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Development of Rotating Liquid Membrane Disk Electrode and Rotating Liquid Membrane Ring-Liquid Membrane Disk Electrode and Evaluation of Characteristics of Ion Transfer Reactions at the Rotating Aqueous/Organic Solution Interface

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A liquid membrane disk electrode, LMDE, and a liquid membrane ring-liquid membrane disk electrode, LMRE-LMDE, were developed by placing a gelled polyvinyl chloride thin membrane impregnated with 2-nitrophenyl octyl ether, NPOE-LM, on the surface of a glassy carbon, GC, disk or ring electrode. The voltammogram for the ion transfer at the interface between an aqueous solution, W, and NPOE-LM was recorded by setting the developed electrode in W and rotating at a rate, ω , between 0 and 4000 rpm. The sensitivity of the ion-transfer current at the W/NPOE-LM interface, I , was enhanced to be more than 100 times better than that at the W/NPOE (solution) interface when LMDE was rotated at ω higher than 200 rpm. The reversibility of the ion transfer reaction could be evaluated based on the dependence of I on ω of LMDE, and the reaction product at LMDE could be identified at LMRE when the rotating LMRE-LMDE system was adopted.

Introduction

The current in the voltammogram at a solid disk electrode is enhanced when the electrode is rotated, since the diffusion layer at the surface of the electrode becomes thinner due to the convective diffusion created by the rotation.¹⁻³ Another characteristic of the rotating electrode is that the shape of the voltammogram at the rotating electrode is sigmoidal instead of having a peak, and hence the theoretical analysis of the voltammogram becomes much easier when the electrode is rotated. The rotation of electrode also makes the investigation of kinetics of fairly fast electron transfer processes possible. When a ring electrode is placed outside the disk electrode, and the ring-disk electrode is rotated, the reaction product at the disk electrode can be detected and identified at the ring electrode.¹⁻⁵ The ring-disk electrode system is also useful for the determination of the life-time of an unstable reaction product at the disk electrode.

The rotating disk electrode or the rotating ring-disk electrodes proposed so far have been solid electrodes that were applied to the investigation of redox reactions, except for a few examples described later. However, voltammetry has expanded its field to the transfer of a charge (ion or electron) between an aqueous solution, W, and an organic solution, O, during the past few decades.⁵⁻⁸ If the voltammogram for the charge transfer could be recorded at the rotating W/O interface, the advantages of the rotating disk and rotating ring-disk electrodes can be utilized for the measurement and elucidation of charge transfer processes at the W/O interface. The voltammetry at the rotating W/O interface is expected to allow new applications of the charge transfer

voltammetry in fields of analytical chemistry, electrochemistry, or membrane chemistry. Examples of works done so far by using the rotating W/O interface are as follows: The rate constants of transfers of tetraalkylammonium ions and a drug ion between W and 2-nitrophenyl octyl ether, NPOE, were investigated based on voltammograms obtained at a rotating net-cloth-supported NPOE-polyvinyl chloride (PVC) gel membrane.⁹ A hydrodynamic study of ion transfer at the W/1,2-dichloroethane (DCE) interface was performed at a rotating W/DCE disk electrode.¹⁰ Here, the electrode was prepared by sealing one end of a glass tube with a polyester track-etched membrane, and filling the glass tube with W. Then, the glass tube was rotated after dipping it into DCE in order to form the W/DCE interface. However, investigations of the rotating W/O interface from the viewpoint of analytical chemistry such as the sensitivity, reproducibility or applicability to the quantitative determination and those of the ring-disk W/O interface have not been done.

In the present work, a liquid membrane disk electrode (LMDE) and a liquid membrane ring-liquid membrane disk electrode (LMRE-LMDE) were developed by placing a PVC gel impregnated with NPOE (NPOE-LM) on the surface of a glassy carbon (GC) disk or ring electrode. Various charge transfer reactions at the W/O interface were investigated by using the developed electrodes, and the characteristics of the electrodes were elucidated from the viewpoint of analytical chemistry.

