Chiral electrode behavior of magneto-electrodeposited Cu-Cu$_2$O films

I Mogi and K Watanabe
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
E-mail: mogi@imr.tohoku.ac.jp

Abstract. Chiral properties were investigated in Cu and Cu$_2$O composite films prepared by magneto-electrodeposition. The Cu-Cu$_2$O films were electrodeposited in a CuSO$_4$ and Na$_2$SO$_4$ aqueous solution under magnetic fields $B$ (2 and 5 T) parallel (+$B$) or antiparallel ($-$+$B$) to the faradaic current. The magneto-electrodeposited films were used as modified electrodes, and the chiral voltammetric behaviors were observed as follows. The 2T-film electrodes of Cu-Cu$_2$O(15%) showed the oxidation current difference between D- and L-glucoses. The voltammograms of L-DOPA (3-(3,4-dihydroxyphenyl)alanine) showed the peak potential difference between the +5T-film and –5T-film electrodes of Cu-Cu$_2$O(40%).

1. Introduction
Recent development of magnetoscience has provided a new strategy for material processing, namely, magneto-processing of materials. Combinations of magnetic fields and conventional processes allow control of mass transfer, molecular orientation, levitation, crystal morphology, etc., however, there remains an intriguing and open issue, that is, magnetic control of chirality. Rikken and Raupach exploited magnetochiral chemistry in a photochemical reaction. They found an enantioselective magnetic field effect in the photo-induced dissociation of the chiral tris(oxalato)-Cr(III) complex and obtained the enantiomeric excess of 0.01% under a magnetic field of 10 T [1].

We have explored chirality in magneto-electrochemical processing. When a magnetic field is imposed to an electrochemical cell, the Lorentz force acting on the faradaic current causes convection of the electrolytic solution. This is well known as the magnetohydrodynamic (MHD) effect [2,3]. The Lorentz force induces spiral structures in the two-dimensional growth of magneto-electrodeposited metals [4-7] and conducting polymers [8], and the three-dimensional helical structures in silicate membrane growth [9].

Chiral structures can be used for the enantioselective recognition of chiral molecules. If the chiral structures can be formed in nanometer scales on the magneto-electrodeposited films, such film surfaces would serve as an enantioselective catalyst. As the first attempt, we tried to prepare chiral conducting polymer films by magneto-electropolymerization and found that such polyaniline films exhibited chiral electrode behavior for the oxidation of ascorbic acid [10,11]. This result suggested that the Lorentz force affected the growth probabilities of right- and left-handed helical polyaniline chains.

The chiral electrode behavior was also found in magneto-electrodeposited Ag films, which exhibited different oxidation currents between D- and L-glucoses [12]. Aogaki pointed out that the micro-MHD effect plays an important role in electrodeposition under the magnetic fields parallel to
the faradaic currents [13]. In electrodeposition processes, non-equilibrium fluctuation produces a lot of humps on the deposit surfaces. The faradaic currents around such humps are not parallel to the magnetic field, so that the Lorentz force could cause vortex-like convections in the local areas around the humps. Such local convections are expected to induce chiral structures on the deposit surfaces. The chirality is thus considered to be an intrinsic feature in magneto-electrodeposition. To confirm this concept, it is necessary to explore various kinds of magneto-electrodeposited films. In this paper, we report the magneto-electrodeposition of Cu and Cu$_2$O composite films and their chiral electrode behaviors.

2. Experimental

All chemicals were reagent grade and were used as received. All aqueous solutions were prepared with distilled water. For electrochemical experiments, a conventional system with the following three electrodes was employed: a platinum disc working electrode with a diameter of 3 mm, a platinum plate counter electrode, a Ag | AgCl | NaCl(sat) reference electrode. A potentiostat (Princeton Applied Research model 263A) was used for all the electrochemical experiments.

Figure 1 shows a voltammogram of Cu$^{2+}$ in a 50 mM (M = mol dm$^{-3}$) CuSO$_4$ aqueous solution containing 0.1 M Na$_2$SO$_4$ as a supporting electrolyte. In a small peak at 67 mV, Cu$^{2+}$ is reduced to Cu(I), forming cuprous oxide Cu$_2$O electrodeposits [14]. In a large peak at –70 mV, Cu$^{2+}$ is reduced to Cu(0), forming Cu electrodeposits. However, Shang et al. reported that the electrodeposition in neutral solutions with pH ~ 7 leads to simultaneous deposition of Cu and Cu$_2$O in a wide potential range [15]. In our experiment, electrodeposition of Cu and Cu$_2$O composite films was conducted at 0 and 40 mV (vs Ag | AgCl) by a passing charge of 0.15 C cm$^{-2}$ in a 50 mM CuSO$_4$ and 0.1 M Na$_2$SO$_4$ aqueous solution. The molar ratios of Cu and Cu$_2$O in the composite films depended on the deposition potential and were determined electrochemically, as mentioned in the next section.

