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CHIRAL CATALYTIC ACTIVITIES IN MAGNETOELECTROCHEMICAL ETCHING

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Chiral catalytic activities of electrode surfaces fabricated by magnetoelectrochemical etching without oxygen adsorption in a vertical magnetohydrodynamic (MHD) flow have been theoretically examined. Then, the following points were clarified: under anionic specific adsorption, such activities arise from the screw dislocations of 2D pits. Their chirality is donated by microscopic vortexes termed micro-MHD flows, which are formed on the free surfaces covered with ionic vacancies. As a result, under upward (+) and downward (−) magnetic fields, D (dextrorotatory)- and L (levorotatory)-activities appear, respectively.

Introduction. The chemical reactivity of catalysts for some fundamental aspects, such as stereoselectivity and chirality, is the issue 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 enantiomeric activities of electrodes cathodically 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 termed micro- and nano-MHD flows arising from the magnetic field and macroscopic rotation [3, 4]. The most important theoretical result concerning the catalytic activity for enantiomeric reagents is that the chiral symmetry tends to be broken to L-active side.

The fabrication process of this type catalyst under the magnetic field and rotation is universal. In view of the fact that stars and nebulae are also evolved under the magnetic field and rotation, whether such type catalysts had contributed to the molecular evolution of amino acids in the cosmic space, would be quite an interesting problem for the origin of homochirality. Furthermore, another question arises: Is anodic etching also possible to bestow the same kind of catalytic activity

to electrode surfaces? Led by this question, Mogi has recently found the enantiomeric activity of a copper electrode anodically etched in a vertical magnetic field [5].

In a vertical magnetic field, it is supposed that micro-MHD flows under a tornado-like stream termed vertical MHD flow emerge over the electrode surface, yielding 2D pits with special chirality. In addition, though copper anodic etching is often accompanied by oxygen adsorption, for simplicity, in the absence of an oxygen-adsorbed film, the formation process of chiral catalytic activity by a vertical MHD flow is theoretically examined.

1. Theory.

1.1. Electrochemical instabilities of 3D and 2D pits. In anodic etching, two types of pits are possible to grow [6]; one is the 3D pit with a diameter of the order of 1 μm, forming a narrow deep hole. The other is the 2D pit with a diameter of the order of 100 μm, forming a shallow hole. Due to a large amount of metallic ions dissolved, the growth of the 3D pit is controlled by the concentration overpotential in the diffusion layer. Since metal dissolution yields the positive nonequilibrium concentration fluctuation of metallic ions, to decrease the reaction resistance for unstable growth, the concentration fluctuation at the pit bottom must take negative values. However, the positive concentration fluctuation is actually provided, so that 3D pits are always stable and randomly grow without special chirality [6].

On the other hand, since 2D pits arise from the electric double layer, the electrostatic potential fluctuations in the electric double layer are newly joined, making the pitting process unstable under the following conditions [6]:

$$-\left(\partial\Phi_1^*/\partial\Phi_2^*\right)_\mu \Phi_2^* < 0, \tag{1}$$

where the sign '–' implies specific (chemical) adsorption of anion, and Φ_1^* and Φ_2^* are the electrostatic overpotentials of the Helmholtz and diffuse layers, respectively. In the anodic reaction, Φ_1^* is required positive. Then, $\left(\partial\Phi_1^*/\partial\Phi_2^*\right)_\mu$ is the differential potential coefficient and the subscript implies that all other quantities are kept constant. In specific adsorption, the coefficient $\left(\partial\Phi_1^*/\partial\Phi_2^*\right)_\mu$ becomes negative, so that Φ_2^* takes a negative value. Fig. 1 represents the potential distributions in the electric double layer in the absence and presence of specific adsorption of anion. In the case of anionic specific adsorption, it is validated that the above unstable conditions are fulfilled. In a vertical magnetic field, only under unstable

