

Research Article

Chiral Recognition of Amino Acids by Magneto-electrodeposited Cu Film Electrodes

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Chiral behavior of magneto-electrodeposited (MED) Cu film electrodes was investigated for the electrochemical reactions of amino acids. The Cu films were electrodeposited under a magnetic field of 5 T perpendicular to the electrode surface. Such MED Cu films were employed as an electrode, and cyclic voltammograms were measured for the electrochemical reactions of several kinds of amino acids. Chiral behavior was clearly observed as oxidation current difference between the enantiomers of alanine, aspartic acid, and glutamic acid. The MED film electrodes with the thickness of 50~500 nm exhibited such chiral behavior, and their surface morphologies had network structures, which could be induced by the micro-MHD effect.

1. Introduction

When a magnetic field is imposed to an electrodeposition process (magneto-electrodeposition), the Lorentz force acting on the faradaic current causes convection of the electrolytic solution. This is well known as the magnetohydrodynamic (MHD) effect [1, 2]. The MHD effect leads to spiral structures in the two-dimensional growth of magneto-electrodeposited (MED) metals [3–6] and conducting polymers [7], and the three-dimensional helical structures in silicate membrane growth [8]. Thus, magneto-electrodeposition has the potential to produce chiral structures. This is called as magneto-electrochemical chirality. Control of chirality is one of the most significant subjects in biochemistry, and considerable effort has been devoted in exploring chiral catalysts. If the chiral structures can be formed in nanometer scales on the MED films, such film surfaces would serve as an enantio-selective catalyst.

Aogaki proposed the micro-MHD effect in the electrodeposition under the magnetic fields parallel to the faradaic current and perpendicular to the electrode surfaces [9]. In electrodeposition processes, nonequilibrium fluctuation produces a lot of humps on the deposit surfaces. The faradaic current around such humps is not parallel to the magnetic

field so that the Lorentz force could cause vortex-like convection in the local areas around the humps. The micro-MHD effect was observed in the circular structures on the MED Cu film surfaces [9] and the network structures in the Ni-alumina composite films [10]. The micro-MHD convection breaks the symmetry of mass transfer around the humps, and such symmetry breaking might lead to the formation of chiral structures on the deposit surfaces [11].

We tried the magneto-electrodeposition of Ag films and employed them as modified electrodes. The MED Ag film electrodes were found to exhibit different oxidation currents between the enantiomers of glucose and cysteine [12, 13]. To demonstrate the universality of magneto-electrochemical chirality, it is necessary to examine the chiral behaviors of the MED films of various kinds of metals. Copper electrodes exhibit electrocatalytic behaviors for the electro-oxidation of alcohols and amino acids in alkaline aqueous solutions [14, 15]. The electrocatalytic reactions are sensitive to the surface structure of the electrode through specific adsorption of reactant molecules. If the reactant has chirality, its electrocatalytic reaction could be sensitive to the chirality of the electrode surface. In this paper, we report the magneto-electrodeposition of Cu films and their characteristic chiral electrode behaviors for amino acids.

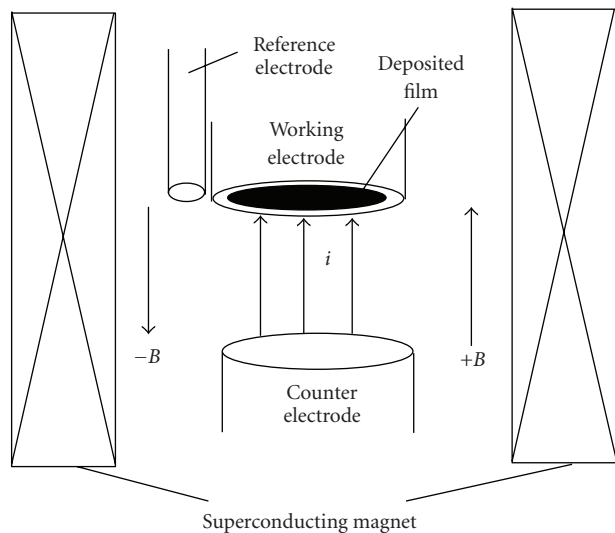


FIGURE 1: Schematic representation of magneto-electrodeposition in a superconducting magnet. Magnetic fields B are applied to parallel (+) or antiparallel (–) to faradaic currents, and they are perpendicular to the electrode surface.