Experimental

Preparation of a liquid membrane disk electrode, LMDE, and a liquid membrane ring-liquid membrane disk electrode, LMRE-LMDE

The LMDE developed is illustrated schematically in Fig. 1(a). The LMDE was prepared by inserting a GC rod (5.4 mm in diameter, 80 mm in length, GC-20, a product of Tokai Carbon Co.) into a tetrafluoroethylene resin (Teflon) cylinder (16 mm in outer diameter, 5.3 mm in inner diameter, 50 mm in length), and

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placing the NPOE-LM (9.2 mm in diameter, 0.3 mm in thick) at the end of the GC rod. The NPOE-LM was obtained by mixing 4 ml of NPOE containing 0.01 M (= mol dm⁻³), decamethylferrocene (DMFc), 0.01 M decamethylferricinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (DMFc⁺TFPB⁻) and 0.03 M TFPB⁻ salt of bis(triphenylphosphoranylidene)-ammonium (BTTPA⁺TFPB⁻) with 12 ml of tetrahydrofuran (THF) containing 1 g of PVC. Then, the mixture was put dropwise over the surface of GC, and the mixture was dried by evaporating THF carefully to make the membrane surface flat. Here, DMFc and DMFc⁺ were added in order to depolarize the NPOE-LM/GC interface by the electron transfer due to the redox reaction. The NPOE worked not only as a solvent but also as a plastitizer.

The LMRE-LMDE illustrated in Fig. 1(b) is composed of an LMRE (13.2 mm in outer diameter, 10.2 mm in inner diameter) and an LMDE (9.2 mm in diameter). The LMRE was prepared by placing NPOE-LM (0.3 mm in thick) on the surface of a GC ring (10.2 mm in outer diameter, 9.2 mm in inner diameter, GC-20, a product of Tokai Carbon Co.) set outside the Teflon cylinder in which the GC rod with LMDE had been inserted. The composition of the NPOE-LM was identical with that of NPOE-LM used for the preparation of LMDE.

The GC ring electrode without NPOE-LM (GCRE) shown in Fig. 1(c) was used for the investigation of redox behaviors of reactants or products at the LMDE.

Measurement of voltammograms at LMDE or LMRE-LMDE

The cell system adopted for the measurement of voltammograms for charge transfer reactions at the W/NPOE-LM interface is described by Eq. (1). The LMDE or LMRE-LMDE, silver-silver chloride reference electrode (SSE) and platinum counter electrode (Pt) were placed in W containing the ion of interest and 0.1 M MgSO₄, which worked as a supporting electrolyte (SE).

In the measurement of the voltammogram, the LMDE or LMRE-LMDE was rotated at a rate, ω , between 0 and 4000 rpm, and the potential difference applied between GC and SSE, E_{W-GC} , was scanned. The amount of charge transferred at the interface was detected as the current, I_{W-GC} , by using Pt and GC. Here, the current due to the transfer of a positive charge from W to NPOE-LM or that of a negative charge from NPOE-LM to W was defined as the negative current, and the charge transfer in the opposite direction as the positive current.

As will be described later, charge transfer reactions proceed at both the W/NPOE-LM and NPOE-LM/GC interfaces in the cell system of Eq. (1). Therefore, E_{W-GC} is the sum of potential differences at the interfaces $E_{W/NPOE-LM}$ and $E_{NPOE-LM/GC}$. In the present work, DMFc and DMFc⁺ of fairly high concentrations were added in NPOE-LM in order to keep $E_{NPOE-LM/GC}$ practically constant by depolarizing the NPOE-LM/GC interface with the aid of the DMFc/DMFc⁺ redox reaction and to make the change of E_{W-GC} reflected directly on $E_{W/NPOE-LM}$.

Fig. 1 (a) Liquid membrane disk electrode (LMDE), (b) liquid membrane ring-liquid membrane disk electrode (LMRE-LMDE) and (c) glassy carbon (GC) ring-liquid membrane disk electrode (GCRE-LMDE). 1, Liquid membrane; 2, GC; 3, Teflon; 4, connecting wire.

In the measurement at a liquid membrane electrode (LMDE or LMRE), it took a rather long time to stabilize the background current by the pretreatment after the preparation of the electrode. For example, when the transfer of tetraethyl ammonium ion, TEA⁺, from W to NPOE-LM was observed by scanning E_{W-GC} between -0.2 and -0.55 V versus SSE, the electrode was pretreated as follows. After the liquid membrane electrode was dipped in W containing only SE, -0.2 V was applied as E_{W-GC} and kept for 15 min. Then, E_{W-GC} was scanned cyclically at a scan-rate of 1 mV s^{-1} . Usually, 4 or 5 cyclic scans were required to get the steady state background current. In this connection, in the measurement of the objective ion transfer, we confirmed that there was no difference between the background current before the measurement and that after the measurement.

