

CHIRAL ELECTRODES OF MAGNETO- ELECTROPOLYMERIZED POLYANILINE FILMS

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Introduction. Magnetic fields induce chiral structures through the Lorentz force acting on currents in electrolytic solutions. Two-dimensional spiral structures were found in the electrodeposition of metals [1, 2] and conducting polymers [3], and three-dimensional helical structures in silicate membrane growth [4], though both structures were on the millimeter scale. If chiral structures on the molecular scale are induced on the surface of the films formed under magnetic fields, such film surfaces would serve as enantioselective catalysts.

Enantioselective recognition of chiral molecules is one of the most important processes in biochemistry; in most cases, it is realized by enzymes. Chiral surfaces of heterogeneous catalysts have the enantioselective properties, and thus considerable effort has been devoted to preparing chiral surfaces by adsorbing chiral molecules [5, 6] or slicing single crystals [7]. Chirality was also introduced into conducting polymers by doping chiral molecules [8, 9, 10], and chiral polyaniline films exhibited enantioselective recognition for several amino acids [9].

We attempted to prepare polyaniline films with a chiral surface by magnetoelectropolymerization (MEP), which is electropolymerization under magnetic fields [11]. Polyaniline is one of the most promising materials for electronic devices, and its films are easily prepared by the oxidative electropolymerization of aniline in acidic aqueous solutions. Aniline monomers are stoichiometrically oxidized in front of the polymer chain, and then electrons are transported from the front to the substrate electrode within the chain. Under magnetic fields, the Lorentz force is expected to act on currents within the polymer chain and induce helical growth. Thus, it is interesting to examine whether the MEP films exhibit chiral electrode properties. Here, we show the voltammetric responses of the MEP polyaniline films to vitamin C (L-ascorbic acid) and its enantiomer, erythorbic acid (D-ascorbic acid).

1. Magnetoelectropolymerization (MEP). 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 | NaCl(sat) reference electrode. Polyaniline films were prepared on the working electrode by potentiostatic electropolymerization at 0.9 V by a passing charge of 0.1 C cm^{-2} in a 0.5 M ($\text{mol} \cdot \text{dm}^{-3}$) sulfuric acid aqueous solution containing 50 mM aniline. The MEP experiments were conducted at 25°C under a magnetic field of 5 T in a cryocooled superconducting magnet (Sumitomo Heavy Industries Ltd.), the schematic illustration is shown in Fig. 1. The applied magnetic fields were parallel or antiparallel to faradaic currents, and the MEP films prepared under these fields are called the +5T-film or the -5T-film, respectively. The MEP films were used as modified electrodes, and their chiral properties were examined by measuring the cyclic voltammograms (CVs) of L-ascorbic acid (L-AA) and erythorbic acid. The latter is the enantiomer of L-AA, and thereby, it is called D-ascorbic acid (D-AA) in this paper. The CVs of 20 mM L- or D-AA were measured in a 0.5 M H_2SO_4 aqueous solution with a potential sweep rate of 50 mV s^{-1} in the absence of a magnetic field. To obtain

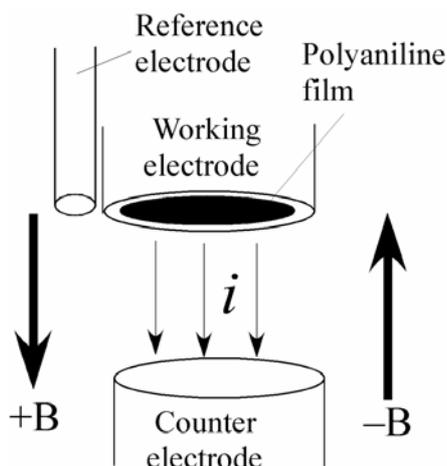


Fig. 1. Electrode configuration in the magnetoelectropolymerization process. Magnetic fields \mathbf{B} are applied parallel (+) or antiparallel (-) to faradaic currents, and they are perpendicular to the electrode surface.

reproducible CVs, the polyaniline films were pretreated with a five-cycle potential sweep in the range of -0.1 to 1.1 V in a 0.5 M H_2SO_4 aqueous solution.

The current-time curves during the MEP at $+5$ T and -5 T were nearly the same as those in the absence of a magnetic field. The CV peak potentials for the redox response of the MEP films themselves were also coincident with those for the redox response of the 0 T-film itself. These results indicate that the magnetic fields affect neither the polymerization rate nor the redox potential of polyaniline.

2. MEP film electrodes. A polyaniline film electrode shows electrocatalytic properties for several organic molecules such as L-AA [12, 13, 14] and hydroquinone [15]. Fig. 2 shows the CVs of L-AA on the 0 T-film electrode and a bare Pt electrode. A small peak at 0.2 V in the CV on the 0 T-film electrode, which is not seen in the CV on the Pt electrode, represents the oxidation of polyaniline. L-AA is irreversibly oxidized to dehydroascorbic acid on the electrodes. This reaction occurs at 0.4 V on the polyaniline electrode, while it occurs at a more positive potential of 0.6 V on the Pt electrode. In addition, the peak current on the polyaniline electrode is much larger than that on the Pt electrode. These observations indicate that the polyaniline film plays a catalytic role in the oxidation reaction of L-AA.

