

**Reactions at oil|water|electrode interfaces by
ion-insoluble polydimethylsiloxane droplet
- the formation of emulsion**

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When a wire electrode pierces an oil|water interface, its side comes in contact with the oil|water interface in a ring shape to form a three-phase boundary, as illustrated in Fig.1(A). This kind of three-phase boundary may be generated when a sensor electrode is inserted in living tissues, piercing oil|water interfaces. A technical key of the electrochemical measurements at the three-phase boundary have been performed by use of a hemispherical oil drop mounted on a planar electrode in aqueous solution^{1,2}, as shown in Fig.1(B). If there is not any electrolyte in the oil phase, a double layer will be formed at the water|electrode interface by the supporting electrolyte. Since the aqueous phase contains no electroactive species, no electrode reaction occurs at the water|electrode interface. Electrode reactions can react only at the three-phase boundary. This anticipation leads us to electrochemical work on the redox behavior of ferrocene at the three-phase boundary. It is expected that the three-phase boundary is as thin as the molecular length because the oil|water interface intersects geometrically the electrode surface to form an infinitesimally thin ring. However, the boundary has micrometer width because of formation of oil-in-water emulsion.

The electrochemical system presented here is the oxidation of ferrocene in the hemispherical droplet of polydimethylsiloxane (PDS) at the ring shape of the oil|water|electrode interface. The PDS phase included ferrocene without supporting electrolyte, whereas the aqueous phase included electrolyte without electroactive species. The voltammogram showed the steady-state anodic wave for the oxidation of ferrocene (Fig.2), independent of potential sweep rates. The limiting current was proportional to the radii of the droplet. These facts indicate that the electrode reaction should occur at the thin annular part on the electrode to which the water and the oil phase merge. The ring width of the three-phase boundary was evaluated from the limiting current on the basis of the microband model to yield 18 and 9 μm for BF_4^- and ClO_4^- , respectively, much larger than a molecular length or thickness of a diffuse double layer predicted geometrically from intersection of two plains. The large values suggest participation in fluctuation of the three-phase boundary. The fluctuation is ascribed to emulsion formed at the oil|water interface owing to forced dissolution of ferricenium ion in the oil phase. The emulsion was observed with a microscope (Fig.3) and was chemically detected.

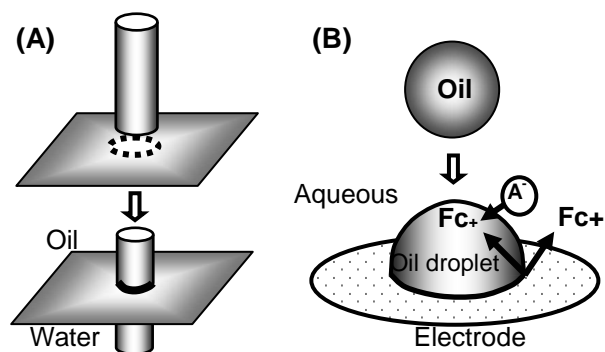


Fig.1. Illustration of generating the oil|water|electrode boundary by (A) piercing a wire electrode for a sensor in an oil|water interface and (B) dropping oil on a planar electrode in aqueous solution.

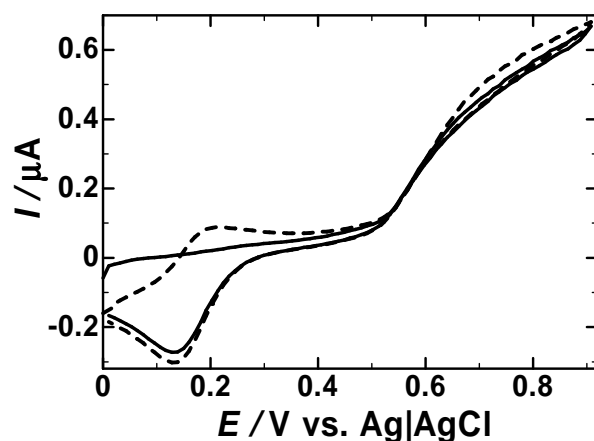


Fig.2. Cyclic voltammogram of the ferrocene-included PDS droplet 0.56 mm in radii on the glassy carbon electrode in 0.05 M NaBF_4 aqueous solution at 10 mV s^{-1} for the first (solid curve) and the second (dotted) scan.

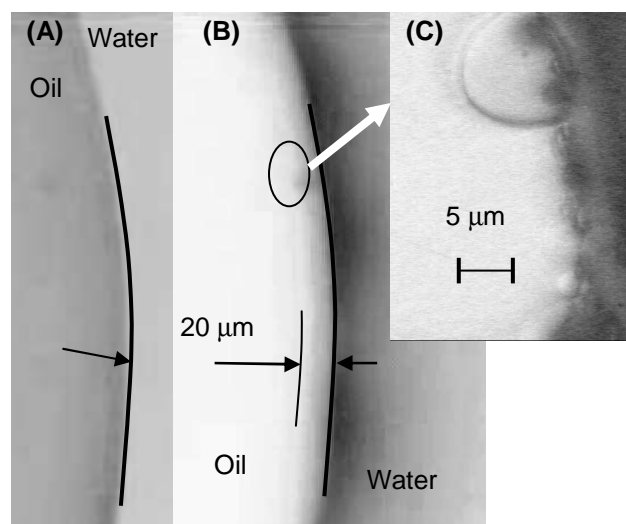


Fig.3. Photographs of the PDS droplet on the electrode in 0.05 M KCl aqueous solution (A) before the potential application, (B) one minute after applying 0.8 V, and (C) 10 minutes after applying 0.8 V.

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