.7 MPa) to $-0.5$ V (at 0.3 MPa) because of the Pt pseudo-RE. According to Nernst equation, $E_{\text{Pt}}$ depends on partial pressure of $H_2$ ($p_{H_2}$). When the concentration of $H^+$ is 0.1 M, $E_{\text{Pt}}$ at 25°C is expressed as $E_{\text{Pt}} = -0.059 - 0.059 \log(p_{H_2})$ and thus the difference between $E_{\text{Pt}}$ at 0.1 MPa and that at 0.7 MPa is only 0.05 V, which is much smaller than the fluctuation range of $E_{\text{Pt}}$. The potential of the Pt pseudo-RE also follows the Nernstian behavior. However, $p_{H_2}$, or activity of $H_2$, at the pseudo-RE was not the same as that at the WE, which thus caused the fluctuation. Besides, the potential was also affected by oxygen molecules that formed on the CE, which was also a factor causing the fluctuation.

3.3 Effect of pressure on $H_2$ bubbles

$I$–$E$ curves were also measured under potential controlled conditions using the high-pressure cell. Figure 4 shows $I$–$E$ curves for a Pt sphere electrode in 0.1 M $H_2SO_4 + 0.05$ M $Na_2SO_4$ measured under potential controlled conditions and snapshots of the electrode taken at the marks shown in the curves. The curves were measured under potential controlled conditions at a scan rate of 0.1 V s$^{-1}$. The pressure: (a) 0.1 MPa and (b) 0.7 MPa.

3.4 Effect of pressure on the constant-current state

Figure 5 shows $I$–$E$ curves for a Pt sphere electrode, obtained at scan rates of 0.1 and 1.0 V s$^{-1}$. The curves changed depending both on the pressure and the scan rate. When the pressure was 0.1 MPa (panels a1 and a2), the constant-current state was observed, that is, the current was limited by diffusive and convective transport of $H^+$ to the electrode surface, both at 0.1 and 1.0 V s$^{-1}$. Besides, a cathodic peak was observed at around $-1.7$ V at 1.0 V s$^{-1}$ (panel a2). The peak can be explained, as done in many textbooks, by considering a change in the concentration profile of the electroactive species, namely $H_2$, near the electrode surface.

When the pressure was 0.7 MPa (panels b1 and b2), the cathodic peak was dominant because the solution-stirring effect, which enhanced the convective transport of $H^+$, was not significant. Therefore, the constant-current state was not observed and the peak was larger at 1.0 V s$^{-1}$ than at 0.1 V s$^{-1}$, supporting the above explanation. It was possibly that the peak was not related to the profile change but to a surface blocking effect caused by the bubble formation. If so, the peak was not dominant at high pressure at which the total volume of hydrogen bubbles was small (see Fig. 4).

Incidentally, at 0.1 MPa, a current fluctuation was induced due to the bubble evolution. The bubble evolution became less intense as the pressure increased, and consequently, at 0.7 MPa, the fluctuation was successfully eliminated, which facilitated this study.

3.5 Is an N-NDR is hidden in $I$–$E$ curves?

As mentioned in the introduction, N-NDR characteristics play crucial roles in the most typical oscillators. However, such characteristics were not involved in HER oscillation, as revealed by measuring $I$–$E$ curves under potential controlled conditions at 0.1 MPa in the following manner. The potential was scanned from 0.1 V at a relatively slow scan rate of 0.01 V s$^{-1}$ in order to eliminate the cathodic peak that became predominant at fast scan rates (see Fig. 5), and then scanned at 0.5 V s$^{-1}$ from a potential in the constant-current region, e.g., $-0.5$ V, $-0.6$ V, $-0.7$ V, and $-0.8$ V.
As shown in Fig. 6, the cathodic peak was not observed because of the slow scan rate (gray curves), and the constant-current state was hardly affected even after the scan rate was increased. If an N-NDR was hidden in the constant-current region, it would appear at the fast scan rate. We thus conclude that any N-NDR characteristics are not involved in HER oscillation, that is, HER oscillation is not an HN-NDR type. Note that an N-NDR type exhibits only a current oscillation while an HN-NDR type does both current and potential oscillations.17–26

3.6 Hysteresis induced by bubble evolution

As explained before, a hysteresis behavior was observed in the constant-current region (see Fig. 1a). This can be explained by the solution-stirring effect caused by the bubble evolution. Figure 7 shows I–E curves for a Pt wire electrode in 0.1 M H2SO4 + 0.05 M K2SO4 measured under potential controlled conditions at a scan rate of 0.01 V s⁻¹. The potential was scanned from 0 V to a low potential and then scanned back to 0 V. When its lower potential limit was −1.06 V or higher (panels a and b), the H2 bubble evolution did not occur at the electrode surface, and hence the current in the constant-current region (Icc) was about −7 mA, which was determined by the diffusion rate of H⁺, for both scan directions.

