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

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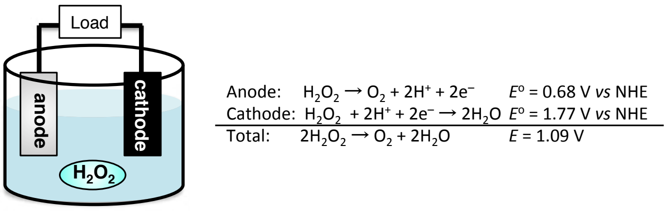
**Performance of an $H_2O_2$ fuel cell employing an Ni mesh and $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ as an anode and a cathode, respectively, was remarkably enhanced in terms of an open circuit potential, a power density and durability by the addition of $Sc^{3+}$ ion to an aqueous $H_2O_2$ fuel.**

Utilisation of solar energy to support our lives instead of fossil fuels merits mitigating environmental issues and realizing sustainable society.[1,2] In this context, hydrogen has been regarded as the most promising solar fuel, however, hydrogen has intrinsic problems such as low volumetric energy density, highly explosive properties etc.[3] As an alternative solar fuel, hydrogen peroxide ($H_2O_2$) has attracted increasing attention in this field.[4] $H_2O_2$ can be produced by reduction of $O_2$ abundant in the atmosphere by using various types of reductants including water.[5,6] The properties of $H_2O_2$ that are liquid under ambient conditions, freely miscible with water, etc, indicate that $H_2O_2$ can be a safe liquid fuel.

An aqueous $H_2O_2$ can be used for electric power generation in various types of fuel cells.[7–12] For example, $NaBH_4$-$H_2O_2$ fuel cells,[7] EtOH-$H_2O_2$ fuel cells,[8] etc in which $H_2O_2$ are used as an oxidant.[9] Additionally, some $H_2O_2$ fuel cells utilise $H_2O_2$ for both oxidant and reductant to achieve a theoretical output potential of 1.09 V, which is slightly lower but comparable to that of a hydrogen fuel cell (1.23 V).[11] A schematic drawing of a typical $H_2O_2$ fuel cell is depicted in Scheme 1. This type of $H_2O_2$ fuel cells emit only water and oxygen which are harmless and recyclable chemicals.[6] An intrinsic serious problem of $H_2O_2$ is decomposition by disproportionation, which causes not only lowering the output potentials of $H_2O_2$ fuel cells but also instability of cell performance, preventing the practical applicatons.[11,12]



**Scheme 1.** A schematic drawing of a one-compartment $H_2O_2$ fuel cell

$H_2O_2$ decomposition can be effectively suppressed in the presence of anionic species including ethylenediamine tetraacetic acid, pyrophosphate and stannate, which sequester contaminated metal ions.[13] However, this type of agents are not suitable to be used in an $H_2O_2$ fuel, because these anionic agents may interact with electrode surfaces to block cationic active sites. In this context, emergence of cationic agents for suppression of $H_2O_2$ decomposition are strongly demanded to treat an aqueous $H_2O_2$ fuel safely and enhance the performance of $H_2O_2$ fuel cells. We report herein high and robust performance of $H_2O_2$ fuel cells using an aqueous $H_2O_2$ fuel containing $Sc^{3+}$ ion in terms of open circuit potentials, power densities, and durability under constant current conditions. The effect of addition of various Lewis acids to an aqueous $H_2O_2$ was also clarified on $H_2O_2$ decomposition.

Performance of an $H_2O_2$ fuel cell employing an Ni mesh as an anode and a piece of carbon cloth modified with

## Broader context

Hydrogen peroxide is a promising candidate as a next-generation energy carrier, because it can be produced from $O_2$ abundant in air by using photoenergy in the presence of a photocatalyst and can also generate electricity by $H_2O_2$ fuel cells. An intrinsic problem of $H_2O_2$ is instability during storage under ambient conditions. We report herein remarkable suppression of the $H_2O_2$ decomposition by adding $Sc^{3+}$ ion to an aqueous $H_2O_2$ solution, resulting in high and robust performance of one-compartment $H_2O_2$ fuel cells in terms of open circuit potentials, power densities, and durability.

