Chirality of magneto-electrodeposited metal film electrodes

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Abstract
The chiral electrode behaviors of magneto-electrodeposited (MED) Ag and Cu films were examined for the electrochemical reactions of D-glucose, L-glucose and L-cysteine. The Ag and Cu films were electrodeposited under a magnetic field of 2 T parallel (+2 T) or antiparallel (−2 T) to the faradaic current. For MED films of both Ag and Cu, the oxidation current of L-glucose was larger than that of D-glucose on the +2 T-film electrodes, and the results were opposite on the −2 T-film electrodes. These facts demonstrate that the MED metal films possess the ability of chiral recognition for D- and L-glucoses. The MED Ag film electrodes also exhibited chiral behavior for the oxidation of L-cysteine.

Keywords: chiral recognition, magnetic field, electrodeposition, metal film

1. Introduction
The magnetic field control of chiral chemical reactions is one of the goals in magnetoscience. Many scientists have studied this subject, however, very few have succeeded in achieving such control. Rikken and Raupach found an enantioselective magnetic field effect in a photochemical reaction and obtained the enantiomeric excess of 0.01% under a magnetic field of 10 T [1]. Their result is significant as a breakthrough in magnetochiral chemistry, and simultaneously the quantity of the obtained enantiomeric excess implies that the direct magnetic field control of chiral reactions is difficult.

We have attempted chirality control by magneto-electrochemical procedures. The Lorentz force induces the formation of spiral structures in the two-dimensional growth of magneto-electrodeposited metals [2–5] and conducting polymers [6], and the formation of three-dimensional helical structures in silicate membrane growth [7]. Chiral structures can be used for the enantioselective recognition of chiral molecules, which is one of the most important processes in biochemistry. If chiral structures can be induced at the nanometer scale on the magneto-electrodeposited (MED) films, such film surfaces would serve as an enantioselective catalyst.

As a first attempt, we attempted 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 [8, 9]. We next attempted to prepare chiral film surfaces by the magneto-electrodeposition of metals [10]. When a magnetic field is applied to an electrochemical cell, the Lorentz force induces convection in the electrolytic solution, resulting in an increase in the faradaic current. This is well known as the magnetohydrodynamic (MHD) effect [11, 12]. Aogaki pointed out that the micro-MHD effect plays an important role in electrodeposition when the magnetic field is parallel to the faradaic current [13]. In electrodeposition processes, nonequilibrium fluctuation produces a large number of humps on the deposited surface. The faradaic current around such humps is not parallel to the magnetic field; thus, a Lorentz force may cause vortexlike convection in the local areas around the humps. Such local convection is expected to induce chiral structures on the deposited surface.

Here, we report the chiral electrode behaviors of MED films of Ag and Cu for the oxidation of D-glucose, L-glucose and L-cysteine.

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, and a Ag/AgCl\((50 \text{mM}/(M = \text{mol dm}^{-3}))\) reference electrode for the Ag electrodeposition or a Ag/AgCl|NaCl(sat) reference electrode for the Cu electrodeposition and the voltammetric measurements. A potentiostat (Princeton Applied Research model 263A) was used for all the electrochemical experiments.

Ag electrodeposition was conducted at a constant potential of \(-100 \text{mV} \) (versus Ag/Ag\(^{+}\)) in 50 mM AgNO\(_3\) aqueous solution containing 0.1 M NaClO\(_4\) as a supporting electrolyte. The Ag films were deposited by passing a charge of 0.2 C cm\(^{-2}\) through the working electrode. Cu electrodeposition was conducted at 0 mV (versus Ag/AgCl) in 50 mM CuSO\(_4\) aqueous solution containing 0.1 M Na\(_2\)SO\(_4\). The Cu films were deposited by passing a charge of 0.15 C cm\(^{-2}\). A schematic illustration of the magneto-electrodeposition process is shown in figure 1. 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. A magnetic field \(B\) was applied perpendicular to the working electrode surface and parallel (+\(B\)) or antiparallel (−\(B\)) to the faradaic current. The MED films were deposited at around \(-100 \text{mV}\), as indicated by arrows in figure 2.

The chiral electrode behavior of the MED films was examined by measuring voltammograms of the chiral species. Figure 3 shows voltammograms of 20 mM D- and L-glucoses in 0.1 M NaOH aqueous solution on the +2 T-film and −2 T-film Ag electrodes. The oxidation peak of glucose appears at 220 mV for the Ag electrode, where silver oxide is simultaneously formed \([10]\). It is known that silver oxide induces electrocatalytic reactions on the Ag electrode through specific adsorption \([14]\) that are sensitive to the surface structure of the electrode.