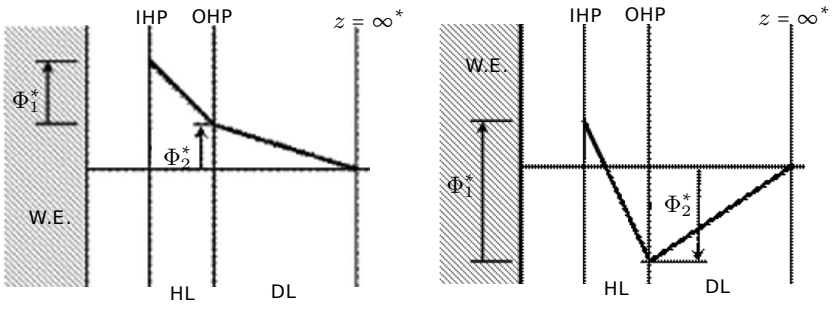


Fig. 1. Potential distributions in electric double layers in 2D pitting. (*a*) The stable case of normal anionic adsorption. (*b*) The unstable case of specific anionic adsorption. W.E. – working electrode, HL – Helmholtz layer, DL – diffuse layer, Φ_1^* – electrostatic overpotential of HL, Φ_2^* – electrostatic overpotential of DL, IHP – inner Helmholtz plane, OHP – outer Helmholtz plane, $z = \infty^*$ – outer boundary of DL.

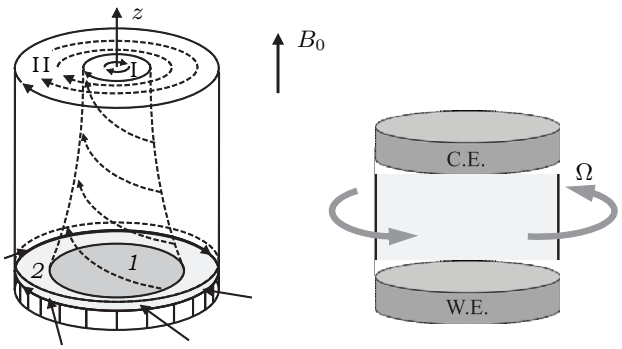


Fig. 2. Macroscopic rotations. (*a*) Vertical MHD flow. (*b*) System rotation. *1* – working electrode, *2* – outer fringe, B_0 – upward (+) magnetic flux density, Ω – angular velocity.

conditions shown in Eq. (1), chiral 2D pits can deterministically grow with time, forming chiral screw dislocations, whereas when the conditions are not satisfied, stochastically random pitting takes place without chirality. Namely, chiral anodic etching under a vertical magnetic field proceeds in the form of 2D pits with the help of specific adsorption of anion. In addition, it should be noted that because of the disturbance of the concentration fluctuation, the fluid motion makes the pit formation less active, which is termed the '1st micro-MHD effect' in magnetoelectrodeposition [7].

1.2. Chiral micro-MHD flows in a vertical MHD flow. 2D pits unstably growing on the electrode surface acquire chirality from microscopic vortexes termed micro-MHD flows under a magnetic field and a macroscopic rotation. Two types of macroscopic rotations in magnetic fields are represented in Fig. 2, i.e. vertical MHD flow and electrode system rotation [4]. In the present paper, as mentioned initially, the case of vertical MHD flow is discussed.

Generally, vortexes are classified in two independent groups, which form, as a whole, a mathematically orthogonal normal pack, i.e. one is formed on rigid surfaces with friction, and the other is on free surfaces without friction. On a solid electrode surface, the free surface requires something like a lubricant. Recently, it has been found that in electrode reactions, ionic vacancies are created [8–10]. Fig. 3 displays a schematic of ionic vacancy, which is a charged free vacuum space of the order of 0.1 nm surrounded by an ionic cloud [8]. Owing to the formation without entropy release to surroundings, ionic vacancies obtain extreme fluidity [11].