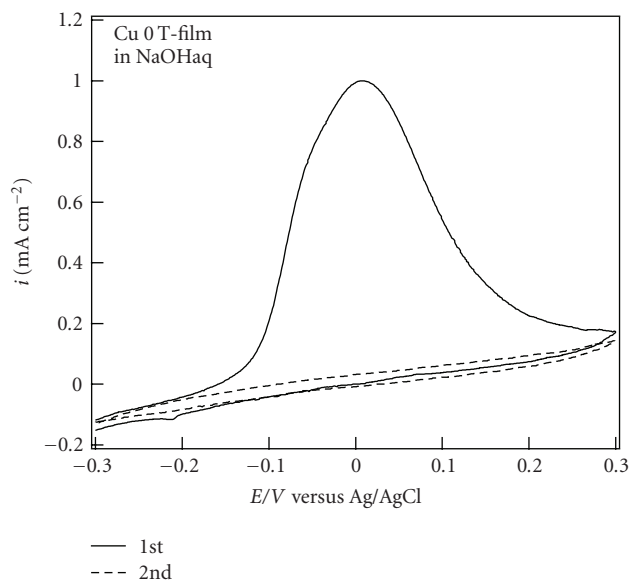


FIGURE 2: CVs of the Cu 0T-film electrode in a 0.1 M NaOH aqueous solution. The 1st sweep (solid line) corresponds to the pretreatment of the Cu film electrode, and the 2nd sweep (dashed line) represents the background current. The potential sweep rate was 10 mV s^{-1} .

2. Experimental

All chemicals were reagent grade and were used as received. For electrochemical experiments, a conventional system with the following three electrodes was employed: a polycrystalline Pt disc working electrode with a diameter of 3 mm, a Cu or Pt plate counter electrode, a Ag | AgCl | NaCl (3 M ($M = \text{mol dm}^{-3}$)) reference electrode. A potentiostat (Princeton Applied Research model 263A) was used for all the electrochemical experiments.

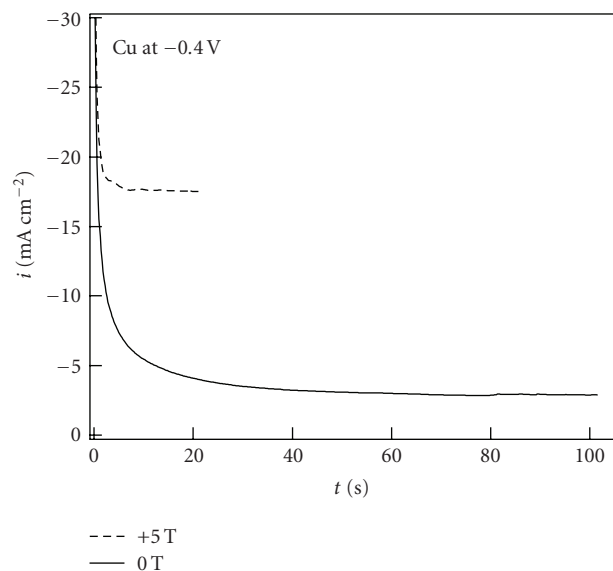


FIGURE 3: Current-time curves during the Cu electrodeposition in 0 T and +5 T.

Cu electrodeposition was conducted in a 50 mM CuSO_4 aqueous solution containing 0.5 M H_2SO_4 . The Cu films were formed on the Pt working electrode by the potentiostatic electrodeposition at a potential of -0.4 V . The film thickness was controlled by a passing charge, and the thickness could be approximately estimated from the density of Cu (8.93 g cm^{-3}), the electrode area and the passing charge. The usual film thickness was c.a. 150 nm at the passing charge of 0.4 C cm^{-2} .