Measurement of voltammograms at the W/NPOE and NPOE/GC interfaces

In order to analyze the voltammogram obtained by scanning E_{W-GC} which is the potential difference between W and GC including the W/NPOE and NPOE/GC interfaces, we recorded voltammograms at the W/NPOE and NPOE/GC interfaces. Here, the NPOE used in this investigation was the solvent but was not a gel.

The observation of the reaction at the W/NPOE interface was performed at the interface formed inside of a Teflon cylinder (9.2 mm in inner diameter). The cell system adopted is given in Eq. (2).

The W contained 0.1 M MgSO₄ as SE and NPOE contained 0.01 M DMFc and 0.01 M DMFc⁺TFPB⁻ as redox reagents and 0.03 M BTTPA⁺TFPB⁻ as SE. The voltammogram was recorded by scanning the potential difference at the W/NPOE interface, $E_{W/NPOE}$, applied by using SSE set in W near to the interface and a tetraphenylborate ion-selective electrode, TPhBE, which worked as a reference electrode in NPOE, and measuring the current at the W/NPOE interface, $I_{W/NPOE}$, by using Pt in W and SSE in NPOE. The configuration of TPhBE is given in Eq. (3).

Here, TPenA⁺ denotes tetrapentylammonium ion.

The GC disk electrode used for the investigation of the reaction at the NPOE/GC interface was prepared by plugging a GC rod (5.4 mm in diameter) into a Teflon cylinder (5.3 mm in inner diameter). The voltammogram at the NPOE/GC interface was recorded by applying the potential difference, $E_{\text{NPOE/GC}}$, referred to TPhBE in NPOE, and measuring the current flowing across the NPOE/GC interface, $I_{\text{NPOE/GC}}$, with the aid of a Pt counter electrode in NPOE. 0.03 M BTPPA⁺TFPB⁻ was added in NPOE as a SE.

Similarly to the measurement at the LMDE or LMRE-LMDE, the current at the WINPOE interface for the transfer of a positive charge from W to NPOE or the current at the NPOE/GC interface for the transfer of an electron (a negative charge) from GC to NPOE was defined as the negative current.

All voltammetric measurements were carried out at $25 \pm 0.5^\circ\text{C}$.

Reagents

The BTPPA⁺TFPB⁻ used as the SE in NPOE (Dojindo Co.) and TPenA⁺TPhB⁻ used for TPhBE were synthesized and purified according to the procedures described previously.¹¹ DMFc⁺TFPB⁻ was prepared by shaking NPOE containing 0.025 M DMFc (Aldrich) and 0.025 M Na⁺TFPB⁻ with W containing 0.025 M K₃[Fe(CN)₆], and oxidizing DMFc based on the coupling of the transfer of electron from NPOE to W with the transfer of Na⁺ from NPOE to W. The W containing DMFc⁺ was prepared by shaking NPOE containing 0.01 M DMFc⁺TFPB⁻ with W containing 5×10^{-3} M BTPPA⁺Cl⁻, and exchanging DMFc⁺ for BDPPA⁺.

The observation of the transfer of K⁺ at the WINPOE interface was performed by adding dibenzo-18-crown-6 (Tokyo Kasei Co., DB18C6) into NPOE. DB18C6 was purified by dissolving it with acetonitrile and then recrystallizing by adding water.

All other reagents used were of reagent grade.

Apparatus

Voltammograms were recorded by using an electrode rotation apparatus (Hokuto Denko Co., Model HR-103A), potentiostats (Hokuto Denko Co., Model HA-151), function generators (Hokuto Denko Co., Model HB-111) and X-Y recorders (Yokogawa Electric Co., Model 3086).