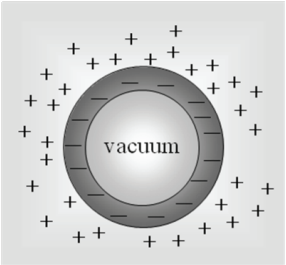
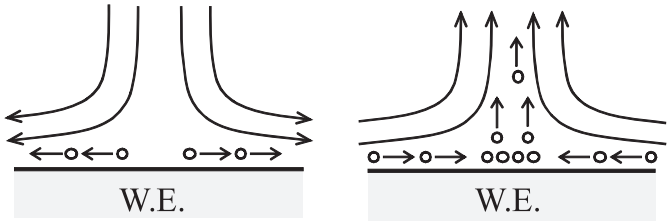
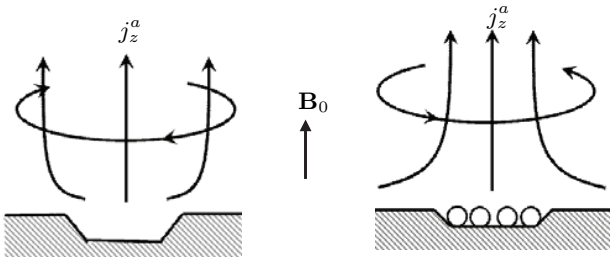


Fig. 3. Ionic vacancy.



(a) (b)

Fig. 4. Rigid and free surface formations by ionic vacancies under downward and upward flows. (*a*) Rigid surface. (*b*) Free surface. ∘ – vacancy.



(a) (b)

Fig. 5. Current lines and activated rotations under an upward magnetic field (+). (*a*) CW rotation on a rigid surface. (*b*) ACW rotation on a free surface. j_z^a – current density fluctuation, ∘ – vacancy, B_0 – magnetic field.

In accordance with ionic vacancies gathered and spread out, as shown in Fig. 4, downward and upward micro-MHD flows locally yield rigid and free surfaces, respectively. On the rigid and free surfaces, the solution stops and continues flowing, respectively. As elucidated above, stationary solutions enhance the pit growth, whereas the fluid motion disturbs the concentration fluctuation, suppressing it, so that, as indicated in Fig. 5, electrolytic current lines are distorted inside and outside on the rigid and free surfaces, respectively. In an upward vertical magnetic field (+), where magnetic fields parallel and antiparallel to current density are defined as '+' and '–', the Lorentz force thus induces clockwise (CW) and anticlockwise (ACW) rotations on the rigid and free surfaces, respectively. Then, the chiral rotations produce mass-flux fluctuations of metallic ion donating chirality to the 2D pits. The power spectra of the mass-flux fluctuations on the free and rigid surfaces are illustrated in Fig. 6. As shown in this figure, the free-surface component is larger than the rigid-surface component, so that it is expected that the

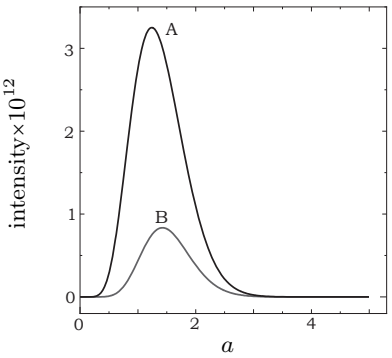


Fig. 6. Power spectra of mass-flux fluctuations on the free and rigid surfaces at +8 T. A – free surface component; B – rigid surface component.*a* – dimensionless wave number.

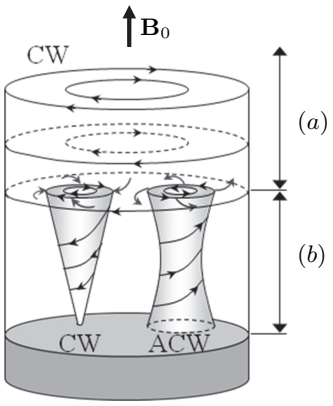


Fig. 7. Reinforcement process by a CW vertical MHD flow. (a) Rotating layer with the vertical MHD flow. (b) Stationary layer. B_0 – upward (+) magnetic flux density, CW – clockwise rotation, ACW – anticlockwise rotation.

chiral screw dislocations on the free surfaces overcome those on the rigid surfaces, determining the enantiomeric activity of the electrode.

