Electrocatalytic Properties of a Modified Electrode with an Asymmetric Nickel(II)-Tetraaza[14]annulene Complex

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Modified electrodes are made by incorporting proper modifiers on electrode surfaces. They are promising for minimizing overpotential, enhancement of selectivity, improvement of sensitivity, and prevention of electrode fouling.[1,2] A large number of tetraaza macrocyclic ligands containing various metals have received much attention due to the usefulness as models for porphyrins and corrin rings in biological systems.[3-5] Many of these complexes have been found to be effective catalysts in the solid state for various substrates such as CO_2, O_2, olefin, alcohol, NO, N_2O, NO_3^-, and dithiodipropionic acid.[6-10]

Most of tetraaza macrocyclic complexes reported have symmetric structure. The macrocyclic complex such as Ni(II)-5,7,12,14-tetramethyldibenzo[b,i] [1,4,8,11]tetraaza-[14]annulene complex can be deposited on the electrode surface by oxidative electropolymerization and the film of which catalyzes the reduction of CO_2.[11] We have synthesized new Ni(II)-tetraaza tetraaza[14]annulene complexes which have asymmetric structures.[12] The asymmetric complexes are expected that the electrochemical characteristics are similar to those of the symmetric ones. Hence we intended to apply the electrochemical characteristics of the newly synthesized complexes to the electrocatalytic analysis of substrates.

In this paper we describe electrochemical catalytic properties of the asymmetric Ni(II)-macrocyclic complex containing dianionic benzotetraaza[14]annulene ligand. The glassy carbon electrodes modified with the asymmetric Ni(II)-tetraaza[14]annulene complex (polymer modified GC electrode) is applied to the electrocatalytic detection for the reduction of oxygen and the oxidations of oxalate and *L*-ascorbic acid. The stability and the effect of the polymer thickness on the responses of the electrodes are also described.

Experimental Section

Preparation of Chemicals. 1,5,8,12-Tetraaza-2,4,9,11-tetramethylcyclotetradecinatonickel(II) was prepared as reported previously.[12] The structure of this complex is shown in Figure 1. Tetraethylammonium perchlorate (TEAP) was prepared and purified as described by Kolthoff and Coetzee.[13] Tetrabuthylammonium perchlorate (TBAP) was purchased from Nakalai Chemicals and used without further purification. Sodium oxalate and *L*-ascorbic acid were bought from Junsei Chemicals and Sigma, respectively. Acetonitrile (AN) was purified according to published procedures.[14] All aqueous solutions were prepared with deionized water purified using a Millipore Milli-Q water system (Bedford, MA).

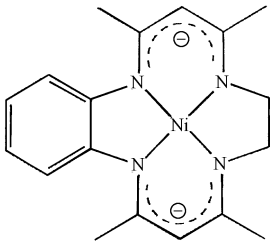

Figure 1. Structure of asymmetric Ni(II)-tetraaza[14]annulene complex studied in this work.

Electrochemical Measurements. Cyclic voltammetry was performed using an EG&G Princeton Applied Research (PAR) Model 174A Polarographic Analyzer and a Bioanalytical Systems (BAS) 100B. For the electrochemical measurements, a three-electrode system consisting of the GC electrode as a working electode, Ag/Ag^+ (0.1 M $AgNO_3$ in AN) as a reference electrode, and a platinum wire as an auxiliary electrode was used. For the investigation of electrocatalytic activity of the modified electrodes, a saturated calomel electrode (SCE) was used as a reference electrode. Electrochemical measurement was carried out at 25.0 ± 0.2 °C for the reduction of dioxygen and the oxidation of oxalic acid, and at 45.0 = 0.2 °C for the oxidation of *L*-ascorbic acid. The constant temperature was achieved by using a Fisher Scientific Model 7305 Digital Circulator.

Modification of Electrodes. In order to fabricate the polymer modified GC electrode, glassy carbon rods (BAS model MF-1000, 2.0 mm in diameter) were employed. Prior to its modification, the GC electrode was polished with alumina slurry (0.05 μm, Buehler) on a microcloth pad, washed with deionized water, and then dried. After polishing procedure, residual polishing material was removed by sonication for one min, and then dried. Electropolymerization of Ni(II)-tetraaza[14]annulene complex was carried out by cycling potential between +1.0 and −2.5 V at 200 mV/s in freshly prepared AN solutions containing 5.0×10^{-4} M Ni(II)-tetraaza[14]annulene complex and 5.0×10^{-2} M TEAP under nitrogen atmosphere. After 9 cycles, the electrode was removed from the solution, rinsed with water, and dried in air.

