

Measurement of gold electrode surface changes in situ by laser photothermal spectroscopy

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Differential MIKE Spectra

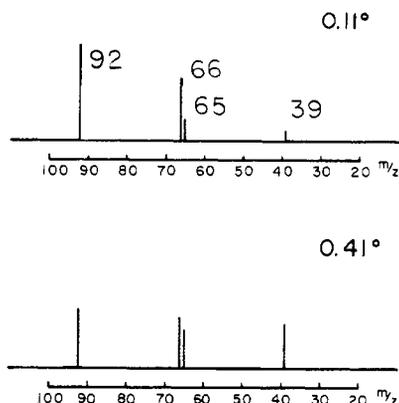


Figure 6. MIKE spectra of the aniline molecular ion (93^+) taken in the presence of collision gas. These differential spectra employ angular selection

spectrometer with very similar results, but distinct advantages, to those obtained using a conventional instrument. The rather limited range of scattering angles used on the MIKES instrument stands in contrast to the much larger range possible with the RMH-2 mass spectrometer. Both this, and the poorer resolution achieved, are simply consequences of the particular configuration chosen. The present modification was carried out to test feasibility and instrumental changes were minimized. For example, no provision was made for varying the angular resolution without breaking vacuum. It is of particular note that this experiment differs fundamentally from those done previously with the RMH-2 instrument in that scattering angle selection is in a plane orthogonal to that of analysis. This amounts to separating angular resolution from mass (or energy) resolution of the collision products. All the advantages of this are not yet apparent, but it is noteworthy that optimization of the position of post-collision analyzer (the magnet in the RMH-2) is avoided.

The concepts developed here provide a convenient method of examining the high energy ion/molecule chemistry of any

selected ion. This includes structural studies by means of collision-induced dissociation as well as thermochemical studies through energy loss spectrometry. The ability to select ion internal energies, which angular resolution provides, should prove a powerful adjunct to the MIKES methodology. The growing importance of collision-induced dissociation in analytical mass spectrometry (16, 17, 19) underlines the potential usefulness of the present results.

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Measurement of Gold Electrode Surface Changes in Situ by Laser Photothermal Spectroscopy

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Photothermal spectroscopy (PTS) using modulated laser excitation was applied to the study of electrode-electrolyte interfaces in situ. Oxidation of an Au electrode in an acid solution and the electrochemical deposition of Cu on Au were studied by the PTS technique. The apparatus and procedure are described and the sensitivity and characteristics of the method discussed.

Photothermal spectroscopy (PTS) (1), is a spectroscopic technique which is particularly useful for obtaining spectra

of highly absorbant samples, e.g., solids, by measuring directly the temperature changes which occur upon absorption of radiation. The purpose of the present work is to demonstrate how PTS can be applied to studies of operating metal electrodes in situ.

In-situ studies of electrode solution interfaces have drawn the attention of a number of investigators for application to corrosion of metals, electrocatalytic reactions, and so on. Usually absorption experiments using optically transparent electrodes (2, 3), internal reflection (4, 5), specular reflection (6, 7), or ellipsometric techniques (8, 9) are used for the characterization of the interfaces or the measurement of the

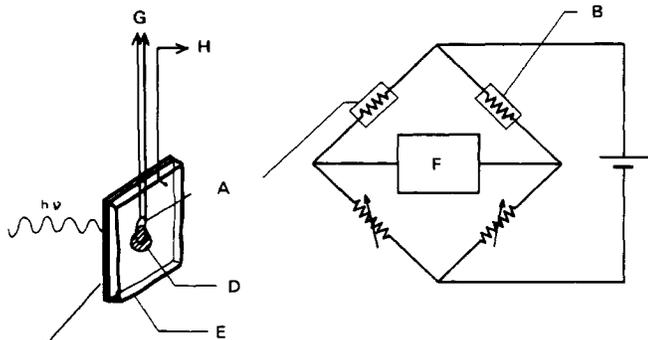


Figure 1. Working electrode and Wheatstone bridge. A, Thermistor for working electrode; B, thermistor for temperature compensation; C, Au plate; D, Ag epoxy; E, epoxy resin; F, lock-in amplifier; G, to bridge; H, to potentiostat

kinetic behavior of electrode reactions. In these conventional techniques, information on the interfaces is obtained optically by detection of a light beam after interaction with the electrode surface, for example as a small difference in absorption between incident and reflected light. PTS, by contrast, involves the detection of temperature changes due to the absorption at the interfaces, and thus has the advantage that it does not count scattering losses. This characteristic is favorable in the practical measurement of electrode-solution interfaces, since the electrode surface need not be highly polished. PTS can also be applied to samples that are difficult to study by conventional spectroscopic methods.