Figure 1 shows a schematic representation of the magneto-electrodeposition. The electrochemical cell was placed at the bore center in a cryocooled superconducting magnet (Sumitomo Heavy Industries Ltd.), which is installed in the High Field Laboratory of Tohoku University and can produce magnetic fields of up to 5 T. An applied magnetic field B was perpendicular to the working electrode surface, and it was parallel (+ B) or antiparallel (– B) to the faradaic current. The films prepared at +5 T or –5 T are called the +5T-film or the –5T-film, respectively. The temperature within the magnet bore was controlled at 25°C by circulating thermoregulated water.

The magneto-electrodeposited (MED) films were used as modified electrodes, and their chiral properties were examined by measuring cyclic voltammograms (CVs) of the enantiomers of several kinds of amino acids (alanine, aspartic acid, lysine, etc.) in a 0.1 M NaOH aqueous solution. Because Cu metal is more easily oxidized than amino acids, the Cu film electrodes underwent a pretreatment of a potential sweep ($-0.3 \sim 0.3 \text{ V}$) in the NaOH solution before the CV measurements, as shown in Figure 2 (the solid line). In this potential sweep, the oxidation from Cu to Cu(I) occurs around -0.05 V , and the oxidation from Cu(I) to Cu(II) occurs around 0.02 V [14], forming a stable oxide film of CuO. The oxidation current became very small in the 2nd potential sweep (the dashed line in Figure 2), indicating that the film surface is covered by CuO after the pretreatment.

