Electrochemical oxidation of sugars at moderate potentials catalyzed by Rh porphyrins†

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In this communication, we demonstrate that certain kinds of Rh porphyrins on carbon black can electrochemically oxidize aldose at low potentials. The onset potential was much lower than those with the other complex-based catalysts. A product analysis suggested that this reaction involves 2-electron oxidation of the aldehyde group.

The significance of the electrochemical oxidation of sugars has been emphasized in the fields of analytical chemistry and fuel cell technology. This reaction is useful for amperometric sensors for sugars[1–4] and HPLC detectors for sugars.[5] The low-potential electro-oxidation of sugars is important for fuel cells which use them as a fuel.[6–9]

The importance of this reaction has inspired many researchers to develop a new catalyst that promotes the electrochemical oxidation of sugars. Metal electrodes[7–15] and enzyme-modified electrodes[1,2,6] have been investigated with regard to their activity to catalyze the electro-oxidation of sugars. Although these catalysts have good electrocatalytic activity for the electrochemical oxidation of sugars, some problems have been pointed out. In the case of Pt and Au, poisoning by adsorbed intermediates has been shown to be a significant problem.[16] The amount of Pt required for glucose oxidation is also a bottleneck. It is somewhat difficult to increase the surface area of Au by preparing stable nano-particles due to its low melting point. Hence, the catalytic current by Au electrocatalysts remains low. Enzyme-modified electrodes can be used only under limited conditions of pH and temperature. Enzyme-modified electrodes sometimes require mediators for electron transfer and the immobilization of enzymes, which can result in complex structures.

These drawbacks of noble-metal and enzyme-modified electrodes have stimulated the study of new electrocatalysts. Complex-immobilized chemically-modified electrodes have attracted much interest as new catalysts.[17] The electrochemical oxidation of sugar by Co phthalocyanins,[5,18–20] Ru complexes,[21,22] and Ni complexes[23,24] has also been examined. However, the overpotentials are much higher than those with metal electrodes. Such high overpotentials reduce their sensitivity in the determination of sugars and the efficiency of fuel cells that use sugars as a fuel.

In this study, we focused on Rh porphyrins adsorbed on a conductive support as an electrocatalyst. Rh N4-macrocycle complexes have been demonstrated to exhibit high activity toward the electrochemical oxidation of CO and HOOC–COOH in low-potential regions in acidic solution.[25–27] The high activities toward these carbonyl compounds encouraged us to examine the electrochemical reactivities of Rh porphyrins toward low-potential sugar (especially aldose) oxidation, since sugar electro-oxidation would occur *via* carbonyl activation.

In this work, we found that certain kinds of Rh porphyrins can act as good catalysts for oxidizing aldose in low-potential regions. These catalysts exhibited higher activity toward aldose than ketose. The overpotential for glucose oxidation was the lowest among those of the complex-based catalysts reported so far. A high catalytic current for glucose oxidation was observed in moderate potential regions.

Rh porphyrins were prepared by reflux of $Rh_2Cl_2(CO)_4$ and the corresponding porphyrin ligands (see ESI†). The abbreviation for the complexes are as follows: $[Rh^{III}(DPDE)]^+$ (DPDE = deuteroporphinate dimethyl ester), $[Rh^{III}(OEP)]^+$ (OEP = octaethylporphinate), $[Rh^{III}(T(–COOCH_3)PP)]^+$ ($T(–COOCH_3)PP$ = 5,10,15,20-tetrakis(4-methylcarboxyphenyl)-porphinate) and $[Rh^{III}(TBPP)]^+$ (TBPP = 5,10,15,20-tetrakis-(4-bromophenyl)porphinate). Rh porphyrins were adsorbed on carbon black with an evaporation-to-dryness method, and the powder was used as an electrocatalyst. The amount of Rh porphyrins adsorbed was fixed at 30 $\mu mol\ g^{-1}$. Carbon-supported platinum (Pt/C) was purchased from Johnson-Matthey Co. Ltd. Powders of these catalysts (0.02 mg) were trapped on a glassy carbon electrode (A = 0.07065 cm^2).

