Chiral recognition of magneto-electropolymerized polyaniline film electrodes

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Abstract

Polyaniline films were prepared by electropolymerization under a magnetic field of 5T parallel (+5T) or antiparallel (−5T) to the faradaic currents. They were used as a modified electrode and their chiral properties were examined for L-3-(3,4-dihydroxyphenyl)alanine (L-DOPA), L-ascorbic acid (L-AA) and D-isoascorbic acid (D-AA) by cyclic voltammetry. The redox currents of L-DOPA on the +5T-film electrode were smaller than those on the −5T-film electrode, and the results for racemic mixture of L- and D-DOPA were the same on the two electrodes. The oxidation current of L-AA on the +5T-film electrode was larger than that on the −5T-film electrode, and the result for D-AA was opposite. These facts demonstrate that the two electrodes have the opposite chirality each other and possess the ability of chiral recognition.

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1. Introduction

Magnetic field control of chiral chemical reactions is one of dreams in magneto-science. Many scientists have challenged this subject, however, almost all have never succeeded. As far as we know, there is one successful report that a chiral photochemical reaction was affected by magnetic fields [1]. In biological systems, it is well known that a chiral site in enzymes allows control of enantioselective reactions. In laboratories, considerable effort has been devoted in preparing chiral surfaces by adsorbing chiral molecules [2,3] or slicing single crystals [4]. Magnetic fields induce chiral structures through the Lorentz force acting on currents in solutions. Two-dimensional spiral structures were found in the electrodeposition of metals [5,6] and conducting polymers [7], and three-dimensional helical structures in silicate membrane growth [8], 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.

Conducting polymers are frequently used as a modified electrode, which shows electrocatalytic properties. Doping of chiral molecules induces helical chain structures in conducting polymers [9–11], and such chiral films exhibit enantioselective recognition for several amino acids [10]. Most electropolymerization processes in conducting polymer syntheses are oxidative polymerization. Monomer molecules 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. Otherwise, if polymer chains tend to form helical structures spontaneously, the Lorentz force is expected to induce the one-handed structure.

We attempted to prepare chiral conducting polymer films by magneto-electropolymerization (MEP), which is electropolymerization under magnetic fields [12]. 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. A previous paper reported that the MEP polyaniline films exhibited chiral electrode properties for the oxidation of ascorbic acid [12]. Here, we show the voltammetric responses of the MEP polyaniline films to L-3-(3,4-dihydroxyphenyl)alanine (L-DOPA).

2. Experimental

All chemicals were reagent grade and were used as purchased. 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 (mol dm\(^{-3}\)) sulfuric acid aqueous solution containing 50 mM aniline.

The MEP experiments were conducted at 25 °C under a magnetic field of 5T in a cryocooled superconducting magnet (Sumitomo Heavy Industries Ltd), the schematic illustration is shown in Fig. 1. The applied magnetic field was parallel (+) or antiparallel (−) to faradaic currents, and the MEP films prepared at +5T or −5T are called the +5T-film or the −5T-film, respectively.

The MEP films were used as modified electrodes, and cyclic voltammograms (CVs) were measured for L-3-(3,4-dihydroxyphenyl)alanine (L-DOPA), L-ascorbic acid (L-AA) and D-isoascorbic acid (D-AA). Their molecular structures are shown in Fig. 2. L-DOPA is a kind of amino acid with a redox functional group of dihydroxyphenyl. The L-AA molecule has two asymmetric carbon atoms numbered as 4 and 5. While L- and D-AA have opposite chirality each other at the carbon atom 5, they have the same chirality at the carbon atom 4. Thus, they are not enantiomers but diastereomers.

The CVs of 20 mM L-DOPA were measured in a 0.05 M H\(_2\)SO\(_4\) aqueous solution with a potential sweep rate of 50 mV s\(^{-1}\) in the absence of a magnetic field. The CVs of 20 mM L- or D-AA were measured in 0.5 M H\(_2\)SO\(_4\) aqueous solution. Chiral electrode properties were examined by comparing the CVs on the +5T- and −5T-film electrodes. To obtain reproducible CVs, the polyaniline films were pretreated with a five-cycle potential sweep in the range of −0.1−1.1 V in a 0.5 M H\(_2\)SO\(_4\) aqueous solution.

3. Results and discussion

The current-time curves during the MEP at 5T and −5T were nearly the same as those in the absence of a magnetic field. This means that the magnetic fields did not affect the polymerization rate of polyaniline under the present condition. This is partly because the magnetic fields were applied parallel to the faradaic currents to minimize the magnetohydrodynamic convection effect, and partly because the electrode potential of 0.9 V was under kinetic-controlled conditions. Fig. 3 shows CVs for the redox response of the polyaniline films themselves in a 0.5 M H\(_2\)SO\(_4\) aqueous solution. The MEP does not affect the redox potential of the polyaniline films but increases the redox currents.