Generally, electrocatalytic reactions are sensitive to the surface structure of the electrode through specific adsorption. If the MEP process induces changes in the surface structure of the polyaniline films, such changes would be reflected in the

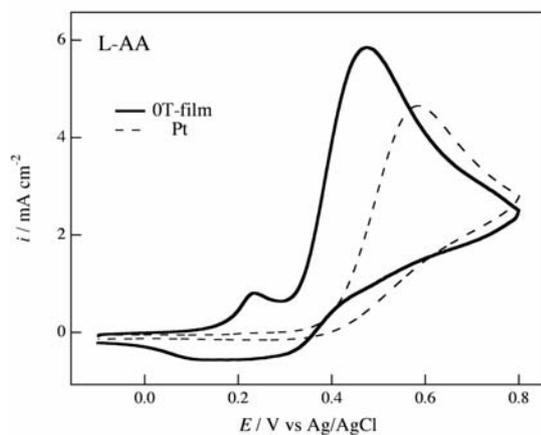


Fig. 2. Cyclic voltammograms of 20 mM L-ascorbic acid (L-AA) in a 0.5 M H_2SO_4 aqueous solution on the polyaniline 0 T-film electrode and a bare Pt electrode. The potential sweep rate is 50 mV S^{-1} .

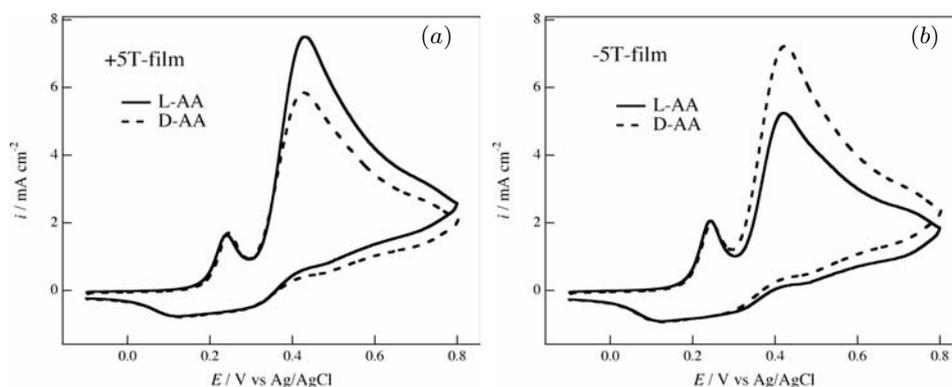


Fig. 3. Cyclic voltammograms of L- and D-ascorbic acids in a 0.5 M H_2SO_4 aqueous solution on (a) the +5T-film and (b) the -5T-film electrodes. The potential sweep rate is 50 mV S^{-1} .

voltammetric response to ascorbic acid. Fig. 3 shows the CVs of L-AA (solid line) and D-AA (broken line) on (a) the +5T-film and (b) -5T-film electrodes. In both Figs. 3a and 3b, the CV curves of the solid and broken lines are coincident for the oxidation peaks of polyaniline at 0.2 V. The difference between the enantiomers is clear on the oxidation peak at 0.4 V. The peak current for L-AA is larger than that for D-AA on the +5T-film electrode (Fig. 3a). In contrast, the result is opposite on the -5T-film electrode; the peak current for D-AA is larger than that for L-AA. This result indicates that the MEP induces the ability of enantioselective recognition for the polyaniline film and that the reverse magnetic field during the MEP process produces the opposite chirality.

It is interesting to compare the redox behaviors on the MEP film electrodes between chiral and achiral species. We examined the CVs of L-AA and hydroquinone (QH_2) on the +5T-film and -5T-film electrodes. The peak current of the L-AA oxidation on the +5T-film electrode was larger than that on the -5T-film electrode, being consistent with the results in Figs. 3a and 3b. On the other hand, QH_2 has no chirality, and it is electrochemically oxidized to p-benzoquinone in aqueous solutions. The polyaniline film also exhibits electrocatalytic properties for QH_2 , namely, rendering the redox reaction more reversible and increasing the redox currents. However, the CV curves of QH_2 were coincident between the +5T-film and -5T-film electrodes. This implies that the MEP produced the chiral structure in the polyaniline film, which is insensitive to achiral species in the electrode reactions.

In the two-dimensional electrodeposition of metals under magnetic fields, the spiral growth direction was reversed by the reversal of the applied magnetic fields because the spiral growth comes from the Lorentz force acting on currents in electrolytic solutions [16]. Similarly, the opposite chirality of the polyaniline film electrode for the reverse magnetic field indicates that the origin of the chirality is the Lorentz force. Shinohara *et al.* showed that the Lorentz force couples with small currents around humps on fluctuated surfaces and produces the vortex structures of electrodeposits [17]. The sizes of the vortices, however, are of the order of micrometers, being much larger than the molecular size. The enantioselective recognition for L- and D-AA implies that the MEP films possess a molecular-level chiral structure. The molecular structure of polyaniline is achiral, and it is incredible that the magnetic field changes the chemical bonds and induces a chiral molecular structure. It is, hence, most feasible that the Lorentz force acts on the currents within the polymer chains and induces the helical coil structures of the chains. The observation of the surface structure of the MEP films is in progress.

3. Conclusion. We showed that the polyaniline film electrodes prepared by the MEP method exhibit the ability of enantioselective recognition for L- and D-ascorbic acids. The films electropolymerized under the reverse magnetic fields showed an opposite chirality. This observation indicates that the origin of the chirality is the Lorentz force, which could induce the helical structure of the polymer chain. Thus, the MEP method is useful in introducing chirality into achiral conducting polymers without chiral dopants, and can be used for the synthesis of new biosensing devices.

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