In situ Spectrocyclic Voltammogram of $[\text{Ru}(\text{terpy})_2]^{2+}$ Incorporated into Coated Nafion Membrane

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In situ spectrocyclic voltammetry (SCV) of $[\text{Ru}(\text{terpy})_2]^{2+}$ incorporated into coated Nafion membrane was carried out utilizing photodiode array spectrophotometer which provides UV-VIS absorption spectra of the redox species during potential sweep. It was found by the SCV that the oxidized state of the complex in the Nafion membrane could function as a water oxidation catalyst under basic conditions and that the reduced complex could catalyze proton reduction. The electrocatalysis of the polymer confined $[\text{Ru}(\text{terpy})_2]^{2+}$ complex was discussed in relevant to its location in the Nafion membrane.

1. INTRODUCTION

Electrochemistry is attracting attention a great deal with its increasing application to various fields, such as electrochemical device, electrocatalysis, photoenergy conversion system and fuel cell. In a conventional electrochemical measurement, only the information about the current is obtained, so that it is not easy to know the exact phenomena taking place on the electrode surface. Simultaneous observation of redox reaction by other methods coupled with the electrochemical measurements is important for the true understanding of the electrochemical events. Recently, various analytical methods have been associated with the electrochemical measurements so as to obtain multiple

information simultaneously¹⁻²²⁾. *In situ* spectroscopic measurements such as UV-VIS¹⁻⁷⁾, FT-IR⁸⁻¹¹⁾, Raman^{12, 13)}, ESR^{14, 15)}, Luminescence¹⁶⁾, PAS (photoacoustic spectroscopy)^{17, 18)}, and EQCM (electrochemical quartz microbalance technique)¹⁹⁻²¹⁾ have been reported which provide important information on the redox or mass transport process occurring on the electrode surface.

Modification of the electrode surface has been one of the most attractive subjects in the field of electrochemistry during the last two decades²³⁻²⁷⁾. Although many kinds of strategy have been attempted to furnish a characteristic function to the electrode, surface modification by polymer coating is the most general and widely applicable method. The polymer coating is also very attractive as a convenient way of modifying the electrodes by functional compounds such as metal complexes, semiconductor particles, or enzymes. The electrochemical properties of transition metal complexes have been intensively studied in terms of their redox activities, electrocatalysis,

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utilization as the electrochromic or photoenergy conversion material and so on. These studies are often carried out in surface modified systems as mentioned above. In-situ UV-VIS spectroelectrochemical measurements are very advantageous particularly for such systems to ascertain the redox reactions taking place on the surface, because we can obtain direct information on the electrochemical processes through the spectral change. In addition, it also facilitates the quantitative estimation of the coverage of the active species on the modified electrode. Recently, diode array spectrophotometer by which a whole spectrum of a sample can be taken in a very short time has become to be used in the spectroelectrochemical studies^{3,7}. Time resolved spectroelectrochemical studies utilizing a diode array spectrophotometer were carried out successfully by the present authors on a Prussian Blue (PB) membrane electrodeposited on an ITO transparent glass electrode⁷. Rapid transient spectral change subsequent to the potential step was shown for the first time on a PB membrane and a new mechanism of the redox process was proposed.

Here we report in-situ spectrocyclic voltammetry (SCV) of a $[\text{Ru}(\text{terpy})_2]^{2+}$ (terpy = 2,2',6',2''-terpyridine) complex incorporated into a coated Nafion membrane. Since the $[\text{Ru}(\text{terpy})_2]^{2+}$ is a transient metal complex which is stable and capable of various reversible redox reactions and has an intense visible light absorption based on its MLCT (metal to ligand charge transfer) process, it is a good candidate for the spectroelectrochemical studies.