Fig. 1A shows voltammograms of a carbon-supported $[Rh^{III}(DPDE)]^+$ (Rh(DPDE)/C) in the absence/presence of glucose. Upon the addition of glucose, the oxidation current drastically increased. The anodic current started to flow at *ca.* −0.75 V (*vs.* Ag|AgCl|KCl(sat.)). This onset potential and those with previous catalysts are shown in Table S1 (ESI†). The onset potential with Rh(DPDE)/C is extremely low compared to those with other complex-based electrocatalysts such as Co macrocycles, Ru bipyridine complexes, and polymerized Ni porphyrins.[5,18–24] The potential is comparable to those with Au-based catalysts, although it is higher than those with Pt-based catalysts.

Fig. 1B shows a comparison of the activities of Rh porphyrins. A significant difference in current was observed between Rh porphyrins. The Rh(DPDE)/C (line a) and Rh(OEP)/C (line b) exhibited high activities, while Rh(T(–$COOCH_3$)PP)/C (line c) and Rh(TBPP)/C (line d) gave relatively low current.

Potential-step chronoamperometry was also performed for the analysis of glucose electro-oxidation. The potential was stepped from −1.0 V to −0.6 V. Fig. 2A shows chronoamperograms of Rh(DPDE)/C. In the absence of glucose, the current approached

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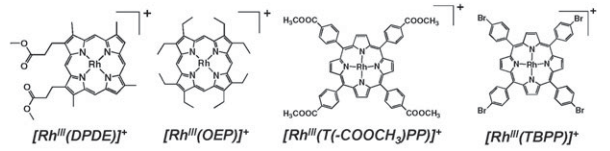

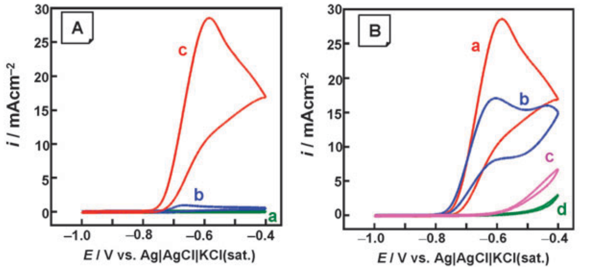

Fig. 1 (A) Cyclic voltammograms of Rh(DPDE)/C at a scan rate of 10 mV s^{-1} in the presence of (a) 0 mM, (b) 10 mM, and (c) 0.5 M glucose. (B) Cyclic voltammograms of (a) Rh(DPDE)/C, (b) Rh(OEP)/C, (c) RhT(–$COOCH_3$)PP/C, and (d) Rh(TBPP)/C in the presence of 0.5 M glucose. Measurements were performed in 1 M NaOH solution under a nitrogen atmosphere at 25 °C.

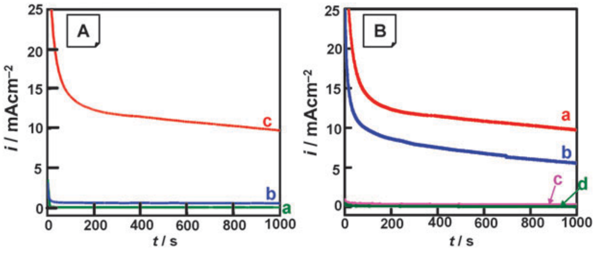

Fig. 2 (A) Potential-step chronoamperograms of Rh(DPDE)/C in the presence of (a) 0 mM, (b) 10 mM, and (c) 0.5 M glucose. (B) Potential-step chronoamperograms of (a) Rh(DPDE)/C, (b) Rh(OEP)/C, (c) RhT(–$COOCH_3$)PP/C, and (d) Rh(TBPP)/C in the presence of 0.5 M glucose. The potential was stepped from −1.0 V to −0.6 V. Other conditions were the same as those in Fig. 1.

virtually zero immediately. In the presence of glucose, the significant currents flowed, indicating that a Faradaic process occurred. The current increased with the increase in the concentration of glucose. Chronomaperograms of other carbon-supported Rh porphyrins are shown in Fig. 2B. The activities of Rh(DPDE)/C and Rh(OEP)/C were much higher than those of Rh(T(–$COOCH_3$)PP)/C and Rh(TBPP)/C. Rh(DPDE)/C, which exhibits the highest activity, was used as an electrocatalyst for further experiments.

