An Electroreflectance Study at the Bottom-Surface of a Mercury Drop Electrode Placed on an Underlying Nafion Film

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Electroreflectance measurement at the bottom-surface of a mercury drop electrode on an underlying Nafion film on a cell bottom has been demonstrated for the redox reaction of heptylviologen in an aqueous solution.

The spectroelectrochemical methods in an external reflection configuration such as UV-vis and IR-reflection spectroscopies provide powerful tools for characterizing both faradaic and nonfaradaic processes of adsorbed molecules on electrode surfaces. The reflection measurement has usually been made at a planar solid electrode. On the other hand, plenty of information about potential-dependent molecular adsorption on a liquid mercury (Hg) electrode has been so far obtained by conventional electrochemical methods. As an electrode material, Hg has merits such as reproducibility of a clean surface and a high overvoltage for hydrogen evolution. However, *in situ* reflection study in the wavelength range from UV to IR at a Hg electrode has been limited. Four types of Hg electrodes have been used in specular reflection optical configurations: (1) hanging Hg drop electrode (HMDE),[1,2] (2) Hg film deposited on a platinum or gold substrate,[3-5] (3) Hg pool electrode with or without an amalgamated platinum ring guide,[6,7] and (4) Hg drop bottom electrode.[8-10] The Hg bottom electrode may be superior among these electrodes in regard to the purity of Hg and the capability of preventing the mechanical vibration, which is a fatal problem in the reflection measurements.[1-3,6] In the use of the Hg bottom electrode, it is absolutely necessary to minimize the solution resistance of the water thin-layer between the Hg bottom and the optical window of the cell. Blackwood *et al.*[8-10] demonstrated IR reflection absorption measurement at a Hg bottom electrode. However, they did not device to minimize the resistance to the level allowing the potentiostatic measurement. Therefore, we suspect whether they really could collect the reflection beam solely from the Hg bottom to the detector.

Applicability of the ac potential-modulation to the electrode is of importance for the aim of tracking the dynamic processes by the reflection measurements.[11] The measurement of redox reaction by UV-vis reflection spectroscopy with ac potential modulation at a Hg electrode was attempted only once by Barker to our best knowledge, though the experimental performance using HMDE was not satisfactory.[1]

In this letter, we demonstrate for the first time the potential-modulated UV-vis reflectance (Electroreflectance: ER) measurement of the redox reaction at the bottom-surface of a Hg drop electrode. The experimental setup is shown in Figure 1. When the Hg drop was in direct contact with the quartz cell bottom, the solution resistance was actually too high to conduct electrochemical measurements, since the water layer between Hg and glass might be too thin. To avoid the huge resistance, an ionically-conductive, optically-transparent polymer film, Nafion®, was sandwiched between the Hg drop and the cell bottom. The steady, monochromatic probe light was irradiated at normal incidence to the bottom-surface of a Hg drop through the cell-bottom and the Nafion film, with care not to illuminate the edge of Hg drop.

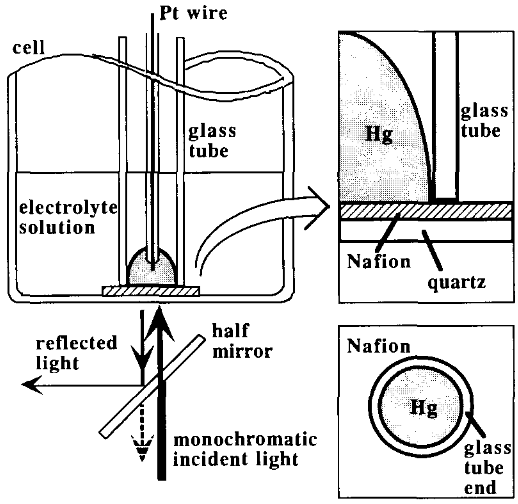

Figure 1. Schematic view of the cell. Lower-right is the bottom-view.

A Nafion 117 film of a 0.175 mm-thickness from Aldrich was cut into a 1 × 1 cm^2-piece, washed with ethanol, rinsed with purified water, and then immersed overnight in 1.0 M (1 M = 1 mol dm^{-3}) KBr solution containing 1 mM heptylviologen dibromide (N,N'-diheptyl-4,4'-bipyridinium dibromide, recrystallized from acetone + ethanol: abbreviated as HV in the remainder). The film was then placed flatly on the bottom of the quartz cell. After filling the cell with electrolyte solution, a glass tube, which plays a roll as a Hg drop holder, was pull down by screw onto the Nafion film. Finally, *ca.* 0.15 ml of Hg (>99.9999% purity) was poured into the tube. The diameter of the edge circle of the Hg in contact with the Nafion film was 6.0 mm. Both the main cell compartment and the tube holding the Hg drop were purged by Ar gas (>99.998%). A Ag/AgCl electrode in saturated KCl in a separated compartment served as the reference electrode. The counter electrode was a coiled gold wire. All the measurements were carried out at 23 ± 2 °C.

