Electronic Supplementary Information

for

High and robust performance of H_2O_2 fuel cells in the presence of scandium ion

Yusuke Yamada,*[,a,b] Masaki Yoneda[a] and Shunichi Fukuzumi*[,a,c,d]

[a]*Department of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, ALCA and SENTAN, Japan Science and Technology (JST), Suita, Osaka 565-0871, Japan. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp; yamda@chem.eng.osaka-u.ac.jp; Fax: +81-6-6879-7370.*

[b]*Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan.*

[c]*Department of Bioinspired Science, Ewha Womans University, Seoul, 120-750, Korea.*

[d]*Faculty of Science and Technology, Meijo University and ALCA and SENTAN, Japan Science and Technology Agency (JST), Shiogamaguchi, Tempaku, Nagoya, Aichi 468-8502, Japan.*

Experimental section

Materials. All chemicals were obtained from chemical companies and used without further purification. Iron(II) sulfate heptahydrate, sodium chloride, perchloric acid (60%), aqueous hydrogen peroxide (30%), calcium(II) nitrate tetrahydrate, and nitric acid (69%) were purchased from Wako Pure Chemical Industries, Ltd. Yttrium(III) nitrate pentahydrate, ytterbium(III) nitrate pentahydrate, and magnesium(II) nitrate hexahydrate were received from Sigma–Aldrich. Potassium hexacyanocobaltate(III) ($K_3[Co^{III}(CN)_6]$), scandium (III) acetate hydrate, and scandium (III) chloride hexahydrate were supplied by Strem Chemicals. Zinc(II) nitrate hexahydrate was obtained from Nacalai tesque. Scandium(III) nitrate tetrahydrate was purchased from Mitsuwa Chemicals. Purified water was provided by a Millipore Milli-Q water purification system (Direct-Q 3 UV) with an electronic conductance of 18.2 MΩ cm.

Preparation of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ with thermal treatment. An aqueous solution of iron(II) sulfate heptahydrate (0.18 M, 10 ml) was slowly added to an aqueous solution of $K_3[Co^{III}(CN)_6]$ (0.12 M, 10 mL) with vigorous stirring. The formed precipitate was collected by filtration and washed with pure water several times. The resulting precipitate was dried *in vacuo* at room temperature, and then, dried at 60 ºC or 120 °C under air for 10 hours.

Characterisation of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$. Powder X-ray diffraction patterns were recorded on a Rigaku MiniFlex 600. Incident X-ray radiation was produced by a Cu X-ray tube, operating at 40 kV and 15 mA with Cu $K\alpha$ radiation ($\lambda = 1.54$ Å). The scan rate was 2° min^{-1} from $2\theta = 10 - 80°$. TG/DTA measurements were performed on an SII TG/DTA 7200. A sample (about 2.5 mg) was diluted with α-Al_2O_3 (about 7.5 mg) and then loaded into an Al pan and heated under air with continuous flowing. The sample temperature was increased with the rate of 1 °C min^{-1}. IR spectra were measured on a Jasco FT/IR 6700 spectrometer. Each sample was prepared as a KBr pellet. Diffuse reflectance UV-vis absorption spectra were recoded by a Jasco V-670 spectrometer equipped with an SIN-768 attachment. $BaSO_4$ was used for recording background spectra.

Evaluation of the performance of an H_2O_2 fuel cell. An aqueous solution of nitric acid or scandium nitrate that contained hydrogen peroxide (0.30 M) and sodium chloride (1.0 M) was placed in a one-compartment electrochemical cell. A small portion (80 μL) of a dispersion of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ in 2-propanol (30 mg mL^{-1}) was dropped on a piece of carbon cloth (1 cm × 2 cm) and dried at room temperature under air for 30 min. An Ni mesh (150 mesh) and the piece of carbon cloth modified with $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ were immersed in the solution of H_2O_2. Cell performance was evaluated by using a KFM 2005 FC impedance meter at 25 °C.

H_2O_2 decomposition catalysed by $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ in the presence of a Lewis acid or Brønsted acid. An aqueous solution (1.0 mL) containing hydrogen peroxide (0.30 M), sodium chloride (1.0 M), and a metal nitrate or nitric acid (50 mM) was flushed with N_2 gas. The solution was then transferred into a vial containing $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ with thermal treatment at 60 °C (0.50 mg) under N_2. Gas in a headspace was analysed by a q-mass spectrometer (Balzers ThermoStar GSD 320 tuned for microanalysis) to determine the amount of evolved O_2 continuously for 15 min.