The currents in Fig. 2B were normalized by charging currents to eliminate the effect of the surface area. Charging currents reflect electrochemically active areas. Hence, the normalized catalytic currents correspond to the activities per surface area. The charging current was determined from cyclic voltammograms in the absence of glucose. The results are shown in Fig 3. The difference in the activity between active catalysts (Rh(DPDE)/C and Rh(OEP)/C) and relatively inactive catalysts (Rh(T(–$COOCH_3$)PP)/C and Rh(TBPP)/C) is not attributed to the difference in the surface area but to that in the intrinsic activity. The lower activity of Rh(T(–$COOCH_3$)PP)/C and Rh(TBPP)/C might be related with the electron transfer rate. The bulkiness of *meso*-phenyl groups prevents the access of these porphyrins to carbon support and makes the electron transfer to electrode slow.

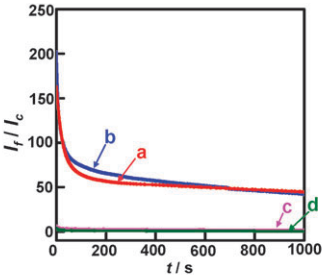

Fig. 3 Normalized potential-step chronoamperograms of (a) Rh(DPDE)/C, (b) Rh(OEP)/C, (c) RhT(–$COOCH_3$)PP/C, and (d) Rh(TBPP)/C in the presence of 0.5 M glucose. Other conditions were the same as those in Fig. 2. I_f and I_c denotes an observed Faradaic current and a charging current, respectively.

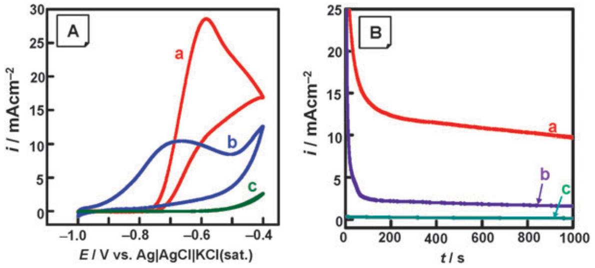

Fig. 4 (A) Cyclic voltammograms of (a) Rh(DPDE)/C, (b) Pt/C, and (c) Au electrodes in the presence of 0.5 M glucose. (B) Potential-step chronoamperograms of (a) Rh(DPDE)/C, (b) Pt/C, and (c) Au electrodes. Other conditions were the same as those in Fig. 1 or 2.

Fig. 4A shows a comparison of electrocatalytic activities for glucose oxidation with several electrodes. Pt/C shows a lower onset potential than Rh(DPDE)/C. However, the current increase in regions of higher potential is sluggish compared to that with Rh(DPDE)/C. The peak current per 1 g catalyst is significantly higher with Rh(DPDE)/C (105 ± 9.5 A g_{cat}^{-1}) than with Pt/C (33.5 ± 6.4 A g_{cat}^{-1}). Since the amount of Rh metal on carbon support is low (in Rh porphyrin catalysts, Rh atoms are highly dispersed at an atomic level), the difference in activity per noble metal is much greater ($3.4 \times 10^4 \pm 3.1 \times 10^3$ A g_{Rh}^{-1} for Rh(DPDE)/C, 84 ± 15.9 A g_{Pt}^{-1} for Pt/C). Rh(DPDE)/C gave high catalytic current even though a very small amount of Rh was used. Under electrode rotation conditions, Rh(DPDE) also exhibited higher current than Pt/C above −0.65 V (Fig. S1, ESI†). The results of potential-step chronoamperometry (Fig. 4B) also indicate that Rh(DPDE)/C has higher activity than Pt/C. The onset potential with Au electrode was also low. However, the catalytic current was much lower than Rh(DPDE)/C in chronoamperometry (Fig. 4B) as well as voltammetry (Fig. 4A). The low current is attributed to the low surface area of gold electrode. Rh(DPDE)/C is a good catalyst in terms of both the overpotential and current.