Results and Discussion

Characteristics of voltammograms at LMDE

The voltammogram illustrated as curve 1 in Fig. 2(a) was recorded by adding 5×10^{-5} M TEA⁺Cl⁻ in W of LMDE system, and scanning $E_{\text{W-GC}}$. Curve 2 is the background current recorded in the absence of TEA⁺. In the voltammetric measurement, the LMDE was not rotated in order to compare the voltammograms at the W/LMDE interface with those at the WINPOE interface that is difficult to rotate. Here, it is interesting that the background current at the interface between W and NPOE-LM that was gelled by PVC [curve 2 in Fig. 2(a)] is much smaller than that at the interface between W and an liquid NPOE [curve 2 in Fig. 2(b)], and therefore the transfer of more dilute ion can be observed when NPOE-LM is used. Curve 1 in Fig. 2(b) illustrates the voltammogram recorded at the interface between

Fig. 2 Voltammograms (a) for the transfer of tetraethylammonium ion (TEA⁺) from aqueous solution (W) to polyvinyl chloride membrane impregnated with 2-nitrophenyl octyl ether (NPOE-LM) at the LMDE, (b) for the transfer of TEA⁺ at the WINPOE interface, and (c) for the redox reaction at the NPOE/GC interface. Composition of W, 0.1 M MgSO₄ in the presence of 5×10^{-5} M (= mol dm⁻³) TEA⁺Cl⁻ (for curve 1) or in absence of TEA⁺Cl⁻ (for curve 2 and 2'); composition of NPOE-LM or NPOE, 0.01 M decamethylferrocene (DMFc) + 0.01 M decamethylferrocenium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (DMFc⁺TFPB⁻) + 0.03 M TFPB⁻ salt of bis(triphenylphosphoranylidene)ammonium (BTPPA⁺TFPB⁻); scan-rate (v) of potential difference between W and GC ($E_{\text{W-GC}}$), W and NPOE ($E_{\text{W-NPOE}}$) or NPOE and GC ($E_{\text{NPOE-GC}}$), 1 mV s⁻¹; rotating-rate (ω) of LMDE, 0 [for curves 1 and 2 in (a) and (b)] and 1000 rpm [for curve 2' in (a)].

W containing 5×10^{-5} M TEA⁺Cl⁻ and NPOE. Curve 2 is the background voltammogram recorded in the absence of TEA⁺Cl⁻. The positive and negative current waves are attributable to the transfer of TEA⁺ between W and NPOE. The large positive and negative currents which determine the potential window (called the final rise and the final descent, respectively, hereafter) are confirmed to be due to the transfer of DMFc⁺ from NPOE to W and that of Mg²⁺ from W to NPOE, respectively. These assignments were carried out based on the dependence of the magnitude of the current on the concentration of TEA⁺, DMFc⁺ or Mg²⁺.

Curve 1 in Fig. 2(c) was recorded at the interface between GC and NPOE containing 0.01 M DMFc, 0.01 M DMFc⁺TFPB⁻ and 0.03 M BTPPA⁺TFPB⁻. The positive and negative currents are attributable to the oxidation of DMFc to DMFc⁺ and the reduction of DMFc⁺ to DMFc, respectively. The current crossed sharply the potential axis since the GC/NPOE interface was depolarized by the redox reaction of DMFc and DMFc⁺ at fairly high concentrations.

Though the positive and negative current waves observed with the LMDE system [curve 1 in Fig. 2(a)] are attributable to the transfer of TEA⁺ at the WINPOE interface, the potential regions for these waves are different from those for the positive and negative currents observed at the WINPOE interface [curve 1 in Fig. 2(b)]. The slopes of the positive and negative current waves observed with the LMDE system are smaller than those with the WINPOE system.

The characteristics of the voltammograms observed with the LMDE system can be understood by considering that 2 aqueous solutions (W1 and W2) are separated by a membrane (NPOE-LM) in the LMDE system, and hence there exist 2 NPOE-

LM|W interfaces in the system.