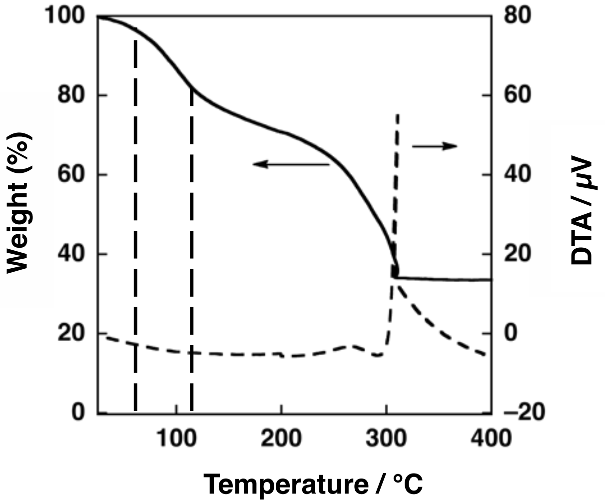

Fig. S1. TG/DTA curves of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$. (TG curve: solid and DTA curve: broken). The temperature increased from 25 °C to 400 °C with a ramp rate of 1 °C min^{-1} under air.

Comments: $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ contains physically adsorbed water owing to its porous structure in the as-prepared state. Thermogravimetric analysis of the complex indicated that gradual decrease in the weight ascribed to water desorption by increasing temperature from room temperature to 150 °C (Fig. S1). A steep decrease observed around 250 °C can be ascribed to oxidative degradation of the cyanide ligand. The formula estimated from the weight loss for the CN ligand is $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2\cdot(H_2O)$. Physisorbed and chemisorbed water molecules (~2.5% and ~17%, respectively) were lost by heating up to 60 and 120 °C, respectively (dotted lines in Figure S1). Thus, the cell performance of H_2O_2 fuel cells were examined by using $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ with thermal treatment at 60 °C and 120 °C as well as without thermal treatment.

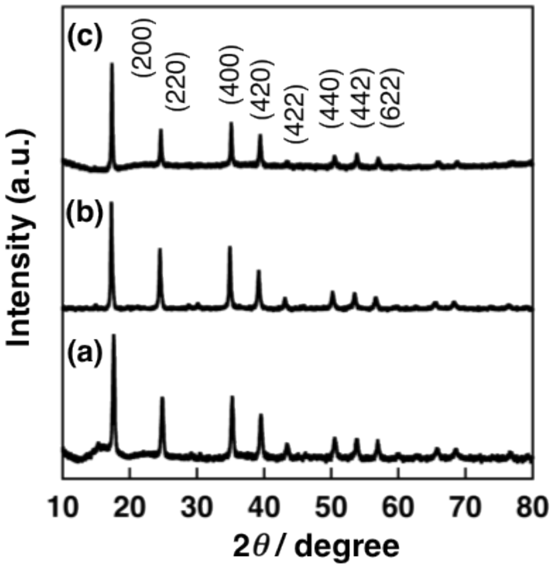

Fig. S2. Powder X-ray diffraction patterns of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ (a) without thermal treatment, and with thermal treatment at (b) 60 °C and (c) 120 °C. The numbers in parenthesis are *hkl* indices.

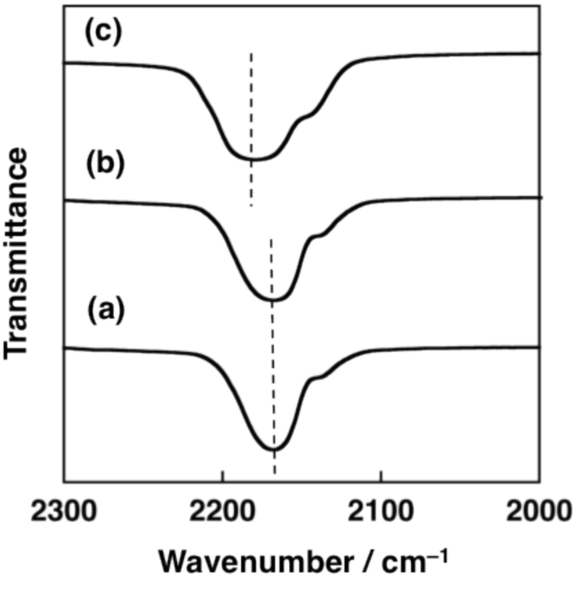

Fig. S3. IR absorption spectra of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ (a) without thermal treatments and with thermal treatment at (b) 60 °C and (c) 120 °C in CN stretching region (2000 – 2300 cm^{-1}).

