Electrochemical Performance of a Glassy Carbon Electrode Anodized in 1-Octanol

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We have recently found that a potential sweep treatment of a glassy carbon electrode at between 0–+2.0 V vs. Ag wire in an alkanol containing 1 M H₂SO₄ can modify the electrode surface with the alkanol probably *via* an ether linkage.¹ A glassy carbon electrode anodized in 1-octanol (C8-GCE) acquired a hydrophobic membrane on its surface similar to a self-assembled monolayer of 1-octanethiol formed on a gold electrode. However, the surface condition was suggested to be totally different from that of a glassy carbon electrode anodized in H₂O (W-GCE) by essentially the same procedure. In order to elucidate the nature of the C8-GCE surface in more detail, the electrochemical performance of C8- and W-GCEs was compared further. In this paper we report on the effects of CaCl₂, butylamine hydrochloride, and hexylamine hydrochloride upon the voltammetric response of Fe(CN)₆³⁻ at C8- and W-GCEs, which is expected to introduce a new concept in designing a modified electrode as an ion-sensor.

A C8-GCE and a W-GCE were prepared as follows. A mechanically polished GCE (3 mm ϕ) was anodized in 1-octanol or H₂O containing H₂SO₄ (0.1 M) by controlled potential electrolysis at +2.0 V vs. Ag wire, instead of the potential sweep method¹, in order to precisely control the amount of electricity consumed during the treatment. After 5 mC electricity was consumed the electrode was successively washed with MeOH and deionized water, and then cathodically treated by sweeping the potential five times from 0––0.5 V vs. SCE in 0.1 M aqueous KCl.

Upon cyclic voltammetry (CV) of an aqueous solution of K₃Fe(CN)₆ (5 mM) and KCl (10 mM) at the thus-obtained C8-GCE, the electrode process of Fe(CN)₆³⁻ used as a marker was completely depressed, which was restored by the addition of dodecyltrimethylammonium bromide. Although a similar behavior was observed at a W-GCE, the surfactant induced no change in the depressed voltammogram. As previously reported¹, the

voltammetric behavior at a C8-GCE could be explained by the formation of an insulating hydrophobic membrane at the surface through its anodic oxidation in 1-octanol, while the surface of a W-GCE is suggested to have been covered by anionic functional groups, such as carboxylate², which induces a depressed response of the anionic marker at the W-GCE due to an electrostatic repulsion.

Since Ca²⁺ is well known to restore the suppressed voltammetric response of an anionic marker at an electrode modified with a membrane containing anionic functional groups^{3–6}, Ca²⁺ can be used as a probe for the existence of anionic sites on an modified electrode. Thus, for each aqueous solution containing K₃Fe(CN)₆ (5 mM), KCl (10 mM), and CaCl₂ of various concentrations (0, 0.5, 1, 4, 7, 10 mM), CV was performed at both the C8- and W-GCEs at a sweep rate of 100 mV/s. The effects of Ca²⁺ upon the electrochemical response of Fe(CN)₆³⁻ was evaluated based on the ratio of the cathodic current at 0 V vs. SCE in the presence of CaCl₂ (*I*)⁷ to that in the absence of the additive (*I*₀).⁸ As shown in Fig. 1, an increase in the current ratio (*I*/*I*₀) with the concentration of CaCl₂ was observed at the W-GCE, demonstrating that anionic functional groups actually exist on its surface, as is generally accepted.² Unexpectedly, the additive exhibited a similar effect at the C8-GCE, which was more pronounced than that at the W-GCE. These results seem to indicate that a C8-GCE possesses more anionic sites than does a W-GCE, contradicting to our conclusion that a C8-GCE has a hydrophobic membrane solely comprising an uncharged alkyl group.

In order to disclose the origin of the phenomena at a C8-GCE, it was examined how the coexistence of butylamine hydrochloride (1) and hexylamine hydrochloride (2) affects the response of Fe(CN)₆³⁻ depressed at C8- and W-GCEs. The reasons for choosing the ammonium ions were as follows: (1) 1 and 2 have no surface-activating ability like that of dodecyltrimethylammoni-

Fig. 1 Effects of CaCl_2 on the response observed on the cyclic voltammetry of $\text{K}_3\text{Fe}(\text{CN})_6$ (5 mM) in aqueous KCl (10 mM) at a C8-GCE (closed circles) and a W-GCE (open circles).

