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Supplementary Information

Stability of Organic Ligands on the Oxygen Evolving Center of Photosystem II and Manganese Oxide Water Oxidation Catalysts

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Synthesis of *a*-MnO₂ Powder

 α -MnO₂ powder was synthesized as previously reported [S1,S2]. 1.10 g of KMnO₄ in 20 ml of water was stirred for 30 min at 60 °C. Separately, 1.89 g of MnSO₄·5H₂O in 25 ml of a 2 M acetic acid aqueous solution was stirred for 20 min at room temperature. The solutions were mixed and heated for 2 h at 80 °C under a stirred condition. The particles thus obtained were collected, washed, and dried overnight at 60 °C.

Preparation of α-MnO₂ Particulate Film Electrodes

Particulate film electrodes of α -MnO₂ were prepared by a spray deposition method as previously described [S3]. The amount of deposited α -MnO₂ was ~0.14 mg cm⁻² unless otherwise noted. In this case, 75 mg of the α -MnO₂ powder was ground in an agate mortar for 5 min, and suspended in 100 mL of highly pure Milli-Q water (18 M Ω cm⁻¹) by a sonicator (Q700, QSonica). The suspension was sprayed by a spray gun (ST-6, Fuso Seiki Co., Ltd.) onto a clean conducting fluorine-tin-oxide-coated glass substrate (SPD Laboratory, Inc.) heated at 200 °C. The electrodes were gently washed with the highly pure Milli-Q water, and calcined in air for 4 h at 500 °C. The deposited amount was controlled by the initial amount of the α -MnO₂ powder.

Details of Measurement Method

Electrochemical Measurement in General

Current density (*j*) and potential (*U*) were controlled and measured with a commercial potentiostat and potential programmer (HZ-5000, Hokuto Denko), using a Pt wire as the counter electrode and a Ag/AgCl/KCl (saturated) electrode as the reference electrode. Sodium sulfate was used as the supporting electrolyte with the concentration set at 0.5 M. Sodium benzoate, imidazole, and guanidine sulfate were used as artificial amino-acid analogs and were introduced by dissolving them into the electrolyte. The electrolyte solution was prepared using the highly pure Milli-Q water and reagent-grade chemicals, and the pH was adjusted using 1.0 M H₂SO₄ and 1.0 M NaOH. Guanidine sulfate and isotopic reagents (D₂O, and D₂SO₄ for pD adjustment) were obtained from Sigma-Aldrich, and all other reagents are obtained from Wako and used without further purification.

O2 Measurement by a Fluorescence-Based Needle-Type O2 Microsensor (OMS)

The concentration of dissolved O_2 in the electrolyte solution was monitored using a fluorescencebased needle-type OMS (Microx TX3-trace, PreSens) under stirred condition.

Tafel Plots

Tafel plots were made by plotting steady-state current at each potential. The electrolyte was filled and stirred by a stir bar at *ca*. 1000 rpm. The amount of deposited α -MnO₂ was decreased to be ~0.056 mg cm⁻² to lessen the effect of pseudo-capacitance. The highest potential was kept for more than 500 s to avoid the effect of pseudo-capacitance. At other potentials, the steady-state current was measured after 90 s. The solution resistance was measured and the resulting ohmic potential loss was corrected.

pH Dependence of Potential under a Constant Current Condition

pH dependence of potential under a constant current condition was measured by plotting the potential during the change of pH by the addition of NaOH aq. The electrolyte was filled and stirred by a stir bar at *ca*. 800 rpm. The amount of deposited α -MnO₂ was decreased to be ~0.056 mg cm⁻² to lessen the effect of pseudo-capacitance. Although ohmic potential loss cannot be corrected because of the change in the composition of the electrolyte, the change in the solution resistance was so small that the slope value was not affected in the experimental accuracy in this time.

Kinetic Isotope Effect (KIE) Measurement

KIE was measured based on the ratio of current density during linear sweep voltammetry. The concentration of sodium benzoate was 0.5 M, and the scan rate was 10 mV s⁻¹. pD was adjusted based on the relationship between pD and pH: pD = pH + 0.4 [S4]. The amount of deposited α -MnO₂ was ~0.056 mg cm⁻². The KIE was calculated at the potentials where the current density reaches 0.25 mA cm⁻² in undeuterated electrolyte. The measurement was conducted twice.

