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Surface Characterization of Glassy Carbon Electrodes Anodized in 1-Alkanols by Their Wettability and Capacitance

Hatsuo MAEDA, Munenori ITAMI, Yuji YAMAUCHI, and Hidenobu OHMORI*

Faculty of Pharmaceutical Sciences, Osaka University, 1–6 Yamadaoka, Suita, Osaka 565, Japan.

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The surface conditions of glassy carbon (GC) electrodes anodized in n-$C_nH_{2n+1}OH$ (n=2, 4, 6, 8: electrodes 1—4), $HO(CH_2)_nOH$ (n=2—5: electrodes 5—8), and $HO(CH_2CH_2O)_2CH_2CH_2OR$ (R=H, Me: electrodes 9 and 10) were explored by measuring the wettability and capacitance as well as the voltammetric response to $Fe(CN)_6^{3-}$; wetting properties were evaluated by the contact angle formed by a drop of water; the ratio between the values of capacitance obtained before and after the anodic modification was used instead of the capacitance itself. The data have revealed that $LiClO_4$ is recommended rather than conc. H_2SO_4 as a supporting electrolyte to fix 1-alkanol molecules more effectively to GC electrode surfaces in the anodic modification. The surface conditions of electrodes 1—10 have reflected the identities of the modifier remarkably: electrodes 1—4 have surfaces with hydrophobicity and thickness correlated to the length of carbon chains of the modifiers; on the other hand, the surfaces of electrodes 5—10 are hydrophilic, which seemed to allow each of the modified electrodes, except for electrode 8, to have a double layer with a thickness similar to a bare GC electrode. The suppression in the electrode reaction of $Fe(CN)_6^{3-}$ was stronger at electrodes 6 and 8 than at electrodes 5 and 7, which can be explained by the invocation of an "odd-even" effect.

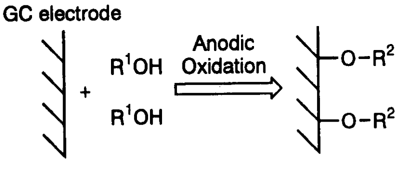
Key words surface characterization; modification; glassy carbon electrode; wettability; capacitance; cyclic voltammetry

Recently, we found that the anodic oxidative treatment of a glassy carbon (GC) electrode in a 1-alkanol containing a small amount of H_2SO_4 allows the alkanol molecules to be fixed on the electrode surface *via* an ether-linkage.[1,2] The method is simple and highly reproducible, providing a useful tool for obtaining a covalently modified GC electrode as a counterpart of a gold electrode covered with a self-assembled monolayer of an alkanethiol. However, it has been suggested that the resulting membrane on a GC electrode anodized in a 1-alkanol is not as densely packed as that on a gold electrode modified by the self-assembly technique.[2,3] Accordingly, 1-alkanol-modified GC electrodes, though not useful as model systems to study the interfacial chemistry of organic surfaces, seem to be applicable to electrochemical sensors, because pinhole defects in the membrane permit an electro-active analyte to reach the electrode surface and show its electrochemical response. In fact, 1-octanol-modified GC electrodes have been shown to provide useful access for the indirect detection of both alkaline earth ions[2,3] and monoalkylamine hydrochlorides[2] by the voltammetric response of $Fe(CN)_6^{3-}$, and a GC electrode anodized in 1,5-pentanediol has proven to be a potent dopamine-sensor.[4]

In order to further develop electroanalytical systems with 1-alkanol-modified GC electrodes, our attention has been directed to evaluating more detailed surface conditions of the modified GC electrodes, although it is expected that the anodic modification of a GC electrode in a 1-alkanol will result in the formation of a characteristic membrane reflecting the identity of the modifier.[1] The results of such a study should be valuable for designing 1-alkanol-modified GC electrodes applicable to proper electrochemical sensing systems of target analytes. In this paper, we describe the results of our attempts to characterize the surface of a GC electrode anodized in a 1-alkanol by measuring its wettability[5-13] and capacitance,[14-18] which have been employed as feasible and general tools for elucidating the surface structure of electrodes modified with organic molecules. The response of $Fe(CN)_6^{3-}$ at the modified electrodes was also adopted for the characterization. It has been suggested that the surface property of the modified GC electrode is controlled by judicious choice of a 1-alkanol in the anodic modification.

