CHIRAL CATALYTIC ACTIVITIES IN MAGNETOELECTROCHEMICAL ETCHING

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Abstract: Chiral catalytic activities of electrode surfaces fabricated by magneto-electrochemical etching have been theoretically examined for the two cases of macroscopic rotation; in the first case, a tornado-like stream called vertical magnetohydrodynamic (MHD) flow rotates the solution over the electrode, and in the second case, the whole electrode system uniformly rotates. As a result, the following three points were clarified; 1) In the absence of oxide layer such as passive film, the activities arise from screw dislocations of 2D pits. 2) For the vertical MHD flow, under upward and downward magnetic fields, D- and L-activities appear, respectively. 3) For the system rotation, only L-activity is obtained.

1. Introduction

The chemical reactivity of catalyst for some fundamental aspects such as stereoselectivity and chirality are issues of paramount importance. Chirality is a fundamental concept in chemistry and life science, and chiral catalysts play the most important scientific and technological roles in modern industry with intense economic impact. In this sense, how to fabricate chiral catalysts is still an open question with important fundamental and technical interest.

Mogi has first found the appearance of the enantiomorphic activities of electrodes deposited in vertical magnetic fields [1,2]. Then, the following studies clarified that the chiral activities are attributed to numerous chiral screw dislocations on 2D and 3D nuclei, which are created with minute vortexes called micro- and nano-MHD flows arising from magnetic field and macroscopic rotation [3,4]. The most important theoretical result concerning the catalytic activity for enantiomorphic reagents was that the chiral symmetry is broken to L-activity side. The fabrication process of this type catalyst under magnetic field and rotation is universal. In view of the fact that stars and nebulae are also evolved under magnetic field and rotation, whether such type catalysts had contributed to the molecular evolution of amino acids in the cosmic space would be a quite interesting problem for the origin of homochirality.

Furthermore, is anodic etching also possible to bestow the same kind of catalytic activity to electrode surfaces? According to this question, in the present paper, with regard to anodic etching, two cases of macroscopic rotation under a magnetic field are theoretically examined; the first case is that a tornado-like stream called vertical MHD flow rotates over the electrode surface, and the second case is that the whole electrode system uniformly rotates.

2. Theory

2.1 Electrochemical instabilities of 3D and 2D pits

In anodic etching, two types of pit are possible to grow; one is 3D pit with an about 1 μm diameter, forming a deep hole. The other is 2D pit with an about 100 μm diameter, forming a shallow hole. Due to a localized large amount of metallic ions dissolved, the growth of 3D pit is controlled by nonequilibrium fluctuation of concentration overpotential. Since a positive overpotential is applied to a metal surface, for the pit to unstably develop with time, the overpotential fluctuation is required negative. However, metallic dissolution always provides a positive overpotential fluctuation, so that 3D pits are stable and cannot grow [5].

On the other hand, 2D pit formation is also under a control of concentration overpotential, i. e., a negative fluctuation of it is inevitable for unstable growth. In this case, since 2D pits arise from electric double layer, the overpotential fluctuations of the electric double layer are newly joined, making the pitting process unstable under the following condition,

$$\left(\partial\langle\Phi_1\rangle/\partial\langle\Phi\rangle\right)_{\mu} \langle\Phi_2\rangle > 0 \tag{1}$$

where, $\langle\Phi_1\rangle$ and $\langle\Phi_2\rangle$ are the average potential fluctuations of the Helmholtz and diffuse layers, respectively, and $\left(\partial\langle\Phi_1\rangle/\partial\langle\Phi\rangle\right)_{\mu}$ is the differential potential coefficient, and the subscript μ implies that all other quantities are kept constant. From these discussions, it is concluded that in anodic dissolution without passive films, only 2D pit can develop with time. In Fig. 1a and 1b, Eq. (1) is represented by the potential distributions in the electric doublw layer, which correspond to the cases of the absence and presence of specific adsorption of anion. On the contrary to cathodic deposition [6], anodic etching can always develop in the form of 2D pits. In addition, it shoud be noted that because of the disturbance of concentration overpotential, fluid motion makes the pit formation less active.