FT-IR spectroscopy

The structure of bases on the surface of α -MnO₂ was analyzed by a Fourier transform infrared (FT-IR) spectrometer (Vertex 70, Bruker). 60 mg of α -MnO₂ powder was immersed in 10 mL of the solution of sodium benzoate or imidazole with 0.1 M deprotonated anions whose pH was adjusted to 7.5 by H₂SO₄ or NaOH. The solution was stirred for 12 h. The powder was then separated by suction filtration with a hydrophilic PTFE membrane filter with a 0.2 µm pore size (JGWP04700, Merck Millipore), followed by vacuum drying in a Schlenk flask. As a control sample, α -MnO₂ powder immersed in the highly pure Milli-Q water was also prepared. After ground in an agate mortar, 20 mg of the dried powder was pressed by a hydraulic press (SSP-10A, Shimadzu) into a pellet with a diameter of 12 mm for the measurement.

Inlet Electrochemical Mass Spectroscopy (EC-MS)

EC-MS was also performed to measure the onset potentials of O_2 and CO_2 evolution. The principle of the EC-MS system was the same as previously reported [S5,S6]. A stainless capillary connected a gastight electrochemical chamber and a quadrupole mass spectrometer (QMG 220 M1, Pfeiffer Vacuum). The end of the capillary in the electrochemical chamber was covered with a microporous polytetrafluoroethylene (PTFE) membrane (Poreflon WP-010-80, Sumitomo Electric Fine Polymer). Before measuring the evolution of O_2 or CO_2 , the electrochemical chambers were bubbled with argon for 30 minutes.

In-situ UV-vis Spectroscopy

Optical absorption of electrodes in contact with the electrolyte was measured by a UV-vis spectrometer (UV-2550, Shimadzu) equipped with a multipurpose large-sample compartment with a built-in integrating sphere (MPC-2200, Shimadzu), by placing electrodes in front of the integrating sphere and collecting diffused transmission light. The amount of deposited α -MnO₂ was decreased to be ~0.056 mg cm⁻² to lessen the original absorption by the catalyst.

Supplementary Figures and Table



Fig. S1 pH dependence of potential at a constant current density (50 μ A cm⁻²) in the absence and presence of 50 mM of benzoate.



Fig. S2 FT-IR spectra of (a) α -MnO₂ after the immersion in the solution of 0.1 M deprotonated benzoate at pH 7.5 adjusted by NaOH for 12 h, (b) the solution of 0.1 M deprotonated benzoate at pH 7.5 adjusted by NaOH, and (c) α -MnO₂. In (b), the observed peaks at 1388 cm⁻¹ and 1541 cm⁻¹ can be assigned to the symmetric and asymmetric stretching mode of COO⁻ (v_s (COO⁻) and v_{as} (COO⁻)), respectively [S7,S8]. The peak at 1594 cm⁻¹ can be assigned to the stretching mode of C-C (aromatic ring) (v(C-C_{ring})) [S7,S8]. The small peak at 1179 cm⁻¹ was assigned to a C-H stretching mode, and those at 1071 cm⁻¹ and 1026 cm⁻¹ were assigned to C-H in-plane bending modes [S9]. In (a), the band of v_s (COO⁻) shifted to higher frequency region, which indicated the chemisorption of benzoate on the surface of α -MnO₂ [S7]. The small shift (8 cm⁻¹), as well as broadening of the bands of v_s (COO⁻) and v_{as} (COO⁻), is in favor of the formation of outer-sphere complexes [S7]. On the other hand, the positions of the bands from the aromatic ring was almost constant. Those results indicate that benzoate formed outer-sphere complexes with the surfaces of α -MnO₂, as shown in Fig. S3, which is a suitable conformation for the induction of CPET.



Fig. S3 Schematic representation of surface complexation of benzoate on the surface of α -MnO₂ [S7].



Fig. S4 Potential dependence of current density and dissolved amount of O_2 in the presence of imidazole or histidine (pH 7.5, Scan rate: 1 mV s⁻¹, Concentration of deprotonated imidazole ring: 50 mM).



Fig. S5 Changes in the UV-Vis spectra of an α -MnO₂ electrode in contact with the electrolyte which contained 500 mM deprotonated imidazole (pH 7.5) at rest potential. The spectrum immediately after the contact with the electrolyte was used as a reference.



Fig. S6 FT-IR spectra of (a) α -MnO₂ after the immersion in the solution of 0.1 M deprotonated imidazole at pH 7.5 adjusted by H₂SO₄ for 12 h, (b) the solution of 0.1 M deprotonated imidazole at pH 7.5 adjusted by H₂SO₄, and (c) α -MnO₂. The number of peaks increased after the interaction with α -MnO₂, compared to the spectra of the imidazole solution. We regard the new peaks can be assigned to the oxidation products. The derivatives of urea or nitronate were shown as oxidation products of imidazolyl groups in the previous studies [S10-12], which can be the candidates of the products in our cases.