On the 0 T-film electrode, the voltammograms of D- and L-glucoses were nearly coincident with each other \([10]\). On the +2 T-film electrode, a difference between the two voltammograms can be seen in the peak currents (figure 3(a)). The oxidation current of L-glucose is larger than that of D-glucose. However, the result is opposite for the MED film prepared under the reverse magnetic field. The oxidation current of D-glucose is larger than that of L-glucose on the −2 T-film electrode (figure 3(b)). These results indicate that the MED process induces chirality in the Ag electrodeposited film and that the origin of this chirality is the Lorentz force.
Figure 3. Voltammograms of 20 mM D- and L-glucoses in 0.1 M NaOH aqueous solution on the Ag electrodes of (a) the +2 T-film and (b) the −2 T-film. The potential sweep rate was 50 mV s\(^{-1}\).

because other magnetic field effects are independent of the polarity of the magnetic field.

The chiral electrode behavior of the MED Ag films was also examined for the electrochemical reaction of an amino acid. Figure 4 shows cyclic voltammograms of 20 mM L-cysteine in 0.1 M NaOH aqueous solution on the Ag film electrodes prepared at ±2 and ±0.5 T. The oxidation peak of L-cysteine appears at around 200 mV for the Ag electrodes. The +2 T-film and −2 T-film electrodes exhibit a clear difference in current (figure 4(a)), and this indicates that the films are able to recognize the chirality of L-cysteine.

On the other hand, the voltammograms of L-cysteine on the +0.5 T-film and −0.5 T-film electrodes are coincident with each other, as shown in figure 4(b). Coincident voltammograms were also observed on the +4 T-film and −4 T-film electrodes. These results suggest that there is an optimal combination of the deposition current and the magnetic field for the formation of a chiral surface.

3.2. MED Cu film electrodes

Figure 5 shows a voltammogram of the reduction of Cu\(^{2+}\) ion in 50 mM CuSO\(_4\) aqueous solution. A small peak at +70 mV shows the reduction from Cu\(^{2+}\) to Cu\(^+\) [15], and Cu deposition occurs at potentials of less than 0 mV. Potentiostatic electrodeposition was conducted at various
 potentials from 0 to $-100 \text{ mV}$ under a magnetic field of 2 T, and chiral electrode behavior was only observed in the films electrodeposited around 0 mV, as indicated by the arrow in figure 5.

Figure 6 shows voltammograms of 20 mM D- and L-glucoses in 0.1 M NaOH aqueous solution on the Cu electrodes of (a) the +2 T-film and (b) the −2 T-film. The potential sweep rate was 50 mV s$^{-1}$.

The voltammograms of D- and L-glucoses were nearly coincident with each other on the 0 T-film electrode. On the +2 T-film electrode, the oxidation current of L-glucose is larger than that of D-glucose (figure 6(a)). In contrast, the current of D-glucose is larger than that of L-glucose on the −2 T-film electrode (figure 6(b)). These facts show that the MED Cu film electrodes also possess the ability of chiral recognition for glucoses.

The comparison of the chirality between the Ag and Cu film electrodes is meaningful. As shown in figures 3 and 6, the +2 T-film electrodes of both Ag and Cu exhibit larger currents for L-glucose, and both the −2 T-film electrodes exhibit larger currents for D-glucose. These facts mean that both MED film electrodes have the same chirality, and it seems that the chirality of the film surfaces is determined by the Lorentz force.

Figure 6. Voltammograms of 20 mM D- and L-glucoses in 0.1 M NaOH aqueous solution on the Cu electrodes of (a) the +2 T-film and (b) the −2 T-film. The potential sweep rate was 50 mV s$^{-1}$.

Figure 7 shows cyclic voltammograms of 20 mM L-cysteine in 0.1 M NaOH aqueous solution on the +2 T-film and −2 T-film Cu electrodes. The oxidation peak of L-cysteine appears at 60 mV for the Cu electrode, and both voltammograms are coincident with each other. In contrast to the case of the Ag electrodes (see figure 4(a)), the MED Cu electrodes do not exhibit chiral behavior for L-cysteine. The chiral recognition in electrocatalytic reactions proceeds through specific adsorption. If the specific adsorption of L-cysteine on the Cu electrode occurs at only the thiol ($-\text{SH}$) site of the cysteine molecule, the Cu electrode cannot recognize the chirality. It is thus considered that the chiral recognition depends on the adsorption structure.

4. Conclusion

We demonstrated that the magneto-electrodeposition process induces chirality in Ag and Cu films, which exhibit the chiral electrode behaviors for the oxidation reactions of D- and L-glucoses. The MED Ag films also exhibit chiral behavior for the oxidation of L-cysteine. The films electrodeposited under a reverse magnetic field possess the opposite chirality. This fact indicates that the origin of the chirality is the Lorentz force, but it remains an open issue as to how the micro-MHD effect causes the formation of the chiral structures on the MED film surfaces. Nevertheless, magneto-electrodeposition is expected to be a useful method for introducing chirality into electrodeposited films without chiral chemical species.

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