Not only for its utility as a redox compound to study SCV but also for its electrocatalytic properties, this complex evoked our interest. $[\text{Ru}(\text{terpy})_2]^{2+}$ is oxidized to $[\text{Ru}(\text{terpy})_2]^{3+}$ at $E^0 = 1.34 \text{ V vs. NHE}$, therefore the oxidized species, $[\text{Ru}(\text{terpy})_2]^{3+}$, might be able to

oxidize water to generate dioxygen ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2 + 4\text{e}^-$, $E^0 = +1.23 \text{ V vs. NHE}$) as far as its potential is concerned. We have reported that the $[\text{Ru}(\text{bpy})_3]^{2+}$ which has the similar structure and oxidation potential to $[\text{Ru}(\text{terpy})_2]^{2+}$ was found to be an effective catalyst for the oxygen evolution from water when it is coupled with RuO_2 ²⁸. Taking account of these features, it is interesting to study the electrochemical reactions of this terpyridine complex in relevant to the bipyridine complex.

On the other hand, the two electron reduced state of this complex, $[\text{Ru}(\text{terpy})_2]^0$, is known to be a good catalyst for the CO_2 electroreduction in a non-aqueous homogeneous solution. We have reported that the closely related metal complex, $[\text{Co}(\text{terpy})_2]^{2+}$, which is an effective catalyst for the CO_2 electroreduction in a nonaqueous medium²⁹, can also catalyze CO_2 electroreduction in an aqueous system by incorporating it into a coated Nafion membrane. Reflectance spectroscopic voltammetry (RSCV) technique employed in this study has clearly shown that the electrochemically generated $[\text{Co}(\text{terpy})_2]^+$ species are the CO_2 reduction catalysts³⁰. The Nafion/ $[\text{Ru}(\text{terpy})_2]^{2+}$ system was expected to show catalytic activity for the CO_2 reduction in an aqueous medium similarly to the Nafion/ $[\text{Co}(\text{terpy})_2]^{2+}$ system. In order to study these interesting aspects of the electrocatalysis of this Nafion/ $[\text{Ru}(\text{terpy})_2]^{2+}$ system, in situ spectrocyclic voltammogram has been adopted and will be reported in this paper.

2. EXPERIMENTAL

The metal complex $[\text{Ru}(\text{terpy})_2](\text{ClO}_4)_2$ was synthesized according to the literature³¹. Nafion solution (Nafion117, 5 wt% aliphatic alcohol solution, Aldrich Chemical Co., Inc.) was purchased and diluted twice by methanol prior to use. Electrolytes were of commercially

available purest grade and used as received. Distilled water was used for all the experiments.

Transparent ITO glass electrode (effective area = 1.0 cm²) was used for the SCV measurement and BPG (basal-plane pyrolytic graphite) electrode (effective area = 0.197 cm²) for the other experiments as a working electrode. To coat the Nafion/complex membrane, first 5 μ l or 10 μ l of the Nafion solution (2.5 wt%) was cast on the electrode surface. After the solvent was evaporated under air at room temperature, the coated electrode was dipped in pure water for 30 min to improve the reactivity of the redox species incorporated in the Nafion membrane³²⁾. It was subsequently soaked into an aqueous solution of the [Ru(terpy)₂](ClO₄)₂ (0.3 mM) for one day to adsorb the complex into the Nafion membrane.

Electrochemical cell used was a conventional single compartment type one equipped with three electrodes, a working, a platinum wire counter, and a saturated calomel reference (SCE) electrode. A 0.1 M KHCO₃ (pH ~ 8.5) or a 0.1 M KNO₃ (pH ~ 6) aqueous solution was used as an electrolyte solution. The cell was purged with Ar gas by bubbling it through the solution for around 30 min before the measurement.