When the lower limit was −1.46 V (panel c), however, the curve showed a hysteresis behavior. During the forward scan, almost no bubbles were observed at E > −1.3 V, and thus Icc was about −7 mA. The bubble evolution suddenly started at −1.3 V, and hence the solution-stirring effect was induced, i.e., the convective transport of H⁺ was enhanced, leading to a rapid increase in the reduction current. The bubble evolution became more vigorous with the decreasing potential. During the reverse scan, the vigorous bubble evolution continued until the potential returned back to ca. −0.4 V, and hence Icc was higher (in absolute value) than that in the forward scan.

As mentioned above, when the pressure was 0.1 MPa, the bubble was started to form on the Pt wire electrode at −1.3 V on the negative-going scan. However, it started on the Pt sphere electrode at a potential more positive than the constant-current region (see top panels in Fig. 4). We can say, based on these results, that bubbles were formed more easily on the Pt sphere electrode than on the Pt wire electrode.

The hysteresis behavior was also dependent on the pressure. When the pressure was 0.7 MPa, at which HER oscillation was

![Figure 5](image-url)

**Figure 5.** I–E curves for a Pt sphere electrode in 0.1 M H2SO4 + 0.05 M Na2SO4 measured under potential controlled conditions. The potential is scanned in the negative direction at scan rates of (right) 0.1 V s⁻¹ and (left) 1.0 V s⁻¹. The pressure: (top) 0.1 MPa and (bottom) 0.7 MPa. An enlarged view of panel b1 is shown in panel b of Fig. 4.

![Figure 6](image-url)

**Figure 6.** I–E curves for a Pt wire electrode in 0.1 M H2SO4 + 0.05 M Na2SO4 measured under potential controlled conditions. The potential was scanned at 0.01 V s⁻¹ from 0.1 V in the negative direction. The scan rate was changed to 0.5 V s⁻¹ when the potential reached at (a) −0.5 V, (b) −0.6 V, (c) −0.7 V, and (d) −0.8 V, which are indicated by dashed lines in each panel. The pressure: 0.1 MPa.
never observed (see Fig. 3), the hysteresis was observed because the bubble evolution in the constant-current region was more vigorous during the positive-going scan than during the negative-going scan. At 10 MPa, very tiny bubbles continuously evolved in the constant-current region only during the positive-going scan, and thus, the hysteresis was still observed: $I_{cc}$ was slightly higher (in absolute value) in the positive-going scan than in the negative-going scan. At 20 MPa, the hysteresis was not observed because almost no bubbles evolved in the constant-current region. Note that at a pressure as high as 40 MPa, no bubbles were observed by the normal-speed camera.

### 3.7 Mechanism of HER oscillation

On the basis of the results shown in the present and previous studies, HER oscillation has the following features:

1. During the oscillation, H$_2$ bubbles evolve more vigorously at low potentials than at high potentials.\(^{14}\)
2. The oscillation is neither a bubble growth and detachment type\(^{14}\) nor an HN-NDR type.
3. The oscillation is associated with the constant-current state where the current is limited by the diffusive and convective transport of H$^+$.\(^{13}\)
4. The vigorous bubble evolution, which induces a hydrodynamic flow around the electrode after a short delay, causes the solution-stirring effect.\(^{14}\)
5. The solution-stirring effect, which enhances the convective transport, leads to an increase in the absolute value of $I_{cc}$, or $|I_{cc}|$.

From the features, we can conclude that HER oscillation is an ERDC type.\(^{29-31}\) Furthermore, $I-E$ curves measured at fast scan rates met the criterion for the type that was suggested by Li et al.,\(^{31}\) i.e., crossing curves were obtained when the potential was scanned at 0.5 V s$^{-1}$ or faster, as shown in Fig. 8. A detailed explanation of the ERDC type and the criterion was given by Orlík in his monographs (Section 4.2 of Volume I\(^{20}\) and Section 5.8 of Volume II\(^{21}\)).