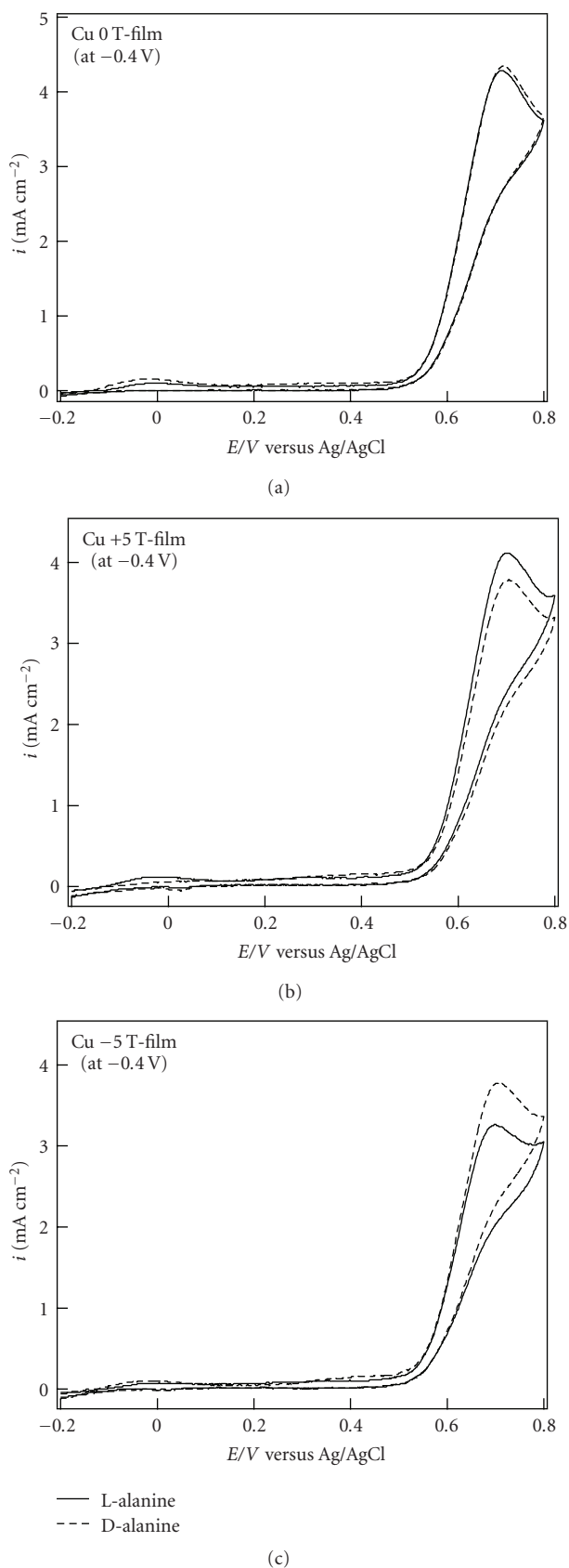


FIGURE 4: CVs of 20 mM L- and D-alanines on the Cu (a) 0T-film, (b) +5T-film, and (c) -5T-film electrodes in a 0.1 M NaOH aqueous solution. The potential sweep rate was 10 mV s^{-1} .

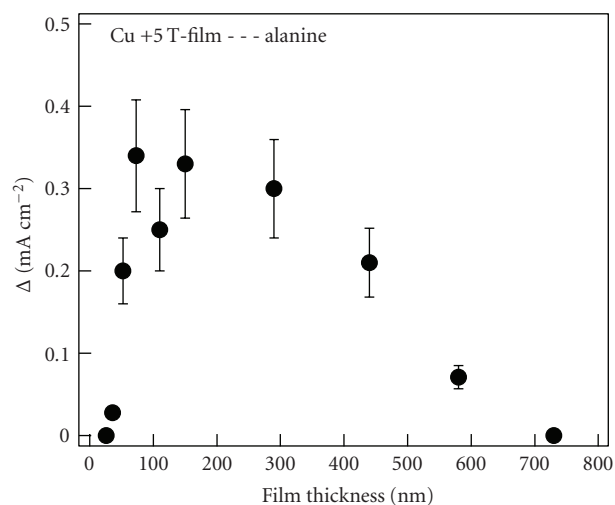


FIGURE 5: Film thickness dependence of the magnetoelectrochemical chirality. Δ is the peak current difference between L- and D-alanines in the CVs on the Cu +5T-film electrodes.

The CVs of amino acids were measured with a potential sweep rate of 10 mV s^{-1} in the absence of a magnetic field.

3. Results and Discussion

Figure 3 shows current-time curves during the Cu electrodeposition in 0 T and +5 T. It shows that the magnetic field considerably enhances the electrodeposition currents, even though the applied field is parallel to the faradaic current. The MHD effect is the minimum in, such a configuration, but it never disappears, because the current is not parallel to the magnetic field at the electrode edge and the fluctuated deposit surface. The latter is the micro-MHD effect [9], as mentioned above.

CVs of several amino acids were examined on the MED Cu film electrodes. Figure 4 shows CVs of 20 mM L- and D-alanines on the Cu (a) 0T-film, (b) +5T-film, and (c) -5T-film electrodes. The oxidation reaction of alanine occurs around 0.7 V, where the amino group ($-\text{NH}_2$) in the amino acid is oxidized [15]. Both CVs of the enantiomers are almost coincident each other on the 0T-film electrode (Figure 4(a)). On the +5T-film electrode, difference between the two CVs is seen in the peak currents. The oxidation current of L-alanine is larger than that of D-alanine (Figure 4(b)). On the contrary, the result is opposite for the MED film prepared under the reversal magnetic field. The oxidation current of D-alanine is larger than that of L- alanine on the -5T-film electrode (Figure 4(c)). These results indicate that the magnetoelectrodeposition induces the chirality in the Cu films and that the MED films possess the ability of enantioselective recognition for L- and D-alanines. The fact that the chiral behavior depends on the polarity of the magnetic fields indicates that the chirality arises from the Lorentz force and micro-MHD effect.