Fig. 2 Effects of butylamine hydrochloride (1) (circles) and hexylamine hydrochloride (2) (triangles) on the response observed on the cyclic voltammetry of $\text{K}_3\text{Fe}(\text{CN})_6$ (5 mM) in aqueous KCl (10 mM) at a C8-GCE (closed marks) and a W-GCE (open marks).

um bromide, and their association with a carboxylate anion is weaker than that with Ca^{2+} ; (2) accordingly, it was expected that the membrane on a C8-GCE would be shown to have anionic sites as does a W-GCE, if these ammonium ions induced no effect on the voltammetric response of $\text{Fe}(\text{CN})_6^{3-}$ at both of the modified electrodes. Cyclic voltammetry was performed at each of the two electrodes in the presence of 1 or 2 of various concentrations, and the I/I_0 value⁷ was estimated in a manner similar to the case of CaCl_2 . As is apparent from Fig. 2, both of the ammonium ions did not reduce the electrostatic repulsion between the anionic marker and the anionic functional groups on a W-GCE sufficiently to induce a distinguishing increment in the I/I_0 value; even upon the addition of 1 or 2 in 10 mM, the ratio was about 1.6. On the other hand, the effects of 1 upon the I/I_0 value at a C8-GCE was similar to those of Ca^{2+} , and the increment in the current ratio caused by the addition of 2 was more than twice as large as that in the case of 1.

The above results suggest that the phenomena observed at a C8-GCE in the presence of Ca^{2+} as well as the ammonium ions can not be explained simply by the ability of the cations to reduce the electrostatic repulsion between the marker and the electrode surface. Although the exact mechanism is not clear at present, one of the origins for the voltammetric results might be ascribed to the packing situation of the hydrophobic membrane on a C8-GCE, which seems not to be as tight as that on an octanethiol-modified gold electrode, as judged from the fact that the restoration of the response of $\text{Fe}(\text{CN})_6^{3-}$ at a C8-GCE attained its maximum upon the addition of dodecyltrimethylammonium bromide in a much lower concentration than that at the modified gold electrode. Namely, a rather loose membrane on a C8-GCE formed by the anodic oxidative treatment in 1-octanol might play an important role to induce the effects⁹ of the cations on the voltammetric behavior of

$\text{Fe}(\text{CN})_6^{3-}$. This hypothesis is supported by the following findings: (1) the cations exhibited similar effects at a gold electrode covered with 1-octanethiol when the modification was performed by dipping a gold electrode in a dilute EtOH solution of the thiol for a short time, that is, when a less-packed membrane was deliberately formed on a gold electrode; (2) the influence of the cations on the voltammetric response of $\text{Fe}(\text{CN})_6^{3-}$ was diminished at a C8-GCE prepared at the expense of more than 5 mC, that is, a GCE modified with a more-packed hydrophobic membrane. Although it was found to be very hard to reproduce a gold electrode covered with an appropriately less-packed membrane of 1-octanethiol, a newly polished glassy carbon electrode was furnished with almost the desired packing situation of the hydrophobic membrane in a highly reproducible manner by only controlling the amount of electricity during the anodic treatment in 1-octanol.

The present study implies that an electrochemical cation-sensing function will be conferred on a system consisting of an anionic marker and an electrode coated with a less-packed hydrophobic membrane. This expectation is very intriguing, since the indirect electrochemical detection of cations like alkaline earth ions has been achieved only by the response of an anionic marker at an electrode covered with a membrane containing anionic functional groups^{3-6,10}, the preparation of which seems to often encounter some difficulty. Further studies to shed light on the mechanism for the observed phenomena and to examine the possibility of the present system as alkylamine- and alkaline earth ion-sensors are under way.

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References and Notes

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7. When the depressed response of $\text{Fe}(\text{CN})_6^{3-}$ was recovered in the presence of the additive to give a well-defined peak at a potential more positive than 0 V, its peak current was employed as I .
8. Background corrections were not made on the values of I_0 and I , since the background currents, observed on CV for a solution containing only KCl (10 mM) at C8 and W-GCEs, were less than 10% of I_0 values at both anodized electrodes.
9. One of the referees suggested that the observed effects may originate from the cation exchange between $\text{K}_3\text{Fe}(\text{CN})_6$ and CaCl_2 , 1, or 2, which allows $\text{Fe}(\text{CN})_6^{3-}$ to permeate the hydrophobic membrane. We agree that the proposal is plausible. At present, however, it is not clear why such an ion-extraction takes place only at a less-packed hydrophobic membrane.
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