Results and Discussion

GC electrodes anodized in n-$C_nH_{2n+1}OH$ (n=2, 4, 6, 8: electrodes **1**—**4**), $HO(CH_2)_nOH$ (n=2—5: electrodes **5**—**8**), and $HO(CH_2CH_2O)_2CH_2CH_2OR$ (R=H, Me: electrodes **9** and **10**), as depicted in Chart 1, were studied in the present work. GC electrodes modified with n-$C_nH_{2n+1}OH$ with n>9 and $HO(CH_2)_nOH$ with n>6 were not prepared because such alcohols are solid and the anodic modification must be performed in an organic



electrode **1**: R^1 and R^2 = $-C_2H_5$
2: R^1 and R^2 = $-C_4H_9$-n
3: R^1 and R^2 = $-C_6H_{13}$-n
4: R^1 and R^2 = $-C_8H_{17}$-n
5: R^1 = $-(CH_2)_2OH$; R^2 = $-CH_2CO_2H$
6: R^1 = $-(CH_2)_3OH$; R^2 = $-(CH_2)_2CO_2H$
7: R^1 = $-(CH_2)_4OH$; R^2 = $-(CH_2)_3CO_2H$
8: R^1 = $-(CH_2)_5OH$; R^2 = $-(CH_2)_4CO_2H$
9: R^1 = $-(CH_2CH_2O)_2CH_2CH_2OH$;
R^2 = $-(CH_2CH_2O)_2CH_2CO_2H$
10: R^1 and R^2 = $-(CH_2CH_2O)_2CH_2CH_2OCH_3$
(electrode **11**: anodized in H_2O)

Chart 1

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* To whom correspondence should be addressed.

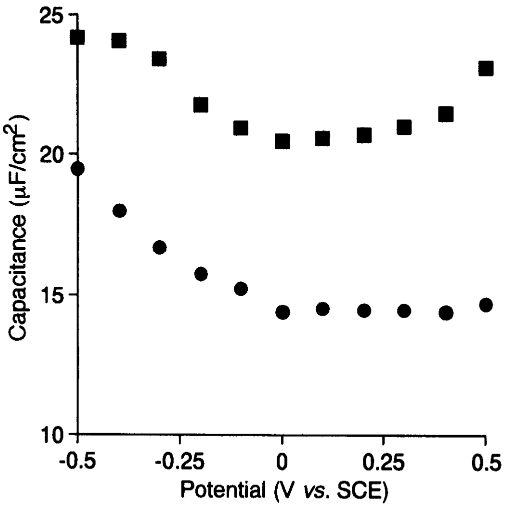

Fig. 1. Capacitance of Bare (Squares) and 1-Octanol-Modified (Circles) GC Electrodes Plotted as a Function of the Potential Applied for the Measurement

Obtained by cyclic voltammetry in a 1 M KCl aqueous solution; for details, see Experimental.

Table 1. Contact Angle (θ) of Water, Relative Capacitance ($C_{\mathrm{mod}}/C_{\mathrm{bare}}$), and Voltammetric Response (E_{cp} and I_{cp}) of $K_3Fe(CN)_6$ at a Bare GC Electrode and Electrodes **1**—**4** and **11** Prepared in the Presence of conc. H_2SO_4

Electrode	θ (°)	$C_{\mathrm{mod}}/C_{\mathrm{bare}}$[a]	E_{cp} (V)[b]	I_{cp} (μA)[b]
Bare	64	—	0.122	71.5
11	39	1.61	0.115	74.5
1	68	1.44	0.097	59.3
2	68	1.23	0.028	49.8
3	74	1.33	—[c]	38.0[d]
4	82	0.76	—[c]	36.0[d]

a) C_{bare} and C_{mod} stand for capacitance values observed for GC electrodes before and after the anodic modification: for details, see the text. *b)* E_{cp} and I_{cp} stand for cathodic peak potential (*vs.* SCE) and current, respectively, observed on a cyclic voltammogram of $K_3Fe(CN)_6$ (5 mM) in aq. KCl (100 mM): sweep rate, 100 mV/s. *c)* No cathodic peak was observed on the voltammogram over the range between 0.6 and −0.2 V. *d)* Cathodic response observed at −0.2 V on the voltammogram.

