CHIRAL SURFACE FORMATION BY MAGNETOELECTROCHEMICAL ETCHING

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Abstract: Chiral surface formation was found in magnetoelectrochemical etching (MEE) as well as magnetoelectrodeposition. The MEE of copper films was conducted in galvanostatic conditions with various etching currents under a magnetic field of 5 T perpendicular to the electrode surfaces. The MEE film electrodes exhibited current difference in voltammograms between alanine enantiomers, and such chiral behavior depended on the etching current and the polarity of the magnetic field at the MEE processes.

1. Introduction

Chirality induction is one of the most attractive functionality in magnetoelectrolysis (electrolysis under magnetic fields). Chiral surfaces of metals and minerals have potentials as chiral catalysts, which could play wide roles in organic syntheses, pharmaceutical industry and molecular evolution of biochemical systems. Thus, studies on chiral surface formation are of great significance, and magnetoelectrolysis can be expected to contribute to the development of novel technique for the preparation of chiral surfaces.

We have reported that magnetoelectrodeposition (MED) is able to produce chiral surfaces of metal films of silver and copper [1-5]. This surface chirality could be induced by the MHD and micro-MHD vortices arising from the Lorentz force acting on faradaic currents [6,7]. The MED films showed chiral recognition for the enantiomers of several amino acids, glucose and tartaric acid [1-3,8].

The micro-MHD effect was also observed in magnetoelectrochemical etching (MEE) [9] as well as in MED. Figure 1 shows a schematic of the micro-MHD and vertical MHD vortices excited in the MEE processes under magnetic fields perpendicular to electrode

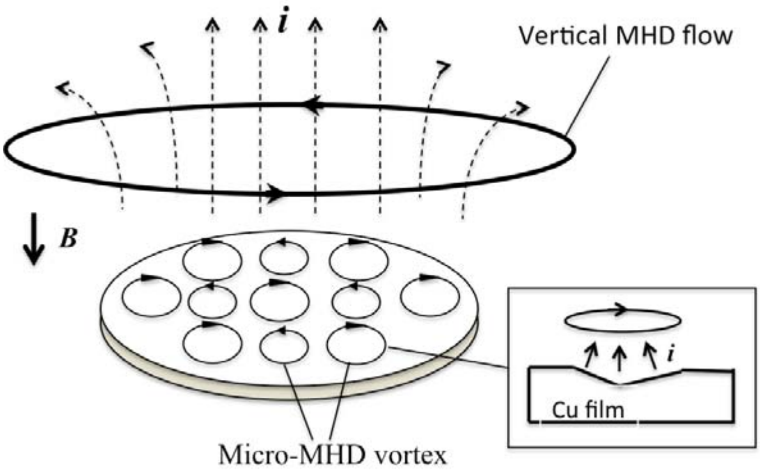

Figure 1: Schematic of the MHD effects in magnetoelectrochemical etching. The magnetic field ***B*** is imposed antiparallel to the faradaic current ***i*** and perpendicularly to the electrode surface.

surfaces. Electrochemical etching is a non-equilibrium process, and non-equilibrium fluctuation produces a number of pits on the etching surfaces. The micro-MHD vortices emerge around such pits (see an inset in Figure 1), and then they form self-organized states on the film surface. The vertical MHD flow is excited around the electrode edge and make interference on the micro-MHD vortices. Thus MEE processes are expected to produce chiral surfaces. In this paper, we report the experiments of MEE of Cu films with galvanostatic conditions and the dependence of chirality of the MEE films on the etching currents and the polarity of magnetic field.

2. Experimental of magnetoelectrochemical etching

In the electrochemical experiments, a conventional three-electrode system was employed: a polycrystalline Pt disc working electrode with a diameter of 1.6 mm, a Cu plate counter electrode, and a Ag | AgCl | 3 M (M = mol dm^{-3}) NaCl reference electrode. Before the etching processes, Cu films with a thickness of approximately 300 nm were prepared by electrodeposition on the working electrode in the absence of magnetic field. The etching of the Cu films was conducted in galvanostatic conditions with various constant currents of 15 – 30 mA cm^{-2} in a 50 mM $CuSO_4$ + 0.5 M H_2SO_4 aqueous solution until the film thickness decreased to approximately 150 nm. The passing charges were 0.8 C cm^{-2} at the electrodeposition and 0.4 C cm^{-2} at the etching. In the MEE process, the electrochemical cell was placed at the bore center in a cryocooled superconducting magnet, and a magnetic field of 5 T was imposed perpendicularly to the electrode surface. Here, the MEE films prepared in the magnetic field parallel and antiparallel to the faradaic currents are called +5T-film and –5T-film, respectively.

