Immobilization of a High-Valent Rhenium Complex on an Indium-Doped Tin-Oxide Electrode: Enhanced Catalytic Activity of a *trans*-Dioxorhenium(V) Complex in Electrochemical Oxidation of Alcohols

Hideki Sugimoto,*[a] Hiroshi Tsukube,[a] and Koji Tanaka[b]

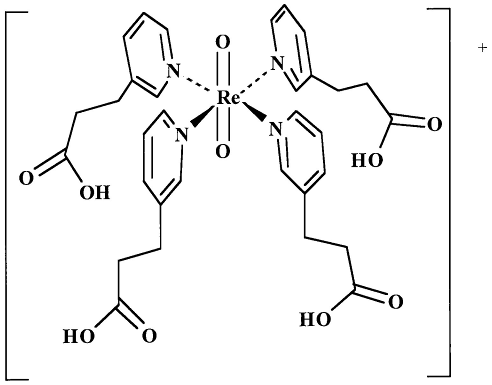
Keywords: Surface analysis / Cyclic voltammetry / Immobilization / Rhenium / Oxidation

A high-valent *trans*-dioxorhenium(V) complex containing pyridine ligands was successfully immobilized on an ITO (indium-doped tin-oxide) electrode. The complex formed a monolayer structure on the electrode surface and promoted electrochemical catalytic oxidation of 1-phenylethanol to acetophenone in CH_2Cl_2. Oxidation hardly occurred in CH_2Cl_2 solution containing the free rhenium(V) complex. Immobilization of other high-valent metal complexes will present opportunities for design of functional electrodes with high activities.

Introduction

One of the most effective strategies in the development of novel molecular devices such as sensors and nanosized catalysts is to immobilize redox- and photo-active metal complexes on semiconductor electrodes by utilizing their well-defined structure.[1] Several ferrocene derivatives[2] and Re^{I},[3] Os^{II},[4] and Ru^{II} [5] complexes have already been immobilized on electrodes and have effectively mediated electron- and charge-transfer processes. Although most of the metal complexes operating in previous electrode systems were limited to those of low oxidation numbers, a few studies have immobilized high-valent compounds.

trans-$[Re^{V}O_2(pys)_4]^+$ (pys = pyridine derivatives) complexes have interesting features as redox- and photo-active catalysts, such as: 1) one-electron oxidation of the $Re^{V}O_2$ complexes affords higher-valent $Re^{VI}O_2$ cores;[6] 2) the two oxygen atoms attached to the Re center are responsible for electrochemical oxidation of organic molecules;[7] and 3) they exhibit microsecond long-lived luminescence based on d-d transitions in the visible region.[7] We have prepared the novel complex *trans*-$[ReO_2(L)_4]PF_6$ [**1**]PF_6 (L = 3-pyridinecarboxylic acid) containing free carboxylic acid groups (Figure 1). Such high-valent Re^{V} complexes have rarely been immobilized. Herein we investigate the immobilization of a series of Re^{V} complexes on ITO (indium-doped tin-oxide) electrodes and their catalytic activity in the oxidation of 1-phenylethanol and related alcohols (Scheme 1).



[**1**]$^+$

Figure 1. Suggested structure of [**1**]$^+$

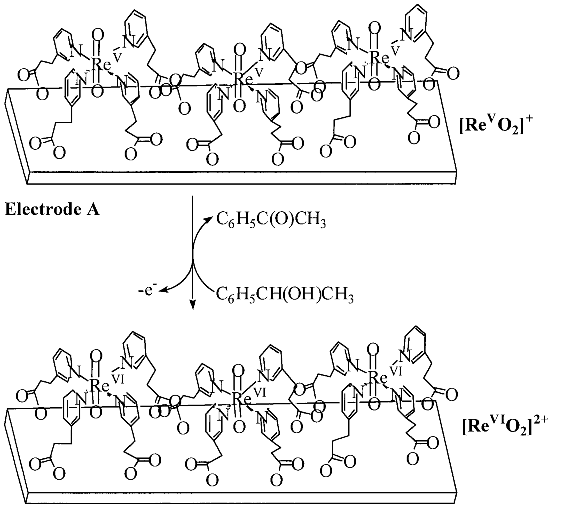
Results and Discussion

In electrochemical experiments, complex [**1**]$^+$ shows a reversible redox wave assignable to a $Re^{VI/V}$ couple at 0.90 V vs. Fc/Fc^+ in CH_3CN. The complex was immobilized on ITO[8] electrodes by three different methods. Electrode **A** was modified by dipping the ITO electrode into a CH_3CN solution of the [**1**]PF_6 complex (2×10^{-4} M) for several days. Electrodes **B** and **C** were modified by combining the [**1**]PF_6 complex with aminoethyl- and aminomethylphosphonic acids by inserting them into the space between the surface of the electrodes and the [**1**]PF_6 complex. In electrode **A**, [**1**]$^+$ can connect with the ITO surface through carboxylate ester bonds [Sn−O−C(O)-] and hydrogen bonds [Sn=O···HO-C(O)-], as observed for the adsorption of ruthenium complexes containing free carboxylic acids