solvent containing one of the alcohols as a modifier, for which no satisfactory procedure has yet been established. As previously reported,[3)] the anodic modification of a GC electrode was carried out by controlled potential electrolysis at 2.0 V *vs.* Ag wire in a 1-alkanol, where 5 mC of electricity had been allowed to be consumed.

The surface conditions of electrodes **1**—**4** and a GC electrode anodized in water, that is, electrode **11**, prepared in the presence of H_2SO_4, were first probed by the measurement of wettability and capacitance. Wettability of these modified electrodes was evaluated through the contact angle (θ) formed by a drop of water on the surface. A larger θ observed at a modified electrode than at a bare GC electrode should mean that the modification resulted in the formation of a more hydrophobic surface, and *vice versa*.

A similar method to that reported[18)] was employed to determine the capacitance (C_{bare} and C_{mod}, respectively; μF/cm²) of bare and modified electrodes: C_{mod} and C_{bare} were estimated by regarding the background currents observed on cyclic voltammograms at the electrodes for 1.0 M KCl aqueous solution as the charging currents, where a fast potential scan (50 V/s) over a small potential range (20 mV) was applied according to the recommendation to minimize the contribution of faradaic currents to the background currents.[19)] Figure 1 compares C_{bare} with C_{mod} at a 1-octanol-modified GC electrode (electrode **4**) over the potential range from −0.5 to +0.5 V *vs.* saturated calomel electrode (SCE). The anodization of the electrode in 1-octanol brought about lower capacitance at each potential, probably as a result of the surface coverage by the insulating molecules of the alkanol, leading to a decrease in the net surface area and/or the formation of a thicker Helmholtz layer. Accordingly, the capacitance measurements turned out to be used as a tool to compare the extent of the surface coverage by 1-alkanol molecules through the anodic modification.

However, a change of more than 20% in C_{bare} was sometimes observed at the same electrode, obtained by careful repolishing, which resulted in a variation of C_{mod} for electrode **4** to a similar extent; thus, it seemed difficult to use C_{mod} itself as a probe for our purpose. Fortunately, it was found that the ratio between C_{bare} and C_{mod} for electrode **4** was quite reproducible, regardless of the value of C_{bare}. Thus, the surface conditions of the modified electrodes were compared by $C_{\mathrm{mod}}/C_{\mathrm{bare}}$ estimated before and after the anodization of a GC electrode in a 1-alkanol; measurements of charging currents to obtain C_{bare} and C_{mod} were carried out at 0 V in order to avoid any contribution of faradaic currents, since the residual currents were minimal at 0 V with both the bare and 1-octanol-modified GC electrodes (Fig. 1).

The contact angle (θ) and capacitance ratio ($C_{\mathrm{mod}}/C_{\mathrm{bare}}$) for electrodes **1**—**4** and **11**, prepared in the presence of H_2SO_4, are summarized in Table 1. The electrochemical performances of these electrodes as monitored by the voltammetric response of $Fe(CN)_6^{3-}$ are also included in Table 1, since the voltammetric sensitivity for the marker anion has previously proved to be a useful criterion for judging the extent of fixation of insulating alkanol molecules on a GC electrode modified through the anodic treatment.[1)] When the anodic modification of a GC electrode was carried out in a 1-alkanol with a longer carbon chain, θ became larger, compared with that for a bare GC electrode. For the electrode anodized in water (electrode **11**), θ was significantly smaller than that for a bare GC electrode. These results demonstrated that the anodization of a GC electrode in a 1-alkanol provides an electrode surface with hydrophobicity correlating to the chain length of the modifier, while hydrophilic functionalities such as hydroxyl and carboxyl groups seem to be introduced on an electrode surface through the anodization in water, as previously proposed.[20,21)]