Electrochemical measurements were carried out on a Hokuto-Denko HA-301 potentiostat and a HB-104 function generator and the voltammograms were recorded on a Rika-Denki RW-21T X-Y recorder. Spectrocyclic voltammetry was performed by combining these apparatuses with a diode array spectrophotometer of Otsuka Electronics IMUC-7000, flexible optical fibers, and a monitoring light source (halogen tungsten lamp). For the SCV measurement, a pair of optical fibers were set on the front and back sides of the coated ITO electrode to measure the transmission spectral

change. The spectral data were stored and processed by the personal computer NEC PC-9801RX and plotted out on a plotter MC-920. For the RSCV measurement, the two optical fibers were positioned at the 45° angle with each other to measure the reflected light from the coated surface of the BPG electrode. The sampling time for the full scale wavelength (350~750 nm) was 20 ms and eight scans of the spectrum was accumulated for the SCV measurement; they were 1 s and one scan for the RSCV measurement. In both the measurements, the spectra were recorded with the interval of 12.5 s during the potential sweep of 2 mVs⁻¹, which corresponds to the spectral recording at 25 mV interval.

3. RESULTS AND DISCUSSION

Results of SCV at the ITO coated with the Nafion/[Ru(terpy)₂]²⁺ membrane dipped in the 0.1 M KNO₃ aqueous solution (pH ~ 6) are shown in Fig. 1. A set of the reversible redox peaks centered at +1.1 V was observed in the cyclic voltammogram (Fig. 1A), which is assigned to Ru(2+/3+) redox couple. Before the potential reaches to +0.9 V, the spectrum did not change showing the maximum absorption peak at 475 nm. The spectrum is almost identical to that of [Ru(terpy)₂](ClO₄)₂ present in an aqueous solution. With the increase of the anodic current, the absorption at 475 nm began to decrease while exhibiting two isosbestic points at 395 and 610 nm (Fig. 1B). The spectral change corresponds to the charges passed up to +1.3 V and the spectrum kept the same absorbance up to +1.4 V. The spectrum at +1.3 V is assigned to the oxidized form of the complex, [Ru(terpy)₂]³⁺, which has the maximum absorption at 735 nm and seemingly at the wavelength shorter than 350 nm. The remaining weak absorption peak at 475 nm shows the residual [Ru(terpy)₂]²⁺ species in the membrane, namely, a few part of the complex

can not be oxidized under these conditions. From the comparison between the original absorbance at 475 nm (at +0.9 V) and that at +1.3 V, we can estimate the percentage of the electroactive species in the membrane; 93 % of the complex was oxidized in this measurement. The broad anodic peak seems to be composed of two processes. However, any other spectral change which can be assigned to these processes could not be observed. We suggest that once the oxidation of the complex takes place, it may accelerate the oxidation of other complexes possibly due to the spatial rearrangement of the complex. In the reverse sweep, the spectrum began to change at around +1.3 V exhibiting the increase of the absorption at 475 nm. Along with the increase of the cathodic current, the spectrum changed rapidly to recover the original absorbance of $[\text{Ru}(\text{terpy})_2]^{2+}$. When the potential reaches +0.9 V, the rate of the spectral change became sluggish but still the spectrum changed continuously and slowly until it regained its initial value perfectly at 0 V. Thus, the complex is simply oxidized and rereduced showing no catalytic reactions under these conditions. The present in situ SCV measurement has proved its usefulness in studying the real change of the redox species.

In contrast, an entirely different result was obtained when 0.1 M KHCO_3 (pH ~ 8.5) was used as an electrolyte instead of KNO_3 . The anodic current appeared at around +0.9 V in CV (Figure 2A), bringing about the spectral change due to the oxidation of $[\text{Ru}(\text{terpy})_2]^{2+}$ to $[\text{Ru}(\text{terpy})_2]^{3+}$ (Fig. 2B). However, the anodic current reached four times as high as that in the KNO_3 solution showing no current peak, while the degree of the spectral change was rather small in spite of the higher anodic current. This characteristic CV feature shows that some electrocatalytic reaction takes place on oxidizing the complex. The spectral change ceased at

Fig. 1 Spectroelectrochemical (SCV) measured at ITO electrode coated with Nafion membrane incorporating $[\text{Ru}(\text{terpy})_2](\text{ClO}_4)_2$ (thickness = ca. $1\mu\text{m}$), dipped in 0.1 M KNO_3 aqueous solution (pH ~ 6) under Ar. A; Cyclic voltammogram at scan rate = 2 mVs^{-1} and absorbance at 475 nm. B; Visible absorption spectra during the potential sweep from 0.9 V to 1.3 V (vs.SCE) at the 25 mV interval. C; Visible absorption spectra during the reverse sweep from 1.3 V to 0.1 V (vs.SCE) at the 25 mV interval.