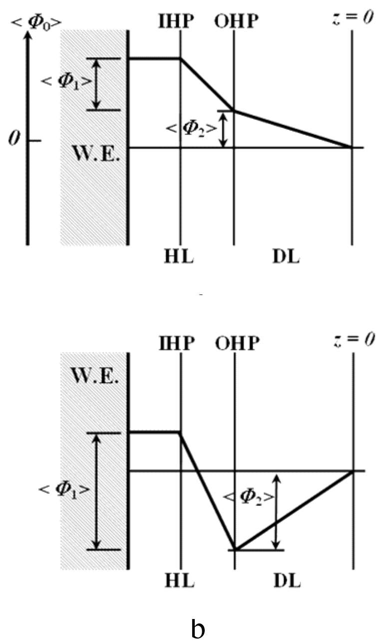


Figure 1: Potential distributions in electric double layers in unstable 2D pitting. a, without specific adsorption; b, with specific anionic adsorption.

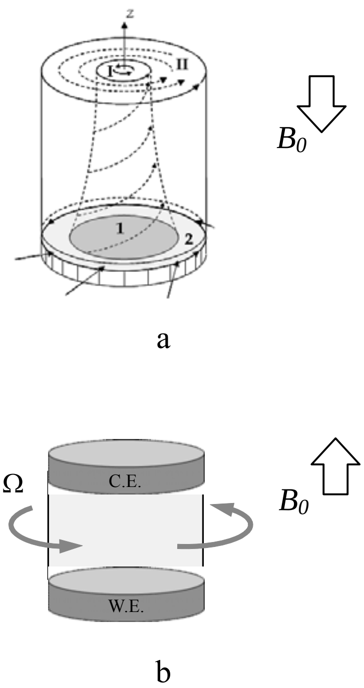


Figure 2: Macroscopic rotations. a, vertical MHD flow; b, system rotation. B_0, the magnetic flux density; Ω, the angular velocity.

2.2 Chiral activity induced by vertical MHD flow

2D pits unstably growing on an electrode surface acquire chirality from microscopic vortexes called micro-MHD flows under magnetic field and macroscopic rotation. Two types of macroscopic rotations in magnetic field are represented in Fig. 2, i.e., a tornado-like rotation over an electrode surface called vertical MHD flow and an electrode system rotation.

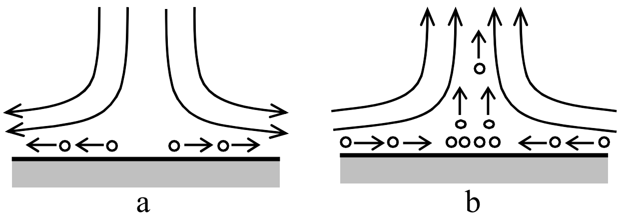


Figure 3: Rigid and free surface formations. a, rigid surface; b, free surface; ○, vacancy.

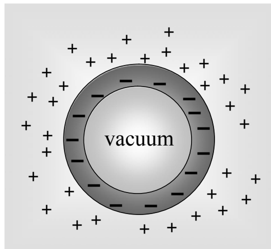


Figure 4 : Ionic vacancy.

In accordance with ionic vacancies gathered and spread out, as shown in Fig. 3, upward and downward micro-MHD flows yield free surface without friction and rigid surface with friction, respectively. Here, ionic vacancy created during electrode reaction works as an atomic-scale lubricant, which is shown in Fig. 4, i. e., a free vacuum space with an about 0.1 nm diameter surrounded by ionic cloud [7]. On the rigid surface, due to friction, micro-MHD flow disappears, and the solution is kept stationary, whereas it can rotate on the free surface without friction. As elucidated above, the stationary solution on the rigid surface assists the unstable growth of 2D pit, whereas the solution flow on the free surface rather suppresses it, so that as indicated in Fig. 5, the current lines are distorted inside and outside on the rigid and free surfaces, respectively. In an upward vertical magnetic field, Lorentz force thus induces clockwise (CW) and anticlockwise (ACW) rotations on the rigid and free surfaces, respectively. Here, on the rigid surfaces with friction, the solution is kept stationary, the vortex rotation is not transcribed to a pit surface. Only on the free surfaces without friction, such a transcription is possible, i. e., under an upward magnetic field, micro-MHD flows with ACW rotation contribute the fabrication of chiral screw dislocations.

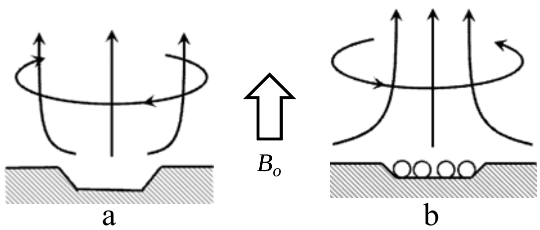


Figure 5: Current lines and activated rotations. a, rigid surface; b, free surface; ○, vacancy.

