Alternative or Simultaneous Electrochemical Access with Micro Water/Oil Phases in a Middle Phase Microemulsion Based on the Hydrophilic/Lipophilic Balance on Electrode Surfaces

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The electrochemical contact with the micro aqueous phase and the micro organic solvent phase in the "middle phase" microemulsion, in which the water phase and the oil phase bicontinuously coexist on a microscopic scale, was alternatively or simultaneously achieved by controlling the hydrophilicity and lipophilicity on electrode surfaces.

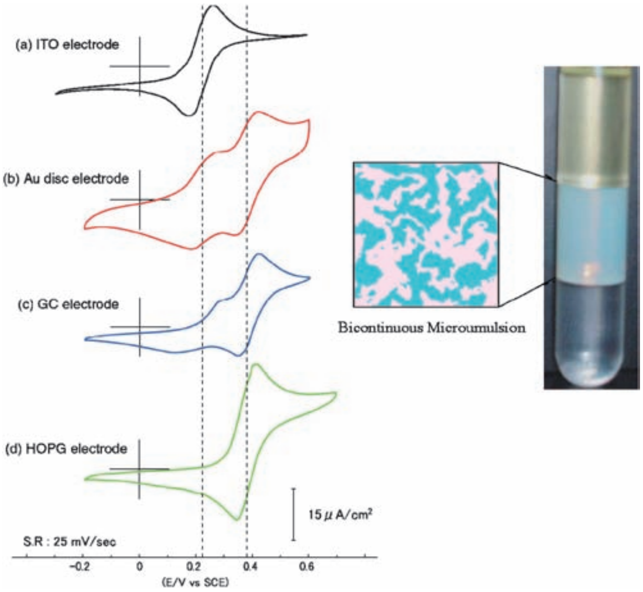

Figure 1. Typical cyclic voltammograms measured using ITO (a), polished Au disc (b), polished GC (c), and cleaved HOPG (d) electrodes in the MPME in the presence of $K_3Fe(CN)_6$ and ferrocene. Scan rate: 25 mV/sec. The right inset shows a picture of three-phase microemulsion.

A microemulsion (ME)[1] is low-viscosity, isotropic, thermodynamically stable, and spontaneously formed solution phase composed of water, organic solvent, and surfactants. The dynamic morphology of a ME is determined by the characteristics of the surfactant in the emulsion system. When the hydrophilicity and lipophilicity of a surfactant in a system are well-balanced, the ME reveals a bicontinuous structure, a so-called middle phase microemulsion (MPME, Winsor III).[2–4] In an MPME, the water phase and the oil phase coexist alternately on a microscopic scale as a bicontinuous structure. As a typical MPME, Guering and Lindman[5] researched details of a ME system composed of saline and toluene microphases with sodium dodecylsulfate (SDS) and *n*-butanol as the surfactant and cosurfactant, respectively. They proved that the diffusion coefficients of both water and the toluene species, which were obtained by PGSE-NMR, were kept at high levels in the MPME. This report directed our attention toward electrochemical research on MPME. In a previous letter, we reported the simultaneous electrochemical response of the $Fe(CN)_6$ ion and ferrocene, which are distributed in the saline and toluene phases, respectively, of the MPME.[7] The unique characteristics of an MPME are essentially based on the very delicate balance between the hydrophilicity and lipophilicity (HLB) of the surfactant system, which is moderated by the concentrations of cosurfactant and salt. It would be expected that the local structure of an MPME on a surface changes according to the characteristics of the surface. Therefore, the electrochemistry of redox molecules in an MPME was investigated using various electrodes, such as indium tin oxide (ITO), gold disc (Au), glassy carbon disc (GC), highly oriented pyrolytic graphite (HOPG), and alkane thiol-modified Au (SAM) electrodes.