The MEE Cu films were used as electrodes after the pretreatment of surface oxidization from Cu to CuO, as described in our previous paper [3]. The chiral behaviors of the MEE film electrodes were examined using the voltammetric measurements of the enantiomers of alanine (an amino acid). The voltammograms were measured in a 20 mM alanine + 0.1 M NaOH aqueous solution with a potential sweep rate of 10 mV s^{-1}.

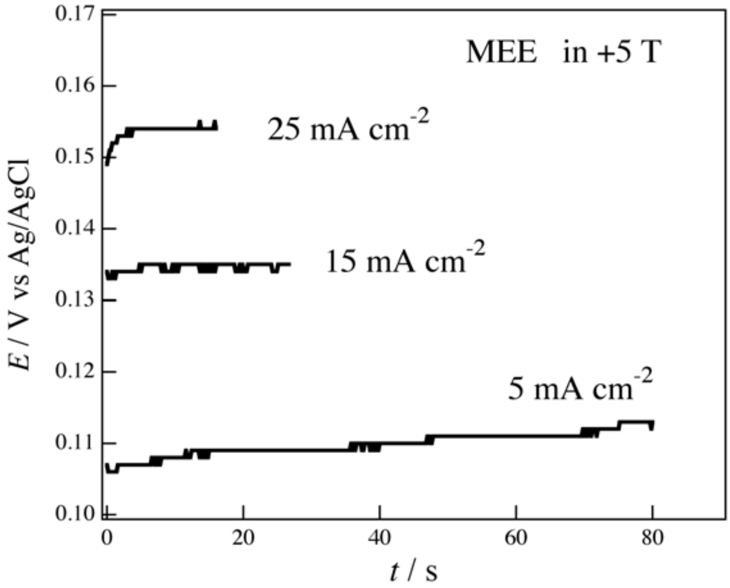

Figure 2: Electrode potential vs time during the MEE processes in +5 T at the etching current of 5, 15 and 25 mA cm^{-2}. The passing charge was 0.4 C cm^{-2}.

3. Results and discussion

Figure 2 shows the time dependence of working electrode potential during the MEE process in +5 T at the etching currents of 5, 15 and 25 mA cm^{-2}. The electrode potentials rise by ~ 5 mV for initial several seconds and then reach constant values at any etching currents. In such steady states, the micro-MHD vortices and the vertical MHD flow could form a self-organized state [7,10]. The steady potential increased almost linearly with increasing etching current in the region of 5 to 30 mA cm^{-2}.

Figure 3 shows voltammograms of L- and D-alanines on the (a) 0T-film, (b) –5T-film and (c) +5T-film electrodes, where all the MEE films were prepared at an etching current of 20 mA cm^{-2}. Alanine molecules are oxidized on the Cu electrodes around 0.7 V [11], where the voltammogram has a current peak. The voltammograms of the alanine enantiomers are coincident each other on the 0T-film electrode, meaning achirality of the film surface. On the other hand, the –5T-film electrode exhibits L-active chirality for the enantiomers; namely, the peak current of L-alanine is greater than that of D-alanine. This fact demonstrates that the MEE process induces the surface chirality on the Cu films.

The chiral sign of the MEE films should depend on the polarity of magnetic field at the MEE process. The reversal of the magnetic field direction is expected to lead to the mirror-image chirality of the MEE films. However, Figure 3(c) shows that the +5T-film electrode exhibit achirality, even though the –5T-film electrode exhibits L-active chirality. On the contrary, when the etching current was 25 mA cm^{-2}, the +5T-film electrode exhibited D-active chirality, and the –5T-film electrode exhibited achirality.