2.2.1. Positive reinforcement by Coriolis force

In the absence of energy supply, micro-MHD flows once activated by magnetic field dwindle with time. Coriolis force by the vertical MHD flow makes special contribution to sustain them. In Fig. 6, the positive reinforcement by the Coriolis force is exhibited; on the electrode surface, two layers are formed. The micro-MHD flows mentioned above are activated in the lower layer by the magnetic field, whereas the Coriolis force yields other vortexes in the

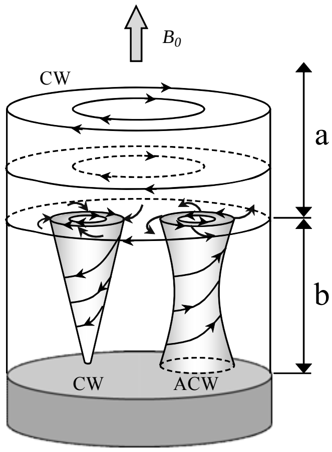


Figure 6: Reinforcement process by the vertical MHD flow. a, rotating layer; b, stationary layer.

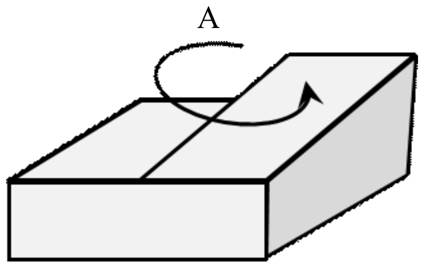


Figure 7: Formation of a screw dislocation. A, the rotational direction of micro-MHD flow.

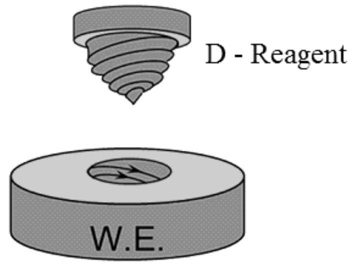


Figure 8: Mirror-image relationship between reagent and dislocation.

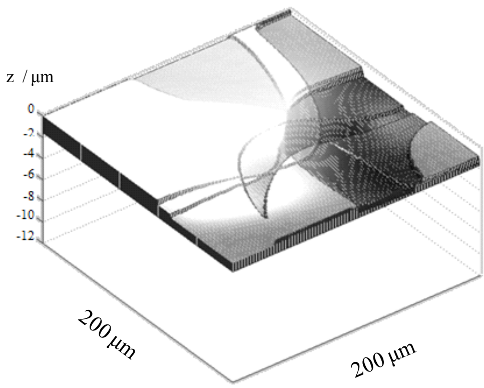


Figure 9: ACW screw dislocations calculated after 10 times pitting.

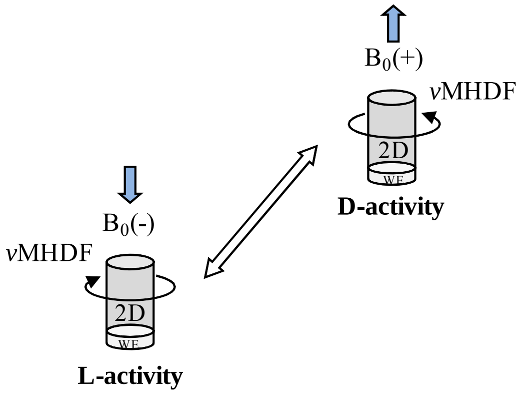


Figure 10: Chiral activity by vertical MHD flow.

upper layer rotating with the vertical MHD flow. As a result, through the vortexes in the rotating upper layer, the kinetic energy of the vertical MHD flow is supplied to the vortexes in the lower layer.

