

## **Supporting Information**

**For**

### **Electrocatalytic oxidation of alcohols by a carbon-supported Rh porphyrin**

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## 1. Experimental Details

### 1.1. Synthesis.

#### 2,3,7,8,12,13,17,18-Octaethylporphyrinato rhodium(III) chloride ([Rh<sup>III</sup>(OEP)(Cl)]).

Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub> (81 mg) and 2,3,7,8,12,13,17,18-octaethylporphyrine (OEPH<sub>2</sub>) (203 mg) were dissolved in toluene (240 mL). The solution was refluxed for 10 hours. After reflux, the suspension was filtered, and the filtrate was collected. The solvent was removed under reduced pressure, and the residue was dissolved in ethanol. The suspension was filtered again. The product was crystallized in the ethanol solution (filtrate). Purple crystals were obtained. ESI-MS (in ethanol): *m/z* 635.2 ([Rh<sup>III</sup>(OEP)]<sup>+</sup>) Anal. Calcd for [Rh<sup>III</sup>(OEP)(Cl)]·H<sub>2</sub>O: C, 62.74; H, 6.73; N, 8.13. Found: C, 62.63; H, 6.66; N, 8.10. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 10.34 (s, 4H), 4.24-4.06 (m, 16H), 2.00 (t, 24H, *J* = 8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 142.9, 140.5, 98.4, 20.1, 18.6.

### 1.2. Catalyst preparation

Rh porphyrins were adsorbed on carbon black (Vulcan XC72R) with an evaporation-to-dryness method. The details of this method have been described elsewhere [1]. Briefly, carbon black (Vulcan XC 72R) (30 mg) was added to ethanol solution (20 mL) containing [Rh<sup>III</sup>(OEP)(Cl)]. After stirring for 30 minutes, the solvent was evaporated, and the residue was collected. The amount of Rh porphyrin was fixed at 30 μmol g<sub>carbon black</sub><sup>-1</sup>.

### 1.3. Electrochemical measurements

The setup for electrochemical measurements was described in the literature [1, 2].

Briefly, a rotating disk glassy carbon electrode was modified with Rh porphyrin-adsorbed carbon black as described elsewhere [1]. The rotating disk glassy carbon electrode ( $A = 0.07065 \text{ cm}^2$ ) modified with catalysts was used as a working electrode. A Ag|AgCl|KCl(sat.) was used as a reference. All of the potentials in the results are vs. a reversible hydrogen electrode (RHE). The potential of Ag|AgCl|KCl(sat.) vs. RHE was measured as described in the literature [1]. Electrochemical measurements, except for the experiments, on pH dependence were performed in a 1 M NaOH solution. pH dependence was examined using several buffer solutions: 1 M NaOH (pH 13.9), 0.1 M NaOH (pH 13.1), and 0.1 M phosphate buffer (pH 11.7, 10.8, 8.9, 6.9). The solution was deaerated with argon gas before the measurements. All voltammograms were measured at a scan rate of 10 mV/s under an argon atmosphere.