The MPME solution prepared for the electrochemical measurements was macroscopically separated into three phases, a toluene phase, a middle phase, and a saline phase, as shown in the right inset of Figure 1. The typical content of the three-phase ME solution was water (19.3 mL), NaCl (1.10 mol/L in water phase), SDS (2.76×10^{-3} mol), *n*-butanol (2.16×10^{-2} mol), and toluene (21.3 mL). The MPMEs with redox compounds were prepared using a 1 mM aqueous of ferrocene solution of $K_3Fe(CN)_6$ and/or a 1 mM toluene solution. No effect was observed following the addition of these redox species in terms of the phase diagram. Electrochemistry in an MPME was conducted using ordinary commercially available equipment. A Pt wire and a saturated calomel electrode (SCE) were also set into the MPME in the solution as counter and reference electrodes, respectively.[7]

Au and GC disc electrodes, which were mechanically polished before experiments, gave typical cyclic voltammograms (CVs) with two independent reversible redox peak couples in the MPME, which are attributed to the redox of $K_3Fe(CN)_6$ and ferrocene, as shown in Figures 1b and 1c. The redox potential of the $Fe(CN)_6$ ion observed in the MPME ($E_{pa} = 0.27$ and $E_{pc} = 0.19$ V vs SCE) is essentially the same as that in an ordinary aqueous solution. Interestingly, ferrocene in the MPME reveals reversible redox peaks at $E_{pa} = 0.43$ and $E_{pc} = 0.36$ V vs SCE, although the electrolyte is not present in the toluene phase. It is reasonable to suppose that the ionic conductivity is maintained via a continuous saline phase in the MPME as an ion-conductive passage. The redox properties of $K_3Fe(CN)_6$ and ferrocene in the MPME are regulated by diffusion control, according to the dependence of the scan rate for peak currents. These results indicate that Au and GC electrode surfaces simultaneously contact both the micro saline phase and the micro toluene phase in the MPME.

Although no electrode influence was observed in terms of the redox potentials and peak separations, redox peak currents changed drastically according to the type of electrode used. When strong hydrophilic or lipophilic (hydrophobic) electrodes were used, it was found that the electrochemical responses from the saline and organic solvent microphases in the MPME differed. Figure 1a shows the CV obtained in the MPME using an ITO electrode. An ITO electrode possesses a strongly hydrophilic, negatively charged surface. No redox peaks due to ferrocene were observed at ca. 0.4 V, although the redox peaks of $K_3Fe(CN)_6$ were clearly observed. For the MPME in the presence of only ferrocene ($K_3Fe(CN)_6$ was absent), a featureless CV, which was the same as that for the MPME in the absence of redox species, was obtained with an ITO electrode. Conversely, strongly lipophilic (hydrophobic) electrodes such as HOPG revealed the opposite electrochemical response in the MPME, as shown in Figure 1d. An HOPG electrode provides an atomically flat neutral surface, which is entirely different from a GC electrode. The surface of a GC electrode is slightly negatively charged by a terminal carboxylic groups. In Figure 1d, only a reversible redox peak couple from ferrocene in the micro organic solvent phase was clearly observed at ca. 0.4 V, and the presence of $K_3Fe(CN)_6$ in the micro saline phase had almost no influence. For the MPME in the absence of ferrocene, a featureless CV was obtained for the solution both with and without $K_3Fe(CN)_6$.