1.3. Positive reinforcement by the Coriolis force. In the absence of energy supply, micro-MHD flows once activated by the magnetic field dwindle with time. The Coriolis force by the vertical MHD flow makes a special contribution to sustain them. In Fig. 7, the positive reinforcement by the Coriolis force is exhibited: under an upward magnetic field (+), on the electrode surface, two vortex layers are formed. The micro-MHD flows mentioned above, i.e. the CW and ACW vortexes on the rigid and free surfaces are activated in the lower stationary layer, whereas in the upper layer rotating in the same CW direction as the vertical MHD flow, in accordance with the meteorological theorem concerning cyclone and anticyclone, the Coriolis force donates CW and ACW precessions to the CW vortex on the rigid surface and the ACW vortex on the free surface in the lower layer, respectively. As a result, through the upper layer rotation, the kinetic energy of the vertical MHD flow is supplied to the vortexes in the lower layer. Such a positive feedback cycle assures steady-state rotations of the micro-MHD flows in the lower layer.

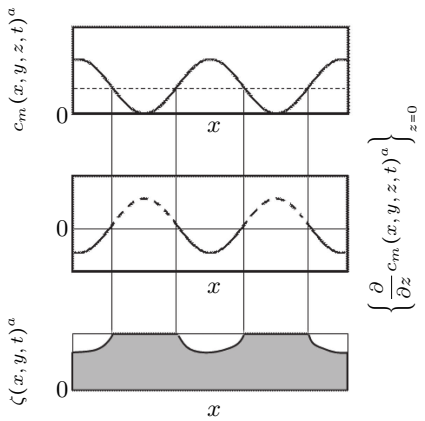
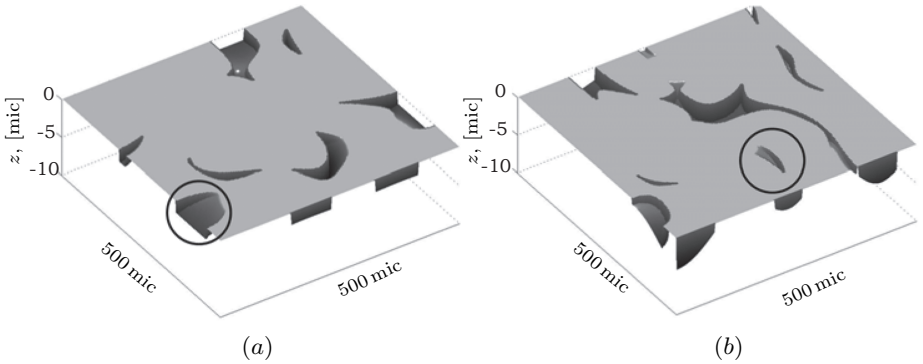


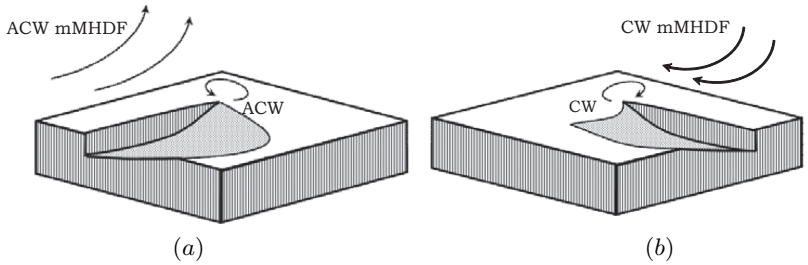
Fig. 8. Formation of a vertical section in pitting dissolution. $c_m(x,y,z,t)^a$ – concentration fluctuation, $\{\partial c_m(x,y,z,t)^a/\partial z\}_{z=0}$ – concentration gradient fluctuation, $\zeta(x,y,t)^a$ – surface height fluctuation.



(*a*) (*b*)

Fig. 9. 2D pits formed on the free surfaces under an upward magnetic field of +8 T. (*a*) Theoretical calculation. (*b*) ACW screw dislocation etched under ACW micro-MHD flow (mMHDF) indicated in a circle in (*a*).