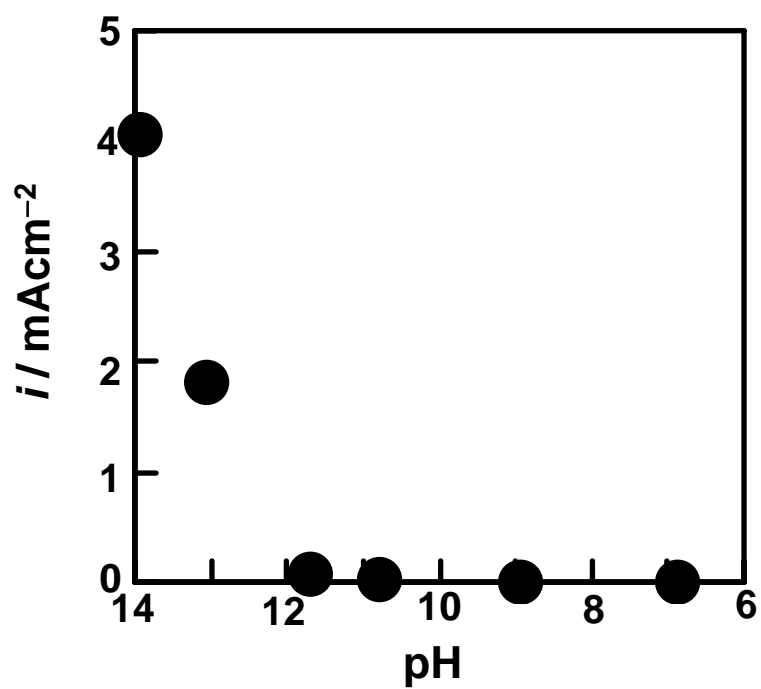
### 1.4. Product analysis

Electrolysis for analysis of the products of alcohol oxidation by  $[\text{Rh}^{\text{III}}(\text{OEP})(\text{Cl})]/\text{C}$  was performed as follows. A 1 M NaOH solution was placed in a cell composed of two compartments separated by a glass filter. The Rh complex-modified working electrode ( $A = 4.5 \text{ cm}^2$ ) and the reference electrode were immersed in one compartment. The counter electrode was immersed in the other compartment. Both compartments were purged with

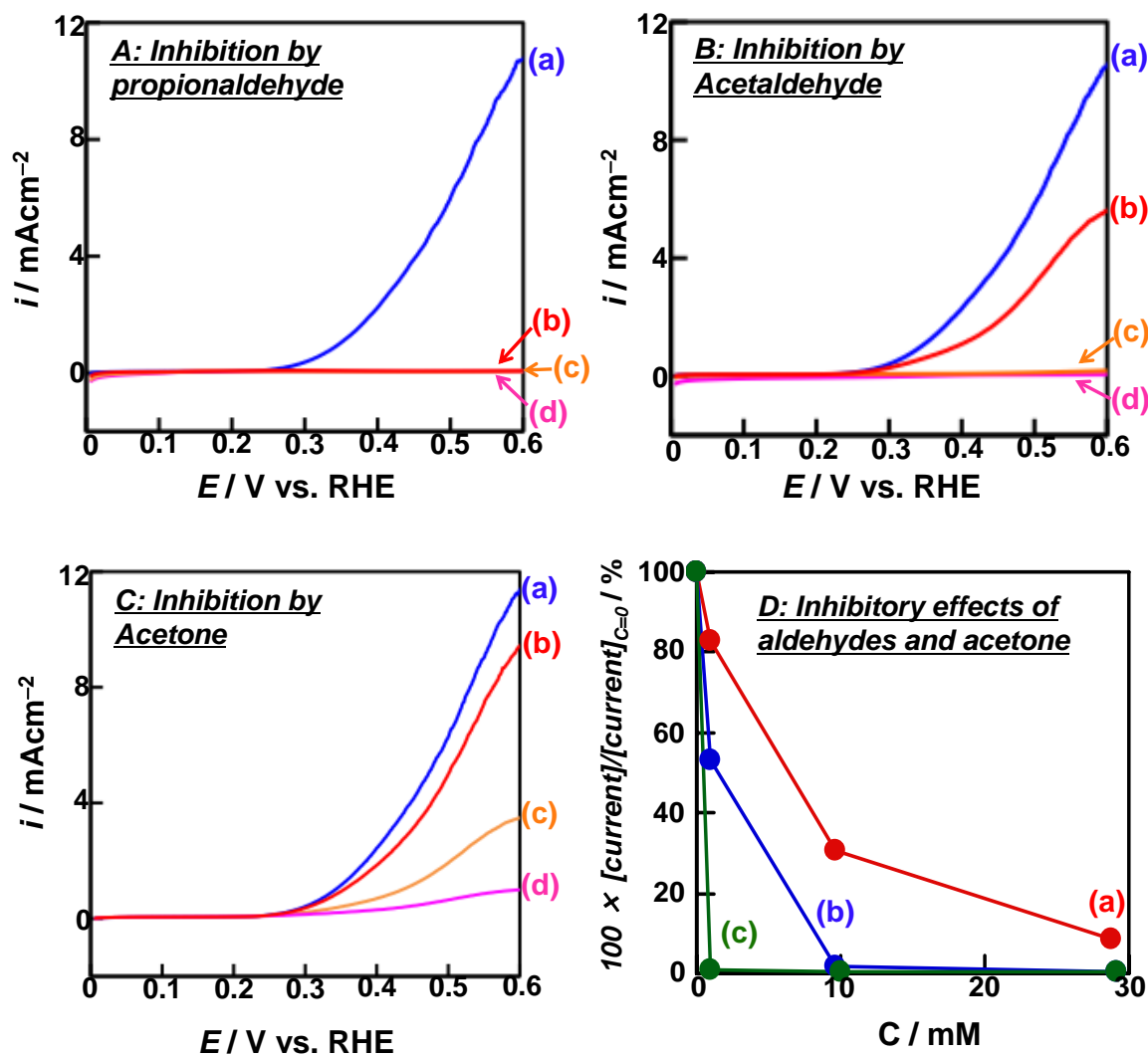
argon gas. The potential of the working electrode was held at 0.61 V (vs. RHE) at 25 °C. After the residual current reached almost zero, benzyl alcohol (10 mM) was added to the working compartment. The charge was recorded during electrolysis. Argon gas was flowed continuously to prevent O<sub>2</sub> contamination during electrolysis. After electrolysis was finished, the solution was neutralized with acetic acid and H<sub>2</sub>SO<sub>4</sub>, and analyzed by HPLC.