2.2.2. Enantiomorphic activity of screw dislocation

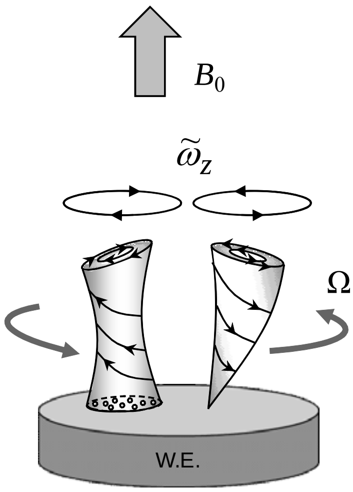
Figure 7 illustrates a screw dislocation formed by a micro-MHF flow. Since dissolution takes place in the same direction as that of the vortex flow, ACW screw dislocation is created from ACW micro-MHD flow. Because enantiomorphic catalysis has a mirror-image relationship with reagent, as shown in Fig. 8, the ACW screw dislocation is active for a D-type (CW) reagent, i. e., having D-activity. Figure 9 shows ACW pits formed on a free surface, which is theoretically calculated after 10 times repeated pitting. The catalytic activities in all cases of magnetic field directions are put in order in Fig. 10, i. e., in an upward magnetic field, D-activity emerges, whereas in a downward magnetic field, L-activity arises.

2.3. Chiral activity induced by system rotation

When an electrode system rotates under a vertical magnetic field, as shown in Fig. 11, Coriolis force is directly imposed to the micro-MHD flows activated by magnetic field, inducing precession of the vortexes. As a result, a cooperative effect arises between Lorentz force and Coriolis force, so that the product of the magnetic flux density and the angular velocity of the system rotation $B_0\Omega$ determines the chirality of the micro-MHD flows. The theoretical calculation indicates that only the case of positive $B_0\Omega$ is allowed for vortexes on free surfaces, and that the following physical parameter called Coriolis vorticity determines the rotational direction of the vortexes.

$$\tilde{\omega}_z = -AB_0\Omega\,\tilde{j}_z \tag{2}$$

where A is a positive constant, and $\tilde{j}_z$ is the extended current density, which is positive in case of anodic etching. Therefore, for a positive $B_0\Omega$, the Coriolis vorticity $\tilde{\omega}_z$ becomes negative, i. e., CW rotation emerges. In accordance with the case of vertical MHD flow, this implies L-activity for enantiomorphic reagents. For a negative $B_0\Omega$, rotational motion on a free surface is not permitted, so that as shown in Fig. 12, chiral activity is not obtained.



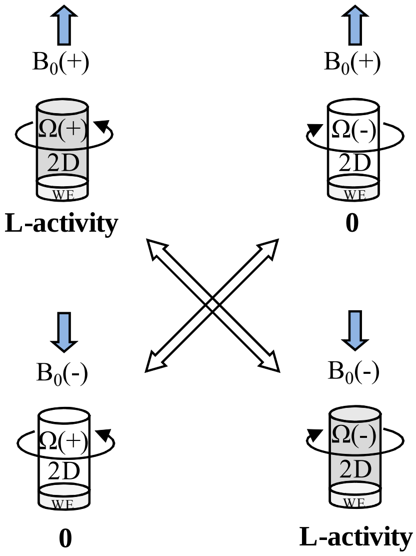


Figure 11: Precession of micro-MHD flow. Figure 12: Chiral activity by system rotation.

3. Conclusion

The following three points were concluded; in the absence of passive film, chiral activity arises from screw dislocation of 2D pit. For vertical MHD flow, under upward and downward magnetic fields, D- and L-activities appear, respectively. On the other hand, for system rotation, only L-activity arises. Namely, in anodic etching also, chiral symmetry is broken to L-activity side.

4. References

[1] Mogi, I.; Watanabe, K.: Chiral electrode behavior of magneto-electrodeposited silver films. ISIJ Int. 47 (2007) 585-587.

[2] Mogi, I.; Morimoto, R.; Aogaki, R.; Watanabe, K.: Surface chirality induced by rotational electrodeposition in magnetic fields. Scientific Reports. 3 (2013) 2574.

[3] Aogaki, R.: Micro-MHD effect on electrodeposition in the vertical magnetic field. Magnetohydrodynamics. 39 (2003) 453-460.

[4] Aogaki, R.; Morimoto, R.: Nonequilibrium fluctuations in micro-MHD effects on electrodeposition. Heat and Mass Transfer: Modeling and Simulation (ed. Hossain, M. : InTech, Croatia) (2011) 189-216.

[5] Aogaki, R.: Instability of Nonequilibrium Fluctuation on Pitting Dissolution (I). J. Electrochem. Soc. 142 (1995) 2954-2966.

[6] Aogaki, R.: Instability of Nonequilibrium Fluctuation in Electrochemical Nucleation I. Occurrence of Instability. J. Chem. Phys. 103 (1995) 8602-8615.

[7] Aogaki, R.: Theory of Stable Formation of Ionic Vacancy in a Liquid Solution. Electrochemistry. 76 (2008) 458-465.