Photoacoustic spectroscopy (PAS) (10-12) is similar to PTS in that it detects the temperature changes due to the radiationless processes following light absorption, but for application to studies of the interfaces, PTS is better because it allows a more flexible sample cell arrangement and is free from external acoustic noise.

The present work involves the study of the surface behavior of metal electrodes by PTS. The change in the electrode-solution interfaces in the course of the electrode reactions was measured by a thermistor attached to the electrode which reacted to the temperature changes resulting from the absorption of light.

EXPERIMENTAL

The working electrode was a 0.1-mm thick flat Au plate with an electrode area of 1.0 cm² manufactured by Ishifuku Kinzoku. The electrode was polished to a bright surface with 3- μ m alumina powder and then washed with distilled water. Detection of temperature changes on the Au electrode surface was accomplished by Shibaura Denshi Model SB-4 thermistors which are 0.8 mm in diameter and 4 mm in length, and have a nominal resistance of 4 k Ω , a sensitivity of 160 Ω /K at 25 $^{\circ}$ C and a time constant in water of 0.4 s. The thermistor was attached to the rear of the Au electrode with Ag epoxy cement as shown in Figure 1 to obtain maximum thermal conductivity, and then coated with epoxy resin. To eliminate the effect of temperature changes in the bulk solution, a differential method was used. Temperature changes in the electrode resulted in an unbalance in a Wheatstone bridge, consisting of a matched pair of thermistors, one attached to the electrode as described above, and one immersed in the electrolyte but out of the light path. By this method, the base-line drift of the temperature change was almost eliminated, so that there was no need to use a well-controlled thermostated bath.

Figure 2 shows the instrumentation used in this experiment. Monochromatic light was provided by a Spectra Physics Model 164 3-W Ar ion laser. The light beam was chopped at 8 Hz and the resulting voltage change in the Wheatstone bridge was detected with a JASCO Model LA-126 lock-in amplifier. Temperature changes resulting from the electrode reaction were thus negligible, because only the ac component of temperature changes was measured by the phase sensitive detection.

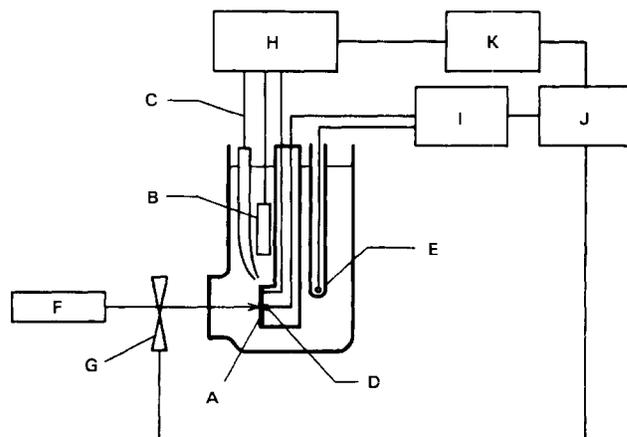


Figure 2. Experimental setup for PTS measurement. A, Working electrode; B, counter electrode; C, reference electrode; D, thermistor for working electrode; E, thermistor for temperature compensation; F, Ar laser; G, light chopper; H, potentiostat; I, bridge; J, lock-in amplifier; K, recorder

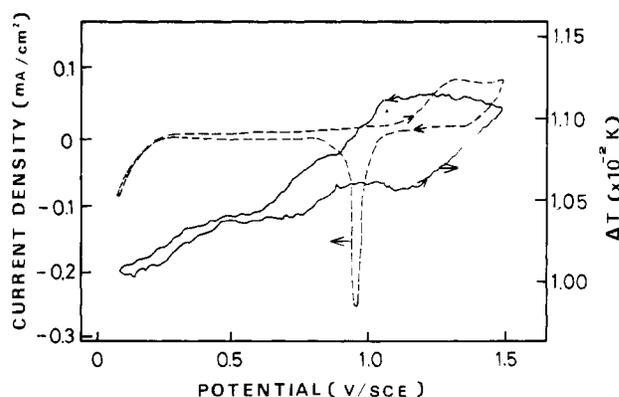


Figure 3. ΔT vs. potential (—) and current vs. potential (---) curves of an Au electrode. 1 M HClO₄, potential sweep rate 10 mV/s, $\lambda = 514$ nm