---

[a] Department of Chemistry, Graduate School of Science, Osaka City University,
Sumiyoshi-ku, Osaka, 558-8585, Japan
Fax: (internat.) + 81-6-6605-2522
E-mail: sugimoto@sci.osaka-cu.ac.jp
[b] Institute for Molecular Science,
Higashiyama, Okazaki, 444-8787, Japan

DOI: 10.1002/ejic.200400546



Scheme 1. *trans*-Dioxorhenium complex [**1**]$^{+/2+}$ immobilized on an ITO electrode and electrochemical oxidation of 1-phenylethanol to acetophenone

onto metal oxides such as SnO_2, TiO_2, and In_2O_3.[5h] In electrodes **B** and **C**, however, [**1**]$^+$ can connect with the amino groups of the spacer compounds through peptide bonds [−NH−C(O)-], and these units, in turn, connect with the ITO surface through phosphate ester bonds [Sn−O−P(O)-], as reported for the adsorption of ruthenium complexes containing free phosphonic acids onto these metal oxides.[5f,5g,9] The only difference between electrodes **B** and **C** is the length of the methylene chain: P−CH$_2$−CH$_2$−N for electrode **B** and P−CH$_2$−N for electrode **C**. The electrode performances were characterized by cyclic voltammetry. The three electrodes **A**−**C** exhibit the same redox potential, $E_{1/2}$, of Re$^{VI/V}$, but with different peak-to-peak separations ($\Delta E_p = E_{pa} - E_{pc}$). Electrode **A** shows a somewhat larger peak separation of 0.11 V than electrodes **B** and **C** (ΔE_p = 0.05 V). The electrodes also exhibit somewhat different surface stabilities. After the electrodes were rinsed for one hour, the current intensity of Re$^{VI/V}$ decreased by 15% for electrode **A**, but decreased by only 5% for electrodes **B** and **C**.

The electron-transfer process of electrode **B**, as characterized by cyclic voltammetry, was typical (Figure 2). The intensities of the anodic and cathodic currents are directly proportional to the increase in scan rate up to 300 mV·s^{-1}; they gradually saturate as the rate increases above 350 mV·s^{-1}. Since electrodes **A** and **C** show similar electrochemical behaviors despite their different construction, the redox processes in these systems must be confined to the surface. The surface coverages of the complexes were calculated by coulometric measurements at 1.2 V. The surface areas were estimated as 2.5×10^{-10} mol/cm^2 for electrode **A**, 1.9×10^{-10} mol/cm^2 for electrode **B**, and 1.8×10^{-10} mol/cm^2 for electrode **C**. Although the crystal structure of [**1**]PF$_6$ is not available, the limiting surface coverage was roughly estimated as 2.9×10^{-10} mol/cm^2 by assuming that spheres based on the bond lengths and angles reported for *trans*-[ReO$_2$(4-picoline)$_4$]ReO$_4$ are packed on a flat surface, and neglecting counteranions.[10] Similar surface coverages have been reported for monolayered electrodes with Ru complexes: [Ru(2,2′-bipyridyl)$_2$(2,2′bipyridyl-4,4′-dicarboxylic acid)]$^{2+}$ = 1.5×10^{-10} mol/cm^2;[9] and [Ru(2,2′-bipyridyl)$_2$(2,2′bipyridyl-4,4′-diphosphonic acid)]$^{2+}$ = 2.5×10^{-10} mol/cm^2.[9] Thus, the employed Re^V complex [**1**]$^+$ is believed to form a monolayer structure on the ITO electrode surface.

The modified electrodes exhibit interesting catalytic behavior in the electrochemical oxidation of 1-phenylethanol. As shown in Figure 3, the intensity of the oxidation current corresponding to Re$^{VI/V}$ increases in the presence of 8.2 mM 1-phenylethanol (see b in Figure 3). Further addition of the alcohol substrate (total 24.5 mM) led to a further increase in the oxidation current, and a corresponding decrease in the reduction current (see c in Figure 3). Electrolysis was carried out at 1.2 V until no oxidation current was observed, and the reaction mixtures were then characterized by GC-MS and HPLC methods, which indicated that 1-phenylethanol had been converted into acetophenone. Electrochemical oxidation of this alcohol hardly occurred in CH$_2$Cl$_2$ solution containing the free complex [**1**]$^+$, in which a glassy carbon electrode having the same surface area as

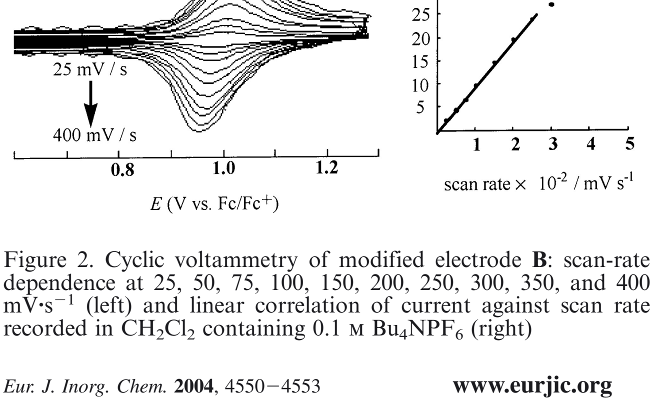


Figure 2. Cyclic voltammetry of modified electrode **B**: scan-rate dependence at 25, 50, 75, 100, 150, 200, 250, 300, 350, and 400 mV·s^{-1} (left) and linear correlation of current against scan rate recorded in CH$_2$Cl$_2$ containing 0.1 M Bu$_4$NPF$_6$ (right)

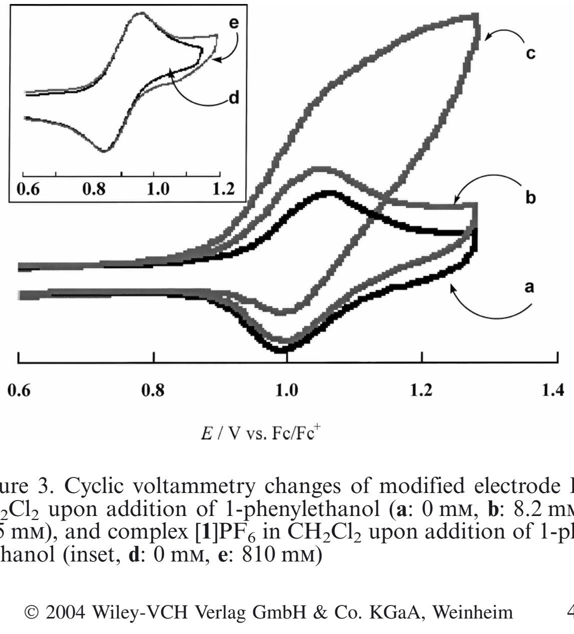


Figure 3. Cyclic voltammetry changes of modified electrode **B** in CH$_2$Cl$_2$ upon addition of 1-phenylethanol (**a**: 0 mM, **b**: 8.2 mM, **c**: 24.5 mM), and complex [**1**]PF$_6$ in CH$_2$Cl$_2$ upon addition of 1-phenylethanol (inset, **d**: 0 mM, **e**: 810 mM)

the employed ITO electrode was used. Also, the current intensity only increased slightly, even in the presence of a large excess of 1-phenylethanol (810 mM) (see inset e in Figure 3). Electrodes **B** and **C** exhibit higher turnover numbers (TON) and current efficiencies in the oxidation of 1-phenylethanol than electrode **A**. Table 1 compares the catalytic profiles of the three modified electrodes. The spacer insertion enhances the catalytic activity of the *trans*-dioxorhenium(V) complexes.

Table 1. Catalytic oxidation of 1-phenylethanol by modified electrodes **A**−**C**

Modified electrode	**A**	**B**	**C**
TON[a]	900	1300	1200
Current efficiency[b]	65	85	80

[a] Turnover number (product mol/complex mol). [b] $2e^-$ per substrate.