+1.3 V, and a considerable amount of the complex was remained unoxidized. It is estimated from the absorption change at 475 nm that about 25 % of the complex in the membrane are not oxidized. However, it would not mean that so large fraction of the complex is electroinactive. More reasonably, when considering the CV in Fig. 2A, it could be inferred that the oxidized complex is rereduced due to some catalytic reactions which compete with the electrochemical oxidation of the complex. Actually in the reverse sweep, the spectrum recovers its 475 nm absorption (Fig. 2C), namely, the $[\text{Ru}(\text{terpy})_2]^{2+}$ species are regenerated although no cathodic current is obtained as shown in CV. Water molecules or related species would be one of the candidates as the reductant to reduce the complex. Such catalysis will be discussed later. After the potential reached +0.9 V in the reverse scan the spectrum changed at a very slow rate regardless of the no cathodic current, but it could not recover its initial absorbance. About 85 % of the divalent complex initially present in the membrane was reproduced by the reverse scan according to the estimation from the spectral

data. The reason for the partial irreversibility of the spectrum might be ascribed to the desorption of the complex accompanying the catalysis, inactivation of the residual trivalent complex in the membrane, or decomposition of the complex.

As for the catalytic oxidation taking place in a KHCO_3 solution, if hydroxyl anion is oxidized, it is quite natural that the higher pH favors the catalysis. Probably on this reason, the complex would have behaved differently between the two electrolyte conditions.

Fig. 2 Spectrocyclic voltammogram (SCV) measured at ITO electrode coated with Nafion membrane incorporating $[\text{Ru}(\text{terpy})_2](\text{ClO}_4)_2$ (thickness = ca. 1 μm), dipped in 0.1 M KHCO_3 aqueous solution (pH $\sim$ 8.5) under Ar. A; Cyclic voltammogram at scan rate = 2 mVs^{-1} and absorbance at 475 nm. B; Visible absorption spectra during the potential sweep from 0.9 V to 1.3 V (vs. SCE) at the 25 mV interval. C; Visible absorption spectra during the reverse sweep from 1.3 V to 0.0 V (vs. SCE) at the 25 mV interval.

The more basic condition of the KHCO_3 solution would enable OH^- oxidation to generate H_2O_2 by two electron oxidation or O_2 by four electron oxidation. Although the oxidized complex $[\text{Ru}(\text{terpy})_2]^{3+}$ is able to work as an only one electron oxidant by itself, it might be possible for such metal complex to catalyze a multi electron process when it is incorporated into a condensed phase such as polymer membrane. The high concentration of the complex in the condensed phase could enable the formation of active sites for the multi-electron catalysis³³⁾. In addition to these explanations, a special effect might be expected for KHCO_3 salt in a catalytic water oxidation. Recently, Arakawa et al. reported that the addition of carbonate or bicarbonate salt to aqueous medium enhances a great deal the photocatalytic decomposition of water in a Pt-loaded TiO_2 suspension system³⁴⁾. Although they are not sure about the role of the carbonate anion yet, it is suggested that the hydrogen atom of water molecule is abstracted by carbonate anion and thus water splitting can take place. We suppose a similar effect might be involved in our system.

