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STUDIES OF ELECTRODE SURFACE CHANGES *IN SITU* BY PHOTOACOUSTIC SPECTROSCOPY

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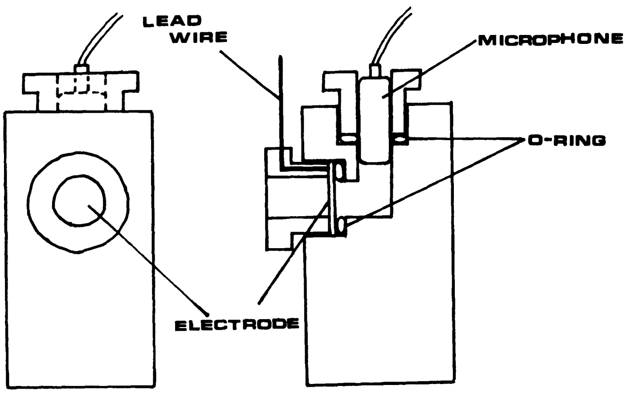
Photoacoustic spectroscopy (PAS) was used for the study of electrode-electrolyte interfaces *in situ*. The design of the PAS cell and the experimental procedure are given. The change in absorption at the interface during electrochemical reaction at Au electrodes, as measured by PAS technique, is described.

In recent years, there has been much interest in the photoacoustic effect, or photoacoustic spectroscopy (PAS)1)-8) as a new tool for the investigation of the surface conditions of various materials. One of the advantages of PAS is that one can obtain absorption spectra even for solid samples that are difficult to measure by conventional spectroscopic techniques on account of light scattering problems. We have noted this characteristic of PAS from the viewpoint of spectro-electrochemistry, and attempted to apply PAS to studies of the electrode surface *in situ*. Generally, spectro-electrochemical behavior is measured by using an optically transparent,9, 10) internal reflective,11, 12) specular reflective electrode,13,14) ellipsometric techniques15,16) and so on for the purpose of characterizing the electrode-electrolyte interfaces, or measuring the kinetic behavior of electrode reactions. It is expected that PAS will be more advantageous than the conventional spectroscopic techniques in observing the electrode-solution interfaces, because preparation of a sample electrode is not difficult, that is the surface does not need to be highly polished. Some works have been described on the application of PAS to electrochemical studies.6, 8) However, PAS was used in these works to measure the absorption spectra of the electrode surface in the air after the electrodes were worked in electrolysis. Here, we have used PAS to study the surface behavior of metal electrodes as the application of the technique to *in situ* observation of electrode surfaces.

Figure 1 shows the design of the PAS cell employed in this study. The cell was constructed from acrylic resin and was used in the electrolyte solution. This internal cell, in which an electret condenser microphone (Sony Model ECM-150) was employed as a pressure transducer, was approximately 0.4 cm^3 in size. The working electrode was a flat gold plate 0.1 mm thick, and 7.0 mm in diameter, which was mounted on one side of the PAS cell by a silicone O-ring to ensure an air-tight seal. The experimental set up is shown in Fig. 2. The light source was a 500 W Xe lamp (Ushio Electric) or a 3W Ar ion laser (Spectro Physics Model 164). In measuring the action spectrum using the Xe lamp, the radiation was focused using a convex lens through a series of 10 nm band width interference filters (Koshin Kogaku). The light beam was chopped by a mechanical light chopper and the photoacoustic signal detected with the microphone was amplified with a lock-in amplifier (Nihon Bunko Model LA-120). A potentiostat (Nikko Keisoku Model NPGS-301) with a potential programmer (Nikko Keisoku Model NPA-2) was used to obtain current-potential curves. A saturated calomel electrode was used as a reference electrode, and the counter electrode was of platinum. Current-potential and photoacoustic signal-potential curves were recorded simultaneously on a X-Y-Y' recorder (Riken Denshi Model D-72).



