Ferrocene redox behavior at nano-scale
three-phase boundary
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In order to comprehend the emulsion system, we investigated the electrode behavior at the oil|electrode|water interface. The behavior varies with the voltammetric variables such as potential sweep rates, concentrations, drop size, area of the electrode, and presence or absence of electrolyte in the droplet [1].

The oil droplet is shown in Fig.1. A nitrobenzene droplet including ferrocene (Fc) was attached to a glassy carbon electrode in aqueous solution so that a three-phase boundary between the water, the oil and the electrode was formed. The oil droplet contained 50 mM tetrabutylammonium perchlorate (TBAClO$_4$) whereas the water phase contained 50 mM sodium perchlorate (NaClO$_4$). The oxidation wave of Fc in the oil droplet (Fig. 2) is controlled by diffusion of Fc, i.e., it is proportional to the concentration, the potential sweep rate for $v < 0.1$ V s^{-1} and the contact area of the droplet on the electrode. The peak current can be expressed in terms of the conventional expression for the reversible peak current, except for the coefficient, if the electroactive area is taken to be the area of the oil|electrode interface. Fig.3 is shows the dependence of i_p at the first scan on the radius and contact area. The proportionality of the peak current with the radius of the circular oil|electrode interface, becomes conspicuous when the scan rate becomes faster without supporting electrolyte. Diffusion of the counterion at a short time restricts the electrode reaction to the edge of the oil|electrode interface. This behavior can be modeled a diffusion current at a microband electrode which this model is shown in Fig 4. With the lapse of time, the diffusion layer extends toward the center of the circular interface, and finally covers the interface. Then the oxidation occurs over the whole interface area, not at the three-phase boundary.
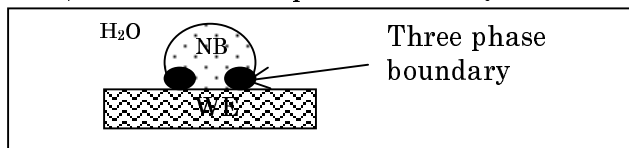

Fig.1 An oil droplet is smaller than the electrode (W) diameter. It exhibits a three-phase boundary in a circle on the electrode Fc is

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1. T.Porntip, C.Jingyuan, A. Koichi,
J.Electrochem. Chem., 533 (2002), 119-126.
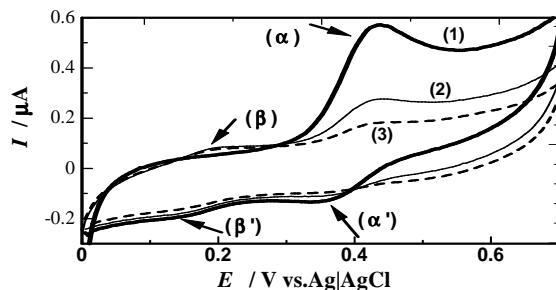
oxidized both in the oil and the water phases.

Fig.2 Cyclic voltammograms of the oil droplet at the potential sweep rate 10 mV/s. The oil phase contained 50 mM TBAClO$_4$ whereas the water phase contained 50 mM NaClO$_4$. Geometry of the droplet was $r_1 = 0.5$ mm and $r_2 = 0.56$ mm. Number (1), (2), and (3) denote the first, the second and the third scan.
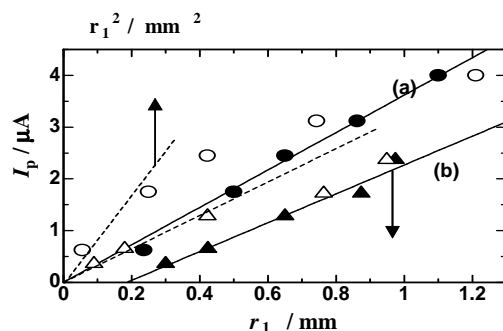

Fig.3 Dependence of i_p at the first scan in cell on the radius, r_1, (on the lower axis, full marks) and contact area, πr_1^2 (on the upper axis, open marks) of the droplet at $c = 5$ mM without supporting electrolyte. Potential sweep rates are (a) 50 and (b) 5 mV s^{-1}. The dashed lines were drawn for the proportionality fitted for $i_p < 1.8$ µA.
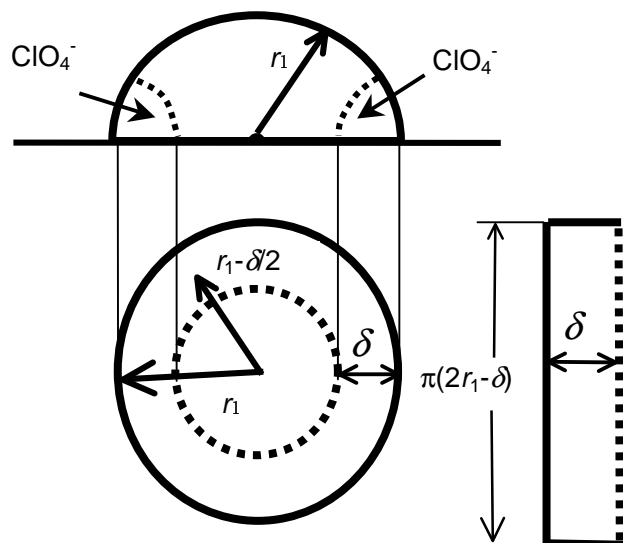

Fig.4 A model of the three-phase boundary. Diffusion of ClO$_4^-$ reaches the ring domain δ wide, at which Fc is oxidized. The left is the band electrode modeled after the ring.