The electrochemical cell was placed at the bore center in a cryocooled superconducting magnet (Sumitomo Heavy Industries Ltd.), which can produce magnetic fields of up to 5 T. An imposed magnetic field $B$ was perpendicular to the working electrode surface, and it was parallel (+$B$) or antiparallel ($-B$) to faradaic currents. The electrodeposited films prepared at +2 T or –2 T, for example, are called the +2T-film or the –2T-film, respectively. The temperature within the magnet bore was controlled at 25ºC by circulating thermo-regulated water.

The magneto-electrodeposited films were used as modified electrodes, and their chiral properties were examined by measuring the voltammograms of 20 mM D- and L-glucoses in 0.1 M NaOH.

![Figure 1. Voltammograms of 50 mM CuSO$_4$ in a 0.1 M Na$_2$SO$_4$ aqueous solution. The potential sweep rate was 10 mV s$^{-1}$.](image)
aqueous solutions and 20 mM L-3-(3,4-dihydroxyphenyl)alanine (L-DOPA) in a phosphate buffer solution with pH = 6.86. Before the voltammetric measurements, the Cu-Cu₂O film electrodes experienced the potential sweeps in the supporting electrolyte solution as a pretreatment, and the background currents were measured for each electrode. The voltammograms of glucose and L-DOPA were measured with a potential sweep rate of 50 mV s⁻¹ in the absence of a magnetic field, and the background corrections were made on each voltammogram.

3. Results and discussion

Figure 2 shows the current-time curves during the Cu-Cu₂O electrodeposition at 0 mV in 0 T and +2 T. The curve at –2 T was quite similar to that at +2 T. The magnetic field increases the electrodeposition rate after 20 sec, even though the applied field was perpendicular to the electrode surface. When the magnetic field is perpendicular to the electrode surface, the MHD effect is the minimum, but it never disappears because the current is not parallel at the edge of the electrode and the fluctuated deposit surface (the micro-MHD effect).

Figure 3 shows the voltammograms of the Cu-Cu₂O 0T-film prepared at 0 mV. The voltammograms were measured several times successively in a 0.1 M NaOH aqueous solution, and the first and the second sweep voltammograms are shown in Figure 3. In the first sweep voltammogram, the oxidation from Cu to Cu(I) occurs around a sharp peak at 0 V, and the oxidation from Cu(I) to Cu(II) occurs around the next peak at 0.2 V [16]. The oxidation current becomes very small in the second sweep voltammogram, implying that the film surface is covered by cupric oxide CuO after the first sweep.

The molar ratios of Cu and Cu₂O in the composite films were determined from the measurements of the passing charges during the film oxidation from Cu to Cu(I) in the NaOH solution. The estimated molar ratios of Cu : Cu₂O are 0.85 : 0.15 for the film prepared at 0 mV, and 0.60 : 0.40 for the film prepared at 40 mV. These ratios were nearly the same as those of the 2T- and 5T-films.

The chiral electrode behaviors of the Cu-Cu₂O(15%) films were examined for the oxidation reaction of 20 mM D- and L-glucoses in a 0.1 M NaOH aqueous solution. In the alkaline solution, CuO covers the surface of the Cu electrode after the pretreatment potential sweeps, and the oxide induces electrocatalytic reactions [16]. Generally, an electrocatalytic reaction includes a specific adsorption process, which are sensitive to the surface structure of the electrode. The voltammograms of D- and L-glucoses were nearly coincident each other on the 0T-film electrode.

![Figure 2. Current-time curves during the electrodeposition of Cu-Cu₂O at 0 mV in 0 T and +2 T.](image1)

![Figure 3. Voltammograms of the Cu-Cu₂O(15%) 0T-film in a 0.1 M NaOH aqueous solution. The potential sweep rate was 50 mV s⁻¹.](image2)
Figure 4 shows voltammograms of D- and L-glucoses on the Cu-Cu$_2$O(15%) electrodes of (a) the +2T-film and (b) the –2T-film. The potential sweep rate was 50 mV s$^{-1}$.

Figure 4 shows voltammograms of D- and L-glucoses on the +2T-film and –2T-film electrodes of Cu-Cu$_2$O(15%). The oxidation peak of glucose appears around 0.7 V. On the +2T-film electrode, the oxidation current of L-glucose is larger than that of D-glucose (Figure 4(a)). On the contrary, the current of D-glucose is larger than that of L-glucose on the –2T-film electrode (Figure 4(b)). These facts indicate that the magneto-electrodeposition induces chirality in the Cu-Cu$_2$O(15%) films and that the origin of this chirality is the Lorentz force because other magnetic field effects are independent of the polarity of magnetic fields. The 2T-film electrodes of Cu-Cu$_2$O(15%) possess the ability of chiral recognition for glucoses.