1.4. Enantiomorphic activity of screw dislocation. An atomic-scale vertical section and spiral slope winding up characterize a screw dislocation. With regard to the vertical section, the discontinuous phase boundary of the concentration gradient fluctuation plays an important role; as shown in Fig. 8, in case of dissolution, only a negative gradient component is allowed, so that at the boundary between positive and negative gradients, in atomic scale, discontinuous vertical sections are apt to be produced. As to the spiral slope formed by micro-MHD flow, since on the upper side of the solution flow dissolution more actively occurs, an uphill slope along the flow is formed. This implies that under the ACW and CW vortexes, ACW and CW screw dislocations are created, respectively. Fig. 9*a* represents 2D pits theoretically calculated for the free surfaces under an upward magnetic field of +8 T. As indicated in the circle, an ACW screw-dislocation-like pit appears, as schematically illustrated in Fig. 9*b*. On the other hand, in Figs. 10a,b, the 2D pitting and CW screw dislocation-like pit simultaneously formed on the rigid surfaces under the same magnetic field are shown. Fig. 11 shows both pits on the rigid and free surfaces, which share their locations without contradiction, forming an orthogonal normal pack. As discussed above, the chiral pit formation on each type of surface depends on the probability determined by the power spectrum of the concentration-gradient fluctuation, so that in accordance with the power spectra in Fig. 6, it is concluded that the ACW screw dislocation on the free surfaces is predominant over the electrode surface. In view of the mirror-image relationship between chiral dislocation and enantiomeric reagent, this means that D-catalytic activity is obtained in an upward magnetic field (+), whereas in a downward



(*a*) (*b*)

Fig. 10. 2D pits formed on the rigid surfaces under an upward magnetic field of +8 T. (*a*) Theoretical calculation. (*b*) CW screw dislocation etched under CW micro-MHD flow (mMHDF) indicated in a circle in (*a*).

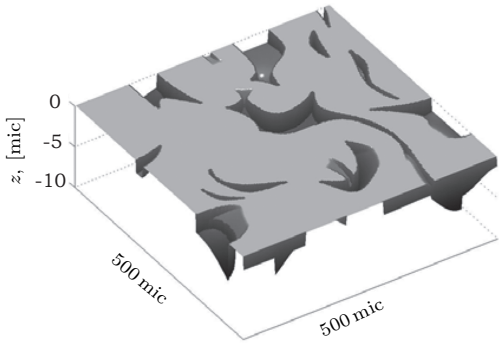


Fig. 11. Complete 2D pitting surface combining the free surface in Fig. 9*a* with the rigid surfaces in Fig. 10*b*.

magnetic field (–), L-activity is predicted. The ratio between the rigid and free surface components of the chiral dislocations at +8 T is obtained from the spectra in Fig. 6, which is equalized to the ratio between the enantiomeric currents for the L- and D-reagents, so that the enantiomeric excess (*ee*) ratio defined by Mogi [5] can be theoretically estimated, i.e. in the present case, $ee = -0.15$, where the sign '–' implies that D-activity is predominant.

In the present paper, though the role of the oxygen-adsorbed film is not discussed, it has been theoretically clarified that the blocking effect of the film on electrode reactions induces the spatial phase inversion of the concentration fluctuation [12]. Accordingly, it can be predicted that etching at high overpotential or current density will give rise to the inversion of enantiomeric activity.

2. Conclusion. Using magnetoelectrochemical etching on a stationary copper electrode, we can obtain chiral catalytic activity of the electrode; under upward (+) and downward (–) magnetic fields, in the absence of oxygen adsorption, D- and L-activities appear, respectively, which agrees with Mogi's experimental result. Such activities arise from screw dislocations of 2D pits formed under anionic specific adsorption, of which chirality is donated by the micro-MHD flows on the free surfaces covered with ionic vacancies. In the presence of oxygen adsorption at high overpotential or current density, on the contrary, inversion of chiral activity can be predicted.

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