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Estimation of the Concentration-Distance Profile within the Electrochemical Diffusion Layer by Raman Microprobe Spectroscopy

by

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The concentration gradient in the diffusion layer has been measured by Raman microprobe spectroscopy. This method has the advantage that it is molecular specific i.e., the Raman spectrum is unique to the species being detected. The ferricyanide/ferrocyanide couple is used as an illustration. Major concentration depletion and accumulation was found in the volume extending from the surface of a gold electrode to 0.2 mm.

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Estimation of the Concentration-Distance Profile within the Electrochemical Diffusion Layer by Raman Microprobe Spectroscopy

(short running: Analysis of the Diffusion Layer by Microprobe Raman)

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Introduction

Knowledge of the concentration-distance profile in the region of space extending between an electrode surface and the bulk of the solution is essential for the understanding of electrode processes. Properties within the diffusion layer, stretching from the inner layer to the bulk of the solution, differ from those of the bulk. Two major optical properties which have been utilized in order to estimate the concentration of species in the diffusion layer are refractive index and absorbance. Interferometry [1,2] is a method based on refractive index change; in general it is nonselective because any component can change the local refractive index. Methods based on absorbance can be selective, particularly for coloured species, or species with a detectable vibration spectrum. Applications of electronic and vibrational spectroscopies have been recently reviewed by McCreery [3]. Greater selectivity, sensitivity, and higher spatial resolution have been achieved with these techniques. Methods which combine interferometry and spectroscopy provide greater selectivity but rely on the possibility of resolving often broad UV-visible bands and cannot be categorized as a routine experiment [4-6].

Here we propose a new method with excellent capability of discrimination between species and for estimation of the local concentration of the species. The method is based on Raman spectroscopy and thus exploits the structural information inherent in the vibrational spectrum. We have been making use of the Raman microprobe to investigate the species adsorbed or formed on electrode surfaces. A Raman signal of an adsorbed species is obtained when the laser beam is focussed through the microscope objective upon the electrode surface. However, when the position of the focus is **above** the surface we observed that the surface-adsorbed species and the bulk-dissolved species gave different intensities. We found that we could characterize a concentration gradient by adjusting the focal point at different heights above the electrode surface.

Here we report our preliminary results of this technique, applied to the ferricyanide and ferrocyanide redox couple.

Experimental

A Dilor OMARS-89 spectrometer with microscope option, interfaced to an IBM PC-AT computer was used for the measurements. The detector is a 512 diode diode-array optically coupled to an image intensifier. As excitation light source, the 514.5 nm line of a Coherent Innova 70 Argon ion laser (100 mW) was used.

A specially designed Raman cell shown in Fig. 1 was used for in-situ measurement of Raman spectra while the working electrode was under potentiostatic control. The schematic illustration of the cell and an outline of the microscopic part of the Dilor spectrometer are shown in Fig. 1. The laser beam enters from point A and is reflected at C to the objective lens, D. Through D, the laser irradiates a surface of the working electrode, E, and its scattered light is collected by the objective lens, D; from B it is directed to the main body of the spectrometer. The objective lens used here has an objective magnification 50 (OLYMPUS IC50/MSPLAN 50, ∞/0 f=180, NA=0.55). A knob I is used to change the distance between the objective lens and a stage (H) to which the cell is attached; thus it can be used to adjust the height of the focus point above the surface of the working electrode. The minimum rotation unit corresponds to a height change of 2 μm and thus the distance profile can, at present, be probed in 2 μm intervals in principle.

A gold working electrode, E, which consisted of a gold rod of 5 mm diameter and 7 mm length, sealed inside an 8 mm diameter Teflon sheath, was used; it was polished with 0.5 and 0.3 μm alumina slurries on metron cloths. Two platinum wires were used for the counter electrode (G) and the reference electrode (F).

The sample solution had the composition 0.2 M $K_4Fe(CN)_6$, 0.2 M $K_3Fe(CN)_6$, and 0.5 M NaCl. In this case, the reactions at the working, the reference, and the counter electrodes are described by the following process:

$$Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-} \tag{1}$$

The reference electrode had an absolute potential equal to the standard potential of the ferrocyanide/ferricyanide redox couple. The working electrode had zero potential relative to the reference electrode. The reaction taking place at the counter electrode was the reverse reaction of that at the working electrode; thus the net composition of the entire solution was not changed.

Both ferrocyanide (2092, 2058) and ferricyanide (2132 cm^{-1}) have Raman-active vibrations as noted; thus the changes of their concentrations could be estimated from their Raman intensities.