Comparison of $C_{\mathrm{mod}}/C_{\mathrm{bare}}$ for electrodes **1**—**4** has demonstrated that the longer the 1-alkanol used in the anodic modification, the thicker the insulating membrane formed on the electrode surface, as can be expected from the results of θ. The dependence of thickness of the membrane formed by the anodic treatment upon the length of a carbon chain in a 1-alkanol was also revealed by the suppression in the voltammetric response of $Fe(CN)_6^{3-}$; the cathodic peak of the marker anion was shifted negatively and its peak current decreased with a GC electrode anodized in a longer 1-alkanol.

Although the trend in C_{mod}/C_{bare} for electrodes **1**—**4** prepared in the presence of H_2SO_4 gave useful information for evaluating the surface conditions of the modified electrodes, C_{mod}/C_{bare} for each of the electrodes **1**—**3** was larger than 1, which was in conflict with the expectation that C_{mod}/C_{bare} should be less than 1 if the anodization would induce only the fixation of 1-alkanol molecules on the electrode surfaces. Some undesired process seemed to take place as well, which increased the background currents. Based on the fact that C_{mod}/C_{bare} at electrode **11** was 1.61 and the voltammetric response of $Fe(CN)_6^{3-}$ was not retarded at all, the introduction of oxygen functionalities on the electrode surface as a side reaction during the anodic treatment was envisioned as plausibly inducing a C_{mod} larger than C_{bare}. Namely, water contamination in a 1-alkanol as a modifier might cause the observation. In addition, the incremental increase in C_{mod}/C_{bare} might be ascribed to an increase of surface roughness induced by the anodization. It was initially proposed that anodic treatment would fix 1-alkanol molecules to the electrode surface through nucleophilic attack of the modifier to carbocations anodically generated on the carbon surface.[1] However, the possibility cannot be ruled out that the surface modification with 1-alkanol molecules may be initiated by the anodic formation of intercalation species such as $C_n^+X^-$ ($X^-=HSO_4^-$ when H_2SO_4 was used for the anodization) instead of simple carbocations.[22] When the intercalation intermediate reacts with nucleophiles such as 1-alkanol and water, not only will a C–O bond be formed, but also, the carbon surface in the basal plain regions will be peeled off, inducing an incremental increase in surface roughness.[21] Accordingly, the initial formation of the intercalation species, as well as water content in the modifier, must be taken into consideration in order to prepare a 1-alkanol-modified GC electrode with low C_{mod} values. The contribution of the formation of the intercalation species to the modification process might be suppressed by using neutral salts instead of H_2SO_4 as a supporting electrolyte for the anodic treatment, since the intercalation reactions seem to proceed more easily in the presence of acids.[22] In addition, the effects of water content would be expected to decrease by performing the anodic modification with a supporting electrolyte less hygroscopic than H_2SO_4. Thus, our attention was turned to the kind of supporting electrolytes to be used for the anodic modification.

Also, from an electroanalytical viewpoint, as small background currents as possible are desirable to achieve high sensitivity. So, it seems worthwhile to develop anodization conditions to prepare a 1-alkanol-modified GC electrode with C_{mod} being much smaller than C_{bare}.

The effects of supporting electrolytes upon the surface conditions of a 1-alkanol-modified GC electrode were estimated from the values of θ and C_{mod}/C_{bare} and from the voltammetric response of $Fe(CN)_6^{3-}$ observed at electrode **4** prepared by the anodization in 1-octanol containing various supporting electrolytes. As supporting electrolytes, $LiClO_4$, $LiBF_4$, and $Mg(ClO_4)_2$ were used in place of H_2SO_4, taking into consideration the solubility in 1-octanol.

