Determination of L-Ascorbate by Electrocatalytic Oxidation on 1,5,8,12-Tetraaza-2,4,9,11-tetramethylcyclotetradecanickel(II) Polymer Modified Glassy Carbon Electrode

Zun U. BAE[†], Jeong H. LEE, Hye Y. CHANG and Sang H. LEE

Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea

Keywords L-Ascorbate, electrocatalytic oxidation, 1,5,8,12-tetraaza-2,4,9,11-tetramethylcyclotetradecanickel(II), polymer modified glassy carbon electrode

A variety of examples of the electrochemical determination of L-ascorbate using enzymes have been proposed.¹⁻³ However, these methods suffer difficulties in the fabrication of electrodes and automatic analysis. Recently, the use of chemically modified electrodes for sensor development has received considerable attention.^{4,5} In principle, the development of chemically modified electrodes provides a means for improving the performance of solid electrodes by incorporating catalytic sites at the electrode-solution interface. They are very promising for minimizing the overpotential effect, enhancing the selectivity, improving the sensitivity and preventing electrode fouling. Some examples have been reported for the determination of alcohols, alditols, aldehydes, amines and amino acids.⁶ Tetraaza macrocyclic ligands have been used as an interesting class of synthetic ligands.⁷⁻¹² A large number of their derivatives containing various metals have received much attention as models for biological systems, such as porphyrins and corrin rings.¹³ For some time, our work has concentrated on the synthesis of new asymmetric nickel(II)-macrocyclic complexes, and these efforts have been aimed at using the resulting polymer modified electrodes as sensors.¹⁴

In the present work, we prepared an asymmetric Ni(II)-macrocyclic polymer-modified glassy carbon electrode by cyclic voltammetric scanning in an acetonitrile solution containing the complex and a supporting electrolyte. The optimum analytical conditions for pH, temperature and polymer film thickness were studied. The calibration curve obtained using the polymer-modified electrode was compared with that obtained by using a bare glassy carbon electrode.

Experimental

Reagents and instrumentation

1,5,8,12-Tetraaza-2,4,9,11-tetramethylcyclotetradecanickel(II) was prepared as previously reported by

the present group.¹⁴ Tetraethylammonium perchlorate (TEAP) was prepared and purified as described by Kolthoff *et al.*¹⁵ Acetonitrile (AN) was distilled according to a published procedure.¹⁶ L-Ascorbate was bought from Sigma. All aqueous solutions were prepared with deionized water purified using a Millipore Milli-Q water system (Bedford, MA).

Cyclic voltammetry and differential pulse voltammetry were performed using a EG&G Princeton Applied Research (PAR) Model 174A polarographic analyzer and a PAR Model 175 universal programmer. Voltammograms were recorded on a PAR Model RE0091 X-Y recorder. In order to modify a glassy carbon electrode, a three-electrode system consisting of a glassy carbon electrode (GCE), an Ag/Ag⁺ (0.1 M AgNO₃ in AN) electrode (EG&G Model 19367) and a platinum wire for a working, a reference and an auxiliary electrode, respectively. For the determination of L-ascorbate, a saturated calomel electrode (SCE, EG&G Model K0077) was used as a reference electrode. A cylinder-type electrochemical cell (EG&G Model G0060) was used for this experiment.

Preparation of glassy carbon modified electrode

In order to fabricate a modified GCE, high-purity glassy carbon rods (Tokai carbon Co., 3.0 mm in diameter) were employed as supports. Prior to its modification, the GCE was polished with 0.05 μm α -alumina suspension on a microcloth pad (Buehler), washed with water and then dried. After a polishing procedure, the residual polishing material was removed by sonication in an acetonitrile bath for 1 min and then dried. Electropolymerization of Ni(II)-macrocyclic complexes was carried out by potential cycling of the clean GCE between -2.0 and $+1.0$ V at 100 mV s^{-1} in freshly prepared acetonitrile solutions containing 5.0×10^{-4} M Ni(II)-macrocyclic complex and 5.0×10^{-2} M TEAP under a nitrogen atmosphere. After 9 potential cycles, the electrode was removed from the solution, rinsed with water, and dried in air. A deep-blue polymer film was then visible on the electrode surface.

[†] To whom correspondence should be addressed.

Fig. 1 Cyclic voltammograms of 2.0×10^{-3} M L-ascorbate at a bare GCE (a) and a polymer-modified GCE (b) in pH 7.0 Tris-HCl buffer solution: dotted line, blank solution; temperature, 45°C ; scan rate, 100 mV s^{-1} .

Fig. 2 Differential pulse voltammograms of 7.0×10^{-4} M L-ascorbate (a) and blank (b) at a polymer-modified GCE in pH 7.0 Tris-HCl buffer solution: temperature, 45°C ; pulse amplitude, 50 mV; pulse interval, 1 s; scan rate, 5 mV s^{-1} .

Results and Discussion

Cyclic voltammogram of L-ascorbate

Figure 1 shows cyclic voltammograms of 2.0×10^{-3} M L-ascorbate in a 0.1 M KCl solution recorded with a bare GCE (a) and a polymer-modified electrode (b). The cyclic voltammogram displayed by the dotted line is for a blank solution. For the polymer-modified electrode, the peak potential of L-ascorbate oxidation shifted by about 200 mV to the negative direction, and the peak current increased by $20 \mu\text{A}$ compared with those for the bare GCE. The observed peak was confirmed to be due to the oxidation of L-ascorbate on the basis of an observed increase in the peak current upon increasing the concentration of L-ascorbate. Increasing the peak current and a positive shift of the peak potential provided a measure of the catalytic activity. The phenomena observed here show clear evidence of a catalytic effect of the GCE modified with an asymmetric Ni(II)-macro-cyclic complex.

Optimum analytical conditions

The effect of the pH on the cyclic voltammogram of 2.0×10^{-3} M L-ascorbate was examined over the pH range from 6.0 to 8.0. The maximum current was slightly increased up to pH 6.7, and then abruptly increased at about pH 7. The current was gradually diminished afterwards. Therefore, pH 7.0 was used for the optimum pH condition for determining L-ascorbate.

The effect of the temperature on the peak currents of the cyclic voltammograms for 2.0×10^{-3} M L-ascorbate in a pH 7.0 solution over the temperature range from 5 to 50°C was studied. The peak current was rapidly increased up to about 45°C , and then slightly increased afterwards. Since we found that renewal of the electrode surface was relatively difficult, and the possible

number of continuous uses of the electrode was reduced at temperatures over 45°C , a temperature of $45.0 \pm 0.1^\circ\text{C}$ was chosen for the optimum temperature condition.

The effect of the polymer thickness on the peak current was investigated by recording cyclic voltammograms of 2.0×10^{-3} M L-ascorbate with increasing the number of scan cycles. Upon increasing the number of scan cycles, the peak potential rapidly shifted to a lower potential up to about 10 cycles, and then remained constant. The maximum peak current was obtained when the number of cycles was 9. The gradual increase in the peak current up to 9 cycles was obviously due to an increase in the complex concentration. The current decrease after maximum current might be attributed to an increase in the electric resistance due to an increase in the polymer thickness. We used a polymer-modified electrode obtained with 9 scan cycles for the determination of L-ascorbate.

The change in the maximum current for 2.0×10^{-3} M L-ascorbate with the number of uses of the electrode was examined, and the results showed that the electrode could be used up to 7 times. After using 7 times, the surface of the electrode was polished with alumina and coated with an electropolymerized polymer film to be used again.

Calibration curve for determining L-ascorbate

In order to prepare a calibration curve to determine L-ascorbate, differential pulse voltammetry was employed. Figure 2 shows differential pulse voltammograms of 7.0×10^{-4} M L-ascorbate (a) and blank (b) in a pH 7.0 Tris-HCl buffer solution obtained with a polymer-modified electrode. The experimental conditions were 45°C , 50 mV and 5 mV s^{-1} for the temperature, pulse amplitude and scan rate, respectively. Figure 3

Fig. 3 Calibration curves for L-ascorbate at a polymer-modified electrode (■) and an unmodified GCE (●) obtained by differential pulse voltammetry: pH, 7.0; temperature, 45°C; pulse amplitude, 50 mV; pulse interval, 1 s; scan rate, 5 mV s⁻¹.

shows the calibration curves for determining L-ascorbate when a bare GCE and a polymer-modified GCE were used. For the bare GCE, the linear range and the detection limit were 4.0×10^{-4} M – 9.0×10^{-2} M and 5.0×10^{-5} M, respectively. On the other hand, when a polymer-modified electrode was used, the linear range and the detection limit were 1.0×10^{-7} M – 5.0×10^{-4} M and 8.8×10^{-8} M, respectively. The correlation coefficient in the linear range for this plot was 0.999. The present results gave a wider linear range and a lower detection limit than those obtained using the poly(indole-5-carboxylic acid)-modified GCE by Somasundrum *et al.*¹⁷, where the linear range was 2.0×10^{-5} M – 1.5×10^{-4} M and the detection limit was 1.0×10^{-6} M.

References

1. R. Stevanato, L. Avigliano, A. Finazzi-Agro and A. Rigo, *Anal. Biochem.*, **149**, 537 (1985).
2. G. M. Greenway and P. Ongomo, *Analyst* [London], **115**, 1297 (1990).
3. R. Q. Thompson, *Anal. Chem.*, **59**, 119 (1987).
4. C. C. Chen, C. Wei and K. Rajeshwar, *Anal. Chem.*, **65**, 2437 (1993).
5. Y.-H. Tse, P. Janda, H. Lam and A. B. P. Lever, *Anal. Chem.*, **67**, 981 (1995).
6. T. R. I. Cadaldi, D. Centonze and A. Guerrieri, *Anal. Chem.*, **67**, 101 (1995).
7. F. V. Lovecchio, E. S. Gore and H. Buch, *J. Am. Chem. Soc.*, **74**, 109 (1974).
8. D. A. Ganzl and R. R. Durand, *J. Chem. Soc., Chem. Commun.*, 697 (1986).
9. A. Deronzier and M.-J. Marques, *Electrochim. Acta*, **39**, 1377 (1994).
10. C. L. Bailey, R. D. Bereman, D. P. Rillema and R. Nowak, *Inorg. Chem.*, **25**, 933 (1986).
11. P. J. Hochgesang and R. D. Bereman, *Inorg. Chim. Acta*, **149**, 69 (1988).
12. C. L. Bailey, R. D. Bereman, D. P. Rillema and R. Nowak, *Inorg. Chim. Acta*, **116**, 45 (1986).
13. C. Bernard, J. P. Giselsbrecht, M. Gross, E. Vogel and M. Lausmann, *Inorg. Chem.*, **33**, 2393 (1994).
14. Y. C. Park, Z. U. Bae, S. S. Kim and S. K. Baek, *Bull. Kor. Chem. Soc.*, **16**, 287 (1995).
15. I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).
16. J. F. Coetzee, *Anal. Chem.*, **34**, 1139 (1962).
17. M. Somasundrum and J. V. Bannister, *J. Chem. Soc., Chem. Commun.*, 1629 (1993).

(Received December 10, 1998)

(Accepted April 5, 1999)