The research group of the present authors observed the transfer of a charge from W1 to W2 through a membrane, M, as the function of the potential difference between W1 and W2, E_{W1-W2} , and the current between W1 and W2, I_{W1-W2} . Simultaneously with the observation of the E_{W1-W2} - I_{W1-W2} curve, the relation between the potential difference at the W1|M or M|W2 interface, $E_{W1|M}$ or $E_{M|W2}$, and I_{W1-W2} was observed as $E_{W1|M}$ - I_{W1-W2} or $E_{M|W2}$ - I_{W1-W2} curve. Then, E_{W1-W2} - I_{W1-W2} curve was compared with $E_{W1|M}$ - I_{W1-W2} and $E_{M|W2}$ - I_{W1-W2} curves taking into account the fact that, when a current flows across the W1|M interface, a current of the same magnitude must flow at the M|W2 interface in order to maintain the electroneutrality in W1, M and W2. We found that E_{W1-W2} was the sum of $E_{W1|M}$, $E_{M|W2}$ and $I_{W1-W2}R_{W1-W2}$.^{13,14} Here, R_{W1-W2} is the resistance between W1 and W2. When 3 phases (W1, M and W2) contain sufficient electrolytes and hence R_{W1-W2} is small, E_{W1-W2} is given as

$$E_{W1-W2} = E_{W1|M} + E_{M|W2} \quad (4)$$

Equation (4) means that the membrane potential (E_{W1-W2}) is determined by both reactions proceeding at the W1|M and M|W2 interfaces under the condition that the 3 phases contain sufficient electrolytes.

When the voltammogram observed with LMDE system [curve 1 in Fig. 2(a)] is compared with voltammograms at the W1|M and M|W2 interfaces [curve 1 in Figs. 2(b) and 2(c)] taking into account the relation of Eq. (4), it can be understood easily that the negative current wave in curve 1 of Fig. 2(a) is caused by the complex of the transfer of TEA^+ from W1 to NPOE-LM and the transfer of an electron from GC to NPOE-LM. Hence, the potential region where the negative current wave appears in curve 1 of Fig. 2(a) is different from that in curve 1 of Fig. 2(b). Similarly, the positive current wave in curve 1 in Fig. 2(a) is caused by the complex of the transfer of TEA^+ , which had been transferred from W1 to NPOE-LM during the negative scan of E_{W-GC} , from NPOE-LM to W [curve 1 in Fig. 2(b)], and the transfer of electron from NPOE-LM to GC due to the oxidation of DMFc [curve 1 in Fig. 2(c)]. Since the current in a voltammogram observed with the LMDE system is caused by the complex of reactions at the W|NPOE-LM and NPOE-LM|GC interfaces, and the $E_{\text{NPOE-LM|GC}}$ depends on I_{W1-W2} even if the NPOE-LM|GC interface is depolarized by the redox reaction, the slope of the current wave in curve 1 of Fig. 2(a) is smaller than that in curve 1 of Fig. 2(b).

As it is obvious from the experimental results and the considerations described above, when we want to keep $E_{\text{NPOE-LM|GC}}$ practically constant and to make the variation of E_{W-GC} reflected mainly on $E_{\text{W|NPOE-LM}}$, the NPOE-LM|GC interface should be depolarized by a redox reaction. In the present work, DMFc and DMFc⁺ of fairly high concentrations (0.01 M) were added in NPOE-LM in order to depolarize the NPOE-LM|GC interface.

Ion transfer reactions at the rotating LMDE

Curves 1 to 6 in Fig. 3 are voltammograms observed at the rotating LMDE (1000 rpm) with the cell system of Eq. (1) in which W contained 10^{-7} to 5×10^{-6} M TEA^+Cl^- . The negative current wave is considered to be due to the complex of the transfer of TEA^+ from W to NPOE-LM and that of an electron from GC to NPOE-LM. When the concentration of TEA^+ was less than 2×10^{-6} M, the voltammogram was of sigmoidal shape and gave a plateau current, I_1 , similarly to the voltammogram for a redox reaction at a rotating solid electrode. Here, the voltammograms shown in Figs. 3 to 5 are those after correction for the background current recorded in the absence of TEA^+Cl^- .

Fig. 3 Voltammograms for the transfer of TEA^+ from W to NPOE-LM at the rotating LMDE. Concentration of TEA^+ in W: 1) 10^{-7} , 2) 2×10^{-7} , 3) 5×10^{-7} , 4) 10^{-6} , 5) 2×10^{-6} , 6) 5×10^{-6} , 7) 0 M; ω of LMDE, 1000 rpm; v of E_{W-GC} , 1 mV s^{-1} .