During HER oscillation, the production rate of H$_2$ molecules is constant because a constant current is applied. However, the evolution rate of H$_2$ bubbles changes synchronously with the potential. The reason for this can be explained by considering the local pH at the electrode surface and the dependence of the solubility of H$_2$ on pH, as done previously.\(^{14}\) The local pH is basic and acidic at low and high potentials, respectively. Since the solubility of H$_2$ in basic solutions is smaller than that in acidic solutions, H$_2$ bubbles evolve more vigorously at low potentials than at high potentials. Note that H$_2$ bubbles are formed when the solution near the electrode surface becomes saturated with dissolved H$_2$ molecules, and also that a part of the dissolved molecules diffuses away from the electrode surface to the solution bulk.

From the above, the mechanism of the oscillation can be intuitively understood by considering changes in $|I_{cc}|$, as illustrated in Fig. 9. The rapid decrease in the electrode potential from a high potential occurs when the applied current is above $|I_{cc}|$ (from mark 1 to 2), because of the depletion of H$^+$ at the electrode surface. At a low potential, the vigorous bubble evolution is initiated and it causes the solution-stirring effect after a short delay. Hence, the convective transport of H$^+$ is enhanced leading to the increase in $|I_{cc}|$ (from mark 2 to 3). This in turn causes the rapid increase in the potential.

---

**Figure 7.** $I-E$ curves for a Pt wire electrode in 0.1 M H$_2$SO$_4$ + 0.05 M K$_2$SO$_4$ measured under potential controlled conditions at a scan rate of 0.01 V s$^{-1}$. The electrode potential was scanned from 0 V to (a) −0.66 V, (b) −1.06 V, and (c) −1.46 V, and then scanned back to 0 V. The pressure: 0.1 MPa.

**Figure 8.** $I-E$ curves for a Pt wire electrode in 0.1 M H$_2$SO$_4$ + 0.05 M Na$_2$SO$_4$ measured under potential controlled conditions. The scan rate: (a) 0.01 V s$^{-1}$, (b) 0.1 V s$^{-1}$, (c) 0.5 V s$^{-1}$, and (d) 1.0 V s$^{-1}$. The pressure: 0.1 MPa.
from a low potential (from mark 3 to 4). At a high potential, the vigorous bubble evolution is absent (or weak). The solution-stirring effect continues until the hydrodynamic flow around the electrode stops (or decreases to a certain level). When the effect stops (or becomes negligible), \(|I_{\text{cc}}|\) decreases (from mark 4 to 1), resulting in the rapid decrease in the potential (from mark 1 to 2). This repeats itself to produce HER oscillation.

As mentioned in the last paragraph of Section 3.1, the continuous stirring of the electrolyte solution resulted in the disappearance of the oscillation. This is because the convective transport of \(H^+\) is continuously enhanced and hence the \(|I_{\text{cc}}|\) stays higher than the applied current, i.e., the electrode potential stays at a high potential where the \(H^+\) reduction occurs.

In our previous study, we have found that the bubble evolves autocatalytically during the potential oscillation. We believe that this autocatalytic bubble evolution plays an important role for HER oscillation. For a deeper understanding of the mechanism, further study is needed, including the role of the autocatalytic effect in the bubble evolution, the clarification of the convection enhancement, and the estimation of the local pH.

4. Conclusions

We have reported previously that the hydrogen evolution reaction (HER) in acidic solutions, or the electrochemical reduction of \(H^+\), shows a potential oscillation. The oscillation, named HER oscillation, was accompanied with synchronous changes in the evolution rate of hydrogen bubbles with the oscillating potential, and was associated with the diffusive and convective transport of \(H^+\) to the electrode surface. The present study revealed that any N-shaped negative differential resistance (N-NDR) characteristics were not involved in HER oscillation. It also showed that the convective transport of \(H^+\) was enhanced by a solution-stirring effect due to the hydrogen bubble evolution. On the basis of these results, we conclude that the oscillation is an electrochemical reactions and diffusion-convection (ERDC) type. The oscillation appears when the applied current is above the diffusion-limited current of the \(H^+\) reduction. The rapid decrease in the electrode potential from a high potential occurs because of the depletion of \(H^+\) at the electrode surface, whereas the rapid increase from a low potential occurs because of the convection enhancement.

Acknowledgments

This work is partially supported by Research Institute for Science and Technology of Tokyo Denki University under Grant Q18E-01. The authors gratefully thank Dr. Masato Moritoki (University of Hyogo) for technical support.