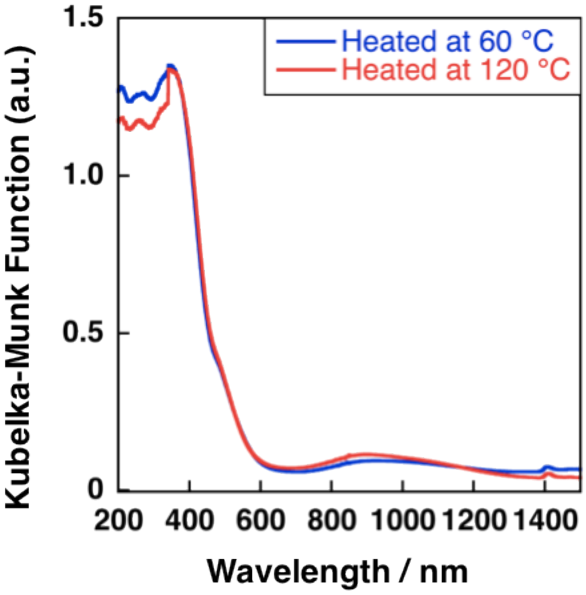

Fig. S4. Diffuse reflectance UV-vis spectra of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ with the thermal treatment at 60 °C (blue) and 120 °C (red).

Comments: CN stretching bands [ν(CN)] appearing around 2200 cm^{-1} keenly reflects the coordination modes of CN ligands.[S1] The ν(CN) bands of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ without and with thermal treatment at 60 °C appeared at 2169 cm^{-1} (Fig. S3). On the other hand, the ν(CN) band of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ pretreated at 120 °C became broader and appeared at 2180 cm^{-1}, which is shifted to higher wavenumber by 11 cm^{-1}. The being broader and higher wavenumber shift of the ν(CN) band indicates that the electron density of π-orbitals of some CN ligands, which possess the highest occupied molecular orbital (HOMO) with antibonding character, was reduced.[S1] Thus, some Fe^{II} ions were oxidised to Fe^{III} ions during thermal treatment at 120 °C. No obvious changes in crystal structures by thermal treatment as evidenced by powder X-ray diffraction (Fig. S2) and in diffuse reflectance near-IR absorption spectra (Fig. S4) suggest that only small portion of Fe^{II} ions were oxidised.

Reference

S1 Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed.; Wiley Interscience: New York, 1986.

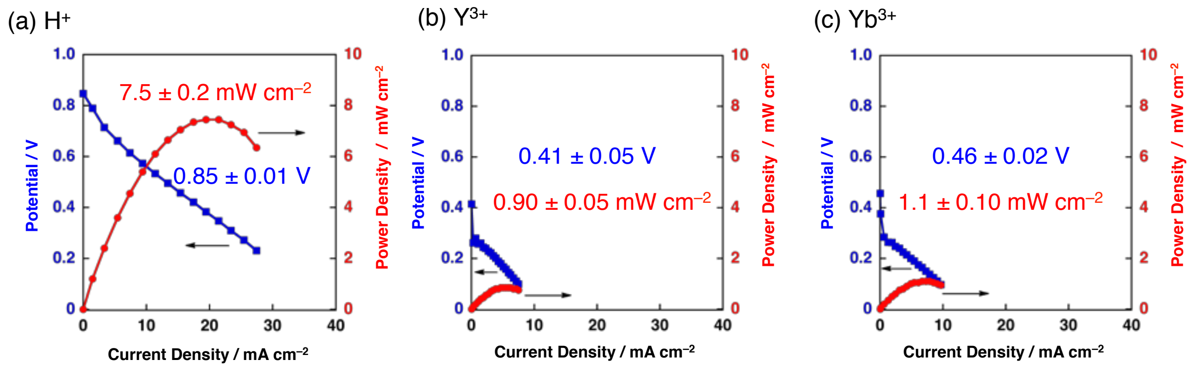

Fig. S5. Average *I*–*V* and *I*–*P* curves of a one-compartment H_2O_2 fuel cell with an Ni anode and carbon cloth electrode modified with $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ in an aqueous solution containing 0.30 M H_2O_2 and 1.0 M NaCl in the presence of (a) H^+ ion (100 mM), (b) Y^{3+} ion and (c) Yb^{3+} ion for triplicate fabricated fuel cells. The values after "±" are the standard deviations.