Results and Discussion

Three sorts of experiments were carried out. Under the open circuit condition, the potential of the gold (working) electrode against the platinum reference electrode was zero. The region of the Raman spectra from 2000 to 2200 cm^{-1} was measured for focal points at different heights from the electrode surface. Spectra are shown in the mid panel (B) of Figure 2. Figure 2-A and 2-C were measured under constant potential electrolysis with the indicated potentials after the potential was applied for at least 20 min, because it has been reported that the concentration gradient in the diffusion layer is almost at steady state after 2 min (7). A Raman intensity measurement at one position requires 40 s (accumulation number 10, time constant 2); thus the measurement for 20 to 25 different height positions requires about 16 min.

Three shaded spectra of Fig. 2 correspond to those measured at the electrode surface (so called, SR spectra). The Raman peak at 2132 cm^{-1} is ascribed to the ferricyanide ion; and those at 2092 and 2058 cm^{-1} are from the ferrocyanide ion. The three SR spectra are different from each other; but spectral changes dependent on the position of the focal point were also observed. In Figure 3, the height profile of the concentration of ferricyanide ion, which is estimated from the intensity of the 2132 cm^{-1} band, and that of ferrocyanide, 2092 cm^{-1}, are shown at the three potentials.

Compared to the plots of open circles corresponding to intensities measured under the open-circuit condition, the intensity of ferricyanide is higher at the oxidation potential +200 mV, and is lower at the reduction potential -200 mV, as shown in Fig. 3-A. Conversely, the intensity of ferrocyanide is lower at the oxidation potential and is higher at the reduction potential than observed for the open circuit condition (3-B). Ferrocyanide ion is consumed by oxidation at the electrode and is transformed into ferricyanide ion. Consequently, in the vicinity of the electrode the concentration of the ferrocyanide decreases and that of the ferricyanide ion increases. For reduction, the concentration of the ferricyanide ion decreases and that of the ferrocyanide ion increases as a result of the reverse reaction. Major concentration depletion and accumulation was found in the volume extending from the surface up to 0.2 mm. This observation is consistent with the report by Jan and McCreery (7) that the diffusion layer thickness at the steady state reaches a limiting value after 2 min of about 220 µm, presumably due to natural convection.

Even for negative distances (i.e., "inside" the electrode), some magnitude of the Raman intensity of both the ferricyanide and the ferrocyanide ion were observed, although those intensities are much lower than those from the solution side. It is probable that the mirror surface of the gold electrode reflects the laser beam creating a focus in the solution when the focal point has been adjusted inside the electrode metal; thus, a low but finite amount of Raman intensity was observed even at negative heights. The loss of laser intensity following reflection and absorption accounts for the lower observed intensity.

The Raman microprobe can give the concentration-distance profile in the electrochemical diffusion layer with no other special elaborate optics; high specificity is possible from the unique vibrational spectra of the species. Further examples and theoretical considerations will be published elsewhere.

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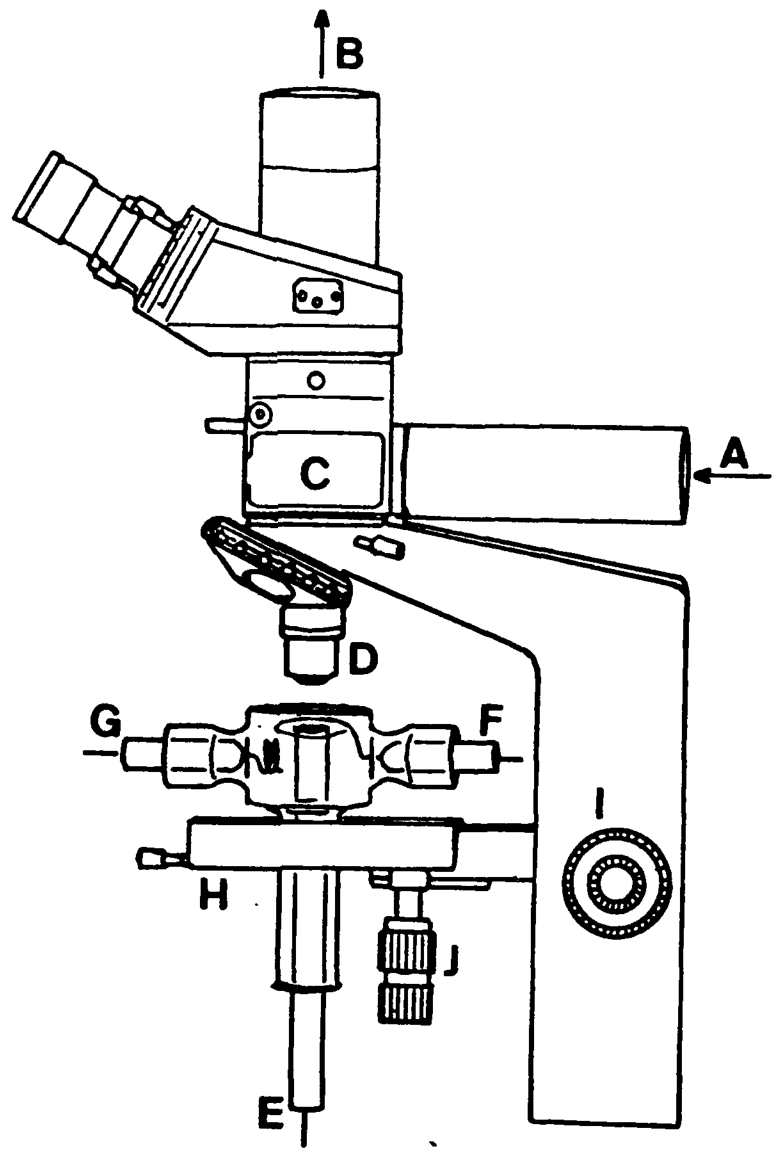
Figure Captions