## References

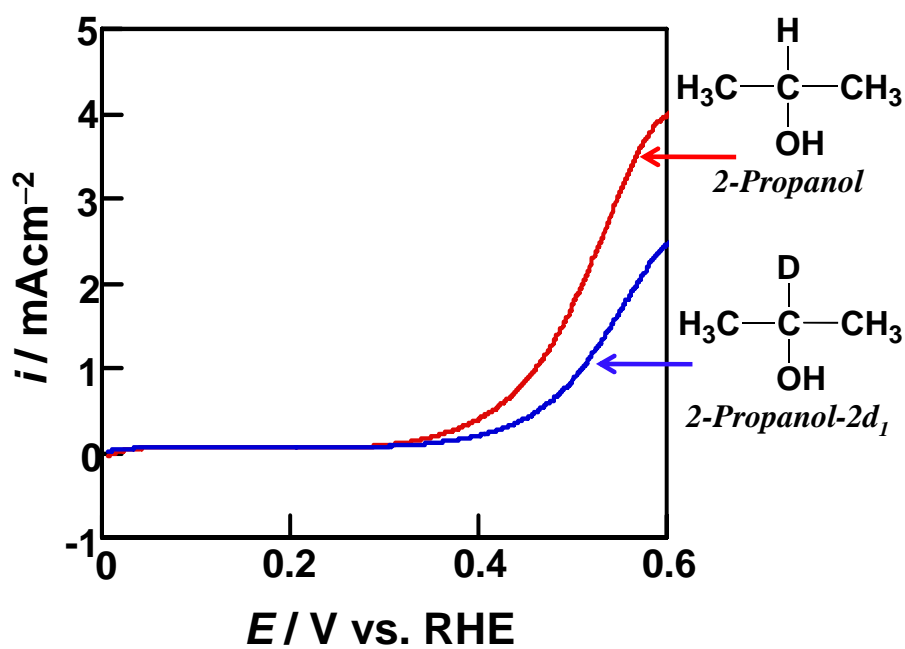
- [1] S. Yamazaki, Y. Yamada, S. Takeda, M. Goto, T. Ioroi, Z. Siroma, K. Yasuda, *Phys. Chem. Chem. Phys.* 2010, **12**, 8968.
- [2] S. Yamazaki, Y. Yamada, N. Fujiwara, T. Ioroi, Z. Siroma, H. Senoh, K. Yasuda, *J. Electroanal. Chem.* 2007, **602**, 96.



**Fig. S1**, pH-dependence of the current in the presence of ethanol (0.48 M) with electrode rotation (6400 rpm) at 0.5 V (vs. RHE). The conditions except for pH were the same as those in Fig. 1.



**Fig. S2.** Inhibition of the [Rh<sup>III</sup>(OEP)(Cl)]/C-catalyzed oxidation of 2-propanol by propionaldehyde, acetaldehyde and acetone. Voltammograms in (A), (B), and (C) indicates inhibitory effects of propionaldehyde, acetaldehyde, and acetone, respectively. (D) The ratio of the current at 0.6 V in the presence of aldehydes or acetone to that in the absence of them. The voltammograms were measured with electrode rotation (6400 rpm) in the presence of 2-propanol (0.48 M) with (a) 0 mM, (b) 1 mM, (c) 10 mM, and (d) 29 mM aldehydes or acetone. Measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV/s) under an argon atmosphere. Other conditions were the same as those in Fig. 1.



**Fig. S3.** Kinetic isotope effect in the oxidation of 2-propanol. Voltammograms of [Rh<sup>III</sup>(OEP)(Cl)]/C with electrode rotation at 6400 rpm in the presence of alcohol (10 mM); (a) 2-propanol and (b) 2-propanol-2d<sub>1</sub>. Measurements were performed in a 1 M NaOH solution at 25 °C (scan rate = 10 mV/s) under an argon atmosphere.