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Electrocatalytic chirality on magneto-electropolymerized polyaniline electrodes

Iwao Mogi · Kazuo Watanabe

Abstract Chiral polyaniline electrodes were prepared by the magneto-electropolymerization (MEP) method. Cyclic voltammograms (CVs) of L-ascorbic acid (L-AA), D-isoascorbic acid (D-AA), and L-3-(3,4-dihydroxyphenyl) alanine were measured on the MEP polyaniline electrodes and their electrode reactions were electrocatalytic. The CV peak currents varied depending on the chirality of the polyaniline and the optically active species, while the peak potentials were independent of the chirality. The CVs of L-AA and D-AA were also measured on a Pt electrode in a (−)-camphor-10-sulfonic acid supporting electrolyte solution, and the chiral behavior was observed in the peak potentials. It is considered that the electrocatalytic process is responsible for the chiral electrochemical behavior on the polyaniline electrodes.

Keywords Polyaniline · Electropolymerization · Magnetic field · Chirality · Electrocatalytic reaction

Introduction

Chiral recognition in an electrode reaction is one of the most important techniques in bioelectrochemistry and electrochemical biosensors. Chiral electrode surfaces possess the enantioselective possibility [1, 2], and thus, much effort has been devoted to prepare the modified electrodes

I. Mogi (✉) · K. Watanabe
Institute for Materials Research,
Tohoku University,
Katahira 2-1-1, Aoba-ku,
Sendai 980-8577, Japan
e-mail: mogi@imr.tohoku.ac.jp

by adsorbing chiral molecules [3–6]. Conducting polymers are frequently used as modified electrodes, and chirality can also be introduced into conducting polymers by doping optically active molecules [7–9]. It is thus possible to prepare chiral-modified electrodes with conducting polymers.

Magneto-electrolysis produces chiral structures of deposits through the Lorentz force. Two-dimensional spiral structures of metal electrodeposits [10–13] and three-dimensional helical structures of silicate membrane [14] were found under magnetic fields, though both structures were on macroscopic scales of millimeter sizes. If chiral structures on molecular scales are induced by magneto-electrolysis, such a surface would serve as an enantioselective electrode, and this would be a breakthrough in magneto-electrochemistry.

Electropolymerization is one of the most powerful methods for the synthesis of conducting polymers, and most cases 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. If magnetic fields are applied to the electropolymerization process [magneto-electropolymerization (MEP)], the Lorentz force is expected to act on currents within the polymer chain and to induce helical growth. Otherwise, if polymer chains tend to form helical structures spontaneously, the Lorentz force is expected to induce a preferred one-handed structure.

We attempted to prepare chiral conducting polymer films by MEP and found that the MEP polyaniline films exhibited chiral electrode properties for the oxidation of ascorbic acid [15]. The polyaniline film electrode shows electrocatalytic properties for several organic molecules such as ascorbic acid [16–18] and hydroquinone [19]. Generally, electrocatalytic reactions are quite 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 voltammograms of electrocatalytic reactions.

In this paper we show chiral voltammetric behaviors on the MEP and chiral polyaniline electrodes. Cyclic voltammograms (CVs) of ascorbic acid and L-3-(3,4-dihydroxyphenyl)alanine (L-DOPA) were examined on the polyaniline and platinum electrodes in chiral and achiral supporting electrolyte solutions.

Materials and methods

Materials

Aniline, ascorbic acids, L-DOPA, catechol, and sulfuric acid were purchased from Wako (Osaka, Japan). Camphor-10-sulfonic acid (HCSA) was purchased from Tokyo Kasei Kogyo (Tokyo, Japan). All chemicals were reagent grade and were used as received. All aqueous solutions were prepared with distilled water.

Instrumentation

Electrochemical measurements were done with an electrochemical analyzer BAS 100BW. A cryocooled superconducting magnet (Sumitomo Heavy Industries, Tokyo, Japan) was used for the MEP experiments, which could generate magnetic fields of up to 5 T in a 220-mm bore.

Methods

Preparation of modified electrodes

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. Sulfate-doped 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. Sulfate-doped chiral polyaniline films were prepared as follows: (+)- or (−)-camphor-10-sulfonate (CSA$^-$)-doped polyaniline films, which have the helical structures of polyaniline [7], were electropolymerized at 1.0 V in a 50-mM aniline and 0.5-M (+)- or (−)-HCSA aqueous solution. (+)- or (−)-CSA$^-$-doped polyaniline films underwent dopant-exchange from CSA$^-$ to SO_4^{2-} during successive redox processes (10 cycles) in the H$_2$SO$_4$ solution, retaining the chiral structures [20].