As another example using a lipophilic electrode, a similar electrochemical contact with the micro organic solvent phase only was obtained by using a self-assembled monolayer (SAM)-modified Au disc electrode with octadecanethiol ($C_{18}SH/Au$), as shown in Figure 2. No redox peaks were observed for $K_3Fe(CN)_6$, only the redox peaks for ferrocene in the MPME were observed using the $C_{18}SH/Au$ disc electrode, as same as the HOPG electrode. SAM electrodes regularly obtained currents that were approximately two times higher than those obtained using HOPG. This might suggest the enrichment of ferrocene into multilayers on the electrode consisting of SAM and surfactants.[8] In fact, the SAM electrode was not stable for electrochemical cycles in the MPME, probably due to disturbance of the alkyl chain packing or partial desorption of the SAM into toluene phase. Just after modification, the SAM modified electrode perfectly blocked the redox activity of $K_3Fe(CN)_6$ in 0.1 M KCl solution. However, the structure of the SAM was destroyed after several tens of cycles of CV measurements in the MPME and broad redox peaks of $K_3Fe(CN)_6$ was observed (Figure 2a). Amazingly, when it was moved back to the MPME again, the imperfect modified electrode revealed the perfect alternate responses in the MPME solution, as same as before. The thermodynamic spontaneous adsorption of surfactant molecules into the SAM would lead to self-complementation of the blocking against hydrophilic $K_3Fe(CN)_6$.

These alternating electrochemical responses in MPME indicate that the bulk bicontinuous structure is thermodynamically discontinuous near the surface, because of the influence of the hydrophilicity or lipophilicity of the electrode surface. Hydrophilic and lipophilic (hydrophobic) surfaces predominantly face toward the micro saline phase and the micro organic solvent phase, respectively, in MPME. Interestingly, surface roughness is not crucial for achieving alternative electrochemical contacts in each micro solution phase in the MPME, because very rough surfaces, such as vapor-deposited ITO and a mechanically polished Au surface modified by SAM both achieved this.

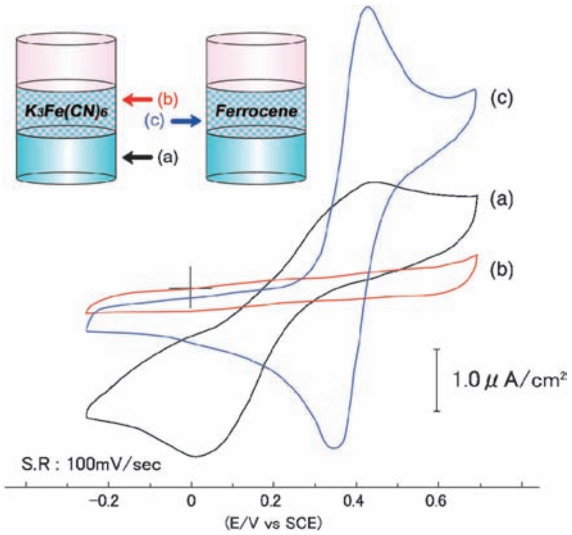

Figure 2. Typical cyclic voltammograms of 0.1 M KCl solution in the presence of 1 mM $K_3Fe(CN)_6$ (a) and the MPME solution in the presence of $K_3Fe(CN)_6$ (b), or 1 mM ferrocene (c) measured using a $C_{18}SH$-modified Au disc electrode. The CVs (b and c) were measured after the experiment to obtain the CV (a). Scan rate: 25 mV/sec.

When the CVs obtained using four different electrodes are compared in Figure 1, it is seen that the peak currents of $K_3Fe(CN)_6$ were decreased, and those for ferrocene were simultaneously increased, in this order: ITO, Au, GC, and HOPG, as shown in Figure 1. This order for the electrodes might be attributed to the expected order of electrode surface hydrophilicity. The lipophilicity of the GC electrode was expected to be much less than that of the HOPG electrode. It is possible to prepare a bicontinuous ME solution, which is macroscopically uniform single phase but not three phases. The ME also gave identical electrochemical responses.

Conclusively, a well-balanced bicontinuous structure of MPMEs is easily changed to a biased or one-sided structure on an electrode surface in order to minimize surface energy. In other words, the local morphology of an MPME near a surface is thermodynamically determined by the HLB of electrode surfaces, but not by ordinary HLB in an emulsion system. The electrochemistry of MPMEs as novel solution systems might provide a unique approach not only to fundamental research into the solution chemistry of organized systems, but also for novel applications such as phase-transfer redox catalytic reactions, analytical systems, and so on.

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