Abs. 69, 206th Meeting, © 2004 The Electrochemical Society, Inc.

The formation of emulsion at water | oil | electrode three-phase boundary

Jingyuan Chen*, Masanori Sato
Department of Applied Physics,
Fukui University,
3-9-1 Bunkyo, Fukui-shi, 910-8507 Japan

There are some electrochemical systems in which an electrode is in contact with both a water phase and an oil phase, exemplified by electrochemical bio-sensors inserted into living tissues and electrode reactions of emulsions[1]. When electroactive species is included even in the oil phase, both electrode reactions and ion-transfer will occur. What behavior of the electrode reaction will be observed in emulsion system. Under this motivation, we generate in this paper the three-phase boundary by use of ferrocene-included silicone oil droplets in $NaBF_4$-included water phase.

A simple system of the competitive behavior is composed of an oil droplet mounted on the electrode in an aqueous solution, as is shown in Fig.1, there the electrode is in contact with the water phase and oil phase. The oil droplet contains neutral electroactive specie ferrocene without deliberately adding supporting electrolyte, whereas the aqueous phase has no electroactive species but contains supporting electrolyte.

In order to evaluate the thickness of the three-phase boundary, an approximate equation for the voltammetric peak current was derived as a function of the width and potential sweep rates on the basis of the band electrode model[2]. The steady-state voltammograms in the domain of $E > 0.5$ V were observed in aqueous solutions. We plotted the limiting current values against the radii, r_1, of droplets in Fig.2 for aqueous solution of $NaBF_4$ and $NaClO_4$. Although the variations contain large scatter, they are approximately proportion to the radii for both the anions. Therefore, the limiting current is caused by the oxidation of the ferrocene at the thin three-phase boundary. The width (9-18 μm) evaluated from the microband model suggests large disturbance of the three-phase boundary. These values of width are much larger than the molecular length predicted mathematically from two intersecting planes. We suggest another cause of extending the three phase boundary. Watching the droplet carefully, we noticed disturbance of the interface by generation of white turbid cloud around the droplet near the electrode after the potential was swept to over 0.5 V. Detailed observation was made through the video microscope perpendicularly to the electrode surface after applying constant potential (0.8 V) to the electrode. The oil|water interface viewed from the top was a well defined circle before the potential was application. When the potential was applied, a color layer developed from the interface toward the aqueous bulk. This layer is obviously the diffusion layer of ferricenium ion. Then a white turbid layer appeared on the side of the oil phase in contact with the oil|water interface (watching video at poster session). After 10 minutes, droplets appeared and developed near the boundary on the oil side, as is shown in Fig.3A. Consequently, water-in-oil emulsion is formed in the oil phase near the boundary, exhibiting the turbid layer; Some small aqueous droplets coalesces to visible droplets because of absence of surfactant. The emulsion may be ascribed to the formation of the intermediate, Fc^+(oil), which draws water droplets into the oil phase.

* Corresponding author. Tel: +81-776-27-8753, fax: +81-776-27-8494
e-mail: d020111@icpc00.icpc.fukui-u.ac.jp.

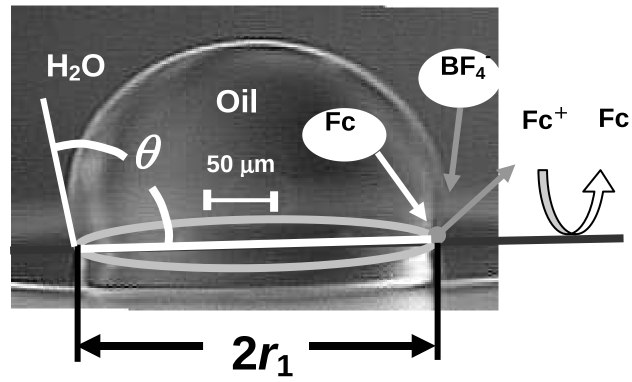

Fig.1 Photograph of the ferrocene-included polydimethylsiloxane droplet on the glassy carbon electrode in 0.1 M $NaBF_4$ aqueous solution. The arrows are the predicted transport of ferrocene, ferricenium ion and BF_4-.

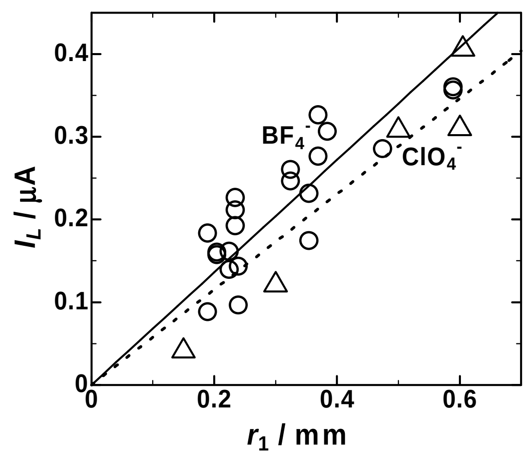

Fig.2 Proportionality of the limiting current with radii of contacting circles of the PDS droplets when the aqueous solution included 0.05 M $NaBF_4$ (circles) and 0.050 M $NaClO_4$. (triangles). The oil phase contained 10 mM ferrocene. Voltammograms were obtained at 10 mV s^{-1}.

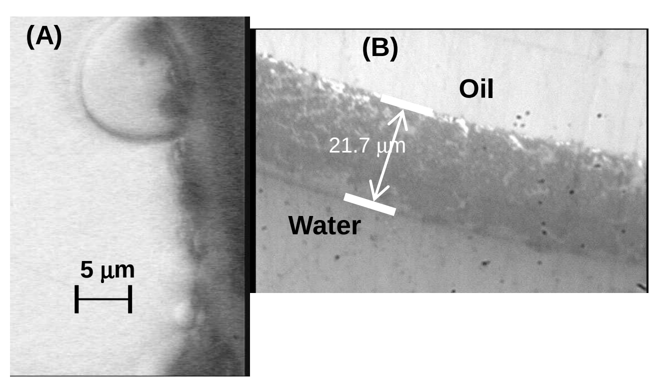

Fig.3 Photographs of the PDS droplet on the electrode in 0.05 M KCl aqueous solution. (A) 10 minutes after applying 0.8 V, (B) 30 minutes after applying 0.8 V, the droplet was rinsed with water several times in order to remove water-dissolved salt before being mounted on the microscope. Then the droplet was dried on the electrode 60 min after the irradiation of the light beam of the microscope.

[1] J. Chen, O. Ikeda, K. Aoki, J. Electroanal. Chem., 496 (2001) 88.
[2] K. Aoki, P. Tasakorn, J. Chen, J. Electroanal. Chem., 542 (2003) 51.