Curve 7 in Fig. 3 is an example of the background current. When the concentration of TEA^+ was higher than 5×10^{-6} M (curve 6 in Fig. 3), the voltammogram showed a peak, which can be understood as follows. When the concentration of an ion becomes large, and hence the rate of the ion transfer becomes large, the electron transfer at the NPOE-LM|GC interface finds it difficult to follow the ion transfer at the W|NPOE-LM interface since the diffusion of DMFc or DMFc⁺ in NPOE-LM is extremely slow.

The I_1 at the LMDE was proportional to the concentration of TEA^+ in the range between 10^{-7} and 2×10^{-6} M when the LMDE was rotated at 1000 rpm. The standard deviation of I_1 observed with 5 measurements of 10^{-6} M TEA^+ was 3.2%. Taking into account this result together with the result that the detection limit in the ion transfer voltammetry at the ordinary W|O interface or at the aqueous solution dropping electrode^{5,6} is 5×10^{-5} M at the best, we see that the detection sensitivity is improved extremely (more than 500 times) when the O is gelled with PVC and the W|O interface is rotated. On the other hand, the sensitivity at the NPOE-LM gelled with PVC is improved about 100 times by the rotation at 1000 rpm. From the viewpoint of analytical chemistry, the improvements in the sensitivity are noteworthy merits of the gelation and rotation.

The transfer of K^+ from W to LMDE facilitated by DB18C6 was also investigated by adding K_2SO_4 and 0.02 M DB18C6 in W and NPOE-LM, respectively, in the LMDE system of Eq. (1). The I_1 in the wave for the transfer of K^+ was proportional to the concentration of K^+ in W in the range between 10^{-7} and 2×10^{-6} M. The standard deviation of I_1 observed with 5 measurements of 10^{-6} M K^+ was 4.2%.

Relation between the rate of rotation of the LMDE and the magnitude of the current for ion transfer

The I_1 observed with the LMDE system of Eq. (1) in which W contained 10^{-6} M TEA^+Cl^- was proportional to $\omega^{1/2}$ when ω was between 200 and 4000 rpm, indicating that the transfer of TEA^+ from W to NPOE-LM is reversible.

The analysis of the voltammogram for ion transfer at the rotating LMDE

The logarithmic analysis of the voltammogram of curve 4 in Fig. 3 [$\log\{(I_1 - I)/I\}$ versus E_{W-GC} plot; I denotes the instantaneous current] gave a straight line with a slope of about 90 mV. The

Fig. 4 Stripping voltammogram of TEA⁺ at the rotating LMDE. Curve 1, the same as curve 3 in Fig. 3; curve 2, stripping voltammogram of TEA⁺ from NPOE-LM to W; concentration, TEA⁺ was concentrated from W containing 5×10^{-7} M TEA⁺ to NPOE-LM by applying E_{W-GC} of -0.5 V at the rotating LMDE ($\omega = 1000$ rpm) for 10 min; stripping voltammetry, after replacing W by that without TEA⁺, E_{W-GC} was scanned positively at v of 1 mV s^{-1} . During the positive scan, LMDE was rotated at $\omega = 1000$ rpm.

slope is different from that (60 mV) obtained by the logarithmic analysis of the voltammogram for the reversible transfer of a monovalent cation at the W|O interface. The slope of 90 mV observed at the rotating LMDE is one of unique characteristics of the membrane system elucidated by the present authors.¹⁵ In a membrane system (W1-M-W2 system), even when the transfer of the monovalent cation from W1 to M is reversible and the M|W2 interface is completely depolarized, the slope of the logarithmic analysis of the current wave for the ion transfer in the $I_{W1-W2}-E_{W1-W2}$ curve is larger than 60 mV since not only the logarithmic plot for $I-E_{W1|M}$ curve at the W1|M interface, but also that for $I-E_{M|W2}$ curve at the M|W2 interface have slopes. When voltammograms were recorded with the same system as that for the voltammogram of curve 4 in Fig. 3 by changing ω in the range between 200 and 4000 rpm, the logarithmic analysis of the voltammograms gave straight lines with slopes of 87 to 95 mV.

The waves observed for the transfer of TEA⁺ from W to NPOE-LM at the LMDE showed the characteristics of the reversible ion transfer even when the LMDE was rotated at 200 to 4000 rpm as described above, which suggests that the rate of the transfer of TEA⁺ is fairly fast.