Table 2. Contact Angle (θ) of Water, Relative Capacitance (C_{mod}/C_{bare}), and Voltammetric Response (E_{cp} and I_{cp}) of $K_3Fe(CN)_6$ Observed at Electrode **4** Prepared in the Presence of Various Supporting Electrolytes

Supporting electrolyte	Time[a] (min)	θ (°)	C_{mod}/C_{bare}[b]	E_{cp}[c] (V)	I_{cp}[c] (μA)
H_2SO_4	33	82	0.76	—[d]	36.0[e]
$LiClO_4$	9	95	0.60	—[d]	36.0[e]
$LiBF_4$	18	89	0.25	−0.093	46.0
$Mg(ClO_4)_2$	21	94	0.37	—[d]	34.3[e]

a) Required to consume 5 mC of electricity during the anodic preparation of electrode **1**. *b*—*e*) Refer to the footnotes *a*—*d*) in Table 1, respectively.

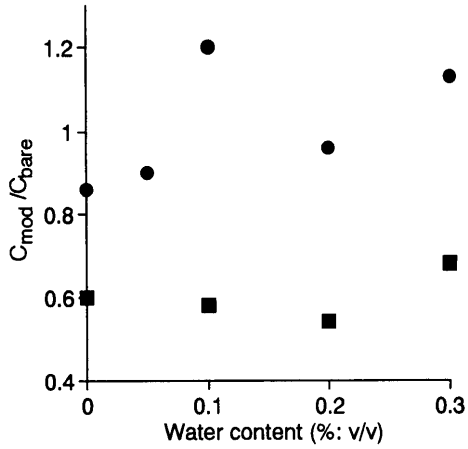

Fig. 2. Values of C_{mod}/C_{bare} Observed at GC Electrodes Anodized in 1-Butanol (Circles) and 1-Octanol (Squares) Containing $LiClO_4$ (0.1 M) and Various Amounts of Water

As apparent from the results summarized in Table 2, the anodic modification utilizing these salts gave electrode **4**, with a larger θ and smaller C_{mod}/C_{bare} than those with H_2SO_4. The results indicate that the anodic fixation of 1-octanol molecules on the electrode surface in the presence of these salts will be achieved with a smaller increase in oxygen functionalities and/or surface roughness compared with that in the presence of H_2SO_4. Electrode **4**, with the smallest C_{mod}/C_{bare}, was prepared by utilizing $LiBF_4$. However, the voltammetric response of $Fe(CN)_6^{3-}$ at electrode **4** prepared in the presence of $LiBF_4$ was the largest, indicating that the extent of surface coverage with 1-octanol molecules was the least among those electrode **4**'s obtained in the presence of the above-mentioned supporting electrolytes. Thus, $LiClO_4$ and $Mg(ClO_4)_2$ seemed to be the supporting electrolytes of choice for the anodic modification of a GC electrode with a 1-alkanol. Since the anodic treatment in the presence of $Mg(ClO_4)_2$ took a longer time to pass 5 mC of electricity than that in the presence of $LiClO_4$, the latter was chosen as a supporting electrolyte to obtain various 1-alkanol-modified GC electrodes for further studies.

The effects of water content in a modifier upon C_{mod}/C_{bare} was examined with electrodes **2** and **4** prepared in the presence of $LiClO_4$. The results are plotted in Fig. 2 as a function of the amounts of water deliberately added to the modifiers. When electrode **2** was prepared in the presence of added water, C_{mod}/C_{bare} was apparently

Table 3. Contact Angle (θ) of Water, Relative Capacitance ($C_{\text{mod}}/C_{\text{bare}}$), and Voltammetric Response (E_{cp} and I_{cp}) of $K_3Fe(CN)_6$ Observed at a Bare GC Electrode and Electrodes **1**—**11** Prepared in the Presence of $LiClO_4$ (0.1 M)

Electrode	θ (°)	$C_{\text{mod}}/C_{\text{bare}}$ [a]	E_{cp} (V) [b]	I_{cp} (μA) [b]
Bare	64	—	0.122	71.5
11	43	1.16	0.100	68.8
1	74	1.11	0.093	63.7
2	85	0.86	0.040	50.7
3	91	0.78	— [c]	41.7 [d]
4	95	0.60	— [c]	36.0 [d]
5	50	0.99	0.103	71.3
6	50	0.91	— [c]	18.5 [d]
7	56	0.95	−0.137	45.0
8	64	0.63	— [c]	3.0 [d]
9	44	0.95	— [c]	41.2 [d]
10	50	0.93	— [c]	40.0 [d]

a—*d*) Refer to the footnotes *a*—*d*) in Table 1, respectively.

