東北大学機関リポジトリ
TOUR
Tohoku University Repository

Determination of the properties of ionic vacancy by magnetic field

Determination of the properties of ionic vacancy by magnetic field

Determination of the properties of ionic vacancy by magnetic field

R. Aogaki [1,10]*, A. Sugiyama [2,3,10], M. Miura [4], Y. Oshikiri [5], M. Miura [6], R. Morimoto [7], I. Mogi [8], S. Takagi [9], Y. Yamauchi [10]

[1]Polytechnic Univ., [2]Yoshino Denka Kogyo, Inc., [3]Waseda Univ. Res. Org. Nano & Life Innovation, [4]Hokkaido Polytechnic College, [5]Yamagata College of Industry and Technology, [6]Polytechnic Center Kimitsu, [7]Saitama Industrial Technology Center, [8]Tohoku Univ., [9]Koriyama Technical Academy, [10]National Institute for Materials Science

*Corresponding author: AOGAKI.Ryoichi@nims.go.jp

Abstract

Ionic vacancy is, being produced as a byproduct in electrode reaction, a polarized free space of the order of 0.1 nm surrounded by oppositely charged ionic cloud. As a perfect gas in electrolyte solution, it does not interplay with other solution particles. On the other hand, magnetic field provides useful means to examine the natures of it. Using a special electrode operated in a magnetic field called cyclotron MHD electrode (CMHDE), we first determined the lifetime of vacancy in copper deposition as 1.2 sec, which is extraordinarily long in comparison with the collision interval of solution particles. Then, using kinetic theory of gas, we measured the collision radius of vacancy gas to be 0.70 nm, which was consistent with theoretical calculation 0.65 nm.

Keywords: ionic vacancy, perfect gas, nanobubble, magneto-dendrite effect, cyclotron MHD electrode.

Introduction

Magnetoelectrochemistry is the electrochemistry in magnetic field. In order to study electrode reactions in magnetic fields, some special electrodes are operated under magnetohydrodynamic (MHD) flow induced by Lorentz force, e.g., under vertical magnetic field, a macroscopic tornado-like vortex called vertical MHD flow arises over a disk-electrode (VMHDE) (Fig.1a), and a circulating solution emerges between a pair of concentric cylinders with electrodes (CMHDE) (Fig. 1b).

In various electrode reactions, unrelated with hydrogen and oxygen evolution, a large number of microbubbles containing dissolved N_2 gas emerge on a VMHDE (Fig.2a,b), which experimentally validates the fact that ionic vacancy is a byproduct of electrode reaction [1-3]. Ionic vacancy is a polarized free space of the order of 0.1 nm surrounded by oppositely charged ionic cloud (Fig. 2a), which is created by electron transfer in electrochemical reaction, emitted to solution side from the conservation of momentum and charge during (Fig. 3A,B) [4]. As shown in Fig.1a, the macroscopic rotation of vertical MHD flow is characterized by two areas, inner and outer regions. In the outer region, the fluid particles rotating at a large distance from the electrode are in hydrodynamic equilibrium under the centrifugal force balanced with the radial pressure gradient. In the inner region, due to friction, the peripheral velocity of the particles near the electrode at rest is reduced, decreasing the centrifugal force materially, whereas the radial pressure gradient directed towards the axis remains the same.
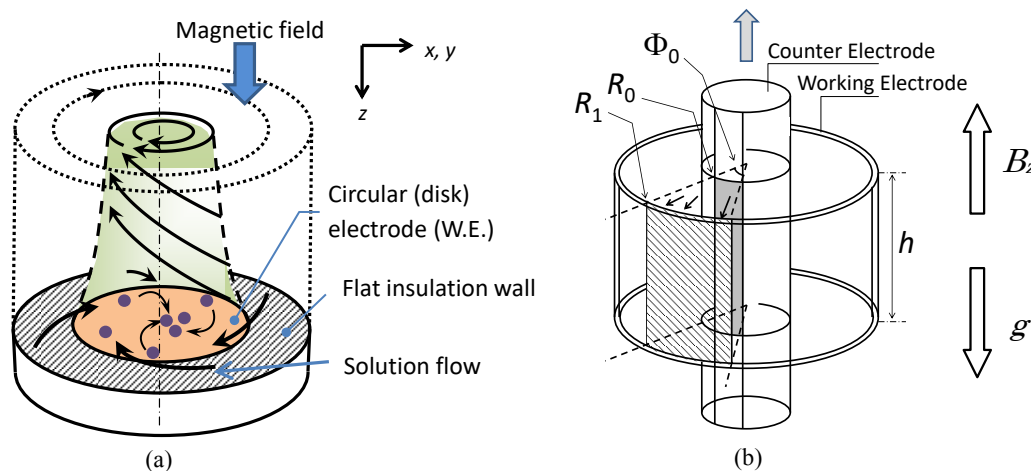