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

Voltammometric measurements

The polyaniline films were used as modified electrodes, and their chiral properties were examined by measuring the CVs of L-ascorbic acid (L-AA), D-isoascorbic acid (D-AA), and L-DOPA. Their molecular structures are shown in Fig. 2. The L-AA molecule has two asymmetric carbon atoms numbered as 4 and 5. While L- and D-AA have chiralities opposite each other at the carbon atom 5, they have the same chirality at the carbon atom 4. Thus, they are not enantiomers but diastereomers. L-DOPA is a kind of amino acid with a redox functional group of dihydroxyphenyl (catechol). The CVs of 20 mM L-AA and D-AA were measured on the polyaniline electrodes in a 0.5-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-DOPA were measured in a 0.05-M H$_2$SO$_4$ aqueous solution. To obtain reproducible CVs, the polyaniline films were pretreated with a five-cycle potential sweep in the range from −0.1 to 1.1 V in a 0.5-M H$_2$SO$_4$ aqueous solution. The CVs of L- and D-AA were also measured on bare Pt electrodes in 0.5-M (−)-HCSA aqueous solutions.
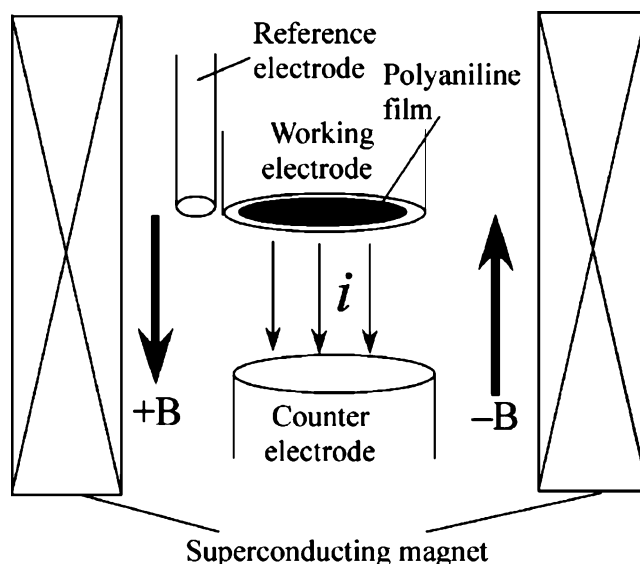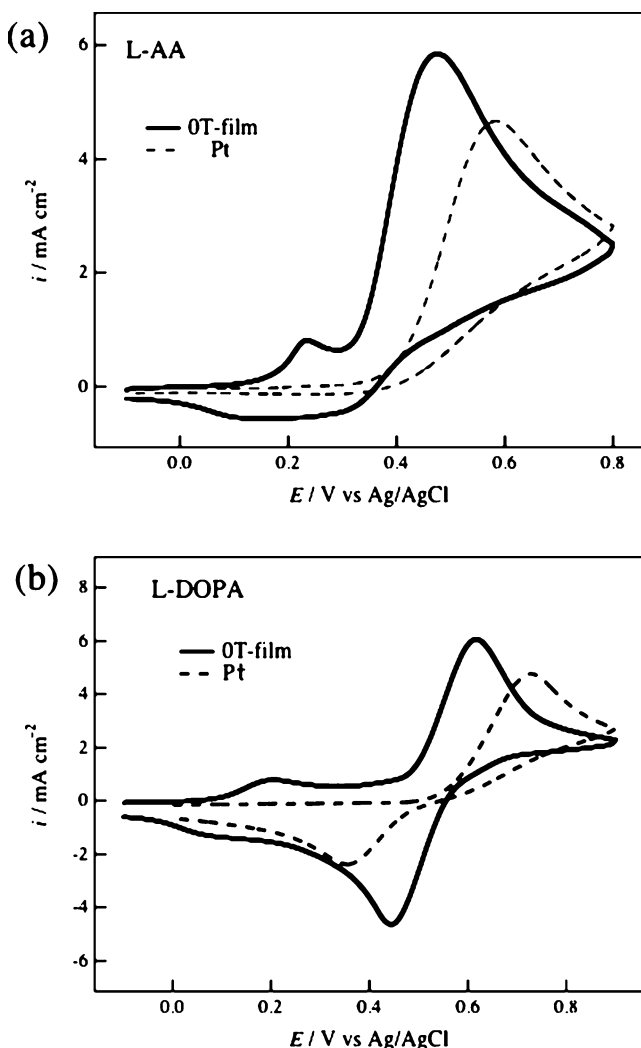