E₁ of Imidazole

Equilibrium between Differently Protonated States of Imidazole and Imidazole Radicals

First, the equilibrium between differently protonated states of imidazole and imidazole radicals are summarized in Scheme S1.



Scheme S1 Protonation equilibrium of imidazole and imidazole radicals.

ImH[•]²⁺, the protonated form of Im^{•+}, is thermodynamically unstable and deprotonates, thus virtually does not exist. Equilibrium constants are given by following equations:

$$K_{a1} = \frac{[Im][H^+]}{[ImH^+]}, K_{a2} = \frac{[Im(-H)^-][H^+]}{[Im]}, K_{r1} = \frac{[Im(-H)^-][H^+]}{[Im^{++}]}$$

 $pK_{a1} = 7.05$ and $pK_{a2} = 14.5$ [S13]; pK_{r1} has not been reported to our knowledge.

Conversion of Vertical Ionization Energy (VIE) to E1

As mentioned in the main text, experimental values of the redox potential of the one-electron oxidation (E_1) of imidazole has not been reported so far to our knowledge. However, an experimental value of the vertical ionization energy (VIE) of imidazole has been reported by a study using photoelectron spectroscopy of liquid microjet [S14]. Thus, the standard E_1 (E_1^0 (Im^{+/}/Im)) can be obtained by subtracting outer-sphere reorganization energy (λ) from VIE.

According to the report, the VIE of neutral imidazole (Im) is +3.98 V vs. SHE [S14]. Here, VIE vs. SHE was calculated by using the reported potential of SHE vs. vacuum, +4.28 V [S15, S16]. λ is estimated to be smaller than 1 eV as for the reactions on electrodes in water with the diameter of the reactant larger than 2 Å [S17]. Thus, E_1^0 (Im⁺/Im) can be estimated to be more positive than +2.98 V vs. SHE.

pH dependence

Analysis of the pH dependence of E_1 requires consideration of the protonation equilibrium and can be estimated by reference to the method reported by Schroeder *et al.*[S18]

Here, [Im]_{total} and [Im[•]]_{total} are defined as follows:

$$[Im]_{total} = [ImH^{+}] + [Im] + [Im(-H)^{-}] = [Im] \cdot \left(\frac{[H^{+}]}{K_{a1}} + 1 + \frac{K_{a2}}{[H^{+}]}\right)$$
$$[Im^{-}]_{total} = [Im^{-+}] + [Im(-H)^{-}] = [Im^{-+}] \cdot \left(1 + \frac{K_{r1}}{[H^{+}]}\right)$$

Thus,

$$[Im] = [Im]_{total} \cdot \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}}$$
$$[Im^{+}] = [Im^{+}]_{total} \cdot \frac{[H^+]}{[H^+] + K_{r1}}$$

Thus, a Nernst equation for E_1 can be written as follows:

$$E_{1} = E_{1}^{0}(\mathrm{Im}^{+}/\mathrm{Im}) + \frac{RT}{F}\ln\left(\frac{[\mathrm{Im}^{+}]}{[\mathrm{Im}]}\right) = E_{1}^{0}(\mathrm{Im}^{+}/\mathrm{Im}) + \frac{RT}{F}\ln\left(\frac{1}{K_{a1}} \cdot \frac{[\mathrm{H}^{+}]^{2} + K_{a1}[\mathrm{H}^{+}] + K_{a1}K_{a2}}{[\mathrm{H}^{+}] + K_{r1}}\right)$$

Note that $[Im]_{total}$ equals to $[Im]_{total}$ at E_1 . By substitution of the pK values, E_1 at the standard condition at pH 7.5 can be calculated as follows:

$$E_1 / V$$
 vs. SHE = $E_1^0(\text{Im}^+/\text{Im}) / V$ vs. SHE - 0.4359 - 0.05916 $\log_{10}(10^{-7.5} + K_{r1})$

Here, E_1^0 (Im⁺⁺/Im) corresponds to the E_1 estimated from the VIE. Therefore, for E_1 to be more negative than E_{onset} (@ 75 µA cm⁻²) in the presence of imidazole at pH 7.5, even when $\lambda = 1$ eV, p K_{r1} have to be less than -27.6. p K_{r1} has not been reported to our knowledge, but considering that the corresponding pK value of histidine is 5-7 [S19], we can safely estimate that p K_{r1} is larger than -27.6. Thus, E_{onset} (@ 75 µA cm⁻²) (Fig. 4) can be estimated to be well more negative than E_1 .

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