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

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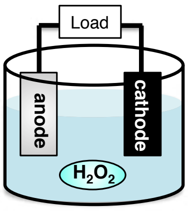
Performance of an H_2O_2 fuel cell employing an Ni mesh and $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ as an anode and a cathode, respectively, was remarkably enhanced in terms of an open circuit potential, a power density and durability by the addition of Sc^{3+} ion to an aqueous H_2O_2 fuel.

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]



Anode: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ $E° = 0.68$ V *vs* NHE
Cathode: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $E° = 1.77$ V *vs* NHE
Total: $2H_2O_2 \rightarrow O_2 + 2H_2O$ $E = 1.09$ V

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

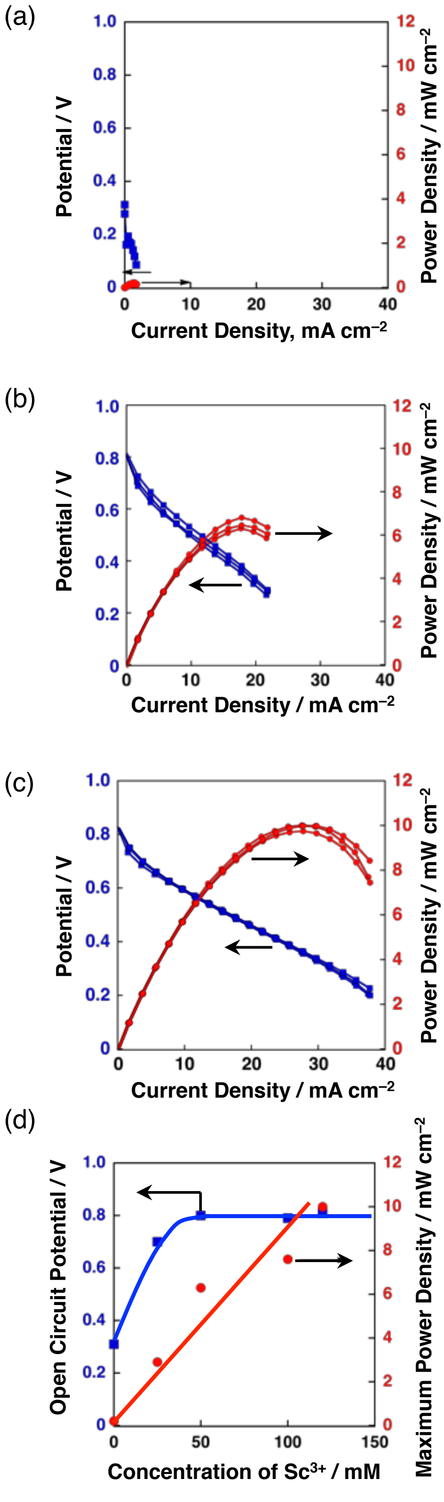


Fig. 1. (a-c) *I*–*V* and *I*–*P* curves of one-compartment H_2O_2 fuel cells with an Ni anode and carbon cloth electrode modified with $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ in an aqueous solution containing 0.30 M H_2O_2 and 1.0 M NaCl in the presence of various concentrations of $Sc(NO_3)_3$ (a) 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 $Sc(NO_3)_3$.

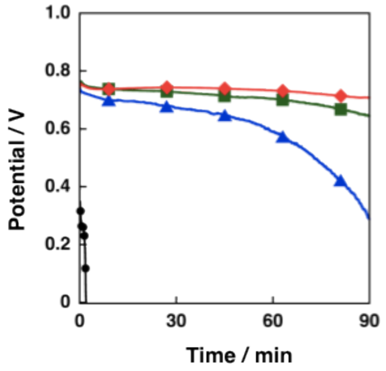


Fig. 2. Time courses of output potentials at 2.0 mA cm^{-2} from H_2O_2 fuel cells using an aqueous solution containing 0.30 M H_2O_2 and 1.0 M NaCl in the presence of various concentrations of $Sc(NO_3)_3$ [0 mM (black circle); 25 mM (blue triangle); 50 mM (green square) and 100 mM (red diamond)].

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.

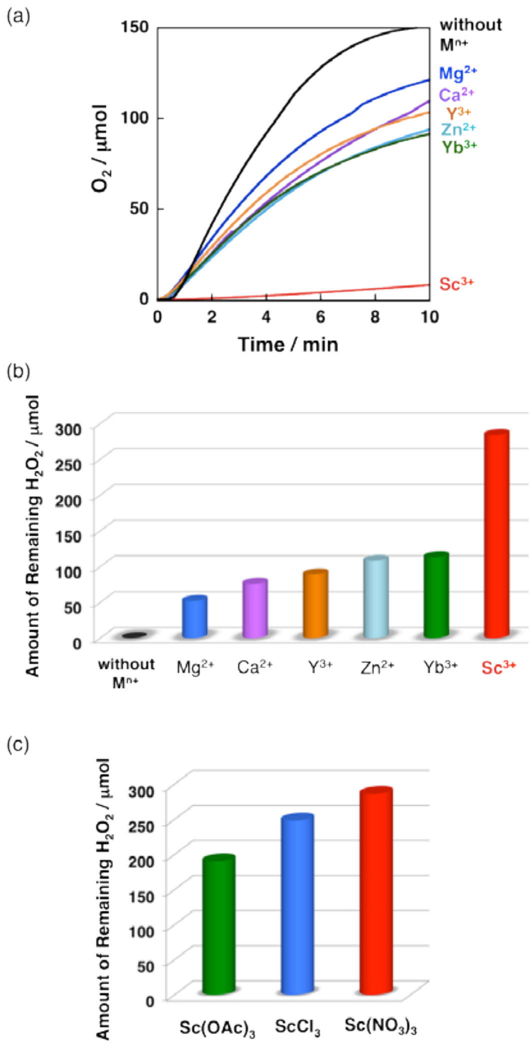


Fig. 3. (a) Time courses of O_2 evolution from aqueous H_2O_2 solutions (0.30 M, 1.0 mL) containing $[Fe^{II}(H_2O)_2]_3[Co^{III}(CN)_6]_2$ (0.50 mg) in the absence (black) or presence of the Lewis acids [50 mM, nitrate salts of Ca^{2+} (purple); Mg^{2+} (blue); Zn^{2+} (light blue); Yb^{3+} (green); 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]

$$H_2O_2 + Fe^{II} \rightarrow Fe^{III} + OH^- + OH^\bullet \qquad (1)$$

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \qquad (2)$$

$$HO_2^\bullet + H_2O_2 \rightarrow OH^\bullet + H_2O + O_2 \qquad (3)$$

$$2\,HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad (4)$$

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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