Fig. 1 Electrode configuration in the MEP process. The magnetic fields, *B*, are applied parallel (*plus sign*) or antiparallel (*minus sign*) to the faradaic currents, and they are perpendicular to the electrode surface

Fig. 2 Molecular structures of L-AA, D-AA, and L-DOPA

L-Ascorbic acid
(L-AA)

D-Isoascorbic acid
(D-AA)

L-3-(3,4-Dihydroxyphenyl)alanine
(L-DOPA)
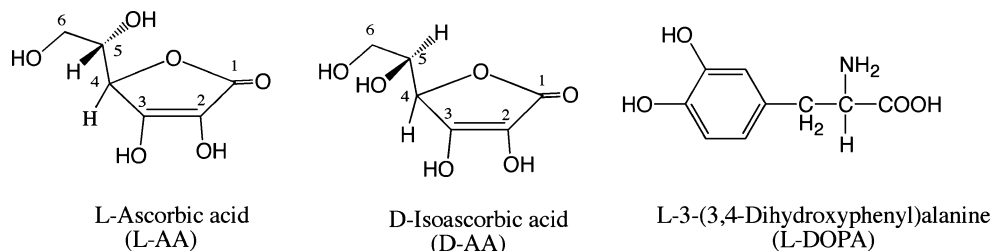
Results and discussion

Ascorbic acid is irreversibly oxidized to dehydroascorbic acid on the electrodes, and this reaction is electrocatalytic on the polyaniline film electrodes [16]. Figure 3a shows CVs of L-AA on the sulfate-doped polyaniline 0 T-film electrode and a bare Pt electrode in a 0.5-M H_2SO_4 aqueous solution. A small peak at 0.2 V in the CV on the polyaniline electrode, which is not seen in the CV on the Pt electrode,
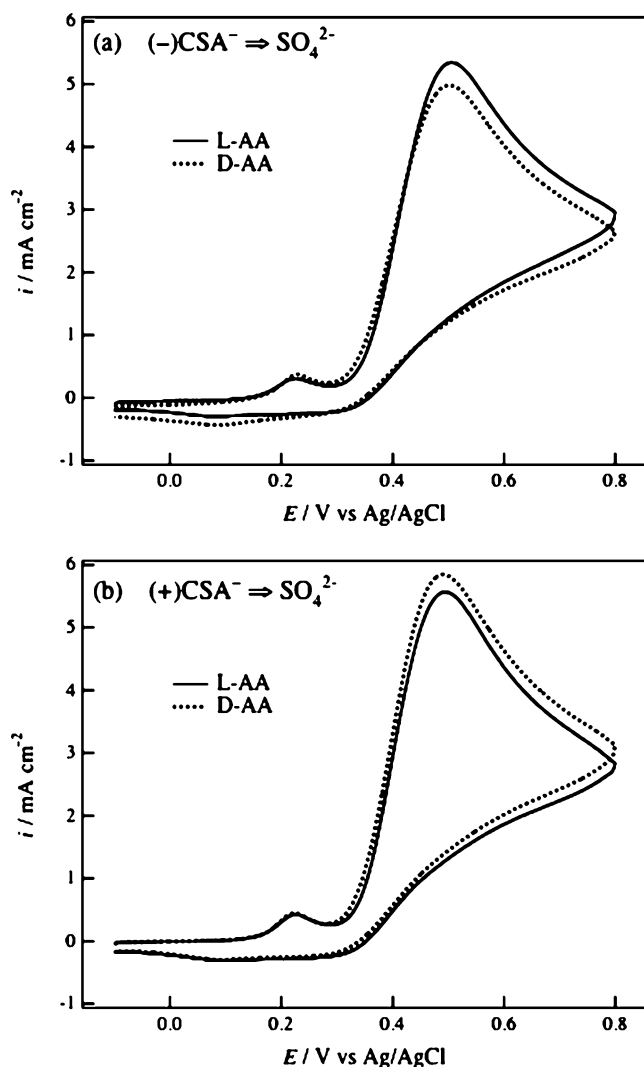
represents the oxidation of polyaniline. The oxidation of L-AA occurs at 0.4 V on the polyaniline electrode, while it occurs at a more positive potential of 0.6 V on the Pt electrode. In addition, the peak current on the polyaniline electrode is much larger than that on the Pt electrode. These facts are characteristics of electrocatalytic reactions.

