Electrosorption of Thiourea on Gold Electrode Studied by Specular Reflectance Measurement

Tsutomu Takamura*, Kiyoko Takamura** and Yumiko Hayakawa**

Adsorption of thiourea on gold electrode has been studied by measuring simultaneously the reflectivity change and the current-potential curves in $1\ M\ H\text{ClO}_4$. Increasing concentration of thiourea caused an increase of the anodic current arising at $1.1\ V$, which is ascribed to the oxidation of thiourea. Cathodic peak due to the reduction of gold oxide was suppressed and broadened but the charge of the peak was found unchanged irrespective of thiourea concentration. The adsorption of thiourea induced a remarkable decrease in reflectivity, the change being associated with the decrease in electron density in the surface. This implies that the adsorption proceeds with its sulphur atom. Adsorbed thiourea was desorbed with the taking place of oxidation of thiourea ($\sim1.1\ V$), which was accompanied by the formation of oxide layer. During the cathodic sweep the oxide layer was reduced at about $1.0\ V$ and the surface just after the reduction was found free from adsorbed thiourea. Adsorption was remarkable in the double layer region, while the adsorbed thiourea was desorbed in the sufficiently negative potential region, giving rise to hydrogen formation. Analysis of the reflectivity-time curve at a constant potential suggests that the adsorption kinetics is not so simple as to be treated with a diffusion controlled process.

I Introduction

In our previous investigation of the properties of electrode-electrolyte interface by in situ optical methods, the usefulness of specular reflectance measurements for the study of adsorption has become evident$^{1}$, $^{2}$, $^{3}$, $^{4}$, $^{5}$, $^{6}$, $^{7}$, $^{8}$. Formation of oxide layers on solid electrodes gave rise to appreciable reflectivity changes even if the thickness was as low as one or two monolayers, and the change was roughly proportional to the amount of the surface oxides$^{12}$, $^{13}$. Adsorption of anions such as halides$^{8}$, phosphates, sulphate and nitrate$^{9}$ causes the reflectivity of gold electrode to decrease, and the decrease may be elucidated in terms of combined effect of the decrease in the electron density in the surface and the increase in refractive index in the double layer together with the internal photoelectric effect of gold$^{10}$. On the other hand, the reflectivity of gold$^{11}$ and palladium$^{12}$, $^{13}$ was found to be changed by the formation of foreign metal adatoms such as Ti, Cd$^{14}$, Bi, Pb, Cu$^{15}$ and Ag$^{16}$, $^{17}$. The change was wavelength-dependent and was proportional to the amount of adsorption unless the coverage is far below a monolayer.

Most contemporary efforts in these subjects have been mainly concerned with the adsorption or desorption of inorganic materials, but recent attention has also been paid to the adsorption of organic substances. Since McIntyre pointed out the possibility of detection of organic adsorptive entities on Pt electrode$^{18}$, a few papers have appeared to treat the organic adsorption. Yeager and his coworkers$^{19}$, and Horkans$^{20}$ have pointed out that the adsorption of benzene or Et$_4$N$^+$ on gold can be detected on the electroreflectance curve. Conway and Gottesfeld reported the adsorption of pyridine and quinoline on amalgamated Au and Pt$^{21}$, Barrett and Parsons published a detailed investigation of adsorption of methanal and formaline on Pt$^{22}$, and Plieth studied the adsorption of methylene blue on Pt$^{23}$.

Adsorption of organic compounds is important in view of the corrosion inhibition where thiourea is considered as one of the representative inhibitor because of its high adsorbability and simplicity in molecular structure. A systematic analysis of the electrosorption of thiourea on gold was carried out by Wroblowa and Green$^{24}$, but their method was based on a tracer analysis which required longer time and special electrode for the determination. It seems, therefore, worthwhile to measure the reflectivity change caused by adsorption of thiourea on Au with a simple potential sweep method. The purpose of the present study is to know what change is caused by the adsorption of thiourea in an attempt to elucidate the reflectivity change and to compare the results of the electrosorption with those obtained by Wroblowa and Green$^{25}$.