Interestingly, in constant-potential amperometry at −0.6 V, Pt/C gave much higher current than Rh(DPDE)/C. The application of more negative potential (−1.0 V) seems to be favourable to increase the activity of Rh(DPDE)/C

The reactivity of Rh(DPDE)/C toward other sugars (Scheme S1, ESI†) was examined, and the results are summarized in Fig. 5. The catalyst oxidized aldose, such as galactose (line a), glucose (line b), maltose (α-D-glucopyranosyl-(1 → 4)-D-glucose) (line c), and lactose (β-D-galactopyranosyl-(1 → 4)-D-glucose) (line d).

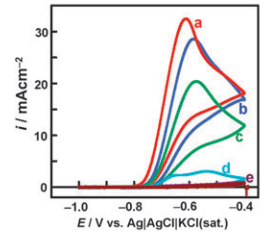

Fig. 5 Cyclic voltammograms of Rh(DPDE)/C at a scan rate of 10 mV s^{-1} in the presence of 0.5 M (a) galactose, (b) glucose, (c) maltose, (d) lactose, (e) fructose, and (f) sucrose. Other conditions were the same as those in Fig. 1.

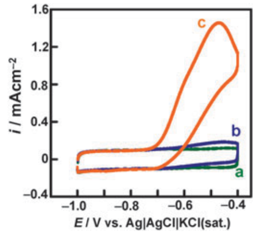

Fig. 6 Cyclic voltammograms of Rh(DPDE)/C at a scan rate of 10 mV s^{-1} in the presence of (a) 0 mM, (b) 10 mM, and (c) 0.5 M sodium gluconate. Other conditions were the same as those in Fig. 1.

The catalyst exhibited little activity toward ketose, such as fructose (line e) and sucrose (α-D-glucopyranosyl-(1 → 2)-β-D-fructofuranoside) (line f). The activity toward monosaccharides (glucose and galactose) was greater than that toward disaccharides (maltose and lactose), but this difference was less significant than that between aldose (a–d) and ketose (e and f). These data suggest that glucose oxidation proceeds *via* aldehyde oxidation. The reactivity toward a variety of aldoses is favorable for the application in HPLC detection.

Electro-oxidation of the aldehyde group in aldoses results in the generation of carboxylic acids. A product analysis of glucose oxidation at −0.5 V was performed to verify the reaction path. Detailed procedures and results are shown in ESI†. An *i*–*t* curve at −0.5 V (*vs.* Ag|AgCl|KCl(sat.)) is shown in Fig. S2†. The amount of electrons transferred to the electrode was evaluated to be 2.1 μmol by integrating this curve. The gluconate concentration after the electrolysis was analyzed by an enzymatic method using gluconate kinase and 6-phosphogluconic dehydrogenase. The result of determination is shown in Fig. S3†. The amount of gluconate in the product solution was determined to be 0.77 μmol. If we assume 2-electron oxidation of glucose, 2.1 μmol of electrons generate 1.05 μmol of gluconate. Actually, the amount of gluconate generated reached 73% of the amount assumed for 2-electron oxidation (1.05 μmol). This indicates that glucose oxidation mainly proceeds *via* 2-electron oxidation. The reactivity of Rh(DPDE)/C toward sodium gluconate was also examined (Fig. 6). Rh(DPDE)/C oxidized sodium gluconate, although the oxidation current was much lower than that with glucose. The maximum anodic current was *ca.* 1/20 of that in the oxidation of glucose. The results indicate that some of the gluconate generated would undergo further oxidation. This is responsible for the finding that the amount of gluconate is lower than is assumed for the 2-electron oxidation of glucose.

In conclusion, we found that Rh porphyrins on carbon black can catalyze the electro-oxidation of glucose at low overpotentials. The onset potential for the electro-oxidation of aldose is the lowest among the complex-based catalysts, and the potential regions are extremely lower than those with conventional complex-based catalysts. A high current density was obtained with this catalyst, even though only a small amount of rhodium was used. These properties make the catalyst a promising candidate for use as an anode catalyst in fuel cells and as an electrocatalyst for sensing sugars. A significant difference in activities was noted between Rh porphyrins. The Rh porphyrin-based catalysts gave higher activity toward aldose than ketose. This high reactivity toward aldose and product analysis suggested that the reaction mainly proceeds *via* 2-electron oxidation of the aldehyde group.

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