Fig. 1: MHD electrodes. (a), Vertical MHD electrode (VMHDE). ○, Ionic vacancy. (b), Cyclotron MHD electrode (CMHDE). R_0; inner radius, R_1; outer radius, h; the electrode height, Φ_0; the angle of the arc electrode surfaces, B_z; the magnetic flux density, g; gravitational acceleration.

This set of circumstances causes the particles near the electrode to flow radially inwards, and for reasons of continuity that motion must be compensated by an axial flow upwards. Ionic vacancies produced on the electrode are carried with the secondary flow to the center, so that coalescence by collision transforms them into microbubbles. Furthermore, in copper electrodeposition under vertical MHD flow, numerous microscopic vortexes called micro-MHD flows are induced on the electrode surface, which create screw dislocations with chirality acting a chiral catalyst for enantiomeric reaction [5].

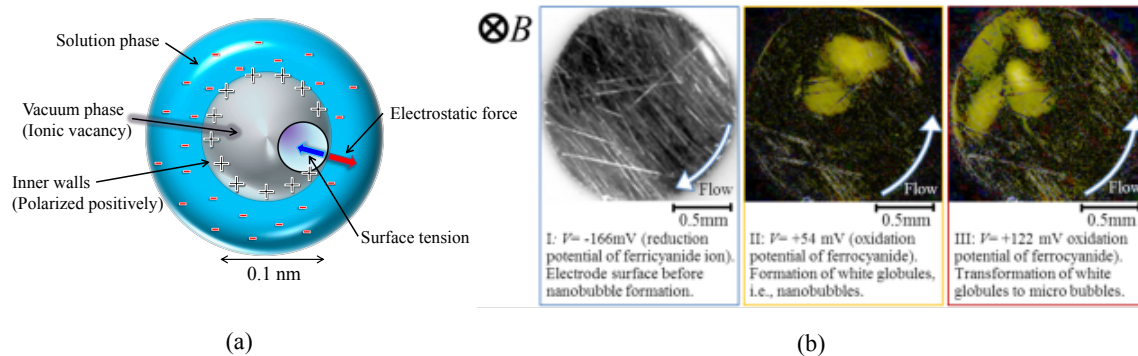(a)   (b)

Fig. 2: Ionic vacancy and microbubble evolution [1]. (a) Schematic of a positive vacancy. (b) Microbubbles on VMHDE. I, Electrode surface during the reduction at an overpotential V = -166 mV (+264 mV vs. NHE); II, Nanobubble-layer formation with refractive variation at V = +37 mV (+467 mV vs. NHE); III, Microbubble formation at V = +122 mV (+552 mV vs. NHE). The images are subtracted and painted by yellow.

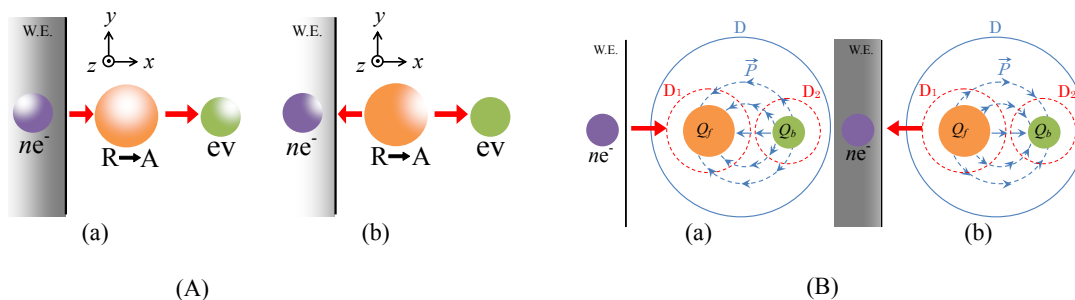(A)   (B)

