



Potential oscillation during electrolysis of water in acidic solutions under numerous conditions



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ARTICLE INFO

Article history:

Received 21 May 2013

Received in revised form 5 September 2013

Accepted 1 November 2013

Available online 1 December 2013

Keywords:

Electrochemical oscillation

Hydrogen evolution reaction

Water electrolysis

pH

Hydrogen bubbles

ABSTRACT

We have revealed that a novel potential oscillation occurs in hydrogen evolution reaction (HER) during water electrolysis, not only when H₂SO₄ solutions are used as electrolytes as has been reported in our earlier papers (Mukouyama et al., 2008; 2013), but also when a large variety of acid solutions are used as electrolytes. When the acid concentration is lower than ca. 0.1 M, the electrode potential oscillates spontaneously under current controlled conditions in a high overpotential region, e.g. more negative than ca. −1.0 V vs. SHE. The oscillation appears by addition of a small amount of salts, such as LiClO₄, Na₂SO₄, K₂SO₄ and MgSO₄, even when the acid concentration is higher than ca. 0.1 M. We have also found that the oscillation occurs not only when Pt, Au or Cu is used as a working electrode as has been reported in the papers but also when various metal substrates such as Rh, Ag, Fe, Ni, W, Zn, Sn and In are used. It was revealed that the local pH at the electrode surface oscillates between acidic and basic synchronously with the potential oscillation. The mechanism of the oscillation can be explained by an autocatalytic bubble evolution and the changes in the local pH and in the concentration of dissolved hydrogen at the electrode surface due to the bubble evolution.

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1. Introduction

Hydrogen evolution reaction (HER) occurs at a cathode electrode during electrolysis of water (2H₂O → 2H₂ + O₂) under a variety of conditions. In the early 20th century, kinetic studies on the HER were conducted by Tafel [1]. Since then, the HER has been extensively studied [2–5] because it is a fundamental electrochemical reaction and also an important reaction for the production of H₂.

Salts, such as Na₂SO₄ and K₂SO₄, are often used as supporting electrolytes for electrochemical reactions because the ions originated from the salts decrease the solution resistance. It was natural, therefore, to expect that the decrease in the solution resistance by the addition of the salts increased the reduction current due to the HER. However we found, as reported in our earlier paper [6], that the reduction current due to the HER on Pt and Au in 0.10 M (M = mol/dm³) H₂SO₄ was anomalously decreased by the addition of the salts in a high overpotential region, e.g. more negative than −0.5 V vs. SHE. The reduction current became low (in absolute value) with increasing concentration of the salts. We also found that a novel potential oscillation, called HER oscillation, appeared accompanying the decrease of the HER current.

As discussed in the earlier paper [6], the decrease in the HER current by adding salts is caused by the presence of cations, Na⁺ or K⁺, which changes the transport velocity of H⁺ to the electrode surface. The transport is caused not only by diffusion and solution-stirring, but also by electromigration, when no salt is added to the solution. When the salt is added to the solution, the cation reduces the electromigration transport of H⁺, resulting in the decrease in the HER current.

We recently studied the HER on Cu in H₂SO₄ solutions and found that the novel potential oscillation appeared without the addition of the salts when the concentration of H₂SO₄ was as low as 0.03 M [7]. In this study, we show that the oscillation appears during the HER not only on Pt, Au or Cu but also on Rh, Ag, Fe, Ni, W, Zn, Sn and In in a variety of electrolytes, such as H₂SO₄, HNO₃ and HClO₄. We also show that the local pH at the electrode surface and the behavior of hydrogen bubbles oscillate synchronously with the novel potential oscillation, and discuss the mechanism of the oscillation.

Electrochemical oscillations have been reported in a variety of systems as summarized in reviews [8–11] including the reduction of metal ions, that of hydrogen peroxide on Pt [12] and Ag [13], that of peroxodisulfate on Pt, Au [14] and Ag [15], and that of iodate on Au [16]. Some potential oscillations were caused by an interaction between the HER and the reduction reaction. Therefore, they were observed in the potential region where the HER occurred.

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What is interesting in the novel potential oscillation in this work is that it appears during the HER without any other side reactions.

It has been reported that hydrogen bubble evolution due to the HER affects the electrode potential. The hydrogen bubble growth and detachment from the electrode under current controlled conditions induced potential fluctuations with a range of up to 0.1 V [17,18] because the active surface area for the HER on the electrode decreased as the bubble grew and recovered when the bubble detached. When microelectrodes were used as working electrodes, the growth of a single bubble and its detachment from the microelectrodes caused a periodical potential oscillation with a large amplitude (up to 0.6 V) [19,20].

The novel potential oscillation in this work, the amplitude of which is as large as about 1 V, also accompanies the H₂ bubble evolution which changes synchronously with the potential oscillation. Therefore, it looks like the oscillations reported in the literature [17–20]. However, the novel oscillation is quite different from the reported ones, as shown in this paper. Namely, not only the amplitude of the novel oscillation is larger than those of the reported oscillations, but also there are definitive differences between them in the oscillation mechanism and in the conditions for the appearance of oscillation.

2. Experimental

2.1. Preparations

We prepared solutions using special analytical grade chemicals (Wako Pure Chemical Industries, Ltd.) and purified water (resistivity: >18 M Ω cm) obtained from a Millipore system.