Results and Discussion

Cyclic Voltammograms and Electropolymerization of Ni(II)-Tetraaza[14]annulene. Figure 2(a) shows a cyclic voltammogram of 5.0×10^{-4} M Nickel(II)-tetraaza[14]annu-

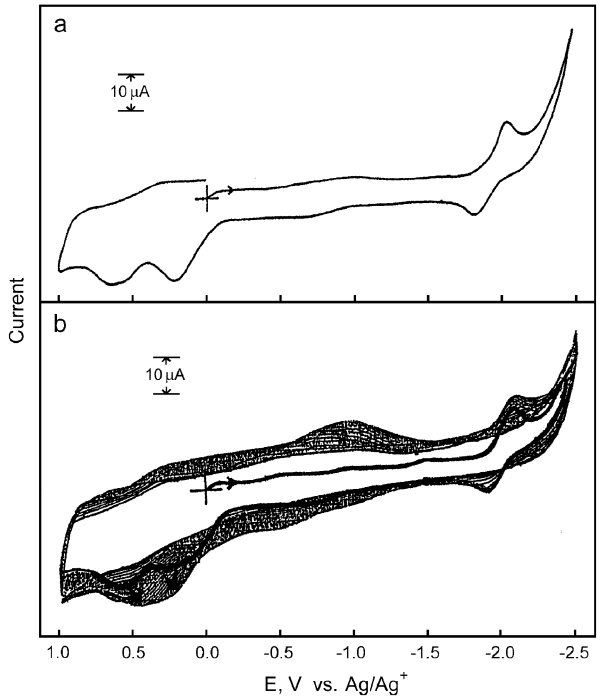

Figure 2. Cyclic voltammogram of 5.0×10^{-4} M 1,5,8,12-tetraaza-2,4,9,11-tetramethyl cyclotetradecinato-Ni(II) complex in 5.0×10^{-2} M TEAP-AN solution (a) and cyclic voltammogram of the complex polymerized at a GC electrode by repeated potential scans between −2.4 and 1.0 volt (b); scan rate, 200mV/s.

lene in AN containing 5.0×10^{-2} M TEAP obtaioned by scaning the potential region from +1.0 to −2.4V *vs.* Ag/Ag^{+}. As shown in Figure 2(a), the complex exhibits two known successive irreversible oxidation peaks (E_{pa}=0.24 and 0.62V) due to the oxidation of the macrocycle ligand and a considerable reversible peak (E_{pc}= −2.0V and E_{pa}= −1.8V) of nickel ion. The cyclic voltammogram of the complex used in this study has similar shape with that for the most symmetric tetraaza[14]annulene complex.[15,16]

Figure 2(b) shows the change of the cyclic voltammograms of the complex with the increase of the number of scans in the potential range from +1.0 to −2.4V *vs.* Ag/Ag^{+}. On increasing the number of scans, the two oxidation peaks start to grow, then combine to one oxidation peak, and finally disappear after 20 scans. In order to determine the number of electrons involved in each oxidation step, the complex were electrolyzed in AN at the more positive potential by 0.2V than that of each oxidation wave. We found that the electron number involved in each oxidation step was one. From this result, we concluded polymer is formed at electrode surface via radical cation and dication. The peak of the nickel ion is observed in the negative potential side up to 10 scans, but the peak disappears after 10 scans. Since this result was also observed for the symmetric tetraaza[14]annulene complex,[17-19] the mechanism for the electropolymerization of the asymmetric complex is thought to be similar to that of the symmetric one.

Electrocatalysis Properties of Polymer Modified GC Electrode. The electrocatalytic activity of the polymer modified GC electrode was examined for the reduction of oxygen and the oxidations of oxalate and *L*-ascorbic acid by cyclic voltammetry. Figure 3 shows cyclic voltammograms for the electrocatalytic effect of oxygen, oxalate and *L*-ascorbic acid obtained with bare and polymer modified electrodes. Figure 3(a) shows that the peak potential of oxygen reduction is shifted positively about 200 mV when the polymer modified electrode is used. The reduction peak current is also 13 μA higher than that for the bare electrode. For the oxidation of oxalate, the modified electrode gives a high oxidation peak while the bare electrode does not give any peak (Figiue 3(b)). For the oxidation of *L*-ascorbic acid, the anodic peak potential obtained with the modified electrode is shifted about 200 mV more negative and its peak currenet increases 33%(20 μA) higher than that for the bare electrode. The peak current or peak potential provides a measure of the catalytic activity and the phenomena observed here are clear evidences of the catalytic effect of the GC electrode modified with an asymmetric Ni(II)-tetraaza[14]annulene complex.