Figure 2 shows the cyclic voltammogram of thus prepared Hg electrode in 1.0 M KBr containing 1 mM HV. The voltammetric feature is almost in accord with that measured at a HMDE, indicating that the contact with Nafion does not largely perturb the redox reaction at the Hg electrode. The spike peak is known to be due to the redox reaction of the monolayer-adsorbed $HV^{++/\cdot+}$ couple synchronized with the phase transition of the adsorption layer.[12] ($HV^{\cdot+}$ is HV radical cation.) The electric charge of this peak enabled us to estimate, using the reported value of the surface excess of HV,[12] that *ca.* 90% of the Hg surface in contact with underlying Nafion film works as the electrode

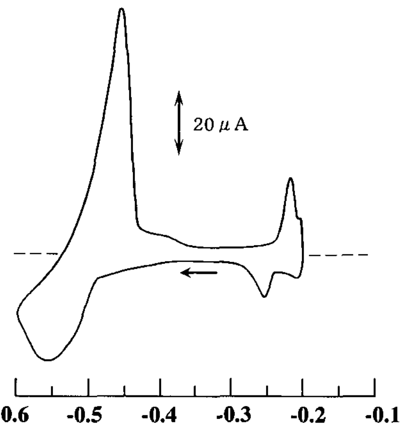

Figure 2. Cyclic voltammogram for HV at Hg electrode on Nafion film in 1 mM HV + 1 M KBr at a scan rate of 0.1 V s^{-1}. Broken line indicates zero-current level.

surface. On the other hand, when not using Nafion, only *ca.* 45 % of the surface, which corresponds to only the edge area of the drop, acted as the electrode. The more negative redox wave corresponds to the reduction of bulk HV^{++}, resulting in the deposition of the $HV^{\bullet+}$, and its reoxidation to HV^{++}.

ER spectrum measured at -0.50 V is shown in Figure 3. The ER spectral profile virtually resembles the absorption spectrum of $HV^{\bullet+}$ (dotted line), which was obtained by reducing HV^{++} by sodium dithionite in an aqueous solution containing β-cyclodextrin.[13] The ER spectral bands at 393 and 606-620 nm are attributable to the absorption by $HV^{\bullet+}$. The ER spectrum should represent the difference absorption spectrum between $HV^{\bullet+}$ and HV^{++}. Since HV^{++} has no absorption bands in this wavelength range, ER spectrum presents the absorption spectrum of $HV^{\bullet+}$ at the Hg/solution/Nafion interface. The band around 550 nm is not pronounced, indicating that most of the $HV^{\bullet+}$ molecules are in the monomeric form.[14] It is important to note that when not using the Nafion sheet, ER spectral response was impossible to be obtained.

The ER voltammogram for the $HV^{++/\bullet+}$ couple was also obtained (data not shown). However, the ER signal at the potential of the spike peak could not be obtained. It is likely either that adsorbed $HV^{\bullet+}$ molecules assume upright orientation or the sensitivity of the present study was not enough to detect the monolayer amount. We are underway of further study to make possible more sensitive measurement with oblique incidence.

We could also measure the ER spectrum and ER voltammogram for the HgO/Hg couple in 1.0 M NaOH solution (data not shown). However, because of the gradual accumulation of HgO-yellow particles between Hg bottom and the Nafion film, ER measurement was possible only in a limited period and potential range. Accumulation of the reaction product as a solid may be a drawback to the use of the Nafion film in the present configuration. For such a reaction, we need to explore how the Nafion affects the electrochemistry at the Hg electrode.

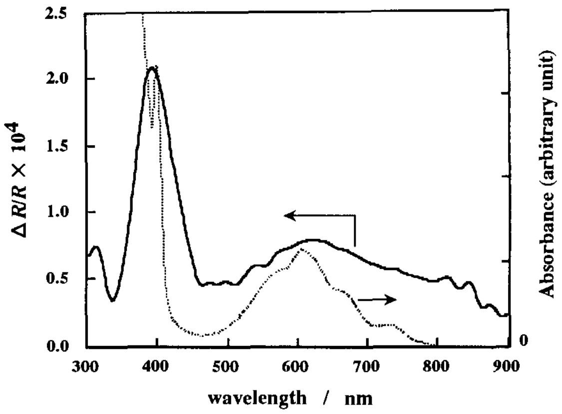

Figure 3. ER spectrum (solid line) for HV at Hg electrode on Nafion film in 1 mM HV + 1 M KBr at -0.5 V. Potential modulation: 50 mV_{rms} and 8 Hz. Dotted line represents absorption spectrum of aqueous solution of $HV^{\bullet+}$ in the presence of excess β-cyclodextrin and sodium hydrosulfite (the latter exhibits absorption at the wavelength < 400 nm).

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