Figure 3b shows the CVs of L-DOPA on the sulfate-doped polyaniline 0 T-film electrode and the Pt electrode in a 0.05-M H_2SO_4 aqueous solution. The redox reaction of L-DOPA occurs at around 0.5 V on both electrodes, where the dihydroxyphenyl group is oxidized to the *o*-benzoquinone group, and the latter is reduced to the former at the reverse potential sweep. The redox peak potential difference on the polyaniline electrode is much smaller than that on the Pt electrode. This means that the electrode reaction on the polyaniline film 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 facts indicate that the polyaniline film also plays a catalytic role for the redox reaction of L-DOPA.

It is interesting how chiral properties appear in electrochemical reactions. Ahmadi et al. investigated the voltammograms of D- and L-glucose on chiral Pt electrodes and showed that the chiral behaviors appear in both the peak potentials and the peak currents [1]. Switzer reported that the chiral behavior appears on the peak potentials in the CVs of L- and D-tartaric acids on chiral CuO electrodes [2]. On the other hand, 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 only in the electrocatalytic peak currents [3].

The CVs of L- and D-AA were examined on the sulfate-doped chiral polyaniline electrodes, which were prepared from (−)- and (+)-CSA⁻-doped polyaniline films by the dopant-exchange technique, as mentioned before. The results in Fig. 4 show that the chiral properties are not seen in the peak potentials but in the peak currents. The oxidation peak potentials of L- and D-AA are the same on both chiral polyaniline electrodes. On the other hand, L-AA shows a larger peak current than D-AA on the chiral electrode prepared from (−)-CSA⁻-doped polyaniline (Fig. 4a), and D-AA shows a larger peak current than L-

Fig. 3 CVs of **a** 20 mM L-AA in a 0.5-M H_2SO_4 aqueous solution and **b** 20 mM L-DOPA in a 0.05-M H_2SO_4 aqueous solution, on the polyaniline 0 T-film electrode and a bare Pt electrode

Fig. 4 CVs of 20 mM L- and D-AA in a 0.5-M H_2SO_4 aqueous solution on the chiral sulfate-doped polyaniline electrodes **a** prepared from (−)-CSA⁻-doped polyaniline and **b** prepared from (+)-CSA⁻-doped polyaniline

AA on the opposite chiral electrode (Fig. 4b). These results indicate that the helical polyaniline film possess the ability of chiral recognition for L- and D-AA.