Fig. 3: Emissions of embryo vacancy in electrode reactions [4]. (A) Emission of embryo vacancy in electrode reaction. (a), Cathodic reaction; (b), Anodic reaction. (B) Charge transfer process by electric polarization.(a), Cathodic reaction; (b), Anodic reaction. ne[-], electrons transferring in the reaction; R, reactant; A, activated complex; ev, embryo vacancy; W.E., working electrode.

Lifetime of ionic vacancy

CMHDE was first developed for measuring the lifetime of ionic vacancy [6]. As shown in Fig. 1b, electrolyte solution is placed between concentric cylinders under a vertical magnetic field. Both cylinders have electrodes, and except for the electrodes, the walls are insulated. As electrolytic current flows, Lorentz force makes the solution rotate between the cylinders. In a weak magnetic field, due to low rotational speed, ionic vacancies disappear on the way returning to the electrode of birth, whereas in a strong magnetic field, due to high rotational speed, they can survive the travel, covering the cylinder walls to form vacancy-rich layers. As a result, the solution flow changes from viscid to inviscid with magnetic field. Figure 4a shows the plots of the limiting diffusion current against magnetic field strength in CMHDE for copper electrodeposition. As the magnetic field increases, the plot changes from a straight line with a slope of 1/2 to a straight line with a slope of 1, corresponding to viscid and inviscid flows, respectively. From the crossing point (critical point), the lifetime of ionic vacancy τ was determined, which is, in Fig. 4b, plotted against the collision efficiency γ. An intrinsic lifetime of ca. 1 sec is obtained in the case without collision for $\gamma = 0$, whereas in the case of one by one collision for $\gamma = 1$, the collision interval with another vacancy τ_{colli} = ca. 10^{-2} sec is obtained. A 1 sec lifetime is extraordinarily long in comparison with a 10^{-10} sec corrosion interval between other solution particles. Due to free space without solid matter, ionic vacancy migrates by repeating creation and extinction together with ionic cloud. In the creation, polarized charge of a vacancy core first induces surrounding ionic cloud. Then, using the

electrostatic energy emitted from the cloud, the core is dynamically expanded up to a given size. In the extinction, disassembling ionic cloud withdraws the energy from dwindling core. In this process, ionic vacancy transfers without entropy production. This implies that ionic vacancy does not interplay with other solution particles but with other ionic vacancies; in other word, ionic vacancy behaves as a perfect gas in electrolyte solution.
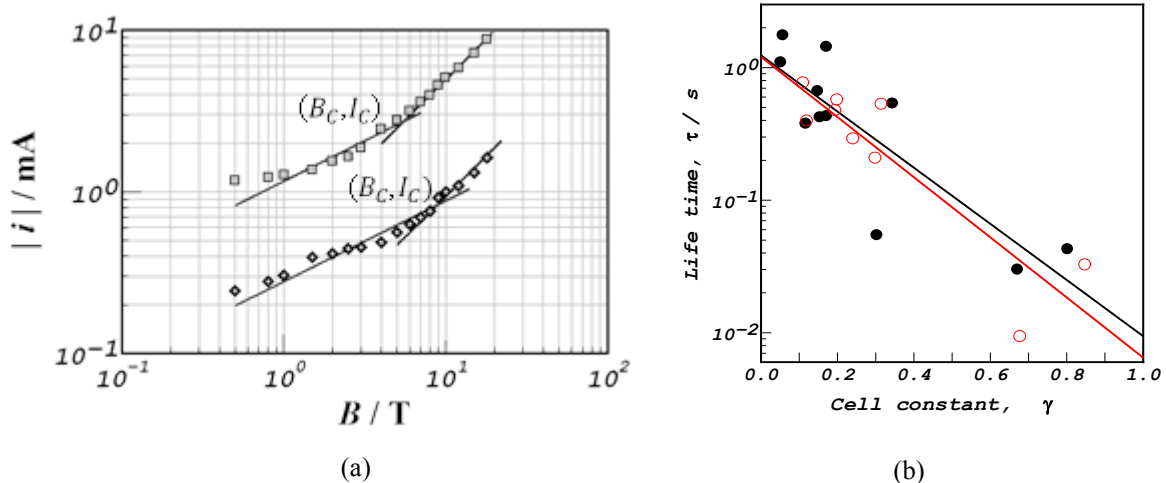