The chiral electrode behaviors of the magneto-electrodeposited Cu-Cu$_2$O(40%) films were examined for electrochemical reactions of an amino acid. L-DOPA is a kind of an amino acid with a redox functional group of dihydroxyphenyl, as shown in Figure 5. The cyclic voltammograms of L-DOPA were measured on the +5T- film and –5T-film electrodes in a phosphate buffer solution with pH = 6.86. The result is shown in Figure 6(a). The oxidation of L-DOPA occurs around 0.3 – 0.4 V on the Cu-Cu$_2$O film electrode. It is noted that the peak potentials are different between the +5T- film and –5T-film electrodes; 351 mV on the +5T-film electrode and 366 mV on the –5T-film electrode. Figure 6(b) shows cyclic voltammograms of the racemic mixtures of D- and L-DOPA on the +5T- film and –5T-film electrodes. The peak potentials of the racemic mixture are coincident each other between the two electrodes. These results indicate that the +5T-film and –5T-film electrodes of Cu-Cu$_2$O(40%) have chirality and possess the ability of chiral recognition of L-DOPA.

![Molecular structure of L-DOPA](image)

**Figure 5.** Molecular structure of L-DOPA
It is known that the chiral voltammetric behavior depends on the electrocataliticity of an electrode reaction. Kashiwagi et al. reported the electrocatalytic voltammograms of R- and S-1-phenylethanols on modified electrodes with a chiral self-assembled monolayer, and showed that the chiral behavior appears in the electrocatalytic currents [17]. On the other hands, if the electrocataliticity is poor, the chiral behavior appears on the peak potentials. Switzer reported that the voltammograms of L- and D-tartaric acids have different peak potentials on chiral CuO electrodes [18]. It seems that the former corresponds to the result of Figure 4 and the latter corresponds to the result of Figure 6. Similar results were observed in the electrocatalytic oxidation of ascorbic acid on magneto-electropolymerized polyaniline film electrodes [11].

4. Conclusion
We have demonstrated that the magneto-electrodeposition induces chirality in the Cu-Cu₂O composite films. The 2T-film electrodes of Cu-Cu₂O(15%) exhibit the oxidation current difference between D- and L-glucoses. The voltammograms of L-DOPA showed the peak potential difference between the +5T-film and –5T-film electrodes of Cu-Cu₂O(40%). These results indicate that the magneto-electrodeposited Cu-Cu₂O films possess the ability of chiral recognition for glucoses and DOPA.

Acknowledgement
The magneto-electrodeposition experiments were performed in the High Field Laboratory for Superconducting Materials, IMR Tohoku University.

References
[1] Rikken G L J A and Raupach E 2000 Nature 405 932
[2] Aogaki R, Fueki K and Mukaibo T 1975 Denki Kagaku 43 504
[3] Fahidy T Z 1983 J. Appl. Electrochem. 13 553
[4] Mogi I, Okubo S and Nakagawa Y 1991 J. Phys. Soc. Jpn. 60 3200
[5] Mogi I, Kamiko M and Okubo S 1995 Physica B 211 319
[6] Coey J M D, Hinds G and Lyons M E G 1999 Europhys. Lett. 47 267
[7] Heresanu V, Ballou R and Molho P 2003 Magnetohydrodynamics 39 461
[8] Mogi I and Kamiko M 1996 Denki Kagaku 64 842
[9] Uechi I, Katsuki A, Dunin-Barkovskiy L and Tanimoto Y 2004 J. Phys. Chem. B 108 2527
[10] Mogi I and Watanabe K 2005 Jpn. J. Appl. Phys. 44 L199
[11] Mogi I and Watanabe K 2007 J. Solid State Electrochem. 11 751
[12] Mogi I and Watanabe K 2007 ISIJ Int. 47 585
[13] Aogaki R 2003 Magnetohydrodynamics 39 453
[14] Wijesundera R P, Hidaka M, Koga K, Sakai M and Siripala W 2006 Thin Solid Films 500 241
[15] Shang W, Shi X, Zhang X, Ma C and Wang C 2007 Appl. Phys. A 87 129
[16] Torto N, Ruzgas T and Gorton L 1999 J. Electroanal. Chem. 464 252
[17] Kashiwagi Y, Uchiyama K, Kurashima F, Anzai J and Osa T 1999 Electrochemistry 67 900
[18] Switzer J A 2004 Interface 13 34