increased, while water had a much smaller effect on $C_{\text{mod}}/C_{\text{bare}}$ at electrode **4**. These results suggest that $C_{\text{mod}}/C_{\text{bare}}$ at a 1-alkanol-modified GC electrode will become larger under the influence of water during the modification as the carbon chain in a 1-alkanol becomes shorter. The exact reason for the observation is not clear at present; the reaction of contaminating water with carbocations anodically generated on the electrode surfaces, introducing oxygen functionalities, might be slower in a more hydrophobic alkanol as a modifier. It is noteworthy that electrodes **2** or **4** obtained in 1-butanol or 1-octanol containing $LiClO_4$ and water showed smaller $C_{\text{mod}}/C_{\text{bare}}$ than those modified electrodes prepared in the presence of H_2SO_4. Therefore, $LiClO_4$ as a supporting electrolyte for the anodic modification, compared with H_2SO_4, seems to inhibit not only the introduction of oxygen functionalities induced by the presence of contaminating water but also the initial generation of the intercalation species which cause the increase in surface roughness.

Table 3 summarizes the values of θ and $C_{\text{mod}}/C_{\text{bare}}$, as well as the voltammetric response of $Fe(CN)_6^{3-}$ observed at GC electrodes anodized in various 1-alkanols containing $LiClO_4$. The surface conditions at GC electrodes modified with n-$C_nH_{2n+1}OH$ ($n=2, 4, 6, 8$), that is, electrodes **1**—**4**, showed a good correlation with the length of a carbon chain in the modifier, similarly to that observed at electrodes **1**—**4** prepared in the presence of H_2SO_4 (*cf.* Table 1): θ became larger, and $C_{\text{mod}}/C_{\text{bare}}$ and the voltammetric response of the marker anion became smaller as a longer modifier was used. However, electrodes **1**—**4** showed remarkably larger θ's and smaller $C_{\text{mod}}/C_{\text{bare}}$ values than the modified electrodes obtained in the presence of H_2SO_4, demonstrating that $LiClO_4$ rather than H_2SO_4 is generally more useful in preparing 1-alkanol-modified GC electrodes with surface conditions reflecting the characteristic of each modifier more exactly, with less side reactions in the modification process.

When GC electrodes were anodized in $HO(CH_2)_nOH$ ($n=2$—5) to prepare electrodes **5**—**8**, the surface conditions were different from those of electrodes **1**—**4**. Comparison of θ between electrodes **1** and **5**, or **2** and **6** clearly indicated that the anodic modification of a GC electrode in a 1,ω-alkanediol results in the formation of a hydrophilic surface on the electrode. It has been proposed that the terminal hydroxyl groups on electrodes **5**—**8** are likely to be oxidized to carboxyl groups during the anodic modification, based on the findings that on cyclic voltammetry at these modified electrodes in a pH 7.0 buffer solution, anodic oxidation of ascorbic acid is totally suppressed while dopamine shows a well-defined anodic peak.[4)] The observed hydrophilic surfaces at electrodes **5** and **6** can be ascribed to the presence of carboxyl groups instead of hydroxyl groups themselves. Although the hydrophilicity of the electrode surface anodized in a 1,ω-alkanediol (electrodes **5**—**8**) diminished in the presence of modifiers with a longer carbon chain, electrode **8** showed similar wettability to a bare GC electrode, and was still more hydrophilic than electrode **2** with a shorter carbon chain. At each of electrodes **5**—**7**, $C_{\text{mod}}/C_{\text{bare}}$ was close to 1 without dependency on the chain length of the modifier, implying that as far as the surface coverage and/or double layer thickness is concerned, these electrodes have almost identical surfaces to that of a bare GC electrode, presumably because the membranes on electrodes **5**—**7** would be disordered by the presence of the terminal carboxyl groups. Such effects diminished in the case of electrode **8**, and the value of $C_{\text{mod}}/C_{\text{bare}}$ is reasonable for the length of the carbon chain.