front side

Fig. 1 PAS cell

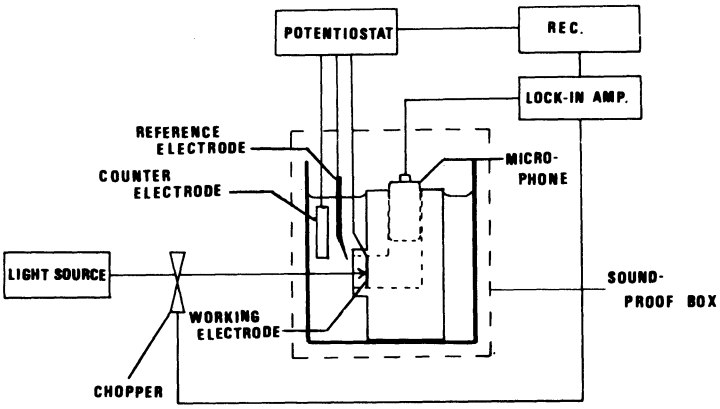


Fig. 2 experimental set up

Figure 3 shows the curve for relative acoustic signal versus applied potential together with a current-potential curve in 1 mol/l $HClO_4$ soltuion on an Au electrode where the photoacoustic signal was measured at a wavelength of 514 nm from the laser with a light intensity 0.8 W. It has been widely reported that oxide layers are formed on the Au electrode with anodic polarization in an acid solution.[17-20] Thus, the anodic current at 1.2 V *vs*. SCE in the anodic sweep was attributed mainly to the formation of the oxide layer of the Au electrode. As shown in Fig. 3, this increase in the acoustic signal began at about the same potential as an increase in current. The rise in the acoustic signal was mainly due to the increase in absorption resulting from formation of an oxide layer at the Au electrode because the absorption coefficient of the oxide layer is greater than that of Au at 514 nm illuminated. On the other hand, in the cathodic sweep, a current peak was observed around 0.9 V due to the reduction of the oxide layer of Au, and at that time the photoacoustic signal decreased gradually depending on the amount of cathodic electricity. When the cathodic current decreased to the original small value around 0.65 V, the acoustic signal also showed the same initial value as it had with the bare Au electrode. When an oxidation potential of 1.30 V was applied potentiostatically to this Au electrode, the photoacoustic signal increased with time, reaching a saturated value at about 500 μ Coul cm^{-2}, at which charge the thickness of the oxide layer was estimated to be about 5 Å.20) From this it can be assumed that an oxide layer of 1 Å or even less can be recognized by means of this PAS-electrochemical system.

Figure 4 shows the second application of PAS to observation of the electrode surface. Cu deposition on the Au electrode was chosen, as shown in Fig. 4. When Cu was deposited near -0.1 V the PAS signal at 514 nm increased in proportion to the amount of electricity of the Cu deposition. The anodic current peak at 0.20 V was attributed to the dissolution of the Cu layer and at this time the acoustic signal began to decreased correspondingly.

Figure 5 shows the photoacoustic spectra of the Au electrode before and after electrolysis at -0.20 V in 1 mol/l $HClO_4$ containing 5 x 10^{-3} mol/l Cu^{2+}. The spectrum of a 0.05 mm thick Cu plate, which was measured separately, in also shown in Fig. 5. Since the spectrum after electrolysis agreed with that of Cu plate, it may be assumed that the Au electrode surface was covered with a Cu layer. The results in Fig. 5 are in accord with those in Fig. 4.

The results reported here are preliminary. Sensitivity can be improved by modification of the PAS cell, *e. g.* a reduction of the size of the internal cell. In addition, PAS is strongly influenced by external acoustic noises, so we feel a major need

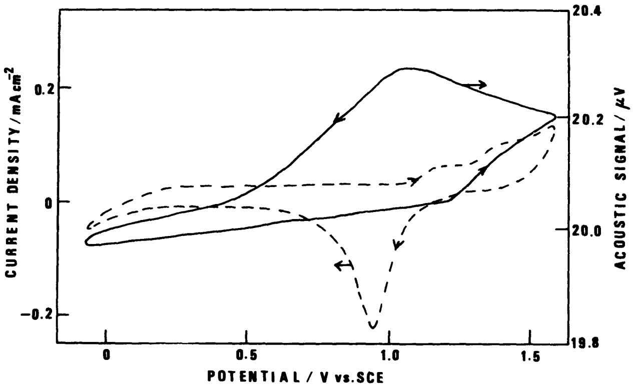


Fig. 3 Acoustic signal-potential (—), and current-potential (---)curves of an Au electrode. 1 mol/l $HClO_4$. Potential sweep rate 40 s/V. λ=514 nm.

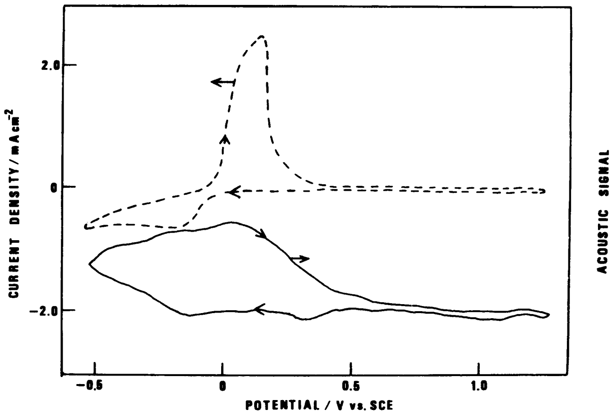


Fig. 4 Acoustic signal-potential (—), and current-potential (---) curves of an Au electrode in the presence of Cu^{2+}ion. $5x10^{-3}$ mol/l Cu^{2+}. 1 mol/l $HClO_4$. Potential sweep rate 40 s/V. λ=514 nm.

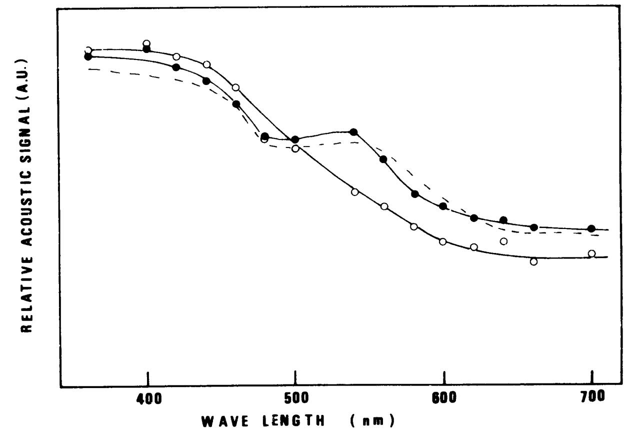


Fig. 5 Photoacoustic spectra of an Au electrode; before (-○-), and after (-●-) electrolysis in $5x10^{-3}$mol/l Cu^{2+}. Photoacoustic spectrum of Cu plate (---).

is for improved instrumentation if more accurate measurement is to be achieved.

It was found, however, that PAS is a useful method for monitoring changes at the electrode-electrolyte interface *in situ*.

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