Microbubble Formation from Ionic Vacancies in Copper Anodic Dissolution under a High Magnetic Field

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ABSTRACT

Ionic vacancies created in copper anodic dissolution has been firstly observed by the conversion to microbubbles using both of cyclotron effect and pinch effect under a vertical magnetic field; in a circulating solution induced by Lorentz force, ionic vacancies collide with each other, changing to nanobubbles. Then, the circulation of the nanobubbles with solution makes further collisions, yielding microbubbles. Based on this result, the lifetimes of ionic vacancy formed in copper electrodeposition were finally determined.

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1. Introduction

For more than 50 years, cavities in polar solvents such as ammonia and water has been paid much attention as trapping regions of free electrons introduced into them.^{1,2} In water, a cavity takes a quasispherical shape with a 2.5 Å radius surrounded by at least six OH bonds oriented toward the negative charge distribution where an equilibrated hydrated electron is transiently confined.^{3,4} The hydrated electron is a key reactive intermediate in the chemistry of water, including the biological effects of radiation. Despite being so reactive, the electron can have appreciable lifetimes of the order of 100 femtoseconds because it is stabilized by the cavity.³ However, the studies using ultrafast laser pulses have confronted the cavity model with many contradictory experimental results.^{3,6} To account for a wide range of properties of the hydrated electron, Larsen et al. have proposed a new model in which the hydrated electron not only penetrates the charge distribution of the water molecules but also is associated with a region of enhanced water density rather than a cavity.^{4,5}

Recently, it has been found that in electrode reactions, absolutely different type of cavity, i.e., ionic vacancies are created.^{7,8,11,12} An ionic vacancy is composed of water molecules and ions, which yield a charged vacuum space of about a 1 Å radius surrounded by an oppositely charged ionic cloud (Fig. 1). The sizes theoretically calculated are in good agreement with experimental data.⁸ Due to creation without any entropy production in the surroundings, the ionic vacancy behaves as a lubricant for providing a free surface without friction. Since ionic vacancy is an iso-entropic particle, such a property is quite different from that of surfaces adsorbing micro- and nano-bubbles.⁹ Then, the nanobubble formation process from ionic vacancies has been also theoretically clarified.¹⁰ Even though nanobubbles, due to their smallness, the direct observation may be difficult, so that for the detection of ionic vacancy, further conversion of nanobubbles to microbubbles (Ostwald ripening) is

Figure 1. (Color online) Structure of ionic vacancy.

required. The microbubbles evolved via nanobubbles have been actually first observed in ferricyanide-ferrocyanide redox reaction.¹¹ In copper deposition, the same kind of microbubble evolution has been also observed,¹² where the measurement of the partial molar volume of ionic vacancy revealed that ionic vacancies are stoichiometrically created with electrode reactions. These experimental results suggest that evolution of ionic vacancy is a universal phenomenon in electrode reactions, and that ionic vacancies emerge with the conservation of momentum as well as electric charge; if ionic vacancy is created in anodic copper dissolution, as shown in Eqs. (1) and (2), according to one-electron or two-electron transfer control, an ionic vacancy with one or two positive unit charges, V_+ or V_{2+} would be formed and then immediately covered with a negatively charged ionic cloud, that is, ionic vacancy totally has no electric charge.

To examine the actual reaction process including ionic vacancies, the size of the ionic vacancy was measured by gravity electrode, which is an electrode system to measure the change of solution density in an electrode reaction under a high gravitational field generated by centrifugal force.^{13–16} In all these measurements, electrolytic currents under diffusion control are utilized. In copper anodic dissolution, however, the current is generally under the mixed control of reaction and diffusion, so that the same electrochemical techniques are too hard to be applied. As a result, though we attempt to develop a new method to treat the mixed-controlling case, whether ionic vacancies occur or not in copper anodic dissolution has not yet been obvious.