* Research and Development Center, Tokyo Shibaura Electric Company (Komukai Toshiba-cho, Kawasaki)

** Tokyo College of Pharmacy (Uenosakuragi, Taito-ku, Tokyo)
2 Experimental

A multiple specular reflection technique using a small number of reflection was applied to obtain a relative reflectivity. Recently, Cahan et al.\textsuperscript{11,17} pointed out that the use of multiple specular reflection to investigate the electrode–electrolyte interface introduced substantial errors due to light scattering and impure wavelengths from the monochromator. Both sources of error may become important when the number of reflections is sufficiently large but can be made negligible by using a small number of reflections. Their experimental data obtained using 1 to 7 reflections showed that within the experimental error the wavelength dependence of reflectivity is independent of the number of reflections used\textsuperscript{12}. In the present study, the number of reflection was kept to be five times to prevent the erroneous results. All the data of $R/R_0$ in the present paper are expressed as the observed relative reflectivity for five–time reflections.

The electrolytic cell for the simultaneous measurements of current–potential ($i$–$E$) and relative reflectivity–potential ($R/R_0$ vs. $E$, where $R_0$ is the maximum reflectivity in each curve) curves are the same as that described in a previous paper\textsuperscript{12}. Two optically polished gold plates (1.5 x 3.5 cm and 1.5 x 4.5 cm) were fixed to Teflon holders which kept them parallel with a separation of 7.0 mm.

Monochromatic light from a Beckman DU spectrophotometer was directed on to the surface of parallel gold plates with an angle of incidence of 50°. After reflection, the light beam passing out of the cell was directed to a photomultiplier. An optical analyzer was placed in front of the detector. The $R/R_0$ vs. $E$ curves were recorded at various wavelengths and optical polarizations for fixed electrolysis condition. The results given in this paper were all obtained at 525 nm with parallel polarization, because such a condition provided the most pronounced change in $R/R_0$.

Electrolysis was carried out with a linear potential sweep method, the potential being applied from a Toshiba potentiostat in connection with a function generator at voltage sweep rates normally between 33 and 100 mV sec\textsuperscript{-1}.

The solution of thiourea was prepared by dissolving reagent grade chemicals (Koso Co., m.p. 180.0°C) in triply distilled water and used without further purification. The supporting electrolyte was usually 1 M perchloric acid, which was prepared with Ultra Pure Reagent from Wako Co. All the measurements were carried out at 25±2°C.

3 Results and Discussions

3.1 Effect of thiourea on $i$–$E$ curve

Potential sweep voltammograms ($i$–$E$ curve) for various amounts of thiourea present are shown in Fig. 1. The influence of thiourea on the $i$–$E$ curves is seen in the following three points: i) Anodic current beginning at around 1 V is enhanced with the increase of thiourea concentration. ii) Cathodic peak in the cathodic branch at around 1 V due to the reduction of the oxide layer decreases in its peak height and shifts towards negative potential, while the change of the cathodic peak was found unchanged irrespective of thiourea concentration. iii) Cathodic current appearing at −0.3 V, which is associated with H$_2$ evolution, shifts towards negative potential with the increase in thiourea concentration.

The above changes will be treated in some detail. The enhanced anodic current is attributed to the oxidation of thiourea\textsuperscript{19}, while the reduction of the oxidized thiourea should occur at the potential more negative than 0.20 V (vs. Ag/AgCl), since $E^\circ$ of the couple between thiourea and its oxidized form is 0.420 V vs. N.H.E.\textsuperscript{20}. When the concentration of thiourea was increased up to 10\textsuperscript{-2}M, a small cathodic current was observed at around 0 V, suggesting the

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Current–potential curves of Au in 1 M HClO$_4$ with various concentrations of thiourea
Thiourea concentrations: (a) 0, (b) 1.0×10\textsuperscript{-4}, (c) 1.0×10\textsuperscript{-3}, (d) 1.0×10\textsuperscript{-4} M
Sweep rate: 100 mV sec\textsuperscript{-1}}
\end{figure}
two possibilities are taken into consideration for the elucidation of the broadening: The one is the adsorption of thiourea at the newly reduced surface, which will retard the further reduction of the neighbouring portion of the oxide layer which is not reduced yet; The other is the stabilization of the oxide during the anodic sweep, owing to the current required for thiourea oxidation. The larger the current, the more the oxide will be stabilized. Comparing Fig. 1 with Fig. 2, we prefer the latter mechanism, but further studies are required to decide which mechanism is more plausible.