It is noteworthy that the voltammetric response of $Fe(CN)_6^{3-}$ was remarkably suppressed at electrodes **6** and **8**, while the marker anion showed its cathodic peak at electrodes **5** and **7**. Based on the trend in the voltammetric response of the marker anion at electrodes **1**—**4**, the electrochemical response should be more depressed at a 1,ω-alkanediol-modified GC electrode with a longer carbon chain. The observed behavior of the marker anion is in contradiction to the expectation. Recently, it has been reported that a silver surface covered with a self-assembled monolayer of an n-alkanoic acid or an n-alkanethiol shows an alternation pattern in the contact angle and IR intensity of the methyl stretching mode, depending on whether the number of the carbon in the adsorbate is odd or even; it was also proposed that the orientation of the terminal methyl groups in the adsorbate with respect to the normal of the surface is remarkably altered by a change in the chain length by one carbon, leading to the observed phenomena.[10—12)] A similar "odd-even" effect might explain the observed fluctuation in the voltammograms of $Fe(CN)_6^{3-}$ at electrodes **5**—**8** by assuming that the terminal carboxyl groups on their surfaces will exist in anionic forms. Namely, the alkyl chain in the modifier with odd numbers (electrodes **6** and **8**) would induce the terminal carboxyl groups in a trigonal shape to point closer to the surface normal, as depicted in Chart 2, leading to a strong retardation of the electrode process of $Fe(CN)_6^{3-}$ through effective electrostatic repulsion, together with blocking by the presence of hydrophobic carbon chains to exclude the marker anion from the surface. However, when the carbon numbers are even (electrodes **5** and **7**), the terminal groups would point away from the surface normal, and the electrostatic effects would be diminished, resulting in the observed voltammetric data at these electrodes being quite similar to those at electrodes **1** and **2**, respectively, which

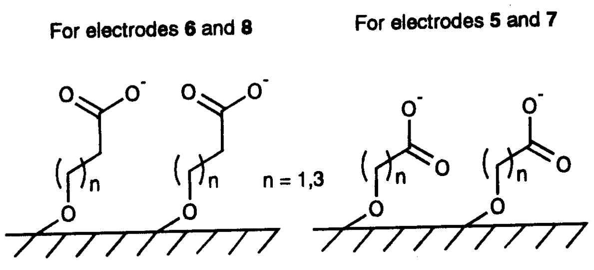

Chart 2

have only hydrocarbon chains on the surfaces.

It seems quite reasonable to speculate, by the following observation, that the membrane on a 1-alkanol-modified GC electrode is not as densely packed as that on a gold electrode modified with a 1-alkanethiol with the same carbon chain length,[1] and that an "odd-even" effect on the IR and contact angle of silver surfaces modified with 1-alkanethiol was recognized more strongly as the alkyl chain of the alkanethiol became shorter.[10,11] The latter can be explained as follows: short alkanethiols form a less ordered membrane on a silver surface, allowing the adsorbate to maintain a tilt orientation, where the direction of the terminal methyl groups with respect to the surface normal alters remarkably depending on whether the alkyl chains have an odd or even number of carbons. The interpretation is of great interest, since it will imply that the length of carbon chains should be taken into consideration in designing a ω-substituted-1-alkanol-modified GC electrode as an electrochemical sensor by recourse of the interaction between the terminal functional groups and the molecules to be analyzed, although further study is needed to draw a definite conclusion.