$[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ as a cathode was examined in an aqueous $H_2O_2$ fuel in the presence and absence of $Sc^{3+}$ ion. No $H_2$ evolution was observed during the examinations. $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ was prepared by the literature method and characterised by TG/DTA, powder X-ray analysis, IR spectroscopy and diffuse reflectance UV-vis spectra (Fig. S1-S4 in ESI†).[11b] We found that catalytic activity of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ was extremely enhanced after thermal treatment at 60 °C.[14] Powder X-ray diffraction peaks of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ after heat treatment at 60 °C became shaper than those of the as-prepared sample, indicating that crystallinity was improved by the heat treatment (Fig. S2). Heat-treatment at higher temperature, 120 °C, in air resulted in the oxidation of $Fe^{II}$ ions as evidenced by the high wavenumber shift of a CN stretching band in IR spectrum (Fig. S3).

The open circuit potential (OCP) and power density of the $H_2O_2$ fuel cell using $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ with the heat treatment at 60 °C were only 0.31 ± 0.02 V and 0.20 ± 0.05 mW $cm^{-2}$, respectively, in the absence of $Sc^{3+}$ ion in an aqueous $H_2O_2$ fuel (Fig. 1a). When the concentration of $Sc^{3+}$ ion in the aqueous $H_2O_2$ fuel was increased to 50 mM or higher, the OCPs increased to 0.81 ± 0.01 V (Fig. 1b). Additionally, the power density increased to more than 9.9 ± 0.13 mW $cm^{-2}$ by increasing the concentration of $Sc^{3+}$ ion to 120 mM (Fig. 1c). The pH of the aqueous $H_2O_2$ solution containing 120 mM $Sc^{3+}$ ion is 1.0, thus, performance of an $H_2O_2$ fuel cell in an aqueous $H_2O_2$ solution acidified with nitric acid (pH 1.0) was examined in terms of power density (Fig. S5a). A slightly low power density (7.5 ± 0.05 mW $cm^{-2}$) suggests that the addition of $Sc^{3+}$ ion is more effective than that of $H^+$.

The effect of other Lewis acids was also examined on performance of the $H_2O_2$ fuel cells. A Lewis acid chosen from $Yb^{3+}$, $Y^{3+}$, $Mg^{2+}$, $Ca^{2+}$ and $Zn^{2+}$ ions was added to an aqueous $H_2O_2$ fuel instead of $Sc^{3+}$ ion. Addition of the trivalent ions of $Yb^{3+}$ and $Y^{3+}$ ions (100 mM) was effective for an improvement in cell performance, however, the obtained OCPs and power densities were lower than 0.5 V and 1.1 mW $cm^{-2}$ (Fig. S5 in ESI†). The improvement obtained by the addition of divalent ions was more modest. Among the divalent ions, $Ca^{2+}$ ion was the most effective, however, the OCP and power density for the $H_2O_2$ fuel cell using an aqueous $H_2O_2$ fuel containing $Ca^{2+}$ ion were as low as 0.47 ± 0.02 V and 0.47 ± 0.05 mW $cm^{-2}$, respectively (Fig. S6 in ESI†). Thus, $Sc^{3+}$ ion is the most effective Lewis acid to improve the performance of the $H_2O_2$ fuel cell in terms of both OCP and power density. The improvement observed in the presence of $Sc^{3+}$ ion would originate from both the suppression of $H_2O_2$ decomposition (vide infra) and the lowering of pH of the aqueous $H_2O_2$, where the $H_2O_2$ reduction readily proceeds by thermodynamical reasons.

Not only OCP and power density but also durability of the $H_2O_2$ fuel cell was improved in the presence of $Sc^{3+}$ ion. The time courses of output potentials of the $H_2O_2$ fuel cells were recorded under the operation at the constant current of 2.0 mA $cm^{-2}$ (Fig. 2). The drop in the output potential mainly results from the detachment of $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ from a glassy carbon electrode, which is caused by bubble formation accompanied with decomposition of $H_2O_2$. When the aqueous $H_2O_2$ fuel contained no $Sc^{3+}$ ion, the output potential dropped to 0 V within 5 min. The durability was remarkably improved in the presence of $Sc^{3+}$ ion at the concentration of 25 mM. The output potential higher than 0.6 V was maintained