Figure 1: Schematic illustration of the microscopic part of the Dilor OMARS-89 Raman spectrometer and the electrochemical Raman cell. A: laser beam inlet; B: scattered beam outlet; C: beam reflector; D: objective lens (magnification X50); E: gold working electrode; F: platinum wire reference electrode; G: platinum wire counter electrode; H: X-Y stage; I: height adjustment knob; and J: X-Y drive control knob.

Figure 2: Height-profile of the Raman spectrum of the ferrocyanide/ferricyanide system in the wavenumber region from 2000 to 2200 cm^{-1}.

Figure 3: Dependence of the Raman intensity of A: ferricyanide ion (2132 cm^{-1}) and B: ferrocyanide ion (2092 cm^{-1}) upon the distance from the electrode surface under controlled potential electrolysis (+200 mV, open circuit, and -200 mV).


B
A
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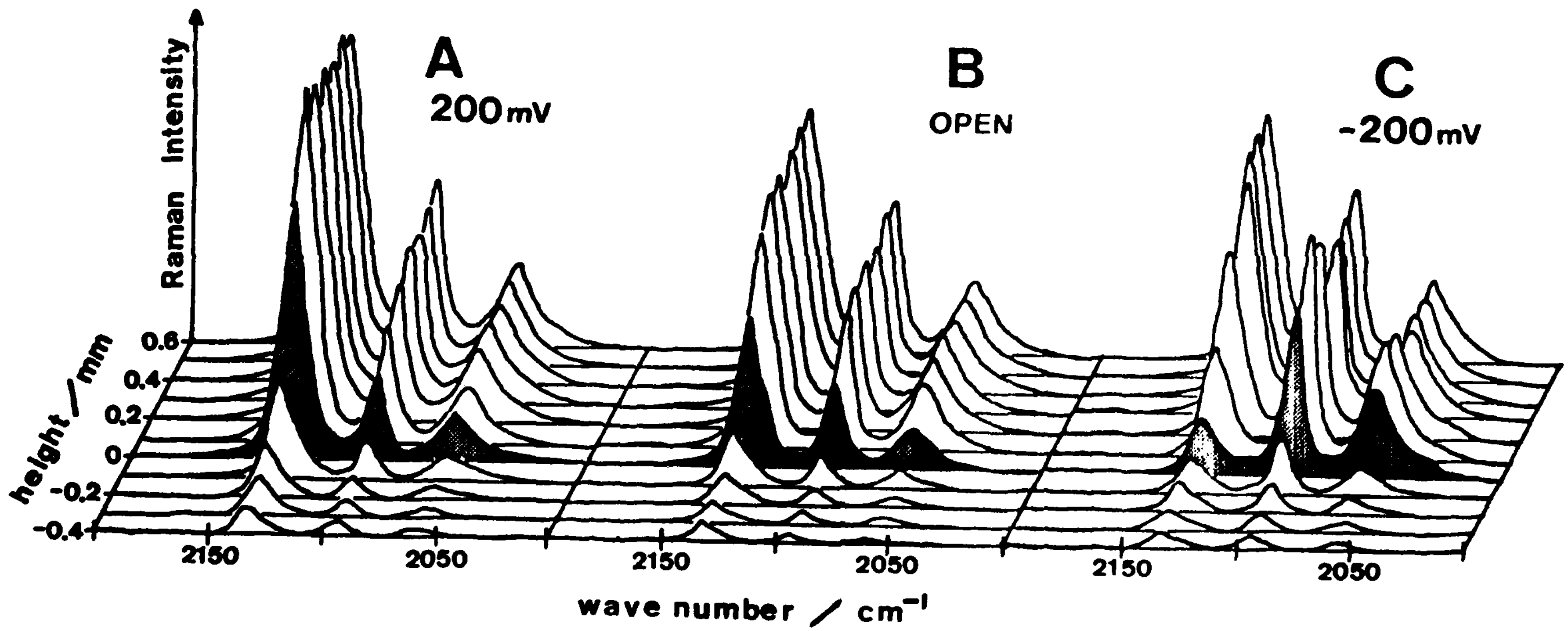
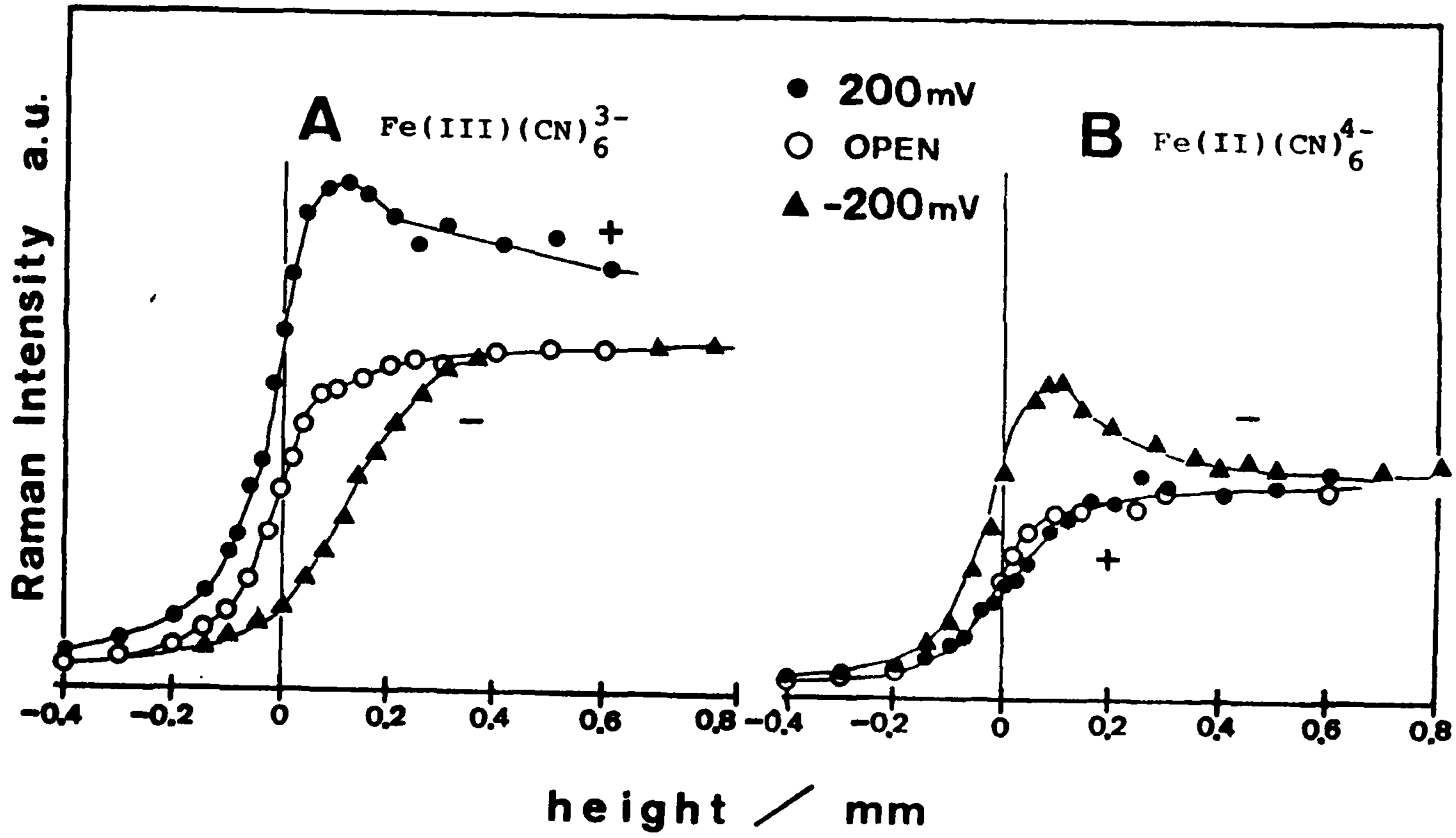

A
200mV
B
OPEN
C
-200mV
Raman Intensity
height / mm
0.6
0.4
0.2
0
-0.2
-0.4
2150
2050
2150
2050
2150
2050
wave number / cm^{-1}


Raman Intensity a.u.
A Fe(III)(CN)$_6^{3-}$
B Fe(II)(CN)$_6^{4-}$
200mV
OPEN
-200mV
+
−
+
−
−0.4
−0.2
0
0.2
0.4
0.6
0.8
height / mm