The ac temperature change resulting from only light absorption is referred to here as ΔT . Under the experimental conditions the ΔT values can be considered to be proportional to the magnitude of absorption at the surface (1). The sensitivity was 60 mV/K with this bridge. Use was made of a Nikko Keisoku Model NPG-301 potentiostat and Model NPS-2 potential programmer to determine current-potential curves. A saturated calomel electrode was used as a reference electrode and the counter electrode was of platinum. Plots of current vs. potential (E) and ΔT vs. potential (E) were simultaneously recorded on a Riken Denshi Model D-72 X-Y-Y' recorder.

RESULTS AND DISCUSSION

Measurements of Formation of an Oxide Layer at Au.

Many studies have been described on the electrochemical oxidation of Au electrodes (14-18). A typical ΔT vs. E curve, together with a current vs. potential curve in 1 M HClO₄ solution is shown in Figure 3. The ΔT vs. E curve was obtained under irradiation at a wavelength of 514 nm and intensity of 0.8 W. At the bare Au surface, the value of ΔT detected by phase-sensitive detection was about 0.1 K, and depended on the condition of the surface. The formation of the oxide layer on the Au electrode began at about +1.2 V vs. SCE on the anodic sweep in the current-potential curve and at the same potential, ΔT began to increase. The increment of ΔT accompanying oxide formation was about 5×10^{-3} K, i.e., about 5% of the value for a bare surface. This suggests that ΔT at the electrode surface increased because of the formation of an oxide layer whose absorption coefficient at 514 nm is greater than that of gold. The large peak in the cathodic sweep is generally attributed to the reduction of the

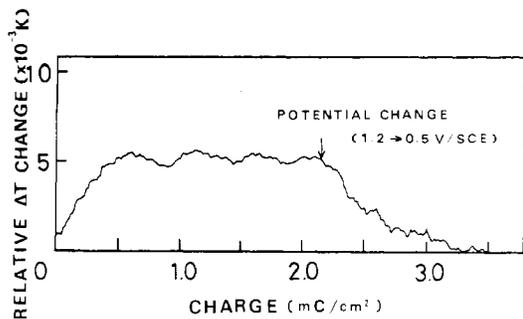


Figure 4. Relative change in ΔT vs. charge for the formation of gold oxide. 1 M HClO₄, potential +1.2 and +0.5 V/SCE, $\lambda = 514$ nm

oxide layer, and ΔT decreased at almost the same potential.

These results pertain to the oxidation region. However, ΔT changes were also observed in the electric double-layer region where no electrochemical reaction occurred. This change in light absorption at the electrode-solution interface as a function of potential has been reported by many investigators (15, 16, 18), and has been explained on the basis of either: (1) a dependence of the reflectivity on the refractive index of the double layer (19); or (2) a change in the 5d band in gold at the surface following the applied potential (18). The results of the present study (Figure 3) do not permit any conclusion as to which interpretation is the correct one. They are qualitatively in accord with those obtained by the specular reflection technique (16). The relationship between the relative change in ΔT and the charge associated with formation or reduction of the oxide layer is shown in Figure 4. The change in ΔT is the value measured against that at the bare Au surface. Changes in ΔT were also recorded, stepping the potential from +1.2 to 0.5 V (at which the oxide layer is reduced). ΔT increased linearly with the quantity of electricity when formation of the oxide layer started at 1.2 V and attained a constant value at about 600 $\mu\text{C}/\text{cm}^2$. If we assume the composition of the oxide layer to be Au₂O₃ with a bulk density of 6 g/cm³ (17), we estimate the thickness of the film to be about 5 Å at 600 $\mu\text{C}/\text{cm}^2$. In a study of Au electrodes using the specular reflection technique, reported by Takamura et al. (16), the change in reflectivity vs. the charge associated with the formation of oxide indicated that the slope of the reflectivity vs. charge curve changed at 500 $\mu\text{C}/\text{cm}^2$, at which charge they concluded that the monolayer coverage of the Au electrode was probably completed. In this work, no clear change in the slope of the ΔT vs. charge curve was observed, perhaps because the time constant in phase sensitive detection was large in terms of the oxidation rate at the Au surface.