Similar chiral behavior was observed in the MED Ag film electrode for the glucose oxidation reaction [12, 13]. Both

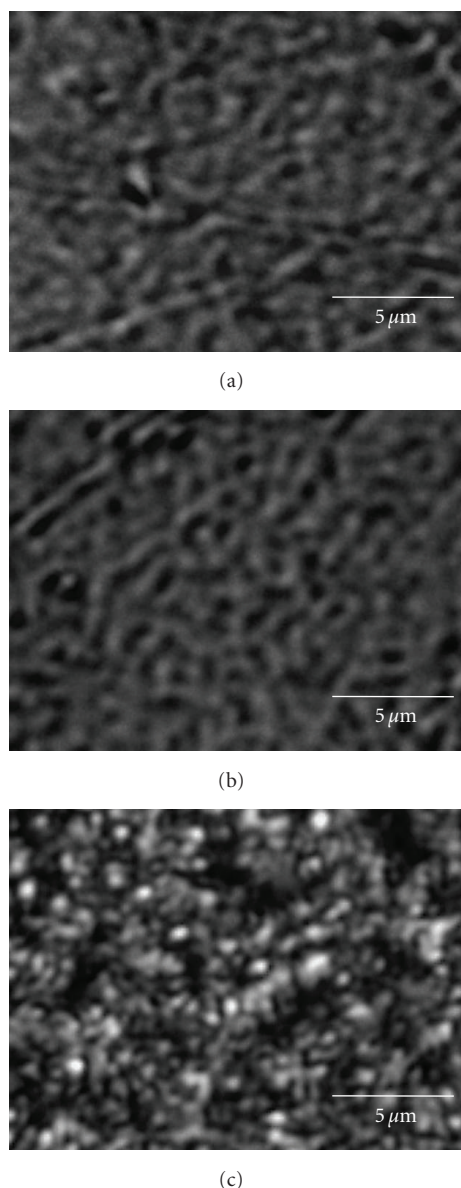


FIGURE 6: Microphotographs of the surface morphology of the Cu +5T-films with the thickness of (a) 150 nm, (b) 440 nm, and (c) 730 nm.

crystal structures of Ag and Cu are face-centered cubic (fcc), and generally, such a highly symmetrical crystal has no chirality. However, Attard et al. pointed out that there exist chiral kinks in certain surfaces, for example, {643}, of the fcc crystal and demonstrated that such a surface exhibits chiral electrode behaviors for the oxidation of D- and L-glucoses [16]. Similarly, they proposed that corner kinks of crystals could be a chiral site [17]. These ideas might be crucial for considering the chiral sites on the MED film surfaces.

The film thickness dependence of the chiral behavior of the +5T-film was examined for the electrochemical reaction of alanine. Figure 5 shows the oxidation current difference $\Delta(= i_p(L) - i_p(D))$ between the enantiomers against the film thickness, where $i_p(L)$ and $i_p(D)$ represent peak currents

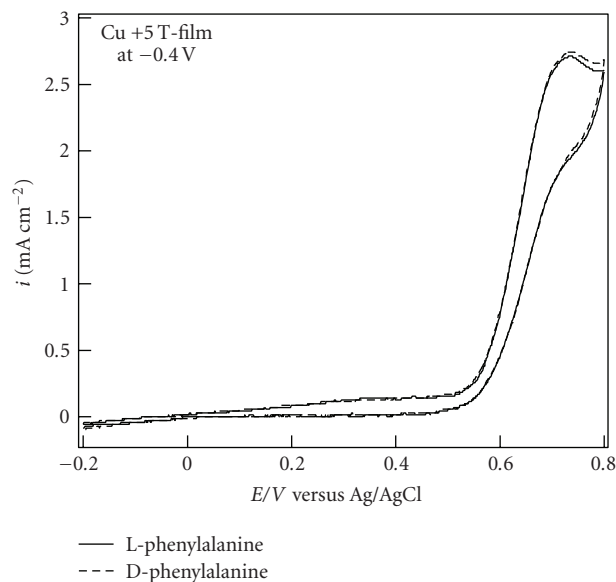


FIGURE 7: CVs of 20 mM L- and D-phenylalanines on the Cu +5T-film electrodes in a 0.1 M NaOH aqueous solution. The potential sweep rate was 10 mV s^{-1} .