Stripping voltammetry by using the rotating LMDE

Stripping voltammetry has often been applied to the sensitive determination of metal ions which are easily reduced or oxidized and can be concentrated in or on the electrode.³

In the present work, considering that even ions in W that are not easily reduced or oxidized could be concentrated to O based on the ion transfer at the W|O interface, the possibility of stripping voltammetry after concentration of an ion into the LMDE was investigated, taking TEA⁺ as an example of the ion.

Curve 1 in Fig. 4 (the copy of curve 3 in Fig. 3) is the voltammogram recorded by adopting the LMDE system of Eq. (1) in which W contained 5×10^{-7} M TEA⁺, and rotating the LMDE at 1000 rpm. Curve 2 is the voltammogram recorded as follows. The LMDE was rotated at 1000 rpm and kept for 10 min after applying -0.5 V as E_{W-GC} in order to concentrate TEA⁺ into NPOE-LM. Here, -0.5 V is the E_{W-GC} available for the observation of I_1 for the transfer of TEA⁺ from W to NPOE-LM. Then W was replaced by W in the absence of TEA⁺, and E_{W-GC} applied to the rotating (1000 rpm) LMDE was scanned to positive at a rate of 1 mV s^{-1} . The positive current peak is due to the release of TEA⁺ concentrated in NPOE-LM to W. The

Fig. 5 Voltammograms observed at the LMRE or LMDE of LMRE-LMDE system. Curve 1, stripping voltammogram of TEA⁺ from NPOE-LM to W observed at LMDE of LMRE-LMDE system (identical with curve 2 in Fig. 4); curve 2, current at LMRE of various E_{W-GC} due to the transfer of species stripped from LMDE; curve 3, current at LMRE of $E_{W-GC} = -0.5$ V due to the transfer of species stripped from LMDE of various E_{W-GC} values; conditions for the concentration of TEA⁺ into NPOE-LM and for the stripping of TEA⁺, the same as those for Fig. 4.

magnitude of the peak current was nearly proportional to the concentration of TEA⁺ in W in the range between 5×10^{-8} and 10^{-6} M. The stripping peak was rather broad, and hence the stripping voltammetry was not very sensitive, as expected originally, though it was a little more sensitive than the voltammetry at the rotating LMDE. The reason for the insufficient sensitivity can be explained as follows. Since TEA⁺ that transferred deep in the NPOE-LM, which was rather thick (0.3 mm), during the concentration procedure could not dissolve out from the NPOE-LM rapidly, the peak was broad and the peak height was not sufficiently high. Here, the diffusion of TEA⁺ in the NPOE-LM which control the dissolution of TEA⁺ is considered to be slower than that in W, since the viscosity of NPOE-LM is large.

The capability of the rotating LMRE-LMDE

Curve 1 in Fig. 5 is the stripping voltammogram observed at the LMDE of the LMRE-LMDE [Fig. 1(b)] set in W containing 10^{-6} M TEA⁺. The procedure to record the voltammogram was identical with that for curve 2 in Fig. 4. Curve 2 in Fig. 5 is the quasi voltammogram which shows the transfer of species, which was released from the LMDE to W, from W to LMRE, at the W|LMRE interface. The quasi voltammogram was obtained as follows. During the measurement of the stripping voltammogram (curve 1), the current at the LMRE to which various E_{W-GC} was applied was recorded. Then, the current at the LMRE at the moment when the stripping voltammogram (curve 1) showed the peak was plotted as the function of E_{W-GC} applied at the LMRE. The half-wave potential ($E_{1/2}$, of curve 2 is identical with that of curve 1 in Fig. 4, which confirms that the species released from the LMDE to W is TEA⁺. This result indicates that the LMRE-LMDE system is useful for the identification of the reaction products at the W|O interface.

The current at the LMRE, to which -0.5 V was applied as E_{W-GC} , was recorded during the measurement of the stripping voltammogram at the LMDE (curve 1 in Fig. 5), and was

plotted as the function of E_{W-GC} at the LMDE (curve 3 in Fig. 5). Curve 3 shows the detection behavior of species, which was released from the LMDE, at the LMRE. The ratio of the magnitude of the peak current in curve 3 to that in curve 1 suggests that, when a species (TEA^+ in the present case) was released from the LMDE and transported by the convective diffusion to the LMRE, the efficiency of detection of the species at the LMRE was 0.35.^{2,16} The efficiency was almost the same (0.34 to 0.35) for ω between 500 and 4000 rpm.