When the oxide layer was reduced by stepping the applied potential from +1.2 to 0.5 V, ΔT decreased to the value at the bare Au surface. The absorption is considered to be proportional to the degree of surface coverage of the oxide layer when the resulting oxide layer is less than a monolayer. Since ΔT varies linearly with absorption at the surface, the change in ΔT of Figure 4 implies an increase in the coverage by the oxide layer.

Measurement of the Electrochemical Deposition of Cu on an Au Electrode. It was expected that ΔT resulting from light absorption would change when different metals were electrodeposited on the bare metal surface. Figure 5 is a plot of the ΔT vs. potential and current vs. potential curves in 1 M HClO₄ containing 5×10^{-3} M Cu²⁺. ΔT was measured at a wavelength of 514 nm and a light intensity of 0.8 W. The reduction current at about 0 V vs. SCE in the cathodic sweep resulted in electrochemical deposition of Cu and at the same potential ΔT began to increase rapidly. On the other hand, the oxidation current on the anodic sweep is attributed to the dissolution of the Cu layer and ΔT decreases correspondingly.

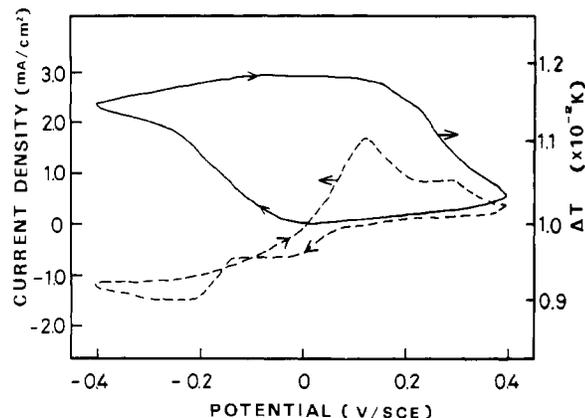


Figure 5. ΔT vs. potential (—) and current vs. potential (---) curves of an Au electrode in the presence of Cu²⁺ ion. 5×10^{-3} M Cu²⁺, 0.1 N Na₂SO₄, potential sweep rate 20 mV/s. $\lambda = 514$ nm

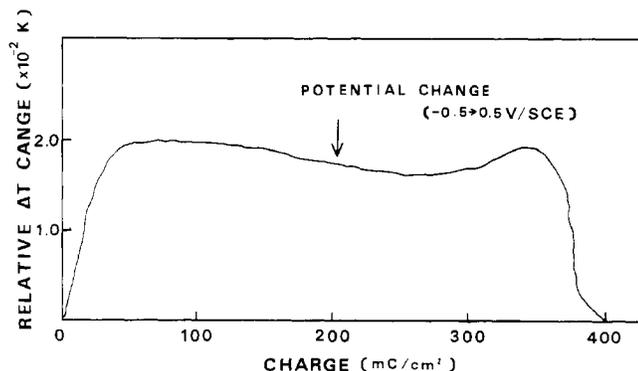


Figure 6. Relative change in ΔT vs. charge for the electrochemical deposition of Cu. 5×10^{-3} M Cu²⁺, 0.1 N Na₂SO₄, potential -0.5 and +0.5 V/SCE

This result is in accord with the difference in reflectivity between gold and copper (20, 21). Figure 6 is a plot of the relative change in ΔT vs. the charge associated with the electrochemical deposition of Cu on the Au surface at -0.5 V. In the case of the dissolution of the Cu layer, a change in ΔT was also recorded at a potential of 0.5 V. In Figure 6, ΔT increases linearly as Cu deposition proceeds and becomes constant at about 50 mC/cm². Assuming the deposition layer to be flat, the thickness of the Cu layer is estimated to be about 200 Å at this charge. In anodic reactions, ΔT decreased on a reverse path until it reached the value for the bare Au surface. The charge consumed for dissolution was exactly equal to that for deposition. In measurement by reflection techniques, the change in reflectivity was reported to be proportional to the thickness of the thin film which was formed on the electrode-electrolyte interface, assuming that the thickness of the film was far less than the wavelength of the incident light (McIntyre-Aspnes approximation) (22). It follows that ΔT can be considered to be proportional to the thickness of the depositing layer. This relationship seems to be valid concerning the region in Figure 6 where ΔT increases linearly. However, ΔT in the flat region would seem to be the result of the absorption at the Cu layer alone.