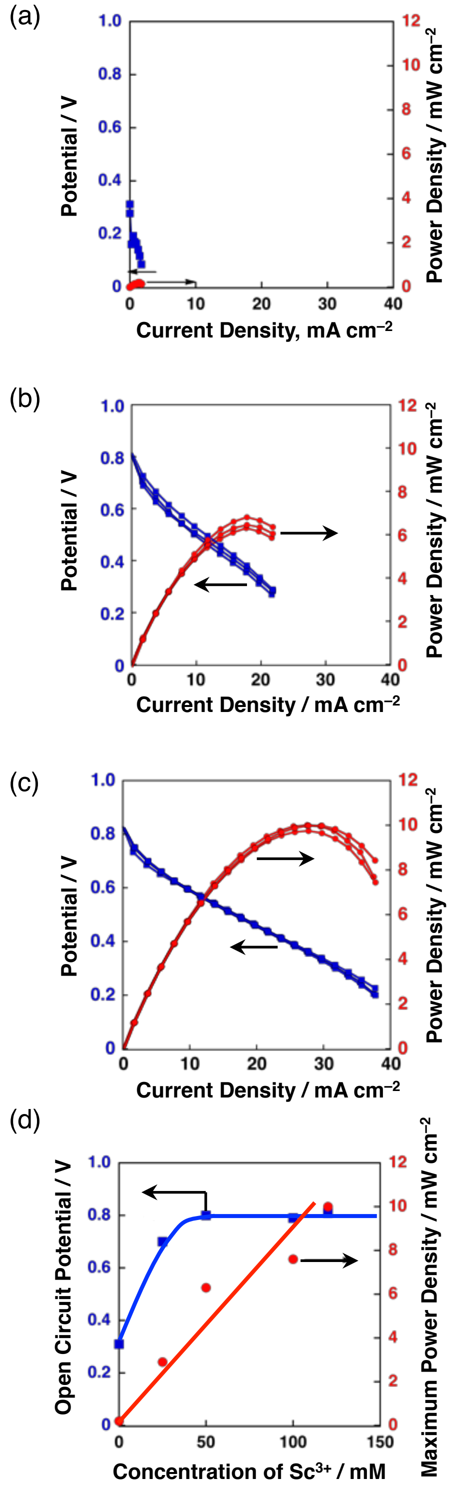


**Fig. 1.** (a-c) *I–V* and *I–P* curves of one-compartment $H_2O_2$ fuel cells with an Ni anode and carbon cloth electrode modified with $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ in an aqueous solution containing 0.30 M $H_2O_2$ and 1.0 M NaCl in the presence of various concentrations of $Sc(NO_3)_3$ (a) 0 mM, (b) 50 mM and (c) 120 mM for triplicate fabricated fuel cells. Currents and powers were normalised by a geometric surface area of the electrodes. (d) Plots of open circuit potentials and maximum power densities *vs*. concentrations of $Sc(NO_3)_3$.

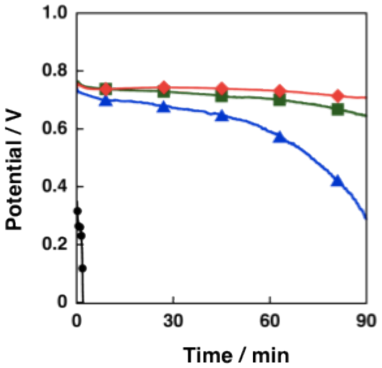


**Fig. 2.** Time courses of output potentials at 2.0 mA cm$^{-2}$ from $H_2O_2$ fuel cells using an aqueous solution containing 0.30 M $H_2O_2$ and 1.0 M NaCl in the presence of various concentrations of $Sc(NO_3)_3$ [0 mM (black circle); 25 mM (blue triangle); 50 mM (green square) and 100 mM (red diamond)].

for nearly 55 min where the initial output potential was 0.74 V. Much improved durability was obtained by further increase of $Sc^{3+}$ ion. The decrease in the output potentials were as small as 97 and 40 mV under the operation for 90 min when the aqueous $H_2O_2$ fuel contained 50 and 100 mM $Sc^{3+}$ ion, respectively. Improvement in the durability was also observed by using an aqueous $H_2O_2$ fuel containing nitric acid (pH 1.5). However, the decrease in the output potential after operation for 90 min was as large as 275 mV (Fig. S7 in ESI†), which is about 3 times larger than that using an aqueous $H_2O_2$ containing 50 mM $Sc^{3+}$ ions although the pH values of aqueous $H_2O_2$ fuels are the same. Thus, addition of $Sc^{3+}$ ion to an aqueous $H_2O_2$ fuel is more effective than that of Brønsted acid for the improvement in the durability of $H_2O_2$ fuel cells.