Retardation of hydrogen evolution is clearly seen on i-E curve and it becomes remarkable with increasing concentration of thiourea as seen in Fig. 1. This is undoubtedly due to the adsorption of thiourea. However, it is not clear whether thiourea becomes desorbed with the increase in cathodic current. The ambiguity will become clear when we compare the results with those obtained in the reflectivity measurement.

3.2 Reflectivity change due to the adsorption of thiourea

The changes in reflectivity due to the presence of thiourea are shown in Fig. 2, where $R/R_o$ in the double layer region is remarkably decreased by the presence of high concentration of thiourea. The decrease is more remarkable at more positive potentials. The decrease is attributed to the adsorption of thiourea. As having been pointed out by Wroblowa and Green[16], thiourea molecule will be adsorbed on gold with its sulphur atom, inducing positive charge in the surface because the electron density on sulphur atom is high. Increased amount of adsorption will decrease the electron density in the surface of gold, resulting in a decrease in the reflectivity through the mechanism as explained in the previous paper[4]. The result that the amount of adsorption is increased at more anodic potential is in accord with that obtained by Wroblowa and Green[16].

On the anodic branch at around 1.1 V, there is a small recovery in $R/R_o$ at high concentration of thiourea. Since the oxidation of thiourea becomes remarkable at this potential, the small recovery is ascribed to the desorption of thiourea due to its oxidation, while the desorption will facilitate the formation of oxide layer, and hence, it is accompanied by the second decrease in $R/R_o$. As already pointed out, the value of $R/R_o$ at the bottom of the hysteresis is nearly constant over the wide range of concentration. This indicates the amount of oxide layer to be essentially unaffected by the presence of thiourea.

Remarkable recovery in reflectivity at the potential of cathodic peak in i-E curve can be seen in the cathodic branch. When the concentration of thiourea

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**Fig. 2** Reflectivity-potential curves of Au in 1 M HClO$_4$ with various concentrations of thiourea obtained at 525 nm with parallel polarization and a sweep rate of 100 mV sec$^{-1}$

Thiourea concentrations: (a) 0, (b) 1.0 × 10$^{-5}$, (c) 5.0 × 10$^{-5}$, (d) 2.0 × 10$^{-4}$M

The changes in reflectivity due to the formation of oxide layer begins to take place.

When we see the cathodic branch, however, the formation of oxide layer during the anodic sweep can be recognized, since the cathodic peak at around 1 V cannot be attributed to any other reason than the reduction of the oxide layer. Although the height of the cathodic peak becomes decreased with the increased concentration of thiourea, the amount of charge for the cathodic peak was found independent of the thiourea concentration. This implies that the formation of oxide layer proceeds without being affected by the presence of thiourea, and this is also supported by the unchanged height of the bottom of the hysteresis on $R/R_o$ - E curves in Fig. 2.

Since the reflectivity decrease due to the oxide layer was verified roughly proportional to the thickness of the layer, only a small reflectivity decrease should be observed if the formation of the oxide layer is retarded.

There is no appreciable current flow on the cathodic branch of i-E curve in the potential region between 1.5 and 1.1 V even though thiourea is oxidized during the anodic sweep in the same region. This is explained in terms of the potential drop across the oxide layer whose thickness does not change during the cathodic sweep until reaching the potential of its reduction. The potential outside the oxide layer, i.e., adjacent to the electrolyte, would not be positive enough to oxidize thiourea during the cathodic sweep. The initiation potential of the main cathodic peak is constant at 1.15 V, independent of the thiourea concentration, while the peak width becomes broadened. The follow-
Fig. 3 Reflectivity–potential curves at varied sweep rates for Au in 1 M HClO₄ containing 5.0 × 10⁻⁵ M thiourea at 525 nm with parallel polarization

Sweep rate: (a) 100 mV sec⁻¹, (b) 33 mV sec⁻¹

is not so high, no adsorbed thiourea would be found on the surface just after the reduction of the oxide layer, and the recovered reflectivity will be nearly the same as that in the absence of thiourea. During the continuation of the cathodic sweep, thiourea in the bulk solution will diffuse and be adsorbed on to the bare surface to cause the reflectivity decrease, as is seen on Fig. 2.