of the CVs of L- and D-alanines, respectively. This figure shows that the chiral behavior appears in the thickness range of 50~500 nm. Figure 6 shows the surface morphologies of the Cu +5T-films with the thickness of (a) 150 nm, (b) 440 nm, and (c) 730 nm, where the photomicrographs were taken just after the magnetoelectrodeposition without the pretreatment. The films (a) and (b) exhibit the chiral behavior for alanine, and their surface morphologies possess network structures, which could be caused by the micro-MHD effect. Similar network structures were observed in the MED Ni- Al_2O_3 composite films [9] and magnetocorrosion of Zn single crystals [18]. On the contrary, the film (c) shows no chiral behavior, and the surface morphology is random aggregates of particles with a size of $\sim 1 \mu\text{m}$. These results imply that the micro-MHD effect induces the self-organization of convections and deposit structures in the film formation and that random fluctuation becomes dominant with increasing film thickness. Such self-organization seems to be significant for the formation of chiral surfaces.

We examined chiral response of the MED Cu film electrodes for several kinds of amino acids. Figure 7 shows CVs of 20 mM phenylalanine on the +5T-film electrode. The two CV curves are coincident each other, thus the MED film exhibits no chiral recognition for phenylalanine. This is contrary to the results of alanine, as shown in Figure 4. When amino acids are represented as $\text{R}-\text{CH}(\text{COOH})(\text{NH}_2)$, R is a methyl group ($-\text{CH}_3$) in alanine, and it is a benzyl group ($-\text{CH}_2\text{C}_6\text{H}_5$) in phenylalanine. The benzyl group is more bulky than the methyl group, and such a steric effect could prevent the specific adsorption at the chiral sites on the electrode surface, leading to the lack of chiral recognition.

Figure 8 shows CVs of 20 mM (a) aspartic acid, (b) glutamic acid, (c) lysine, and (d) arginine on the +5T-film electrode. While the MED film exhibits the chiral recognition