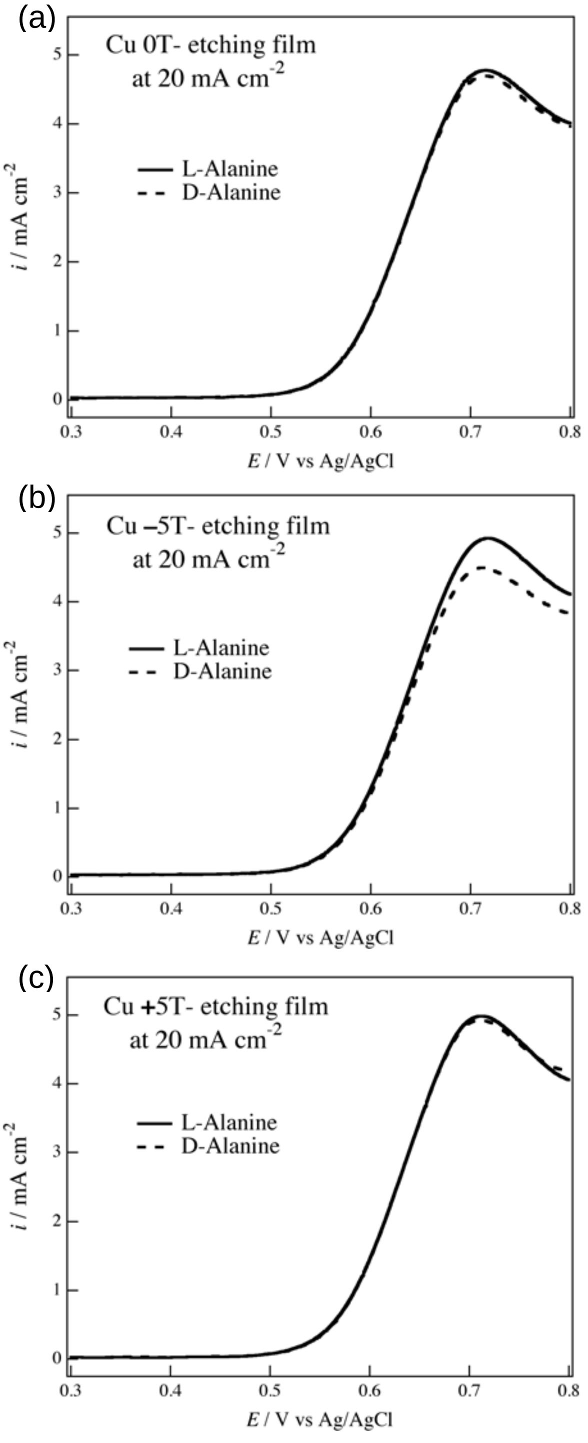

Figure 3: Voltammograms of L- and D-alanines on (a) the 0T-film electrode, (b) the MEE –5T-film and (c) the +5T-film electrodes, where the films were prepared at the etching current of 20 mA cm^{-2}.

In the case of magnetoelectrodeposition (MED) of Ag and Cu films, the reversal of the magnetic field direction induces the mirror-image chirality of the MED films [1-4]. For example, Cu MED +5T-films exhibit L-active chirality, and the –5T-films exhibit D-active one. This is why the direction of vertical MHD flow is determined by the magnetic field direction and the interference of the vertical

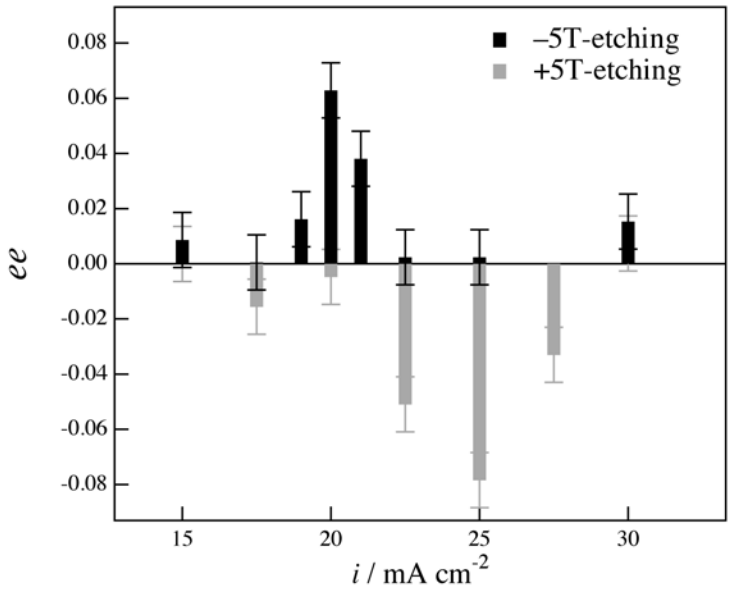

Figure 4: The ee ratios of +5T-film and –5T-film electrodes for alanine enantiomers versus the etching currents at the MEE processes.

MHD flow breaks the symmetry of the micro-MHD vortices [7]. However, the results in these MEE experiments suggest that the reversal of the magnetic field direction at the same etching current does not lead to the mirror-image chirality but lead to achirality.

We examined the etching current dependence of the chirality of the MEE 5T-films, and the result is shown in Figure 4, where enantiomeric excess (*ee*) ratios are plotted against the etching current for both polarities of magnetic field. The *ee* ratio in the voltammograms of enantiomers can be defined as $ee = (i_p^L - i_p^D) / (i_p^L + i_p^D)$, where i_p^L and i_p^D represent the peak currents of L- and D-alanines, respectively. The positive sign of ee ratio represents the L-activity, the negative sign represents the D-activity. While the –5T-film exhibits the maximum L-activity at 20 mA cm^{-2}, the +5T-film exhibits the maximum D-activity around 25 mA cm^{-2}. These results indicate that the optimal electrochemical condition for the L-active film formation is not the same as that for the D-active film formation. As a result, the chirality of the MEE films disappears in the films prepared in the opposite magnetic field at the same etching current, as shown in Figures 3(b) and 3(c). The asymmetric feature in the optimal conditions for L and D active surfaces implies symmetry breaking in the chiral surface formation, being of great interest in connection with the homochirality in molecular evolution.

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