In case of the ordinary rotating ring-disk solid electrodes' system, the efficiency of the detection of the species, which was produced at the disk electrode, at the ring electrode was reported to depend on the ratio of the radius of the disk electrode and the inner and outer radii of the ring electrode, and a theoretical equation for the detection efficiency was proposed.^{2,16} When the dimensions of the LMRE-LMDE used in the present work were substituted for those in the theoretical equation, 0.38 was obtained as the efficiency. The reason why the efficiency obtained experimentally was smaller was considered to be that the surface of the LMRE-LMDE was not sufficiently flat and smooth.

The capability of the GCRE-LMDE

In the background current at the LMDE of the composition given in Eq. (1) recorded by scanning E_{W-GC} positively to 0 V and then negatively to -0.6 V, a fairly large negative current was observed in the range between 0 and -0.2 V when the LMDE was not rotated (see curve 2 in Fig. 2). The current disappeared, however, when the LMDE was rotated at ω of e.g., 1000 rpm (see, curve 2' in Fig. 2). The negative current was considered to be due to the transfer of $DMFc^+$ in W, which was released from the LMDE to W during the positive scan of E_{W-GC} , to the LMDE. This consideration was supported by the experimental result obtained with the aid of the GCRE as follows. The GCRE-LMDE [Fig. 1(c)] was rotated at ω of 1000 rpm in W containing only the supporting electrolyte, and the E_{W-GC} was scanned from -0.3 to 0 V after keeping E_{W-GC} of the LMDE at -0.3 V for 10 min. During the scanning of E_{W-GC} of the LMDE, the current at the GCRE to which a definite E_{W-GC} was applied was measured. Then, the current observed at the GCRE only when the E_{W-GC} of the LMDE had been 0 V was plotted as the function of the E_{W-GC} of the GCRE. This plot is the so-called quasi-voltammogram at the GCRE for the species released from the LMDE. On the other hand, the voltammogram for the reduction of $DMFc^+$ was recorded by using only the GCRE in W containing 10^{-4} M $DMFc^+$. Here, the GCRE was rotated at ω of 1000 rpm. The $E_{1/2}$ in the quasi-voltammogram agreed well with that in the voltammogram at the GCRE for the reduction of $DMFc^+$, indicating that the species released from the LMDE was $DMFc^+$. This result suggests that the rotating GCRE-LMDE system will be useful for the identification of the reaction product at the WIO interface when the product was easily reduced or oxidized.

Conclusion

In the present work, the LMDE was prepared by gelling NPOE with PVC, and the ion transfer reaction at the WIO interface was observed by using the LMDE set in W. It was demonstrated that the detection sensitivity based on the current due to the ion transfer was improved more than 2 orders when the measurement was performed at the rotating LMDE. The reversibility of the interfacial ion transfer could be evaluated

from the dependence of the limiting current on the rotation rate of the LMDE. When the rotating LMRE-LMDE or GCRE-LMDE was adopted, the reaction product at the LMDE could be identified.

The following difficulties were also found. (1) Since the oxidant ($DMFc^+$) added in the NPOE-LM in order to depolarize the NPOE-LM/GC interface was not sufficiently hydrophobic, a part of $DMFc^+$ was released to W, resulting in a narrow potential window. (2) Though the limiting current proportional to the concentration of the objective ion was observed when the concentration was low, the current showed a peak instead of the limiting current when the concentration was higher than 2×10^{-6} M. (3) The stripping voltammetry was not so sensitive as expected. In order to overcome the difficulty of (1), it is necessary to find a more hydrophobic oxidant. The difficulties of (2) and (3) are due to the slow diffusion of the ion in the NPOE-LM gelled with PVC. An idea to decrease the viscosity of the NPOE-LM and to make the diffusion faster is required. As one of the ideas to overcome the difficulty of (3), the thickness of the NPOE-LM was reduced. It was found, however, that the NPOE-LM was easily detached from GC when the thickness was less than 0.1 mm. Further efforts are required to make the NPOE-LM thinner. In this connection, the NPOE-LM of 0.3 mm thick adopted in the present work was confirmed to be stable for at least three days.

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