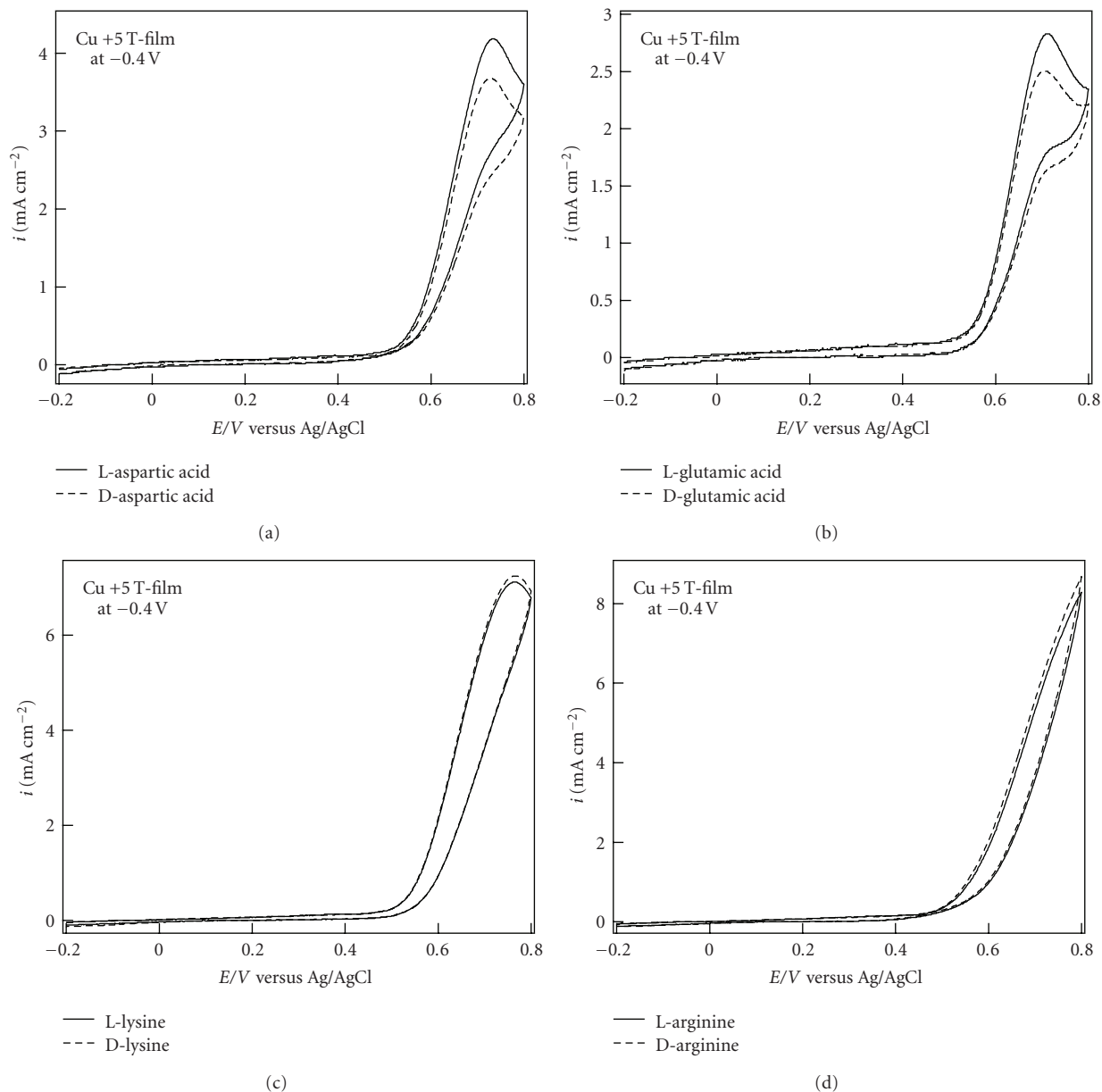


FIGURE 8: CVs of the enantiomers of (a) aspartic acid, (b) glutamic acid, (c) lysine, and (d) arginine on the Cu +5T-film electrodes in a 0.1 M NaOH aqueous solution. The potential sweep rate was 10 mV s^{-1} .

for aspartic and glutamic acids, it shows no chiral behavior for lysine and arginine. The molecular structures of R-groups are clearly different between the formers and the latters. The R-groups of aspartic and glutamic acids involve a carboxyl group ($-\text{COOH}$), on the contrary, those of lysine and arginine involve an amino group ($-\text{NH}_2$). These facts suggest that the carboxyl group promotes the specific adsorption on the electrode surface, leading to the chiral recognition. On the other hands, the amino group participates in the electrode reaction and contributes to the large oxidation currents, as shown in Figures 8(c) and 8(d). This seems to be crucial for the lack of chiral recognition for lysine and arginine.

There remains interesting open issues where the chiral site is on the MED film surface, why such a chiral site can survive after the surface oxidation in the pretreatment process, and how the chiral site recognizes the molecular chirality of amino acids. To elucidate these issues in future studies leads to a design of electrocatalytic chiral surface using the magnetoelectrodeposition technique.

4. Conclusion

We have shown that the MED Cu film electrodes exhibit chiral behaviors for the oxidation of the enantiomers of alanine,

aspartic acid, and glutamic acid and that such magnetoelectrochemical chirality depends on the film thickness. Taking account of our previous results of the chirality of the MED Ag films [12, 13], the observation of the chirality in the MED Cu films implies that the magnetoelectrochemical chirality is a universal phenomenon in the magnetoelectrodeposition of metals. It is noteworthy that the magnetoelectrodeposition is able to provide chiral surfaces without any chiral chemicals, and this novel technique would be applicable to new design of chiral catalysts and sensors.

Acknowledgment

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