— Article —

In Situ Observation of Ferroin and Ferriin in Vicinity of ITO Electrode Surface by Slab Optical Waveguide Spectroscopy

Kouji TAKAHASHI* and Fumiyo KUSU

Department of Analytical Chemistry, School of Pharmacy, Tokyo University of Pharmacy and Life Science (1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan)

Received August 29, 2005 ; Accepted October 31, 2005

Slab optical waveguide (SOWG) spectroscopy was carried out for an *in situ* observation of ferroin and ferriin formed at an electrode/solution interface during electrolysis on an indium-tin oxide (ITO) electrode. A new spectroelectrochemical cell for SOWG spectroscopy was developed to observe *in situ* absorption spectra of species in the vicinity of the ITO electrode surface. A cyclic voltammogram (CV) of 5 mmol·dm⁻³ ferroin in 1 mol·dm⁻³ potassium nitrate aqueous solution was obtained as the potential swept from +1.4 to +0.4 V and then from +0.4 to +1.4 V. Furthermore a cathodic and anodic peaks appeared at +0.82 and +0.92 V, respectively. The SOWG spectra were obtained every 0.05 mV during the sweep. The SOWG spectra at the potential of +0.4 and +1.4 V were identical to the UV-VIS spectra of ferroin and ferriin, respectively. The concentration profiles near the electrode during cyclic voltammetry of ferroin were discussed based on the absorbance at 510 and 650 nm on SOWG spectra. Furthermore, *in situ* real-time monitoring of absorption during potential step experiment of ferroin was made at various incident angles from 70 to 77° using SOWG spectroscopy.

Key Words : Slab Optical Waveguide, Ferroin, Ferriin, Spectroelectroscopy

1 Introduction

Slab optical waveguide (SOWG) spectroscopy is a powerful technique for *in situ* observation of chemical species present at the liquid/solid interface.¹⁻⁵⁾ The technique has widely been applied to study adsorption behavior especially on an electrode surface. Many reports on the adsorptions of cytochrome c, myoglobin and hemoglobin on quartz and glass surfaces exhibited excellent results when using SOWG spectroscopy equipped with a thin-layer cell of small inner volume.¹⁻⁴⁾ For *in situ* observation of solution species in the vicinity of an electrode surface, the SOWG has been combined with various spectroelectrochemical methods such as optically transparent thin-layer electrode method (OTTLE),^{6, 7)} long optical path length thin-layer cell method (LOPTLC),⁸⁾ internal reflection spectro-electrochemistry,⁹⁾ and infrared spectroscopy (IRS).¹⁰⁾ In fact, the OTTLE, LOPTLC, and IRS were only applicable to thin-layer electrochemical cells, and not always sensitive and selective to the solution species present on the surface. Therefore, it is difficult to examine mass transfers of solution species during electrolysis by cyclic voltammetry or potential step method.

We have developed a bulk-type electrochemical cell for SOWG spectroscopy and applied it into both the measurement of electrochemical reactions and the adsorption behaviors of methylene blue on an indium-tin oxide (ITO) electrode.¹¹⁾ When light transmits from quartz coated with ITO (*i.e.*, a media with high refractive index) into an electrolyte solution (*i.e.*, a media with low refractive index) at a certain incident angle, it will be totally reflected at the interface, and results in an evanescent wave, which exponentially decreases along the interface in the electrolyte solution. Only species near the electrode sur-

face, usually within a layer less than 100 nm in thickness, can interact with the light in the evanescent field. By changing the angle of incident light, the penetration depth of an evanescent wave can be changed and thus the monitoring distance from the electrode surface may be controlled. According to the above principle, a concentration depending on the distance from the electrode surface could be measured using the SOWG spectroscopy equipped with the bulk-type electrochemical cell. The cell might be capable of examining the diffusion-controlled electrochemical reactions of the sample whose absorption spectrum exhibits in visible region. In this study, a new bulk-type electrochemical cell for use in SOWG spectroscopy was developed and SOWG spectroscopy with the cell was applied to the analysis of the electrochemical behavior of a Tris (1,10-phenanthroline) iron(II) (ferroin)/Tris (1,10-phenanthroline) iron(III) (ferriin) system during cyclic voltammetry and controlled potential electrolysis.

2 Experimental

2.1 Chemicals

Ferroin solution (15 g·dm⁻³) potassium nitrate (>99.5%) were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used without further purification. Deionized and distilled water was used throughout.

2.2 SOWG spectroelectrochemical cell and SOWG spectrometry system

The SOWG spectroelectrochemical cell developed is shown in Fig. 1. A quartz plate (15 mm × 65 mm × 1.0 mm, edge angle: 60°), which was coated with an ITO (Atock, Ibaraki, Japan), was used as the SOWG. The

Fig. 1 Schematic diagrams of the slab optical waveguide (SOWG) spectroelectrochemical cell.

SOWG was mounted on the cell and the ITO coated side was in contact with an electrolyte solution in a polyacetal container (30 mm × 10 mm × 3.0 mm, cell volume 0.9 ml) and served as the working electrode. The cell was set in a SOWG spectrometry system (SIS-50, System Instruments, Tokyo, Japan). A white light beam coming from a Xe lamp light source entered into the edge of the quartz plate, traveled by internal reflection through the quartz, and exited from the other edge of the plate. The intensity of the transmitted light beam was measured by the photodiode array detector of the SOWG system. Both edges of the glass plate were at an angle of 60°. The incident angle of the light beam from the quartz plate with ITO to an electrolyte solution was available within 65 and 79° using the cell and system.

2.3 Cyclic voltammetry (CV) and potential step method

CV and potential step method were performed in the SOWG spectroelectrochemical cell with conventional methods. The working electrode was the ITO coated glass plate, the counter electrode was platinum wire, and the reference electrode was a silver/silver chloride electrode (Ag/AgCl). Potential to the working electrode was applied with a potentiostat (HAB-151, Hokuto Denko, Tokyo, Japan). When CV was performed, the electrode potential was scanned at a rate of 0.01 V/s and the initial potential was +1.4 V vs. Ag/AgCl.

3 Results and Discussion

3.1 Simultaneous measurements of cyclic voltammograms and SOWG spectra for ferriin/ferriin system

The ferriin/ferriin system, shown in Fig. 2, was chosen as a simple electrochemical redox couple without adsorption and/or chemical reactions. Cyclic voltammetry and SOWG spectrometry of ferriin were performed. Figure 3 shows the cyclic voltammogram (Fig. 3A) and SOWG spectra (Fig. 3B and C) of 5.0 mmol · dm⁻³ ferriin in 1 mol dm⁻³ potassium nitrate aqueous solution. When the potential was swept from +1.40 to +0.40 V and then from +0.40 to +1.40 V, a cathodic peak and an anodic peak appeared at +0.82 and +0.92 V, respectively. The mid potential of +0.87 V was essentially correspondent with the standard electrode potential for ferriin/ferriin couple. Thus, these peaks were due to the redox reaction of ferriin shown in Fig. 2. The SOWG spectra were

Fig. 2 Chemical structure of ferriin and its electrochemical reaction.

Fig. 3 Cyclic voltammogram (A) and SOWG spectra obtained on potential negative scanning (B) and on potential positive scanning (C) of 5.0 mmol · dm⁻³ ferriin in 1 mol · dm⁻³ potassium nitrate aqueous solution. Working electrode, indium-tin oxide coated glass plate; counter electrode, platinum wire; reference electrode, silver/silver chloride electrode; initial potential, +0.1 V; scan rate, 0.01 V/s; SOWG spectra detected at (a) +1.4, (b) +0.9, (c) +0.85, (d) +0.8, (e) +0.75, (f) +0.7, (g) +0.4, (h) +0.8, (i) +0.85, (j) +0.9, (k) +0.95, (l) +1.05, (m) +1.1 and (n) +1.4 V vs. Ag/AgCl.

Fig. 4 Schematic illustration for concentration profiles near the electrode during cyclic voltammetry in Fig. 3(A). The shaded areas show absorbance at 510 nm of SOWG spectra in Fig. 3(B) and (C) are attributed to ferroin molecules present near the electrode surface. The horizontal-striped areas show absorbance at 650 nm of SOWG spectra in Fig. 3(B) and (C) are attributed to ferriin molecules present near the electrode surface.

obtained at the potentials of (a) +1.4, (b) +0.90, (c) +0.85, (d) +0.80, (e) +0.75, (f) +0.70 and (g) +0.40 V on the potential negative scanning and of (h) +0.80, (i) +0.85, (j) +0.90, (k) +0.95, (l) +1.05, (m) +1.1 and (n) +1.4 on the potential positive scanning. The SOWG spectra (a) and (g) were identical to the UV-VIS spectra of ferroin and ferriin, respectively. At +0.9, +0.85, +0.8, +0.75 and +0.7 V on the negative scanning, spectra (b), (c), (d), (e) and (f), and at +0.8, +0.85, +0.90, +0.95, +1.05 and +1.1 V on positive scanning, spectra (h), (i), (j), (k), (l) and (m), which were medium spectra between spectra (a) and (g), were obtained. From these results, the physical situation in the solution adjacent to the electrode during the potential scan is illustrated by the concentration-distance profiles in Fig. 4 for selected potentials from Fig. 3. These concentration profiles near the electrode during cyclic voltammetry (Fig. 4) are similar to the profile reported by Kissinger *et al.*¹²⁾ It is understood that the intensity of absorbance near 510 and 650 nm on SOWG spectrum represent the ferroin and ferriin concentration in the vicinity of the electrode for each potential during the negative and then positive scans, respectively.

From these results, electrochemical and optical information of diffusion-controlled electrochemical reaction at the electrode/electrolyte interface were available with SOWG spectroscopy. The repeatability of SOWG and

Table 1 Repeatability of absorbance on the SOWG spectra and peak currents and peak potentials on the voltammograms.

	Average	SD ($\times 10^{-3}$)	RSD, (%) (n=5)
Cyclic voltammograms			
Oxidation peak current	0.0632 (mA/cm ²)	1.91	3.02
Reduction peak current	0.0669 (mA/cm ²)	1.92	2.87
Oxidation peak potential	0.921 (V)	2.24	0.243
Reduction peak potential	0.821 (V)	2.24	0.272
SOWG spectra			
Absorbance	0.0126	0.778	6.16

SOWG spectra and cyclic voltammograms were obtained at 5 mM ferroin in 1 M KNO₃. WE, ITO coated glass plate; CE, Pt wire; RE, Ag/AgCl; initial potential, +1.4 V; scan rate, 10 mV/s; absorbance measured at 510 nm during electrolysis at +0.4 V.

cyclic voltammogram of 5.0 mmol · dm⁻³ ferroin in 1.0 mol · dm⁻³ potassium nitrate were examined using the cell. As shown in Table 1, the relative standard deviations (RSD) for absorbance, peak current and peak potential less than 6.2 % implied good repeatability.

3. 2 *In situ* real-time monitoring of ferroin during potential step experiment

In situ real-time monitoring of ferroin during potential step experiment was performed. The initial potential was +0.4 V, where no faradic process occurred. The transition from +0.4 to +1.4 V, where the kinetics for oxidation of ferroin predicted was so rapid that no ferroin coexisted with the electrode and its surface concentration went nearly to zero, was made in 5.0 mmol dm⁻³ ferroin in 1 mol dm⁻³ potassium nitrate aqueous solution at the planar ITO electrode. Figure 5(A) shows a diagram of the waveform applied in this potential step experiment, 5(B) the current flow versus time curve for the oxidation of ferroin, and 5(C1), (C2) and (C3) the absorbance ratio of ferroin-time ($A_t/A_0 - t$) curves, respectively. The ferroin absorbance was measured at 510 nm by SOWG spectroscopy. Where A_0 is the ferroin absorbance at 0 s, A_t is the ferroin absorbance at t s, t is the time after electrolysis started. The penetration depth of an evanescent wave (dp) is calculated using the following expression (1):

$$dp = \lambda / 2\pi n_1 (\sin^2 \theta - (n_2/n_1)^2)^{1/2} \quad (1)$$

where n_1 is the refraction index of OWG, n_2 is the refraction index of the electrolyte solution, λ is the wave length of incident light and θ is the angle of incident light. This expression indicates that the penetration depth of an evanescent wave can be changed by changing the incident angle. Therefore, the ferroin absorbances were measured at three different angles for observation under various penetration depths. The incident angles for absorption measurement in an evanescent field were 77, 73 and 70° (when the angles of θ_1

Fig. 5 Change in absorbance during potential step experiment using SOWG spectrometry for $5.0 \text{ mmol} \cdot \text{dm}^{-3}$ ferroin in $1 \text{ mol} \cdot \text{dm}^{-3}$ potassium nitrate. (A) Wave form for a step experiment, (B) current flow versus time, (C) absorbance profiles observed by the light beam at several incident angle in response to the step from $+0.4 \text{ V}$ to $+1.4 \text{ V}$ vs Ag/AgCl .

shown in Fig. 1 were fixed at $5, 10$ and 15°), respectively (Fig. 5(C1)-(C3)). Each penetration depth of the evanescent waves (dp), which were calculated using expression (1), were approximately $150, 170$ and 220 nm , respectively ($n_1 = 1.47, n_2 = 1.33, \lambda = 510 \text{ nm}$). As shown in Fig. 5(B), a large anodic current flowed at first after the transition to $+1.4 \text{ V}$, the potential to be in a mass transfer region, and then the current declined in magnitude on the I - t curve. Absorbance also decreased along with the electrochemical oxidation of the ferroin proceeding. However, the shapes of absorbance decay depend on the incident angles. These results indicate that the present method was capable of *in situ* real-time monitoring of ferroin during chronoamperometry. The current and absorbance were plotted against a reciprocal value of the square root of the time, respectively (Fig. 6). The plots of current display a straight line in the time range between 0.5 and 5 s . The straight line suggests that the I - t curve obeys the Cottrell equation.¹³⁾ Moreover the plots of absorbances also display straight lines in the time range between 0.1 and 5 s , and the slopes of the curves increased in order in Fig. 6(B) < (C) < (D). The concentration ratios of ferroin (C_t/C_0) were calculated using the following expression (2) :

$$C_t/C_0 = A_t/A_0 \quad (2)$$

These results indicate the concentration changes within

Fig. 6 I - $t^{-1/2}$ curve ((A)) and A_t/A_0 - $t^{-1/2}$ curves ((B)-(D)). The straight lines were determined in the time range by using the least-square method.

the area of different distances from the electrode surface. Based on Fick's Second Law, the concentration profiles on the surface of the electrode were made. The profiles were obtained by plotting the data calculated using the following expression (3) :

$$C(x, t) = C_0 \operatorname{erf}(x/(2(Dt)^{-0.5})) \quad (3)$$

where x is the distance from electrode surface, t is the time after electrolysis started, D is the diffusion coefficient, C_0 is the concentration of ferroin at 0 s , $C(x, t)$ is the concentration of ferroin at a given location x at a time t . The evanescent wave reaches up to a distance of 3dp . In addition the absorbance of the species existing within the penetration depth of the evanescent waves was measured by the present method. A schematic illustration for concentration profiles is shown in Fig. 7. As shown in Fig. 7, we demonstrated that when the penetration depth of the evanescent wave became larger, the decrease in the concentration ratio per unit time became larger. When the penetration depth was the shortest of the three angles examined, the decrease in concentration ratio and the slope of C_t/C_0 - $t^{-0.5}$ were smallest (Figs. 5 and 6).

Although the penetration depth examined was limited within a relatively small range in this system, it was noted that the present method easily offered an important measure concerning the surface concentration in the vicinity of the electrode. A wide variation in penetration depth could be realized by further improvement of the SOWG system. This new SOWG spectroelectrochemical method with bulk-type cell was a powerful tool to investigate a more detailed concentration-distance profile.

Fig. 7 Schematic illustration for concentration profiles near the electrode during potential step experiment in Fig. 5(B). The incident angles were (A) 77, (B) 73 and (C) 70°, respectively. Each penetration depth of the evanescent waves (3dp) was approximately 450, 510 and 660nm, respectively.

4 Conclusion

In situ real-time monitoring of ferroin, which showed diffusion-controlled electrochemical reaction during CV and potential step method in the bulk-type cell, was observed by measuring the absorbance of ferroin. The SOWG method using the new spectroelectrochemical cell for electrolysis on a stationary planar electrode could be applied to the examination of a diffusion-controlled elec-

trochemical reaction. Moreover, this method can be employed to measure more detailed concentration profiles of colored species.

References

- 1) J. H. Santos, N. Matsuda, Z. M. Qi, T. Yoshida, A. Takatsu, and K. Kato, *Surf. Interface Anal.*, **35**, 432 (2003).
- 2) T. Yoshida, H. Asano, J. H. Santos, Z. M. Qi, L. X. Sun, A. Takatsu, K. Kato, and N. Matsuda, *Chem. Lett.*, **32**, 270 (2003).
- 3) N. Matsuda, T. Yoshida, H. Asano, J. H. Santos, Z. M. Qi, A. Takatsu, and K. Kato, *Hyomen Gijutsu*, **53**, 912 (2002).
- 4) J. H. Santos, N. Matsuda, Z. M. Qi, T. Yoshida, A. Takatsu, and K. Kato, *Anal. Sci.*, **19**, 199 (2003).
- 5) N. Matsuda, J. Zheng, D. K. Qing, A. Takatsu, and K. Kato, *Appl. Spectrosc.*, **57**, 100 (2003).
- 6) W. R. Heineman, *Denki Kagaku (Electrochemistry)*, **50**, 142 (1982).
- 7) R. W. Murray, W. R. Heineman, and G. W. O'Dom, *Anal. Chem.*, **39**, 1666 (1967).
- 8) Y. Gui and T. Kuwana, *Langmuir*, **2**, 471 (1986).
- 9) T. Takamura, K. Takamura, W. Nippe, and E. Yeager, *J. Electrochem. Soc.*, **117**, 626 (1970).
- 10) F. Kitamura, N. Nanbu, T. Ohsaka, and K. Tokuda, *J. Electroanal. Chem.*, **452**, 241 (1998).
- 11) K. Takahashi, M. Koitabashi, and F. Kusu, *Talanta*, **65**, 1120 (2005).
- 12) P. T. Kissinger and W. R. Heineman, *J. Chem. Education*, **60**, 702 (1983).
- 13) A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, New York, NY, p.143 (1980).