Figure 5 shows the CVs of L- and D-AA on the (a) sulfate-doped polyaniline 0 T-film, (b) +5 T-film, and (c) −5 T-film electrodes in a 0.5-M H_2SO_4 aqueous solution. The CVs of L-AA and D-AA are coincident with each other on the 0 T-film electrode. The difference is clearly seen in the oxidation peak at 0.4 V on the MEP film electrodes. The peak current of L-AA is larger than that of D-AA on the +5 T-film electrode (Fig. 5a). The result is the opposite on the −5 T-film electrode; the peak current of D-AA is larger than that of L-AA (Fig. 5b). The oxidation peak potentials of L- and D-AA are the same on both MEP film electrodes. These chiral behaviors of L- and D-AA on the MEP film electrodes are quite similar to those on the helical polyani-
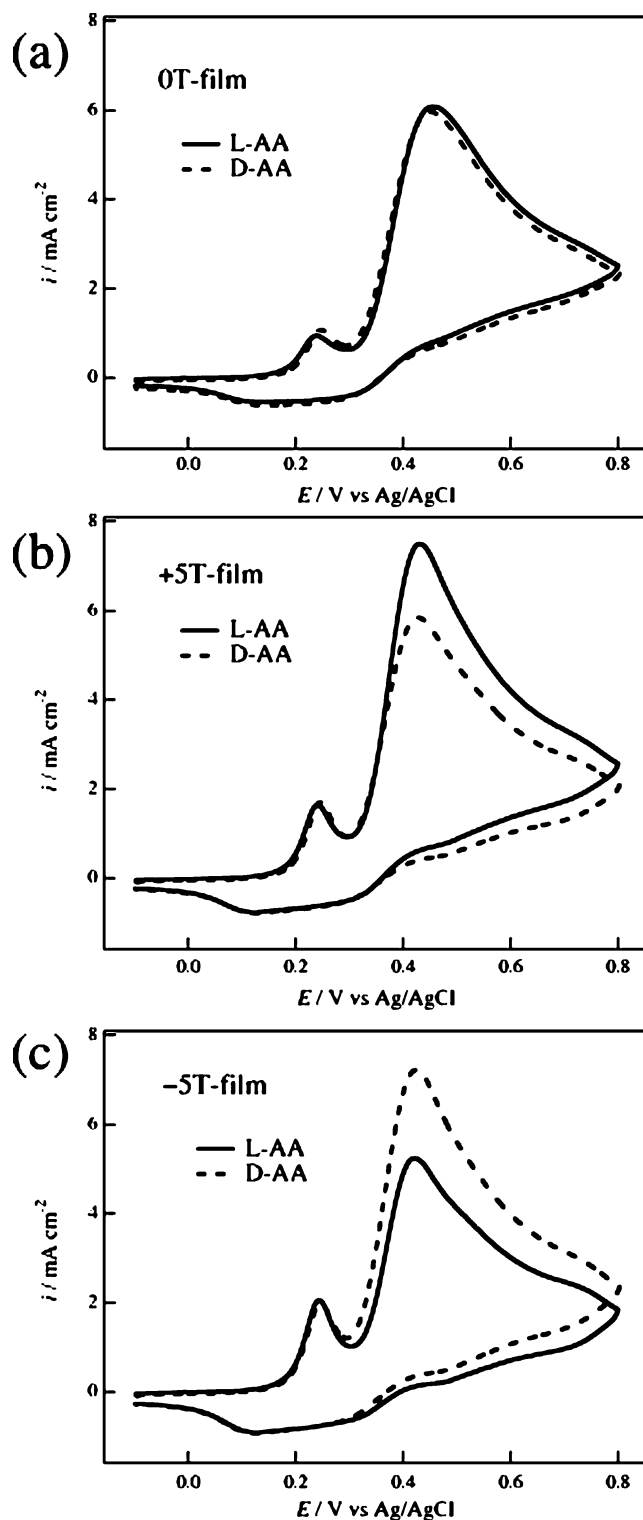
Fig. 5 CVs of 20 mM L- and D-AA in a 0.5-M H_2SO_4 aqueous solution on **a** the sulfate-doped polyaniline 0 T-film, **b** the +5 T-film, and **c** the −5 T-film electrodes

line electrodes, as shown in Fig. 4. This suggests that the MEP polyaniline films also have helical structures.

To examine the electrochemical chiral properties without an electrocatalytic process, the CVs of L- and D-AA were

measured on a bare Pt electrode in an aqueous solution containing 0.5 M (−)-HCSA as an optically active supporting electrolyte. It is expected that the electrode surface adsorbed by the (−)-CSA$^-$ anions would serve as a chiral electrode. The result is shown in Fig. 6. The oxidation peak currents of L- and D-AA are almost the same, but the peak potentials are different, ca. 0.85 V for L-AA and 0.73 V for D-AA. This result is similar to that of tartaric acids on chiral CuO electrodes [2].

Figure 7a shows the CVs of L-DOPA on the +5 T-film and −5 T-film electrodes in a 0.05-M H_2SO_4 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 −5 T-film electrode are larger than those on the +5 T-film electrode. Figure 5b shows the CVs of achiral catechol on the two electrodes, and the two CVs are coincident with each other. Recently, Nagasaka et al. examined the CVs of L- and D-DOPA on chiral electrodes with a self-assembled monolayer of homocyctein and reported that the chiral behavior appears in the peak potential difference, namely, the reversibility of the electrode reactions [21].

