Chiral surface formation by magnetoelectrolysis

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1. Introduction

Chiral surfaces of catalysts are responsible for asymmetric synthesis of organic materials. Particular concern is that surfaces of minerals could play chiral catalytic roles for prebiotic synthesis of amino acids in molecular evolution. A study of chiral surface formation is thus of great significance from wide viewpoints of chiral catalysts, pharmaceutical industry and the origin of life on the early earth.

When a magnetic field is imposed to an electrochemical cell, the Lorentz force acting on the faradaic currents causes convections around the electrodes in the electrolytic solutions. This is well known as the MHD (magnetohydrodynamic) effect. There exists two kinds of MHD flow in the magnetic fields perpendicular to the electrode surface; micro-MHD vortices on a fluctuated surface of the electrodeposits and a macroscopic flow around the electrode edge (the vertical MHD flow). The micro-MHD vortices could produce chiral defects such as screw dislocations on the electrodeposit surfaces, and the vertical MHD flow breaks the symmetry in the micro-MHD vortices, leading to the induction of surface chirality. Our previous papers[1,2] reported that the magnetoelectrodeposition (MED) induces surface chirality of Ag and Cu films. Here we show two new methods for the chiral surface formation; magnetoelectrochemical etching (MEE) and rotational MED.

2. Magnetoelectrochemical etching

The symmetry breaking mechanism in the coupling of micro-MHD and vertical MHD flows would be applicable to magnetoelectrochemical etching, thus we have tried to explore chiral surface formation in MEE processes. The MEE experiment was a galvanostatic dissolution of a copper film in a 50 mM $CuSO_4$ + 0.5 M H_2SO_4 aqueous solution under a magnetic field of 5 T perpendicular to the film surfaces. The MEE copper films were used as an electrode, and the chirality of such electrodes was examined by voltammetric measurements of enantiomers of alanine (an amino acid). The MEE film electrodes exhibited the difference in oxidation currents between the enantiomers, and such a chiral behavior depended on the magnetic field direction and the etching current. The former result shows that the MEE process could induce chirality on the etching film surfaces, and the latter suggests that the chirality induction is responsible for the combination of the micro-MHD vortices and the vertical MHD flows, as proposed in the MED processes.

3. Rotational magnetoelectrodeposition

Another method for the symmetry breaking in the micro-MHD vortices is Rotational MED,[3] in which the electrochemical cell was rotated in a magnetic field of 5 T during the electrodeposition with a frequency of 2 Hz in a clockwise or anticlockwise direction. The MED copper film electrodes exhibited chiral behavior for the electrochemical reaction of alanine enantiomers, and the direction of rotation allowed control of the chiral sign.[4] This chiral induction arises from the asymmetric influence of the system rotation on the cyclonic and anticyclonic micro-MHD vortices around the electrode surfaces.

References

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