References

1. J. Tafel, Z. Phys. Chem., 50U, 641 (1905).
2. B. E. Conway and B. V. Tilak, Electrochim. Acta, 47, 3571 (2002).
3. A. Lasaia, Handbook of Fuel Cells: Fundamentals, Technology, Applications (Eds. W. Vielstich, A. Lamm, and H. A. Gasteiger), Vol. 2, John Wiley & Sons, p. 416 (2003).
4. L. A. Kibler, ChemPhysChem, 7, 985 (2006).
5. F. Salzadeh, E. Ghali, and G. Houlachi, Int. J. Hydrogen Energy, 40, 256 (2015).
6. A. Eftekhari, Int. J. Hydrogen Energy, 42, 11053 (2017).
7. H. Wang and L. Gao, Curr. Opin. Electrochem., 7, 7 (2018).
8. J. Wei, M. Zhou, A. Long, Y. Xue, H. Liao, C. Wei, and Z. J. Xu, Nano-Micro Lett., 10, 75 (2018).
9. C. Gabrielli, F. Huet, M. Keddam, and A. Sahar, J. Appl. Electrochem., 19, 683 (1989).
10. C. Gabrielli, F. Huet, and R. P. Nogueira, J. Electrochem. Soc., 149, E71 (2002).
11. P. Kristof and M. Pritzker, J. Appl. Electrochem., 27, 255 (1997).
12. D. Fernández, M. Martine, A. Meagher, M. E. Möbius, and J. M. D. Coey, Electrochem Commun., 18, 28 (2012).
13. Y. Mukoyama, M. Kikuchi, and H. Okamoto, J. Electroanal. Chem., 617, 179 (2008).
14. Y. Mukoyama, R. Nakazato, T. Shiono, S. Nakanishi, and H. Okamoto, J. Electroanal. Chem., 713, 39 (2014).
15. J. L. Hudson and T. T. Tsotsis, Chem. Eng. Sci., 49, 1493 (1994).
16. M. T. M. Koper, Adv. Chem. Phys. (Eds. I. Prigogine and S. A. Rice), John Wiley & Sons, Inc., p. 161 (1996).
17. K. Krischer, Modern Aspects of Electrochemistry (Eds. B. E. Conway, J. O. M. |
Bockris, and R. E. White), Kluwer Academic/Plenum Publishers, New York, p. 1 (1999).

18. K. Krischer, Advances in Electrochemical Science and Engineering, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, p. 89 (2003).

19. I. Z. Kiss, T. Nagy, and V. Gáspár, Solid State Electrochemistry II, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, p. 125 (2011).

20. M. Orlik, Self-Organization in Electrochemical Systems I, Springer-Verlag Berlin Heidelberg, Berlin (2012).

21. M. Orlik, Self-Organization in Electrochemical Systems II, Springer-Verlag Berlin Heidelberg, Berlin (2012).

22. M. T. M. Koper, J. Electroanal. Chem., 409, 175 (1996).

23. P. Strasser, M. Eiswirth, and M. T. M. Koper, J. Electroanal. Chem., 478, 50 (1999).

24. Y. Mukouyama, S. Nakanishi, T. Chiba, K. Murakoshi, and Y. Nakato, J. Phys. Chem. B, 105, 7246 (2001).

25. Y. Mukouyama, S. Nakanishi, H. Konishi, Y. Ikeshima, and Y. Nakato, J. Phys. Chem. B, 105, 10905 (2001).

26. Y. Mukouyama, H. Kawasaki, D. Hara, Y. Yamada, and S. Nakanishi, J. Electrochem. Soc., 164, 10675 (2017).

27. A. Bîrzu and V. Gáspár, Electrochim. Acta, 55, 383 (2009).

28. C. Zensen, K. Schönleber, F. Kemeth, and K. Krischer, J. Phys. Chem. C, 118, 24407 (2014).

29. J. G. Bell and J. Wang, J. Electroanal. Chem., 754, 133 (2015).

30. Z.-L. Li, B. Ren, X. M. Xiao, Y. Zeng, X. Chu, and Z. Q. Tian, J. Phys. Chem. A, 106, 6570 (2002).

31. S. Chen, W. Huang, Z. Niu, and Z. Li, Chem. Phys. Lett., 421, 161 (2006).

32. K. Maeda, K. Maeno, K. Fukui, M. Moritoki, and H. Kuramochi, J. Chem. Eng. Data, 58, 264 (2013).

33. K. Maeda, N. Arakawa, S. Matsuda, K. Fukui, and H. Kuramochi, J. Electrochem. Soc., 162, A21 (2015).

34. Y. Nobuyoshi, T. Yamamoto, K. Maeda, N. Fukumuro, and S. Yae, Kagaku Kogaku Ronbunshu, 44, 35 (2018).