In both cases of ascorbic acids and L-DOPA, the chiral behavior appears in the CV peak currents on the chiral and MEP polyaniline electrodes, and it appears in the peak potentials on the Pt electrodes adsorbed by optically active molecules. The polyaniline electrodes play an electrocatalytic role in both electrode reactions, as is shown in Fig. 3. The electrocatalytic process includes specific adsorption, in which the molecular conformation is fixed on the polyaniline film. This could be the reason why the CV peak potentials on the polyaniline electrodes are independent of the chirality. Similar chiral behavior was observed in the electrocatalytic oxidation of 1-phenylethanols on chiral self-assembled monolayer electrodes [3].
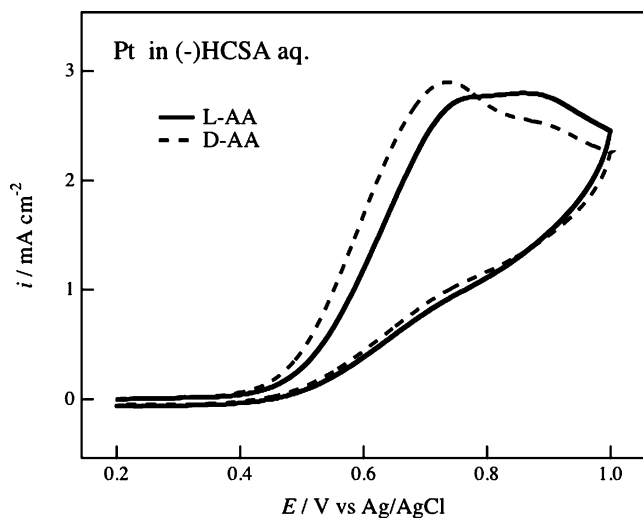
Fig. 6 CVs of 20 mM L- and D-AA on a Pt electrode in a 0.5 M (−)-HCSA aqueous solution
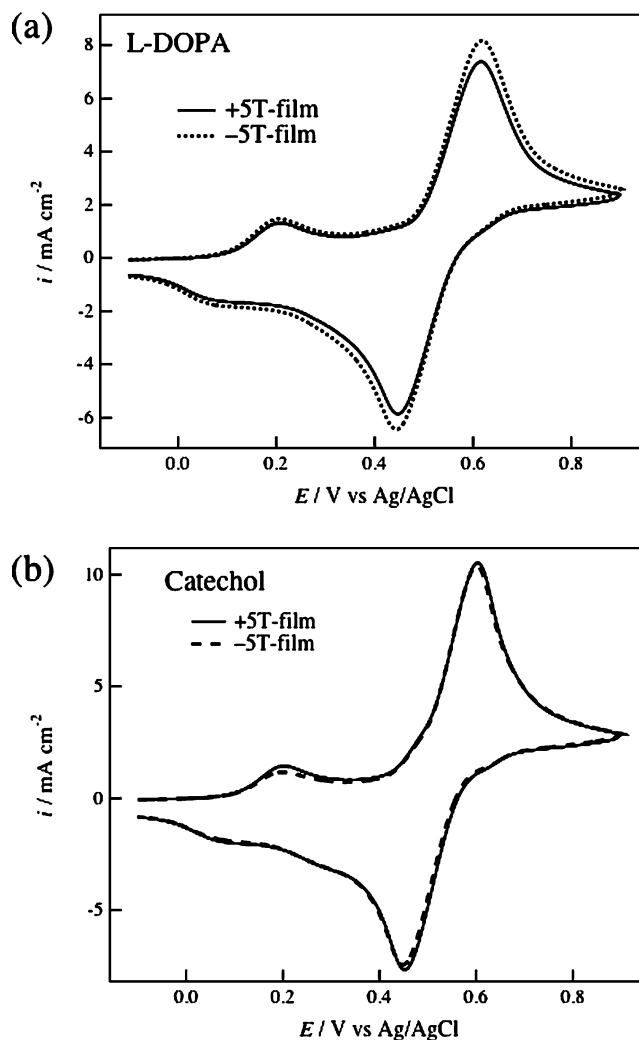
Fig. 7 CVs of **a** 20 mM L-DOPA and **b** 20 mM catechol in a 0.05-M H_2SO_4 aqueous solution on the +5 T-film and −5 T-film electrodes

Conclusion

We have shown that the sulfate-doped MEP and chiral polyaniline electrodes exhibit chiral recognition for ascorbic acids and L-DOPA in their electrochemical reactions. The chiral electrochemical behavior does not appear in the CV peak potentials but appears in the peak currents on the polyaniline electrodes. This result is different from that on the Pt electrodes adsorbed by optically active molecules. The electrocatalytic process on the polyaniline electrodes is considered to be responsible for such chiral electrochemical behavior.

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