A polyaniline film electrode shows electrocatalytic properties for several organic molecules such as L-AA [13–15] and hydroquinone [16]. Fig. 4 shows the CVs of L-DOPA on the polyaniline 0T-film electrode and a bare Pt electrode. A small peak at 0.2 V in the CV on the 0T-film electrode, which is not seen in the CV on the Pt electrode, represents the oxidation of polyaniline (see Fig. 3). The redox reaction of L-DOPA occurs around 0.5 V on both electrodes, where dihydroxyphenyl group of L-DOPA is oxidized to \(\alpha\)-benzoquinone group and the latter is reduced to the former at the reverse potential sweep. The peak potential difference on the 0T-film electrode is much smaller than that on the Pt electrode. This means that the electrode reaction on the 0T-film electrode is more reversible than that on the Pt electrode. In addition, the redox peak currents on the polyaniline electrode are larger than those on the Pt electrode. These observations indicate that the polyaniline film plays a catalytic role in the redox reaction of L-DOPA.

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 voltammetric response to L-DOPA. Fig. 5(a) shows the CVs of L-DOPA on the +5T-film and −5T-film electrodes in...
a 0.05 M H₂SO₄ aqueous solution. The difference is not seen in the peak potentials but in the redox currents of L-DOPA. The redox peak currents on the K₅T-film electrode is larger than those on the C₅T-film electrode. Fig. 5(b) shows the CVs of racemic mixture of L- and D-DOPA on the both electrodes, and the two CVs are completely coincident each other.

If the Lorentz force induces a helical structure in the MEP polyaniline films, the reverse magnetic fields cause the opposite helical structure. Other magnetic field effects, such as the Zeeman effect, magnetic force and magnetic orientation, are independent of the reversal of the magnetic fields. Hence, the CV difference in Fig. 5(a) indicates the chiral recognition of L-DOPA on the MEP film electrodes, and this is consistent with the CV coincidence of racemic DOPA on the both electrodes.

L-AA is irreversibly oxidized to dehydroascorbic acid on the electrodes, and this reaction occurs at 0.4 V on the polyaniline electrode [13]. Fig. 6(a) shows CVs of L-AA on the +5T-film and −5T-film electrodes in a 0.5 M H₂SO₄ aqueous solution. Clear chiral properties are seen in the oxidation peak of L-AA. The peak current on the +5T-film electrode is larger than that on the −5T-film electrode. In contrast, the result is opposite for the CVs of D-AA as shown in Fig. 6(b), where the peak current on the −5T-film electrode is larger than that on the +5T-film. These results demonstrate that the opposite chiral molecules exhibit the opposite chiral electrode properties.

The chiral recognition for L-DOPA, L- and D-AA implies that the MEP films possess a molecular-level chiral structure. A molecular model study suggests that polyaniline easily forms a helical structure as shown in Fig. 7. Ashraf et al. suggests that such a helical structure is stabilized by hydrogen bonds between N=C–H and dopant anions [17]. In the absence of a magnetic field, the electropolymerization produces the racemic state of right-handed and left handed helical chains.
The experimental results in Figs. 5 and 6 indicate that the Lorenz force changes the growth probabilities of right-handed and left-handed helical chains, causing chirality.

In both species of DOPA and ascorbic acids, the asymmetric carbon sites do not directly participate in the redox reactions. Nevertheless, the MEP polyaniline films distinguished these chiral species. This implies that the asymmetric sites contribute to the specific adsorption; the amino acid site in L-DOPA and the –OH group of the asymmetric carbon 5 in L- and D-AA. It is considered that the chirality of the adsorbing parts is reflected in the configuration of the redox parts against the polyaniline backbone. A more detailed mechanism for chiral recognition is a future study.

4. Conclusion

We demonstrated that the MEP polyaniline film electrodes exhibit chiral recognition for L-DOPA, L-and D-AA. These chiral species exhibited different CV currents on the +5T-film and −5T-film electrodes, which possess opposite chirality each other. The oxidation current of L-AA on the +5T-film electrode was larger than that on the −5T-film electrode, the result for D-AA was opposite. The asymmetric carbon sites in these species do not directly participate in the redox reactions. Thus, the specific adsorption of the asymmetric sites in the electrocatalytic processes is responsible for the chiral recognition.

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