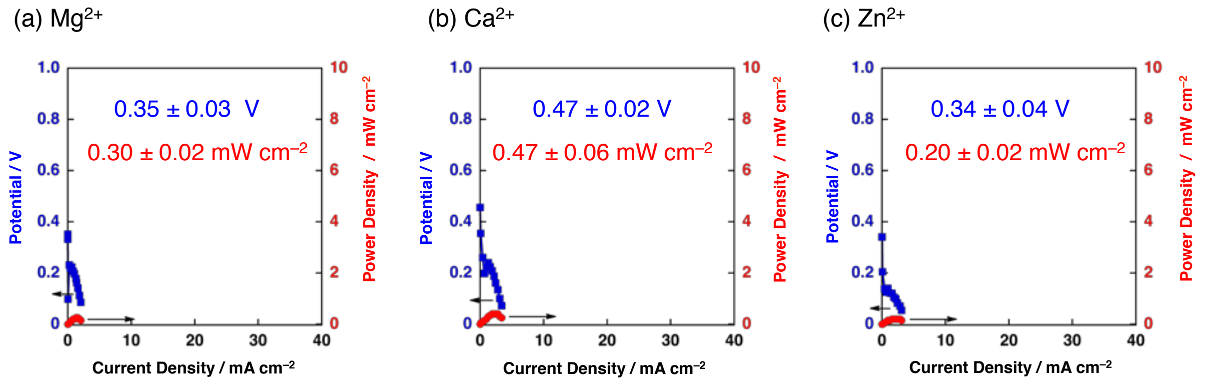

Fig. S6. Average *I*–*V* and *I*–*P* curves of a one-compartment H_2O_2 fuel cell with an Ni anode and carbon cloth electrode modified with $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ in an aqueous solution containing 0.30 M H_2O_2 and 1.0 M NaCl in the presence of (a) Mg^{2+} ion, (b) Ca^{2+} ion and (c) Zn^{2+} ion (100 mM) for triplicate fabricated fuel cells. The values after "±" are the standard deviations.

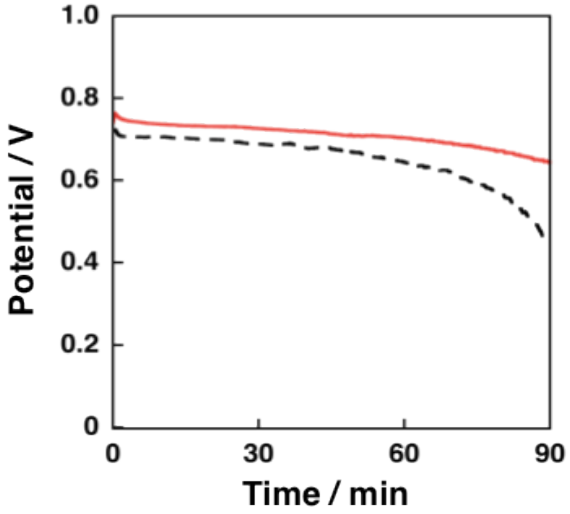

Fig. S7. Time courses of output potentials at 2.0 mA cm^{-2} from H_2O_2 fuel cells using an aqueous solution containing 0.30 M H_2O_2 and 1.0 M NaCl in the presence of 50 mM $Sc(NO_3)_3$ (red solid) or 25 mM HNO_3 (black dash) (pH 1.5).

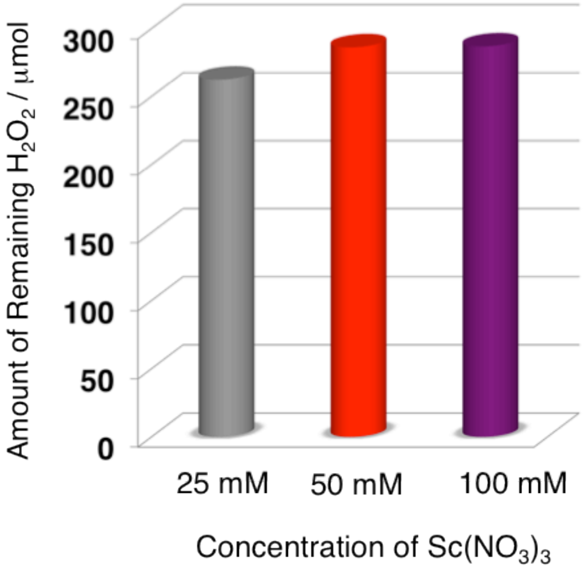

Fig. S8. Amounts of remaining H_2O_2 in aqueous H_2O_2 solutions (0.30 M, 1.0 mL) containing $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ (0.50 mg) in the presence of $Sc(NO_3)_3$ in various concentrations 25 mM, 50 mM and 100 mM after the reaction for 10 min.