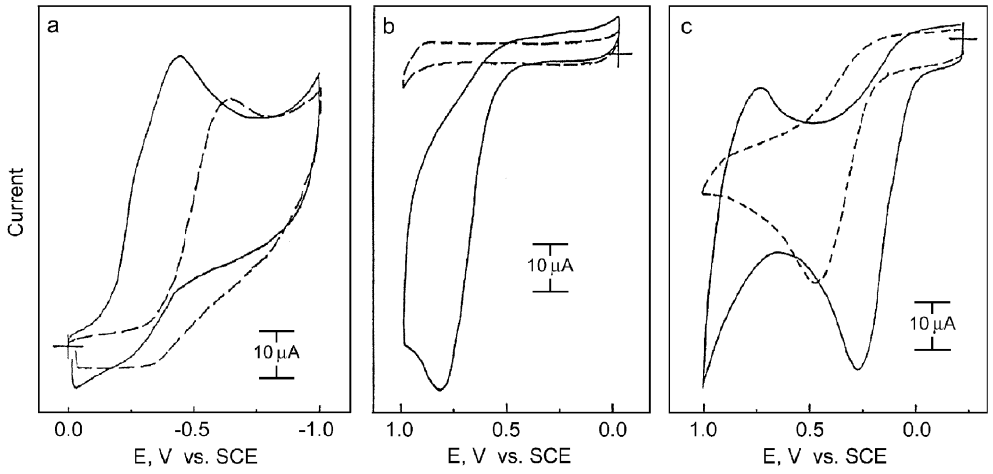

Figure 3. Electrocatalytic effect of the polymer modified GC electrode for substrates: oxygen in 0.05 M KCl (a), 5.0×10^{-4} M oxalate in 0.05 M KCl (b) and 2.0×10^{-3} M *L*-ascorbic acid in pH 7.0 (c); scan rate, 100 mV/s. Dashed lines are for bare glassy carbon electrodes and solid lines are for the polymer modified GC electrode.

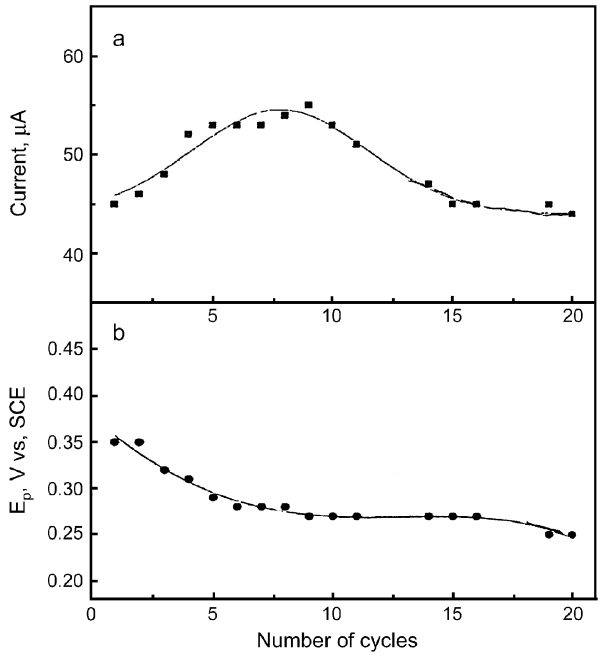

Figure 4. Dependence of cycling numbers on oxidation peak current (a) and peak potential (b) for 2.0×10^{-3} M *L*-ascorbic acid with a polymer-modified electrode of complex: pH. 7.0; temperature, 45 °C; scan rate, 100 mV/s.

Since the nickel ion peaks remain in the negative potential side up to 10 scans (Figure 2(b)), the catalytic activity of the polymer modified electrode is thought to be due to the catalytic function of nickel metal in various oxidation-reduction reactions.

Response Dependence of Polymer Modified GC Electrodes. The effect of polymer thickness on the electrocatalytic response of the polymer modified electrode was examined for *L*-ascorbic acid by using different numbers of potential cycling to electropolymerize. The plots of peak current and anodic peak potential of *L*-ascorbic acid versus number of cycles are shown in Figure 4. On increasing the number of cycles, the peak potential was rapidly shifted about 200 mV to negative potential up to about 9 cycles and then remained constant. The peak current was found to be constant in the range from 4 to 10 cycles within the experimental error of ± 3%. The gradual increase of the peak current up to 4 cycles is obviously due to the increase of the concentration of polymerized complex. The current decrease after 10 cycles may be attributed to the increase of electric resistance due to the increase of the polymer thickness.

The effect of temperature in the range of 5-50 °C on the response of the polymer modified GC electrode for *L*-ascorbic acid in pH 7.0 solution was investigated. The peak current rapidly increased up to about 45 °C and was constant afterwards. Since we observed that renewal of the electrode surface was relatively difficult and the possible number of continuous uses of the electrode was reduced at temperature over 45 °C, the appropriate temperature to use this electrode is 45 °C.

The stability of the polymer modified GC electrode for substrate was examined. The result showed that the electrode could be used up to 7 times for the determination of *L*-ascorbic acid.

The results obtained in this study shows that an electrode can be easily modified with the asymmetric Ni(II)-tetraaza[14]annulene complex by cycling the potential in a constant potential range. Since a small amount of modifier is used and the automation in the fabrication of a small electrode is possible, this method is suitable for the electrode to used in a flow injection analysis system. The electrocatalytic ability observed for dioxygen, oxalate, and *L*-ascorbic acid indicates that this type of electrode can be applied to the amperometric determination of these compounds.

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