As mentioned in the introduction section, electrochemically generated $[\text{Ru}(\text{terpy})_2]^0$ can reduce CO_2 molecule catalytically in a non-aqueous solution system. The cyclic voltammograms of the 1 mM $[\text{Ru}(\text{terpy})_2](\text{ClO}_4)_2$ / DMF solution under Ar as well as CO_2 are shown in Fig. 3. Two well-defined redox couples were observed in the CV under Ar at -1.16 and -1.39 V corresponding to $\text{Ru}(+2/+1)$ and $\text{Ru}(+1/0)$ redox processes, respectively. Under CO_2 atmosphere, while the reduction wave for $\text{Ru}(+2/+1)$ remained unaltered, the cathodic current for $\text{Ru}(+1/0)$ process was enhanced manyfolds and both the reoxidation peaks in the reverse sweep were diminished. Considering the fact that CO_2 reduction to stable products requires at least two electrons, it

is reasonable that the monovalent complex $[\text{Ru}(\text{terpy})_2]^+$ has no catalytic activity in a homogeneous solution system similarly to $[\text{Co}(\text{terpy})_2]^{2+30)}$.

Fig. 3 Cyclic voltammogram of 1 mM $[\text{Ru}(\text{terpy})_2](\text{ClO}_4)_2$ / (0.1M TBAP/DMF) (TBAP; tetra buthyl ammonium perchlorate) solution under [A] Ar or [B] CO_2 at BPG electrode. Scan rate = 5 mVs^{-1} .

The cyclic voltammograms at BPG electrode coated with a Nafion/ $[\text{Ru}(\text{terpy})_2]^{2+}$ membrane dipped in a 0.1 M KHCO_3 aqueous solution and measured under Ar and CO_2 in a negative potential range are shown in Fig. 4. The cathodic current appearing at the potential more negative than -1.5 V in the CV under Ar is considered due to the proton reduction. The redox peaks arising from the redox process of the complex are not apparent in the CV, though the applied potential range is negative enough to reduce the complex as inferred from the CV in DMF (Fig. 3). In the CV under CO_2 , a considerable enhancement of the cathodic current was observed following a cathodic wave at -1.3 V. This current enhancement is supposed to be based on some catalytic reduction. It was expected that CO_2 is reduced catalytically by this modified electrode.

However, in a potentiostatic electrolysis at -1.55 V, CO_2 reduction product such as formic

acid or carbon monoxide could not be detected in GC and HPLC analyses, and only the hydrogen gas evolution was confirmed. Thus, we conclude that proton instead of CO_2 is reduced by the complex in the membrane. The greater cathodic current under CO_2 shown in the CV (Fig. 4) is probably arising from the favored proton reduction by the lower pH due to carbonic acid than the pH under Ar. By employing the same method, it has been successfully shown that $[\text{Co}(\text{terpy})_2]^{2+}$ ³⁰⁾ and $\text{Re}(\text{terpy})(\text{CO})_3\text{Br}$ ³⁵⁾ incorporated in a Nafion membrane catalyze CO_2 reduction in an aqueous electrolyte solution probably owing to the hydrophobic environment around the active site brought about by the Nafion structure.

Fig. 4 Cyclic voltammogram at BPG electrode coated with Nafion membrane incorporating $[\text{Ru}(\text{terpy})_2](\text{ClO}_4)_2$ (thickness = ca. 35 μm), dipped in 0.1 M KHCO_3 aqueous solution (pH $\sim$ 8.5) under [A] Ar or [B] CO_2 . Scan rate = 50 mVs^{-1} .

RSCV technique was employed for this system to study the electrochemical reaction. If the proton reduction is mediated by the complex, spectral change should not be observed or should be suppressed when the reduced complex is rapidly reoxidized by H^+ reduction. The results are shown in Fig. 5. At a slow (2mVs^{-1}) scan rate, two irreversible

cathodic peaks are observed in the CV (Fig. 5A) and it is assumed that these peaks correspond to the redox couples of $\text{Ru}(+2/+1)$ and $\text{Ru}(+1/0)$. Because of the low intensity of the reflected light from the sample, the spectra measured during the cyclic voltammetric scan (Fig. 5B) are rather noisy compared to the transmittance spectra (Figs. 1 and 2), but the reflectance spectrum was the same as the transmittance one. Along with the increase of the cathodic current, the reflectance spectrum changed showing the decrease of the maximum absorption at 475 nm as well as the increase of the absorption in the wavelength region shorter