The cathode material, $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$, is active for $H_2O_2$ decomposition as well as $H_2O_2$ reduction by disproportionation resulting in $O_2$-bubble formation (movie 1 in ESI†). However, very little $O_2$-bubble formation was observed for aqueous $H_2O_2$ fuels containing $Sc^{3+}$ ion. Thus, the effect of Lewis acids on prevention of $H_2O_2$ disproportionation was systematically investigated. An aqueous $H_2O_2$ solution (0.30 M, 1.0 mL) containing a Lewis acid selected from nitrate salts of $Ca^{2+}$, $Mg^{2+}$, $Zn^{2+}$, $Yb^{3+}$, $Y^{3+}$ and $Sc^{3+}$ ions (50 mM) was slowly poured onto $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ (0.50 mg, 213 $\mu mol_{\text{-Fe}}$) under $N_2$ in a sealed bottle. The amount of $O_2$ evolved in the bottle was continuously monitored by a q-mass spectrometer (Fig. 3a). When no Lewis acid was contained in the reaction solution, the stoichiometric amount (150 μmol) of $O_2$ evolution based on the amount of $H_2O_2$ was observed in 10 min. On the other hand, the $O_2$ evolution was decelerated by the addition of $Mg^{2+}$, $Ca^{2+}$, $Y^{3+}$, $Zn^{2+}$, $Yb^{3+}$ and $Sc^{3+}$ ions to the reaction solutions. Among these ions, the most effective additive was $Sc^{3+}$ ion, in which more than 96% of original amount of $H_2O_2$ remained in a reaction solution after 10 min. The efficient suppression of $H_2O_2$ decomposition was also observed for the solution containing $Sc^{3+}$ ions in lower (25 mM) or higher (100 mM) concentration (Fig. S8 in ESI†). The effect of a counter anion of $Sc^{3+}$ ion on the $H_2O_2$ decomposition was also examined by using $Sc(OAc)_3$ and $ScCl_3$ instead of $Sc(NO_3)_3$ under otherwise the same experimental conditions. The amounts of remaining $H_2O_2$ in the reaction solution were 190, 250 and 290 μmol for the reaction solutions containing $Sc(OAc)_3$ and $ScCl_3$ instead of $Sc(NO_3)_3$, respectively (Fig. 3c). The dependence of the catalysis on counter anions indicates the importance of the solution structures of $Sc^{3+}$ ion.