As indicated by their θ values, electrodes **9** and **10** modified with triethyleneglycol and its monomethyl ether, respectively, also showed large wettability against water, although electrode **10** will be covered just by poly-ether molecules without the assumed terminal carboxyl groups, and the surface of electrode **9** was the most hydrophilic among those of the modified electrodes examined here. These electrodes had $C_{\mathrm{mod}}/C_{\mathrm{bare}}$ values around 0.94, possibly showing that they have double layers with similar thickness to a bare GC electrode, as electrodes **5**—**7** did, while their response to $\mathrm{Fe(CN)}_6^{3-}$ resembled those of electrodes **3** and **4**. It has been reported that hydrophilic surfaces incorporating oligomers of ethylene glycol, as constituents of bio-compatible materials, can be conferred on gold by forming a self-assembled monolayer of $\mathrm{HS(CH_2)_{11}(OCH_2CH_2)_{\mathit{n}}OH}$ ($n=3$—7).[9] However, it is a complicated process to synthesize such thiols. In addition, carbon electrodes are more common than gold electrodes for electroanalytical purposes. Thus, the anodic modification in poly-ethylene glycols will provide a simple and easy tool to prepare a GC electrode with hydrophilic and biocompatible surfaces. Further studies on thus point are underway.

The results described so far have demonstrated that the surface conditions of 1-alkanol-modified GC electrodes are altered by changes in hydrophobicity, hydrophilicity, and the length of carbon chains of the modifiers, and that $\mathrm{LiClO_4}$ as a supporting electrolyte is recommended in place of $\mathrm{H_2SO_4}$ for the anodic modification in order to obtain modified electrodes with surfaces reflecting the characteristics of the modifiers in higher degrees. Thus, the present study is believed to provide a useful criterion for further application of 1-alkanol-modified GC electrodes as novel electrochemical sensors in the near future.

Experimental

Reagents Deionized water was distilled and used throughout the present study. All other reagents were of reagent grade and used without further purification.

Apparatus A GC electrode was polished using a Maruto polishing system, Model ML-150P. Electrochemical modification of a GC electrode with 1-alkanols or water was performed using a Hokuto Denko potentiostat/galvanostat, Model HA 301, connected to a Hokuto Denko coulomb/amperehour meter, Model HF 201. Cyclic voltammograms were recorded with a Huso potentiostat, Model 315 A, equipped with a Riken Denshi X-Y recorder, Model F-5C. A three-electrode configuration was employed: glassy carbon disk (7.07 $\mathrm{mm^2}$) with or without modification as the working electrode, SCE as the reference electrode, and a platinum wire as the counter electrode. GC disks (GC 30, 3 mm i.d.) were obtained from Tokai Carbon. The preparation of GC electrodes has been described previously.[23] Contact angles were determined at room temperature with a Kyowa Interface Science contact angle meter, Model CA-D.

Electrode Modification and Measurements A GC electrode modified with 1-alkanols or water was prepared as follows: a GC electrode polished and washed as previously reported[3] was subjected to anodic treatment at +2.0 V *vs.* Ag wire in either of the alkanols (5 ml) containing conc. $\mathrm{H_2SO_4}$, $\mathrm{LiClO_4}$, $\mathrm{LiBF_4}$, or $\mathrm{Mg(ClO_4)_2}$ as a supporting electrolyte (0.1 M), where the electricity consumption was 5 mC. After the treatment, the modified electrode was washed with MeOH and water and treated by cyclic voltammetry in 0.1 M aqueous KCl with five repetitive sweeps between 0 and −0.5 V *vs.* SCE, which guaranteed stable background currents at the modified electrodes. The procedure for the measurements of capacitance of a bare or modified GC electrode at 0 V is representative: cyclic voltammetry was carried out for a 1 M KCl aqueous solution from +10 to −10 mV at 50 V/s of a potential scan rate at room temperature. The currents from the positive and negative scan directions at 0 V *vs.* SCE were summed, divided by twice the scan rate, and normalized by the geometric area of a GC electrode to obtain C_{bare} and C_{mod}. The voltammetric response of $\mathrm{Fe(CN)}_6^{3-}$ at bare and modified GC electrodes were obtained by cyclic voltammetry for a 0.1 M KCl solution of $\mathrm{K_3Fe(CN)_6}$ (5 mM) at room temperature with a sweep rate of 100 mV $\mathrm{s^{-1}}$. The reported data for contact angle, capacitance, and the voltammetry of $\mathrm{Fe(CN)}_6^{3-}$ are the average values of more than three measurements obtained using freshly prepared electrodes.

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