Fig. 5 Reflectance spectrocyclic voltammogram (RSCV) measured at BPG electrode coated with Nafion membrane incorporating $[\text{Ru}(\text{terpy})_2](\text{ClO}_4)_2$ (thickness = ca. 2.5 μm), dipped in 0.1 M KHCO_3 aqueous solution (pH $\sim$ 8.5) under Ar. A; Cyclic voltammogram at scan rate = 2 mVs^{-1} . B; Visible absorption spectra at 0.0 V and during the potential sweep from -1.35 to -1.6 V (vs. SCE) at the 50 mV interval.

than 430 nm. However, the degree of the spectral change was very little and the change was irreversible. Since the potential is enough negative to reduce the complex in the membrane and that it was confirmed by the SCV measurement described before (Fig. 1) that the most part of the complex is electroactive, this little change of the spectrum should be attributed to the catalytic proton reduction taking place in the membrane. The reduced complex generated electrochemically in the membrane would be reoxidized so soon by H^+ reduction that only very little spectral change could be observed. The irreversibility of the spectral change may come from a irreversible reaction of the complex to some other compounds occurring competitively with the catalytic proton reduction. No significant difference could be observed in the same measurement under CO_2 atmosphere. Taking account of all these results, it can be concluded that the $[Ru(terpy)_2]^{2+}$ complex in the membrane functions as a proton reduction catalyst.

As mentioned above, the effects of polymer matrix should be considered to study the electrocatalysis by polymer confined metal complexes. The interesting electrocatalysis of the $[Ru(terpy)_2]^{2+}$ complex in the present study could be discussed in terms of the location of the complex in the Nafion membrane. It is known that a Nafion membrane has three different kinds of domains, the hydrophobic region consisted of fluorocarbon main chain, the hydrophilic ion cluster composed of the pendant sulfonic acid groups, water molecules, and electrolytes, as well as their interfacial region consisted of the side chain and the sulfonic acid groups isolated from the ion cluster^{36, 37)}. When a compound like a metal complex is incorporated into a Nafion membrane, it will be distributed to these three domains according to its hydrophilic and

hydrophobic affinities. In addition, once the complex is oxidized or reduced, the change of the hydrophilicity and hydrophobicity of the complex will cause a spatial rearrangement of the complex achieved by its cross domain migration. In the study of electrocatalytic reduction of CO_2 by the Nafion/ $[Co(terpy)_2]^{2+}$ coated electrode system³⁰⁾, the $[Co(terpy)_2]^{2+}$ complex is supposed to exist in the interfacial region according to its amphiphilic properties, i.e., hydrophilicity due to a divalent cation and hydrophobicity due to the terpyridine ligand. The reduced complex $[Co(terpy)_2]^+$ which is the active species for the CO_2 electrocatalytic reduction in a membrane system becomes more hydrophobic, and thus would migrate to more hydrophobic region of the Nafion membrane. However, the present Nafion/ $[Ru(terpy)_2]^{2+}$ coated membrane system showed no catalytic activity for the CO_2 reduction in an aqueous medium contrary to our expectation. We suppose that the Ru complex is incorporated into a more hydrophilic region than the Co complex and is likely to react with water to generate hydrogen gas instead of reducing CO_2 . Actually, catalytic water oxidation by this system was shown in the former part of this paper. These electrocatalytic reactions with water mediated by the oxidized and the reduced states of the $[Ru(terpy)_2]^{2+}$ complex in the Nafion membrane show that this Ru complex is feasible to react with water in the Nafion membrane.

4. CONCLUSION

It has been shown in this study, how effective the in situ spectroscopic voltammetry is to understand the electrocatalysis taking place on a modified electrode surface. By analyzing the spectral change during potential scan, it is expected to explain the complicated processes quantitatively, such as redox reactions, catalyses, or mass transport. Moreover, this

method can easily be applied to other systems, particularly to surface modified electrodes.

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