The electrochemical measurements were done by using a three electrode system. A polycrystalline Pt (99.99%) disc of ca. 2.0 mm in diameter and polycrystalline Pt (99.99%) and Ag (99.99%) wires (0.5 mm in diameter) of ca. 4.0 mm in length were used as the working electrode. Polycrystalline Rh (99.9%), Au (99.99%), Cu (99.999%), Ni (99.9%), W (99.95%), Zn (99.99%), Sn (99.9%) and In (99.99%) wires (0.5 mm in diameter) of ca. 4.0 mm in length and a Fe (99.9%) wire (0.25 mm in diameter) of ca. 4.0 mm in length were also used as the working electrode. A Pt plate (10 × 10 mm²) was used as the counter electrode and a saturated mercury–mercurous sulfate electrode (MSE, 0.64 V vs. SHE at 25 °C), Hg|Hg₂SO₄|sat. K₂SO₄, was used as the reference electrode; however, the potentials were referred to the SHE.

A Pt disc was polished with 0.06-μm alumina powder and rinsed with purified water. Then it was immersed in 60% HNO₃ for about one day to remove the surface contaminations. A Pt wire was annealed in a hydrogen flame for about 20 s in order to clean the electrode surface. Rh and Au wires were immersed in 60% HNO₃ for one hour. Before electrochemical measurement with Rh and Au wires, the cyclic potential scans between the onset potential of hydrogen evolution reaction and that of oxygen evolution reaction were repeated at a sweep rate of 0.1 V s⁻¹ in 0.1 M H₂SO₄ for about 30 min in order to clean the electrode surface. The remaining wires, Ag, Cu, Fe, Ni, W, Zn, Sn and In wires, were immersed in about 6% HNO₃ for approximately 20 s to clean the electrode surface.

2.2. Measurements

The electrochemical measurements were done using a potentiostat/galvanostat (Hokuto-Denko Co., Ltd., HA-501G or Princeton Applied Research, Model 363) and a function generator (Hokuto-Denko Co., Ltd., HB-105). The values of the potential (*E*) and the current (*I*) were acquired using a data acquisition instrument (National Instruments, NI PCI-6034E) at a sampling rate of

10 kHz. They were then saved after taking an average of every 100 points. A high-speed camera (Shinano Kenshi, PLEXLOGGER) was used to observe behavior of H₂ bubbles evolved from the working electrode. The recording frame-rate was 500 fps (=frames per second).

The electrochemical measurements were done at room temperature (around 25 °C) because there was little effect on the current (*I*) – potential (*E*) curves when the solution temperature ranged between 20 and 30 °C. The electrical conductivities of solutions were measured by a conductivity meter (Horiba, F-55) at room temperature.

3. Results and discussion

3.1. Local pH oscillation

We, first, show that the local pH at the electrode surface oscillates between acidic and basic synchronously with the potential oscillation. Fig. 1 shows the *I*–*E* curves for the Pt-disc electrode in 0.10 M H₂SO₄, 0.10 M H₂SO₄ with 0.03 M Na₂SO₄, and in a basic solution (0.10 M NaOH with 0.10 M Na₂SO₄), measured under potential and current controlled conditions. As shown in Fig. 1a, the reduction of H⁺ (2H⁺ + 2e⁻ → H₂) started to occur at ca. -0.1 V in a 0.10 M H₂SO₄ solution. In the absence of Na₂SO₄, the reduction current almost linearly increased (in absolute value) during the HER in 0.10 M H₂SO₄ with decreasing potential under potential controlled conditions. The constant-current state, where the current was almost constant even if the electrode potential decreased, appeared by adding 0.03 M Na₂SO₄. In the earlier paper [6], we called the state a low-current state.

In the potential region below the constant-current state, i.e., *E* < -1.8 V, the reduction current increased again with decreasing potential. We attributed the increase to the reduction of H₂O molecule (2H₂O + 2e⁻ → H₂ + 2OH⁻) [6]. To confirm that the H₂O reduction, which should occur if the solution at the electrode surface is not acidic, occurred during the HER in H₂SO₄ solutions, we compared the HER in the acidic solution with that in the basic solution. The H₂O reduction started to occur at ca. -0.8 V in the basic solution. The *I*–*E* curve observed in 0.10 M H₂SO₄ with 0.03 M Na₂SO₄ was almost identical to that for the basic solution in a

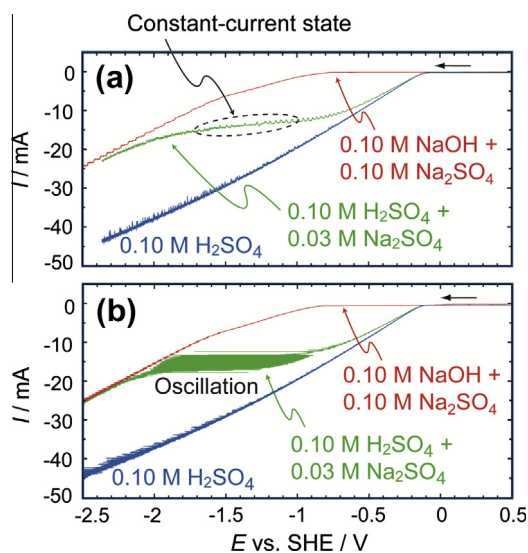


Fig. 1. The *I*–*E* curves for the Pt-disc electrode in 0.10 M H₂SO₄, 0.10 M H₂SO₄ + 0.03 M Na₂SO₄ and 0.10 M NaOH + 0.10 M Na₂SO₄, measured (a) under potential controlled conditions at a sweep rate of 0.01 V s⁻¹ and (b) under current controlled conditions at a rate of 0.1 mA s⁻¹.

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