CONCLUSION

The PTS technique is useful for studies of electrode-electrolyte interfaces in situ. This method can monitor effectively the changes at interfaces. Sensitivity with modulated laser light is the order of monolayer changes, which is somewhat better than that found for PTS studies of electrodes using a xenon-lamp/monochromator source with very slow chopping. Since the temperature changes observed in this work were of the order of 10⁻³ K, the method shows promise

of greater increases in its sensitivity, because the limit in detection of temperature changes has been reported to be about 10^{-6} K (23). The PTS technique requires only simple instrumentation and is advantageous in terms of sample preparation, because it is unaffected by scattering losses. In addition, PTS would be useful for studying rough and porous surfaces which are difficult to examine by conventional spectroscopic techniques.

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Application of Photothermal Spectroscopy to in-Situ Studies of Films on Metals and Electrodes

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The technique of photothermal spectroscopy (PTS) with improved instrumentation was used to study films, such as paints and dyes, on metal substrates. PTS was also used to monitor in situ the formation and spectra of surface layers on electrodes. PTS investigations of the electrodeposition of Cu and heptylviologen bromide on a Pt electrode are reported. The technique as described can detect surface layers ~75-100 monolayers. A one-dimensional thermal diffusion model of the PTS effect is also described.

The search for spectroscopic methods which can be used for opaque samples has led to investigations of techniques such as photoacoustic spectroscopy (PAS) (1-5) where absorption of radiation is detected by the pressure fluctuations induced in a gas by thermal changes in the sample. There is particular interest in possible spectroscopic techniques for the study of solid samples immersed in a liquid, such as electrodes in electrochemical cells. Such methods would complement the powerful electron spectroscopic techniques (6, 7), which require removal of the sample from the cell and placement in a high vacuum environment, and the widely-used spectroelectrochemical and reflectance techniques (8, 9), which place rather severe requirements upon the nature of the electrodes employed. While direct PAS techniques, utilizing microphone detectors are not very sensitive for measurements of solids immersed in liquids, recently described techniques employing piezoelectric detectors (10) appear quite promising. A recent report from this laboratory (11) introduced the technique of photothermal spectroscopy (PTS) in which a thermistor in contact with a sample is employed to detect temperature changes caused by radiationless transitions resulting from the absorption of light by the sample. By

studying the relative temperature change as a function of irradiation wavelength (provided by a high intensity source), the absorption spectra of optically opaque samples can be obtained. The previously reported PTS studies have focused mainly on the characterization of various semiconducting materials (single crystal and polycrystalline) and the study of photoelectrochemical reactions at semiconductor electrodes (12).

The principles for the application of PTS to the in-situ study of metal electrodes is as follows. A highly polished metal electrode absorbs only a small amount of radiation (with the generation of heat) for most of the visible-near UV region. Therefore, when light-absorbing species are generated on or near the electrode, a photothermal signal will be obtained upon irradiation whose magnitude depends upon the molar absorptivity of the species, the amount of species generated, and the thermal properties of the system.

In this paper we present a theoretical model of the PTS effect and describe the application of PTS to studies of films (dyes and paints) on metal foil substrates as well as electro-generated layers on platinum foil electrodes. The latter experiments involved the electrodeposition of copper and the formation of a precipitate of diheptylviologen radical cation bromide. Electrochemical experiments in which the spectra of generated layers and the variation of the PTS signal with potential during slow scan cyclic voltammetry were obtained, were employed to estimate detection limits for this technique.

EXPERIMENTAL

Apparatus. The basic cell used for the spectroelectrochemical experiments is shown in Figure 1. While the design is similar to that previously described (11), a differential thermistor arrangement was used to compensate for changes in ambient temperature. This change greatly improved base-line stability. One thermistor (the working thermistor) was attached to the rear of