In the present paper, therefore, to clarify such ambiguity, the microbubble formation in copper dissolution under a high magnetic field is first attempted for detecting the evolution of ionic vacancy. Then, the anodic vacancy evolution completely denies the relationship with hydrated ion. Finally, in accordance with the experimental result, the lifetime of ionic vacancy in copper deposition is reexamined.

2. Theoretical

To determine the lifetime of the ionic vacancy in copper deposition, whether the ionic vacancy is created or not in copper anodic dissolution on the counter electrode is a quite important problem. As have been discussed in the preceding papers,^{17,18} the lifetime of an ionic vacancy is measured by a new electrode system termed cyclotron magnetohydrodynamic (MHD) electrode, where, as shown in Fig. 2A, the solution together with ionic vacancies circulates between the circular walls of concentric electrodes under a vertical magnetic field. In a weak magnetic field, due to low circulation velocity, the vacancies created become extinct on returning to the initial electrode, and the rigid surfaces of the walls bring about a viscous flow. However, as the velocity increases with magnetic field, the vacancies can return to their starting area, so that the walls are covered with them. Due to the lubricant nature, the ionic vacancies change the rigid surface with friction to a free surface without friction, so that the viscous flow is transformed into an inviscid flow.¹⁷ By measuring the corresponding diffusion current, the lifetime is calculated. However, two types of inviscid flow exist, i.e., only working electrode is free, and working and counter electrodes are free. As shown in Fig. 2B, the two cases provide quite different velocity distributions yielding different diffusion currents, so that the calculated values of the lifetime depend on the inviscid modes, that is, whether copper dissolution on the counter electrode yields ionic vacancies or not.

Based on the thermodynamic calculation concerning the nanobubble formation from ionic vacancies,¹⁰ the critical potential for the nanobubble evolution is of the order of 100 kJ per a unit mole of ionic vacancy, and the critical radius is about 10 Å. The size smaller than the mean free path of gas molecules leads to the vacuum space of ionic vacancy, whereas the inside of nanobubble is filled with gases dissolved in the solution at an atmospheric pressure. However, even if nanobubbles are obtained, which are too small to optically observe, so that they must be further transformed to larger microbubbles. To carry out this requirement, a tornado-like stream called vertical MHD flow under a vertical magnetic field¹⁹ thus plays an important role, and two types of electrodes effective in forming microbubbles were prepared; one is fringe-type, and the other is sheath-type. As shown in Fig. 3, on the fringe-type electrode, Lorentz force and friction of electrode fringe make an inward radial flow conveying nanobubbles, which are compressed at the center of the electrode until supersaturation, changing to microbubbles (pinch effect), whereas on the sheath-type electrode, the exact circulation of the solution inside the sheath makes ionic vacancies collide with each other (cyclotron effect). The validity of

Figure 2. (Color online) Cyclotron MHD electrode and velocity distributions of two types of inviscid flow modes.¹⁶ A, Cyclotron MHD electrode in the case of one free surface; B_z , Magnetic flux density, $\circ$, Ionic vacancy. B, Velocity distribution; (a) Viscous flow, (b) Inviscid flow with one free surface, (c) Inviscid flow with two free surfaces. W.E., Working electrode; C.E., Counter electrode.

Figure 3. Vertical MHD flow. (a) Fringe-type electrode; (b) Sheath-type electrode. a, Working electrode; b, Fringe; c, Sheath; i , Current; G , Gravitational field; B_z , Magnetic flux density.

these electrodes has been proved by the preceding experiments.^{11,12} Then, the microbubbles are in situ observed by optical microscope. To ensure the process mentioned above, the origin of the gas contained in the microbubbles is examined by the following blank

Figure 4. Experimental apparatus. a, Superconducting magnet; b, N₂ gas; c, CCD camera; d, Cable wire to personal computer; W.E., Working electrode; C.E., Counter electrode; R.E., Reference electrode; B_z, Magnetic flux density.

test; prior to experiment, all the gases including dissolved gases are removed from the electrode cell with vacuum pump, which makes nanobubble formation impossible and will prepare the electrode surface without microbubble evolution. In the blank test also, the fringe-type and sheath-type electrodes can be utilized. In this paper, the sheath-type one is used, of which validity have been already proved in the foregoing paper.¹²

3. Experimental

The experimental apparatus was, as shown in Fig. 4, consisted of a home-made electrode cell and a CCD camera (Multi-function USB Portable Digital Microscope B003+, Shenzhen D&F Co., Ltd.) equipped with white LED lights which has a frame rate of 3.3 fps. The cell had a flat bottom covered with an optical glass, through which the surface of a downward-oriented circular copper electrode was optically observed. To provide a smooth surface covered with ionic vacancies, as mentioned above, two types of electrode surface were adopted; one is a bright copper surface with a 3 mm diameter surrounded by an acrylic fringe of a 2.5 mm width (fringe-type) and the other is the same surface surrounded by a 5 mm high sheath of thermal shrinkage tube (sheath-type). The former was used for the observation of microbubble evolution, whereas the latter was for the blank test. On the downside of this working electrode, a spiral copper wire with a 1 mm diameter was placed as counter electrode. Through the opening of the counter electrode, the surface of the working electrode was observed by the CCD camera. As a reference electrode, the same copper wire was inserted in the neighborhood of the working electrode, which was, immediately after experiments, calibrated by a Ag/AgCl reference electrode (RE-1B BAS Co., Ltd.). The CCD camera was capable of a magnification power of ca. 200, connected with a personal computer for the monitoring of bubble evolution. The whole apparatus was settled in the bore space (with an upward-oriented magnetic field) of a 10 T cryocooled superconducting magnet at the High Field Laboratory for Superconducting Materials, IMR, Tohoku University. 10 mol m⁻³ and 30 mol m⁻³ CuSO₄ solutions with a 100 mol m⁻³ H₂SO₄ supporting electrolyte were used for anodic dissolution. Prior to experiment, the

Figure 5. Current response against potential sweep in anodic direction. A, Electrode potential of +400 mV vs. N.H.E. where the photos in Fig. 6 were taken; B, Electrode potential of +750 mV vs. N.H.E. where oxygen gas started evolving. The fringe-type electrode was used. Sweep rate, 1 mV s⁻¹; Magnetic flux density, 1 T; [CuSO₄], 10 mol m⁻³; [H₂SO₄], 100 mol m⁻³.

absence of H₂ gas evolution from the counter electrode was ascertained. For the evacuation of dissolved oxygen, N₂ gas bubbling was performed. Then, during the experiment, N₂ gas was continuously supplied to the solution via a hollow fiber filter (M40-200, Nagayanagi Co., Ltd.) at atmospheric pressure. For the blank test, the N₂ gas supply was stopped, and the gas was evacuated from the inside of the cell by a rotary vacuum pump (model G-50 SA, ULVAC Co., Ltd.). For observing microbubbles, under a 8 T magnetic flux density, various anodic overpotentials of 20 mV (= 270 mV vs. N.H.E.) to 150 mV (= 400 mV vs. N.H.E.) were applied, where the overpotentials are defined by the differences from the rest potential. Temperature of the solution was kept at 22 ± 1°C.

4. Results and Discussion

In Fig. 5, with the fringe-type electrode, after 10 min bubbling of N₂ gas, the current response against the potential sweep at a 1 T magnetic flux density is exhibited. From the video image of the CCD camera, oxygen gas evolution was ascertained about at a 500 mV overpotential (= 750 mV vs. N.H.E) (Point B), which was much higher than the higher limit of the overpotential step, 150 mV (= 400 mV vs. N.H.E.). Before Point B, the diffusion current component fluctuates with time, whereas beyond Point B, the oxygen evolution seems to periodically disturb local electrode potentials, yielding fluctuation.

Then, with the fringe-type electrode, after 10 min bubbling of N₂ gas, at a 8 T magnetic flux density, the overpotential steps of 20 mV to 150 mV were applied. At a 150 mV overpotential step, as shown in Fig. 6, the globules of microbubble continuously emerged ascending from the electrode surface and faded from view after several anticlockwise circulations. Just after the experiment, with the sheath-type electrode, the blank test was performed under the same electrochemical conditions at 8 T after evacuating the dissolved gases. In Fig. 7, the electrode surface in the blank test is represented, where any fragment of the microbubble globules cannot be observed. Namely, it is concluded that in copper anodic dissolution also, ionic vacancies are created.

As a result, for the lifetime calculation of ionic vacancy in copper deposition by means of cyclotron MHD electrode, the inviscid mode of two free surfaces must be used. Figure 8 represents the plot of the lifetime against the cell constant based on this result, where the cell constant is defined as the conversion efficiency of the work of the Lorentz force to the kinetic energy of the MHD flow and implies a collision efficiency of ionic vacancy.¹⁷ For comparison, a regression line from the data based on one free surface in the preceding paper¹⁷ is also exhibited, which is about 10 times larger than that of two free

Figure 6. Microbubble evolution during copper dissolution at 8 T. A, Microbubble globules arising from a copper surface during copper dissolution at an overpotential $V = 150$ mV (+400 mV vs. N.H.E.); B, Continuous images of microbubble globules, which were taken at a 0.33 s interval. The length of arc arrow indicates the angular velocity of solution flow. The fringe-type electrode was used. For clear visualization, all the images of microbubbles are painted in yellow.

Figure 7. Electrode surface during copper dissolution after evacuating a dissolved gas. The sheath-type electrode was used. Except for gas evacuation and sheath-type electrode, the same experimental conditions as those in Fig. 6 were used.

surfaces. Almost the same regression line corresponding to two free surfaces has been obtained in the case of ferricyanide-ferrocyanide redox reaction.²⁰ The experimental result obtained here completely denies that ionic vacancy is a relevant phenomenon with hydrated electron. Namely, hydrated electrons, even if possible, would arise from cathodic reactions, whereas the microbubbles observed evolve from copper anodic dissolution.

Figure 8. Plot of the lifetime of ionic vacancy vs. cell constant in copper deposition from various copper sulfate solutions containing $100 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4$, $[\text{CuSO}_4]$, 10 to 50 mol m^{-3} ; ●, Correct data obtained from two free surfaces; Solid line, Regression line of the correct data. Dotted line, Reference regression line of the data from one free surface.¹⁷

Furthermore, the circulating velocity was of the order of 10 cm s^{-1} , which denies the possibility of cavitation by high-speed rotation. All these events occurred at electrode potentials much lower than that of oxygen gas evolution. The variation of the solution temperature was kept within $\pm 1^\circ\text{C}$, so that the contribution of the endothermic or exothermic effect of the reaction on gas solubility is also denied. The magnetization energy in the present case is estimated at most of the order of 1 kJ mol^{-1} , which is much smaller than conventional chemical activation energies. The light source was white LED without infrared and ultraviolet components, which also excludes the possibilities of bubble evolution from other reasons.

5. Summary

The microbubbles arose from the supersaturated nanobubbles formed by the collision between ionic vacancies in copper anodic dissolution in a $30 \text{ mol m}^{-3} \text{ CuSO}_4$ solution with $100 \text{ mol m}^{-3} \text{ H}_2\text{SO}_4$ supporting electrolyte. Namely, ionic vacancies are created in copper anodic dissolution in a sulfuric acid solution. This result absolutely denies the relationship between ionic vacancy and hydrated electron. Based on this experimental result, the lifetime of ionic vacancy formed in copper deposition was correctly calculated.

Acknowledgments

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