(a)   (b)

Fig. 4: Measurement of the lifetime of vacancies by CMHDE [6]. (a) Plot of current vs. magnetic flux density for copper deposition in a 100 mol m^{-3} H$_2$SO$_4$ solution. I_c and B_c are the critical current and critical magnetic flux density, respectively. (b) Plots of the lifetime of ionic vacancy vs. cell constant (collision efficiency). ○, Ferrocyanide-Ferricyanide redox reaction, and ●, Copper deposition.

Magneto-dendrite effect

Owing to continuous supply of newly created vacancies, using CMHDE as well as VMHDE, we cannot always control the vacancy concentration in the vacancy layer on the electrode, but also examine the chemical nature of ionic vacancy in electrode reactions. Figure 5A,B shows a 'magneto-dendrite effect' observed in copper deposition using CMHDE, where instead of hydrogen molecules, nanobubbles arising from coalescent vacancies are adsorbed on copper 3D nuclei, blocking nucleation [7]. As a result, unrelated with hydrogen gas evolution, characteristic copper dendritic growth occurs with a drastic anodic potential shift of rising current from hydrogen evolution potential (Fig. 5b).

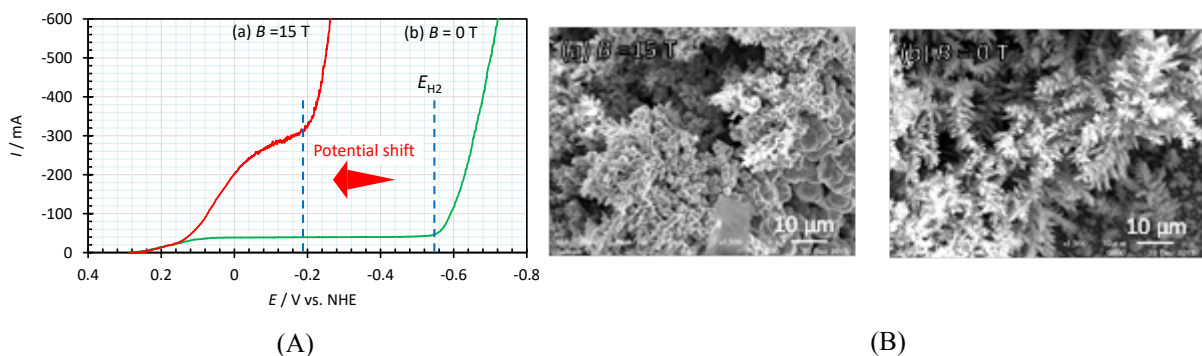(A)   (B)

Fig. 5: Potential shift in anodic direction observed in copper deposition by cathodic potential sweep at a 15T magnetic field and SEM images of the corresponding dendritic deposition [7]. (A) Current vs. potential curves; (a) Red solid line, B = 15 T; (b) Green solid line, B = 0 T. E_{H2}, Hydrogen evolution potential; [CuSO$_4$], 300 mol m^{-3}; [H$_2$SO$_4$], 500 mol m^{-3}; Sweep rate, 5 mVs^{-1}. Electrode, Copper-CMHDE. (B) SEM images of copper dendrites obtained after the potential sweeps. (a) B = 15 T without hydrogen gas evolution. (b) B = 0 T with hydrogen gas evolution.

Ionic vacancy as a perfect gas

The extraordinarily long lifetime measured in Fig. 4b strongly suggests that ionic vacancy behaves as a perfect gas. As a result, using kinetic theory of gas, we can measure the collision radius of ionic vacancy from the experimental data of CMHDE. When an ionic vacancy that is circulating around the cylinder walls collides with other vacancies newly created on the electrode, its kinetic energy as well as linear momentum changes after the collision. By means of the kinetic model, we calculate the frequency with which vacancy collisions occur and the distance a vacancy travels on average between collisions $V_V\tau$, where V_V and τ are the mean speed and lifetime of vacancy, respectively. We count a 'hit' whenever the center of two vacancies come within a distance d of each other, where d, the collision diameter, is of the order of the actual diameter of vacancy. In Fig. 6a, b, a collision tube swept out by a returning vacancy and its collision process in CMHDE are exhibited. In Fig. 6b, the vacancy layer takes a very thin thickness of several µm depending on the diffusion coefficient and the collision lifetime. Due to the gas behaviour without interaction with other solution particles, the vacancy layer can circulate without viscosity, so that the neighbouring part of solution can take a fluid motion without friction. This is the reason why as shown in Fig. 4a, inviscid flow corresponding the plot of a slope 1 emerges in CMHDE. Figure 6c exhibits the plot of collision radius vs. collision efficiency obtained in copper deposition in copper sulfate + sulfuric acid solution. For comparison, theoretical value is also plotted by a dotted line. The experimental data 0.70 ±0.07 nm are in good agreement with the theoretical estimation 0.65 nm, which assures the validity of the theoretical analysis of vacancy gas.
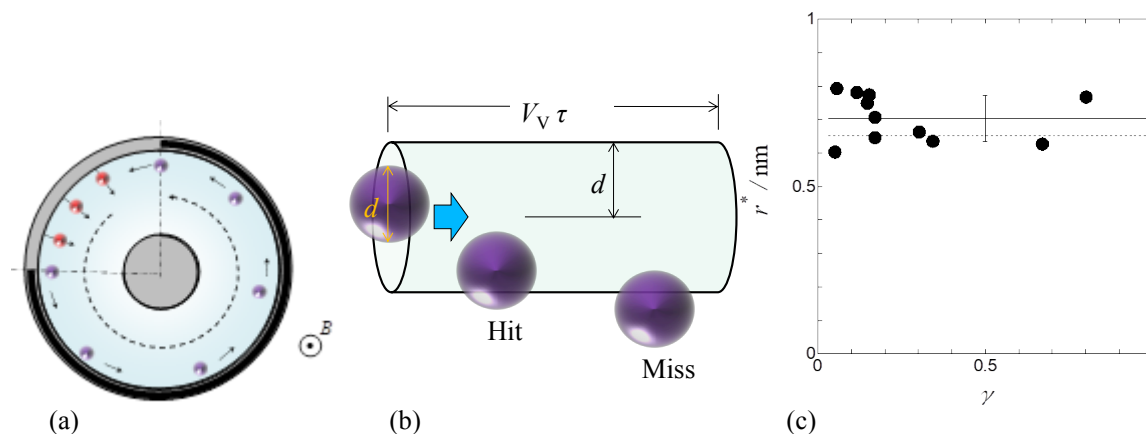

Fig. 6: Collision process of vacancy gas. (a) Collision tube swept out by a returning vacancy. V_V, mean speed; τ, lifetime; d, collision diameter. (b) Collision of ionic vacancies at the critical state in CMHDE. B, applied magnetic field. (c) Plot of the collision radius r^* vs. collision efficiency γ for the ionic vacancy created in copper deposition. Solid line is the average value, and dotted line is the

References

1.   A. Sugiyama, *et al., Electrochemistry* **81** (2013), 890-892.
2.   M. Miura, *et al., Electrochemistry* **82** (2014), 654-657.
3.   Y. Oshikiri, *et al., Electrochemistry* **83** (2015), 549-553.
4.   R. Aogaki *et al, Sci. Rep.*, **6** (2016), 28927.
5.   I. Mogi *et al, Sci. Rep.*, **3**, (2013), 2574.
6.   A. Sugiyama *et al, Sci. Rep.*, **6** (2016), 19795.
7.   M. Miura *et al, Sci. Rep.*, **7** (2017), 45511.