At the cathodic potential of 0.2 V the adsorbed thiourea begins to be desorbed to give rise to an increase of \( R/R_0 \), and at the same time, the cathodic current due to the hydrogen formation becomes remarkable. Desorption of organic molecules at far negative potentials has been discussed by many authors and elucidated in terms of the replacement reaction by the solvent molecule or cationic species of supporting electrolyte\(^{22,23}\). As is usually expected, the potential at which thiourea is desorbed shifts towards negative direction with increase of thiourea concentration. When we compare Fig. 1 with Fig. 2, we can recognize that the adsorption of thiourea retards the cathodic reaction of hydrogen formation.

The effect of sweep rate on \( R/R_0-E \) curve was examined, the example being shown in Fig. 3, where the concentration of thiourea was kept at 5.0 × 10⁻⁵ M. Slow rate of potential sweep gave rise to a more pronounced decrease in \( R/R_0 \). Since the concentration is sufficiently low, the rate of adsorption would be slow enough to compete the sweep rate. Accordingly, the increased amount of adsorption is expected at slower sweep rate.

Wavelength dependence of \( R/R_0-E \) curve is shown in Fig. 4, where curves obtained in the absence of thiourea are also shown by dotted lines as a comparison.

Fig. 4 Reflectivity–potential curves at various wavelengths in the absence (dotted lines) and the presence (solid lines) of 5 × 10⁻⁸ M of thiourea

Sweep rate: 105 mV sec⁻¹

Fig. 5 Reflectivity-time curve of Au in 1 M HClO₄ in the presence of 5.0 × 10⁻⁵ M thiourea (525 nm, parallel polarization)

Potential sequence: held at 1.42 V for 30 sec, then set at 0.9 V, and finally set at 0.26 V

Reflectivity change vs. \( t^{1/2} \) plot following potential step is shown in the lower figure

Adsorption of thiourea caused \( R/R_0 \) to decrease at any wavelength studied and the shape change of the curve was found more remarkable at longer wavelengths.
where the absolute reflectivity of gold tended to 100%. The decrease in \( R/R_0 \) at any wavelength owing to thiourea adsorption supports the previous explanation that the decrease is associated with the decreased electronic charge in the surface and the increase in refractive index of double layer. In both curves obtained at shorter and longer wavelengths, there is a hysteresis in the cathodic desorption range, and the hysteresis will be explained on the basis of the same mechanism as that of halide adsorption\(^{10}\). Because of the low concentration of adsorptive entities, the adsorption rate is rather slow, giving rise to hysteresis when the potential sweep rate is comparable to the rate of adsorption.

The slow rate of adsorption was examined by measuring the change in \( R/R_0 \) with the lapse of time at constant potential, the results being shown in Fig. 5. At first the potential was set at 1.42 V to oxidize the adsorptive entities for 30 sec., then at 0.9 V to reduce the oxide which was formed during the previous treatment, and finally, the potential was set at 0.26 V and \( R/R_0 \)-time curve was recorded (upper figure). The change in \( R/R_0 (\Delta R/R_0) \) is plotted against the square root of time, giving two successive straight lines of different slopes.

By assuming that the rate of adsorption is controlled by diffusion and the observed \(-\Delta R/R_0\) was proportional to the amount of adsorption\(^{10}\), the diffusion coefficient of thiourea was estimated from the initial slope of the line in Fig. 5. The obtained value of about \( 5 \times 10^{-6} \) cm\(^2\) sec\(^{-1}\) seems not so unreasonable. The later parts of the curve in Fig. 5 remains to have further analysis. The reflectivity measurements have been shown to be applicable also to the adsorption kinetics of organic entities.

References: