Supporting Information

For

Electrochemical Oxidation of Sugars at Moderate Potentials Catalyzed by Rh porphyrins

Shin-ichi Yamazaki†*, Naoko Fujiwara†, Sahori Takeda‡, and Kazuaki Yasuda†

Research Institute for Ubiquitous Energy Devices†, Research Institute for Innovation in Sustainable Chemistry‡ National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan.
Experimental Procedures

General. \( \text{Rh}_2\text{Cl}_2(\text{CO})_4 \) was purchased from Wako Chemical. Corresponding ligands were purchased from Tokyo Kasei or Frontier Scientific. All other chemicals were obtained commercially and used as received. Vulcan XC 72R was obtained from Cabot Co. UV-vis spectroscopy was conducted using a Shimadzu UV-1500 PC photodiode array spectrophotometer equipped with a quartz cell (light path = 1 cm) at room temperature.

Synthesis. Rhodium(III) deuteroporphine IX dimethyl ester carbonyl chloride ([\( \text{Rh}^{\text{III}}(\text{DPDE})(\text{CO}) \)]Cl). \( \text{Rh}_2\text{Cl}_2(\text{CO})_4 \) (10.0 mg) and deuteroporphine dimethyl ester (DPDEH₂, 24.8 mg) were dissolved in ethanol (83 mL). The suspension was refluxed for 5 hours. After reflux, the solvent was removed under reduced pressure. The residue was washed with water and hexane, and extracted with ethanol. The solution was used for the preparation of catalyst. The solution was evaporated and the resulting powder was recrystallized in ethanol. ESI-MS (in ethanol): \( m/z \) 639.0 ([\( \text{Rh}^{\text{III}}(\text{DPDE}) \)]⁺), \( m/z \) 667.0([\( \text{Rh}^{\text{III}}(\text{DPDE})(\text{CO}) \)]⁺), \( m/z \) 731([\( \text{Rh}^{\text{III}}(\text{DPDE})(\text{C}_2\text{H}_5\text{OH})_2 \)]⁺). Anal. Calcd for [\( \text{Rh}^{\text{III}}(\text{DPDE})(\text{CO}) \)]Cl·0.5\( \text{H}_2\text{O} \): C, 55.67; H, 4.67; N, 7.87. Found: C, 55.71; H, 4.82; N, 8.04.

Rhodium(III) octaethylporphine ethanol chloride ([\( \text{Rh}^{\text{III}}(\text{OEP})(\text{C}_2\text{H}_5\text{OH}) \)]Cl). \([\text{Rh}^{\text{III}}(\text{OEP})(\text{C}_2\text{H}_5\text{OH})\text{Cl}] \) was synthesized according to the method of Ogoshi et al. [1] with some modification. \( \text{Rh}_2\text{Cl}_2(\text{CO})_4 \) (200 mg) and 2, 3, 7, 8, 12, 13, 17, 18-octaethyl-21\( \text{H}, 23\text{H} \)-porphine (OEPH₂) (248 mg) were suspended in toluene (300 mL). After the suspension
was stirred for 3h at around room temperature to produce a clear solution, the solvent was removed under reduced pressure to give a brown residue. The desired product was extracted from the residue with EtOH and recrystallized from hot EtOH. ESI-MS (in mixed solvent (water : ethanol = 1:1)): \( m/z \) 635.4 ([Rh\textsuperscript{III}(OEP)])\(^+\). Anal. Calcd for [Rh\textsuperscript{III}(OEP)(C\textsubscript{2}H\textsubscript{5}OH)]Cl·H\textsubscript{2}O: C, 62.08; H, 7.13; N, 7.62. Found: C, 61.72; H, 6.78; N, 7.60.

**Rhodium(III) 5, 10, 15, 20-tetrakis(4-carboxyphenyl)porphine tetrasyethyl ester carbonyl chloride** ([Rh\textsuperscript{III}(T(-COOCH\textsubscript{3})PP)(CO)]Cl). Rh\textsubscript{2}Cl\textsubscript{2}(CO)\textsubscript{4} (45.4 mg) and 5, 10, 15, 20-tetrakis(4-carboxyphenyl)porphine tetrasyethyl ester (T(-COOCH\textsubscript{3})PPH\textsubscript{2}), 178.5 mg) were dissolved in toluene (200 mL). After the suspension was refluxed for 5 h to produce a clear solution, the solvent was removed under reduced pressure to give a purple residue. The residue was washed twice with hexane, and extracted with ethanol. Ethanol was removed under reduced pressure to give a purple crystalline powder. ESI-MS (in ethanol): \( m/z \) 947.4 ([Rh\textsuperscript{III}(T(-COOCH\textsubscript{3})PP)]\(^+\), \( m/z \) 975.5([Rh\textsuperscript{III}(T(-COOCH\textsubscript{3})PP)(CO)]\(^+\)). Anal. Calcd for [Rh\textsuperscript{III}(T(-COOCH\textsubscript{3})PP)(CO)]Cl·H\textsubscript{2}O: C, 61.85; H, 3.72; N, 5.44. Found: C, 61.57; H, 3.98; N, 5.19.

**5, 10, 15, 20-tetrakis(4-bromophenyl)porphinato rhodium(III) carbonyl chloride** ([Rh\textsuperscript{III}(TBPP)(CO)(Cl)]\textsubscript{3}). Rh\textsubscript{2}Cl\textsubscript{2}(CO)\textsubscript{4} (11.8 mg) and 5, 10, 15, 20-tetrakis(4-bromophenyl)porphine (TBPPH\textsubscript{2}, 51.4 mg) were dissolved in toluene (170 mL). The suspension was refluxed for 14 hours. The suspension after reflux was filtered and the filtrate was collected. The solvent of the filtrate was removed under reduced pressure. The
residue was washed with distilled water (twice) and hexane (three times). ESI-MS (in CHCl₃ solution): m/z 952.9 ([Rh³⁺(TBPP)-Br+H]+), m/z 1030.8 ([Rh³⁺(TBPP)]⁺), m/z 1058.7 ([Rh³⁺(TBPP)(CO)]⁺). Anal. Caled for [Rh³⁺(TBPP)(CO)(Cl)]·0.5 H₂O: C, 48.97; H, 2.28; N, 5.08 Found: C, 48.99; H, 2.35; N, 5.01.

**Adsorption of Rh porphyrins on carbon support (carbon black, Vulcan XC 72R) by an evaporation-to-dryness method.** The preparation of carbon-supported Rh porphyrins by an evaporation-to-dryness method was performed as follows. Carbon black (Vulcan XC 72R) (30 mg) was added to 20 mL of appropriate solvent containing 0.9 μmol of Rh complexes (the amount of Rh complexes adsorbed is 30 μmol per 1 g carbon). Ethanol was used for Rh(DPDE) and Rh(OEP), and CH₂Cl₂ was used for Rh(TBPP) and Rh(T(-COOCH₃)PP). The suspension was homogenized by an ultrasonic generator for 5 minutes, and vigorously stirred for 30 minutes. The solvent was removed under reduced pressure. The resulting powder was collected and used as a catalyst.

**Electrochemical measurements.** Electrochemical experiments were performed using by an ALS electrochemical analyzer (Model 627B) equipped with a rotation controller (BAS RDE-2). Catalyst powders (0.02 mg) were immobilized on a glassy carbon (GC) electrode (BAS, geometric area = 0.07065 cm²) with Nafion according to the literature [2]. Voltammograms were measured in a 1 M NaOH solution at a scan rate of 10 mV s⁻¹ in a three-electrode system under a nitrogen atmosphere. A modified electrode (as described above) or gold electrode (BAS, geometric area = 0.07065 cm²) was used as a working
electrode. A Ag|AgCl|KCl(sat.) was used as a reference electrode. A platinum coil was used as a counter electrode.

The evaluation of catalytic currents per catalyst and noble metal. The peak current in the voltammetry was divided by the amount of the catalyst and the noble metal used. The amount of the catalyst is 0.02 mg throughout this work. The amount of Rh in Rh porphyrin catalysts was calculated based on the ratio of 30 μmol/g. The amount of Pt in Pt/C catalyst was calculated from the Pt ratio (40%).

Electrolysis for product analysis. Electrolysis was performed in a two-compartment electrolytic cell. The compartments are separated with a glass filter to prevent exchange of the solutions. Both sides of a GC plate (1.5 × 1.5 cm²) were modified with Rh(DPDE)/C, and the plate was used as a working electrode. A Ag|AgCl|KCl(sat.) was used as a reference electrode. A platinum coil was used as a counter electrode. The working and reference electrodes were immersed in one compartment, and the counter electrode was in the other compartment. The electrolyte solution (15 mL, 1 M NaOH) containing 10 mM glucose was purged with argon gas. Electrolysis was conducted by a potentiostatic method in which the potential was fixed at –0.5 V (vs. Ag|AgCl|KCl(sat.)) for 3 hours. During electrolysis, the electrolyte solution was stirred by a magnetic stirrer, and anaerobic conditions were maintained by purging with argon gas.

Determination of gluconate. After electrolysis, the solution was subjected to a product
analysis. The concentration of gluconate in the test solution was determined by an enzymatic method. The solution after electrolysis was neutralized by the addition of sodium dihydrogen phosphate. The gluconate in the solution was converted to ribulose-5-phosphate by gluconate kinase (GK) and 6-phosphogluconic dehydrogenase (6-PGDH) concomitant with NADPH generation as follows.

\[
\text{Gluconic acid} + \text{ATP} \rightarrow \text{6-Phosphogluconate} + \text{ADP} \quad \text{(GK)}
\]

\[
\text{6-Phosphogluconate} + \text{NADP} \rightarrow \text{6-Phosphogluconate} + \text{NADPH} \quad \text{(6-PGDH)}
\]

The amount of NADPH generated is equal to gluconic acid in the test solution. The NADPH concentration was determined by UV-vis spectroscopy. Gluconolactone, which is a possible product of glucose oxidation, is easily changed to gluconate under such basic conditions (1 M NaOH).

NADP⁺(0.96 mM), 6-PGDH, ATP (3.6 mM), and MgCl₂ (1.0 mM) was added to the test solution after electrolysis. The absorbance of NADPH in the solution was monitored at 340 nm using a UV-vis spectrophotometer (Fig. S3). After the addition of GK, the absorbance increased gradually and reached a steady state, The increase in the absorbance corresponds to the amount of gluconate in the test solution.

References


Scheme S1. Chemical structures of sugars used.
### Table S1. Performances of conventional catalysts for glucose electro-oxidation.

| Electrode                          | Onset potential (vs. Ag|AgCl|KCl(sat.)) | Onset potential (vs. NHE) | Conditions | Ref* |
|-----------------------------------|------------------------|----------------------|--------------------------|--------|-----|
| Rh(DPDE)/C                        | ca. –0.75 V            | ca. –0.55 V          | 1 M NaOH                 | This work |     |
| Co phthalocyanin                  | ca. 0.15 V             | ca. 0.4 V            | 0.15 M NaOH              | [18]    |     |
| Polymerized Ni porphyrin          | ca. 0.45 V             | ca. 0.65 V           | 1 M NaOH                 | [24]    |     |
| Ru bipyridine complex             | ca. 0.45 V             | ca. 0.65 V           | 0.1 M NaOH               | [22]    |     |
| Silver-modified Au                | ca. –0.7 V             | ca. –0.5 V           | 0.3 M NaOH               | [7]     |     |
| Au                                | ca. –0.6 V             | ca. –0.4 V           | 0.3 M NaOH               | [7]     |     |
| Au (111)-($\sqrt{3}\times\sqrt{3}$) R30° Ag one third monolayer electrode | ca. –0.7 V | ca. –0.5 V | 0.1 M NaOH | [12] |     |
| Pt                                | ca. –1.0 V             | ca. –0.8 V           | 0.2 M NaOH               | [15]    |     |

*See references in the text.*
Fig. S1. Voltammograms of (a) Rh(DPDE)/C and (b) Pt/C in the presence of 0.5 M glucose with electrode rotation at 6400 rpm (scan rate = 10 mV/s). The measurements were performed in 1 M NaOH under a N₂ atmosphere.
**Fig. S2.** An Amperometric $i$-$t$ curve for glucose oxidation by Rh(DPDE)/C. The potential was maintained at –0.5 V (vs. Ag|AgCl|KCl(sat.)). The electrolyte solution (15 mL, 1 M NaOH) containing 10 mM glucose was purged with argon gas, and anaerobic conditions were maintained by purging with argon gas during electrolysis. The electrolyte solution was stirred using a magnetic stirrer.
**Fig. S3.** A profile of absorbance at 340 nm of the solution after electrolysis. The solution contains NADP\(^+\) (0.96 mM), 6-PGDH, ATP (3.6 mM), and MgCl\(_2\) (1.0 mM). The solution of GK was added at arrow \(a\). The increase in the absorbance corresponds to the amount of gluconate.