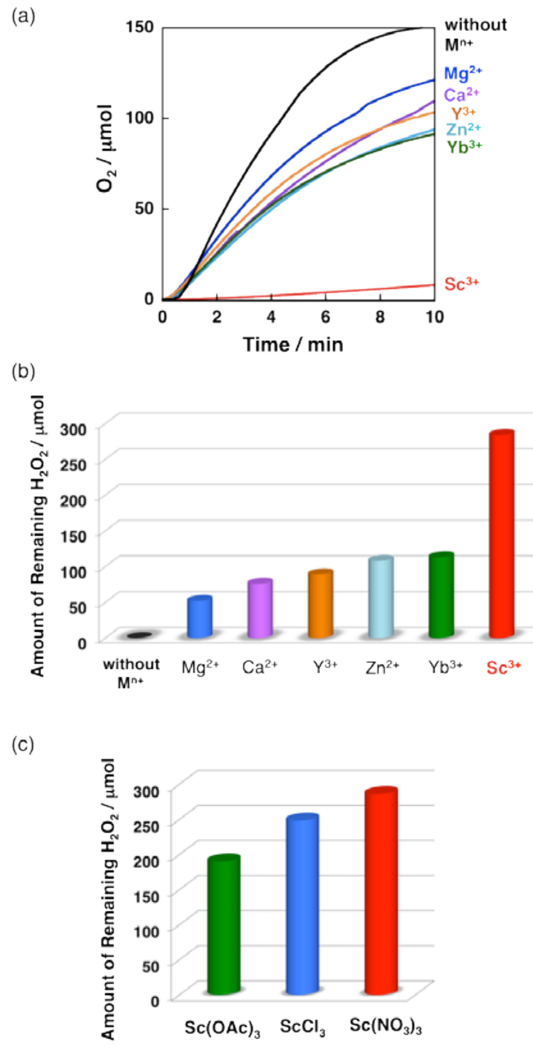


**Fig. 3.** (a) Time courses of $O_2$ evolution from aqueous $H_2O_2$ solutions (0.30 M, 1.0 mL) containing $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ (0.50 mg) in the absence (black) or presence of the Lewis acids [50 mM, nitrate salts of $Ca^{2+}$ (purple); $Mg^{2+}$ (blue); $Zn^{2+}$ (light blue); $Yb^{3+}$ (green); $Y^{3+}$ (orange) and $Sc^{3+}$ (red)]. (b) Amounts of $H_2O_2$ remaining in the reaction solution containing the Lewis acids estimated from the volume of evolved $O_2$ after reaction for 10 min at room temperature. (c) Amounts of $H_2O_2$ remaining in the reaction solution containing $Sc(OAc)_3$, $ScCl_3$ or $Sc(NO_3)_3$ (50 mM) after reactions for 10 min at room temperature.

The well known Haber Weiss mechanism of $H_2O_2$ decomposition initiated by $Fe^{II}$ ions is given by equations (1)-(4): [15]

$$H_2O_2 + Fe^{II} \rightarrow Fe^{III} + OH^- + OH^{\bullet} \tag{1}$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \tag{2}$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow OH^{\bullet} + H_2O + O_2 \tag{3}$$

$$2\ HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{4}$$

The radical chain reactions (eqns 2 and 3) are initiated by the reduction of $H_2O_2$ by $Fe^{II}$ to produce $OH^{\bullet}$ (eqn 1), which reacts with $H_2O_2$ to produce $HO_2^{\bullet}$ (eqn 2). $OH^{\bullet}$ is reproduced by the reaction of $H_2O_2$ with $HO_2^{\bullet}$ (eqn 3). The radical chain is terminated by the bimolecular reaction of $HO_2^{\bullet}$ (eqn 4). The chain carrier ($HO_2^{\bullet}$) is trapped by $Sc^{3+}$ to produce $Sc^{3+}$–bound $O_2^{\bullet -}$, which is much more stable than $HO_2^{\bullet}$ as evidenced by EPR measurements in literature.[16,17] Thus, the radical chain decomposition of $H_2O_2$ is retarded by the presence of $Sc^{3+}$ to improve the durability of the $H_2O_2$ fuel cell (Fig. 2). The positively charged $Sc^{3+}$ ion may assist the reduction of $H_2O_2$ (eqn 1) due to the strong binding of $Sc^{3+}$ to $OH^{-}$, resulting in the high output potential of the $H_2O_2$ fuel cells (Fig. 1).

## Conclusions

The power density of a one-compartment $H_2O_2$ fuel cell was dramatically improved to 9.9 ± 0.13 mW $cm^{-2}$ by the addition of $Sc^{3+}$ ions to an aqueous $H_2O_2$ fuel. The high power density allows to drive a propeller (movie 2 in ESI†). The $H_2O_2$ decomposition in the reaction solution can be dramatically suppressed by the addition of $Sc^{3+}$ ion, resulting in high power densities and durability. This finding is an important piece of work to utilise $H_2O_2$ as a promising solar fuel.

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† Electronic Supplementary Information (ESI) available: Movie files for $O_2$ evolution by $H_2O_2$ decomposition (movie 1) and for driving a propeller (movie 2), experimental section, TG/DTA (Fig. S1), powder X-ray diffraction patterns (Fig. S2), IR spectra (Fig. S3), diffuse reflectance UV-vis spectra (Fig. S4), *I-V* and *I-P* curves (Fig. S5 and S6), durability test (Fig. S7), amount of remaining $H_2O_2$ in the presence of $Sc^{3+}$ ion with various concentrations (Fig. S8). See DOI: 10.1039/c000000x/

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