The rate constants for the system $v = k[\mathrm{Re^V}$ on electrodes][1-phenylethanol] of electrodes **A**−**C** were roughly determined to be about 1 $\mathrm{M^{-1}\,s^{-1}}$ using Equation (1)

$$i = nFAk\Gamma_{\mathrm{p}}C_{\mathrm{A}} \qquad (1)$$

where n = number of electrons, F = Faraday constant, A = surface area, Γ_{p} = surface coverage, k = rate constant, and C_{A} = concentration of substrate, which has been previously applied to heterogeneous systems.[11] The current intensities independent of the scan rates were entered as i in this equation. Since these three electrodes have almost identical surface coverages and rate constants, their catalytic activities must depend on the presence, or absence, and nature of the spacers introduced between the electrode surface and complex $[\mathbf{1}]^+$.

These electrodes also catalyze the oxidation of 1-heptanol and 2-propanol to give 1-heptanealdehyde and acetone, respectively. Although the detailed mechanism is unclear,[12] the catalytic cycles may contain redox and acid-base reactions of the *trans*-$\mathrm{ReO_2}$ unit as suggested in a *trans*-$[\mathrm{ReO_2(py)_4}]^+$ system,[7] in which the active $\mathrm{Re^{VI}}$ state was significantly involved (Scheme 1).

Conclusion

We have presented the first example of high-valent metal complexes immobilized on an electrode surface. The *trans*-dioxorhenium(V) complexes immobilized on the electrode surface enable catalytic oxidation of 1-phenylethanol to acetophenone with high turnover and high current efficiency. A combination of high-valent metal complexes with electrodes could provide a new generation of electrochemical catalysts.

Experimental Section

***trans*-$[\mathrm{ReO_2(L)_4}]\mathrm{PF_6}$ ([1]$\mathrm{PF_6}$; L = 3-pyridinecarboxylic acid):** A suspension containing $[\mathrm{ReOCl_3(PPh_3)_2}]$ (0.50 g, 0.60 mmol) and 3-pyridinecarboxylic acid (1.80 g, 12 mmol) in acetone/$\mathrm{H_2O}$ (20:1 v/v) was refluxed for 90 minutes to give an orange solution. After filtration, the orange solution was concentrated to 5 mL. After silica-gel column chromatography ($\mathrm{CH_3OH}$ eluent), addition of $\mathrm{NH_4PF_6}$ (300 mg, 1.80 mmol) in $\mathrm{H_2O}$ (10 mL) gave an orange powder. The collected powder was dried in air (yield: 126 mg, 22%). $\mathrm{C_{32}H_{36}F_6N_4O_2PRe}$ (967.84): calcd. C 39.71, H 3.75, N 5.79. found C 39.79, H 3.89, N 5.42. ESI-MS: m/z = 823 $[\mathrm{M - PF_6}]^+$. IR: $\tilde{\nu}$ = 799 $\mathrm{cm^{-1}}$ $\nu_{(\mathrm{O=Re=O})}$. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.52 (t, J = 7.7 Hz, 8 H, $\mathrm{CH_2}$), 2.81 (t, J = 7.4 Hz, 8 H, $\mathrm{CH_2}$), 7.49 (t, J = 5.8 Hz, 4 H, py), 7.74 (d, J = 7.7 Hz, 4 H, py), 8.84 (d, J = 5.8 Hz, 4 H, py), 8.92 (s, 4 H, py) ppm. UV/Vis ($\mathrm{CH_3CN}$): λ = 430 nm (ε = 1250 $\mathrm{M^{-1}{\cdot}cm^{-1}}$), 346 (19800), 254 (15600).

Preparation of ITO Electrodes: Before surface modification, each ITO electrode was washed with a 5:1:1 solution of $\mathrm{H_2O}$, $\mathrm{H_2O_2}$, and $\mathrm{NH_4OH}$ and thoroughly rinsed with purified water. After heating at 120 °C for 60 minutes, the electrode was cooled and stored under dry $\mathrm{N_2}$.

ITO Electrode A: The dried ITO electrode was dipped in a $\mathrm{CH_3CN}$ solution of [**1**]$\mathrm{PF_6}$ (2×10^{-4} M) for several days. The electrode was then rinsed in ethanol to remove the adsorbed salt.

ITO Electrodes B and C: The dried ITO electrode was dipped in a $\mathrm{CH_3CN}$ solution of aminoethyl- or aminomethylphosphonic acid; after 24 hours, the electrode was picked up from the solution. The electrode on which the phosphonic acid was immobilized was again dipped in a solution of complex [**1**]$\mathrm{PF_6}$ (2×10^{-4} M) in the presence of four equivalents of DCC (1,3-dicyclohexylcarbodiimide) as a coupling agent for 3−4 days. The electrodes were then rinsed in ethanol to remove the adsorbed salt; in the absence of DCC the complex was not immobilized.

Acknowledgments

This work was partly supported by the Joint Studies Program (2004) of the Institute for Molecular Science, Japan, and by CREST of the Japan Science and Technology Agency. The authors are grateful to Prof. Akio Ichimura of Osaka City University for helpful discussion and to Central Glass Co., Ltd., Japan, for supplying the ITO electrodes.

---

[1] [1a] *Interfacial Electrochemistry: Theory, Experiment, and Applications* (Ed.: A. Wieckowski), Marcel Dekker, New York, **1999**. [1b] E. Palomares, R. Vilar, J. R. Durrant, *Chem. Commun.* **2004**, 362−363. [1c] J. Garcia-Canadas, A. P. Meacham, L. M. Peter, M. D. Ward, *Angew. Chem. Int. Ed.* **2003**, *42*, 3011−3014.

[2] [2a] C. E. D. Chidsey, *Science* **1991**, *251*, 919−922. [2b] J. J. Hickman, *Science* **1991**, *252*, 688−691.

[3] R. Argazzi, C. A. Bignozzi, T. A. Heimer, G. J. Meyer, *Inorg. Chem.* **1997**, *26*, 2−3.

[4] C. Kleverlaan, M. Alebbi, R. Argazzi, C. A. Bignozzi, G. M. Hasselmann, G. J. Meyer, *Inorg. Chem.* **2000**, *39*, 1342−1343.

[5] [5a] J.-K. Lee, S.-H. Lee, M. Kim, H. Kim, D.-H. Kim, W.-Y. Lee, *Chem. Commun.* **2003**, 1602−1603. [5b] B. O'Regan, M. Gratzel, *Nature* **1991**, *353*, 737−740. [5c] S. A. Trammell, J. C. Wimbish, F. Odobel, L. A. Gallagher, P. M. Narula, T. J. Meyer, *J. Am. Chem. Soc.* **1998**, *120*, 13248−13249. [5d] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakkeruddin, R. H-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G. B. Deacon, C. A. Bignozzi, M. Gratzel, *J. Am.*

Chem. Soc. **2001**, *123*, 1613−1624. [5e] K. Wang, M. Haga, M. D. Hossain, H. Shindo, K. Hasebe, H. Monjushiro, *Langmuir* **2002**, *18*, 3528−3536. [5f] B. M. Nakhle, S. A. Trammell, K. M. Sigel, T. J. Meyer, B. W. Erickson, *Tetrahedron* **1999**, *55*, 2835−2846. [5g] S. M. Zakeeruddin, M. K. Nazeeruddin, P. Pechy, F. P. Rotzinger, R. Humphry-Baker, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* **1997**, *36*, 5937−5946. [5h] T. J. Meyer, G. J. Meyer, B. W. Pfenning, J. R. Schoonover, C. J. Timpson, J. F. Wall, C. Kobusch, X. Chen, B. M. Peek, C. G. Wall, W. Ou, B. W. Erickson, C. A. Bignozzi, *Inorg. Chem.* **1994**, *33*, 3952−3964.

[6] M. S. Ram, L. M. Skeens-Jones, C. S. Johnson, X. L. Zhang, C. Stern, D. I. Yoon, D. Selmarten, J. T. Hupp, *J. Am. Chem. Soc.* **1995**, *117*, 1411−1421.

[7] [7a] J. R. Winkler, H. B. Gray, *J. Am. Chem. Soc.* **1983**, *105*, 1373−1374. [7b] H. H. Thorp, J. V. Houten, H. B. Gray, *Inorg. Chem.* **1989**, *28*, 889−892.

[8] ITO-coated glasses of 10 Ω/cm^2 were used in this study.

[9] S. A. Trammell, J. A. Moss, J. C. Yang, B. M. Nakhle, C. A. Slate, F. Odobel, M. Sykora, B. W. Erickson, T. J. Meyer, *Inorg. Chem.* **1999**, *38*, 3665−3669.

[10] J. W. Johnson, J. F. Brody, G. B. Ansell, S. Zentz, *Inorg. Chem.* **1984**, *24*, 2415−2418.

[11] A. J. Bard, L. R. Faulkner, *Electrochemical Methods 2nd ed*, John Wiley & Sons, New York, **2001**.

[12] There are two possibilities of hydrogen transfer and hydride transfer processes (see ref.[7]).

Received June 22, 2004