Electrocatalysis of Heat-treated Mn–Porphyrin/Carbon Cathode for Synthesis of H$_2$O$_2$ Acid Solutions by H$_2$/O$_2$ Fuel Cell Method

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Mn–porphyrin supported on active carbon, which was activated by heat-treatment in Ar, electrochemically catalyzed reduction of O$_2$ to H$_2$O$_2$ by the H$_2$/O$_2$ fuel cell method. The electrocatalytic activities were strongly dependent on the heat-treatment temperatures. The maximum H$_2$O$_2$ concentration of 3.5 wt % with 47% current efficiency was obtained for the catalyst treated at 450 °C, and a TON (Mn) for the H$_2$O$_2$ formation was over 1000 h^{-1}.

Hydrogen peroxide is expected a major oxidant for Green Sustainable Chemistry. Price of H$_2$O$_2$ is expensive to use for chemical process. Most of all H$_2$O$_2$ is manufactured by the anthraquinone process through multisteps operation with a large amount of energy consumption.[1] Therefore, it has been desired for development of new direct catalytic synthesis method of H$_2$O$_2$. It is well known that Pd[2] and Au–Pd[3,4] catalyze H$_2$O$_2$ formation from H$_2$ and O$_2$ in acid solutions. We have recently reported the effective H$_2$/O$_2$ fuel cell method for H$_2$O$_2$ synthesis.[5–7] Reduction of O$_2$ to H$_2$O$_2$ at the three-phase boundary (gaseous O$_2$, aqueous electrolyte, and solid cathode) is the character of the fuel cell method. O$_2$ gas is directly supplied to the active site at the three-phase boundary. Therefore, the reduction of O$_2$ to H$_2$O$_2$ is accelerated to compare with the successive reduction of H$_2$O$_2$. We have performed the efficient production of H$_2$O$_2$ of 7 wt % with a 94% current efficiency by using the [VGCF + XC72 + PTFE][8] cathode and NaOH electrolyte (2 mol L^{-1}).[7] When we chose acid electrolyte (0.5 mol L^{-1} H$_2$SO$_4$) and the [AC + VGCF + PTFE][8] cathode, the maximum concentration of H$_2$O$_2$ was 1.1 wt %.[6] The successive reduction of H$_2$O$_2$ to H$_2$O was competitive to the reduction of O$_2$ to H$_2$O$_2$, and the two rates were balanced at 1.1 wt % over the cathode. We have to find and develop a new electrocatalyst and cathode for accumulation of H$_2$O$_2$ > 1.1 wt % in acid electrolyte.

Electrocatalysts prepared from Fe– and Co–porphyrin or phthalocyanine on carbon by heat treatment in inert gas have been expected as nonprecious metal electrocatalyst for four-electron reduction of O$_2$ to H$_2$O for PEMFC.[9] Our idea was that uneffective metal–porphyrin derivatives would be candidate for the H$_2$O$_2$ formation by our fuel cell method.

Electrocatalysts were prepared from metal–porphyrin[10] CH$_2$Cl$_2$ solutions and AC by a conventional impregnation method, stirring the mixture for 6 h and dried at 50 °C. This metal–porphyrin/AC powder was activated by heat treatment at T = 200–800 °C in Ar stream for 2 h, omitted as M–Por/AC (T °C). The cathode and anode (electrode areas = 1.34 cm^2) prepared by the hot press-method[11] were attached the two compartment cell reactor.[6,12] A yield of H$_2$O$_2$ was determined by the KMnO$_4$ titration or the Ce^{4+} titration method. A current
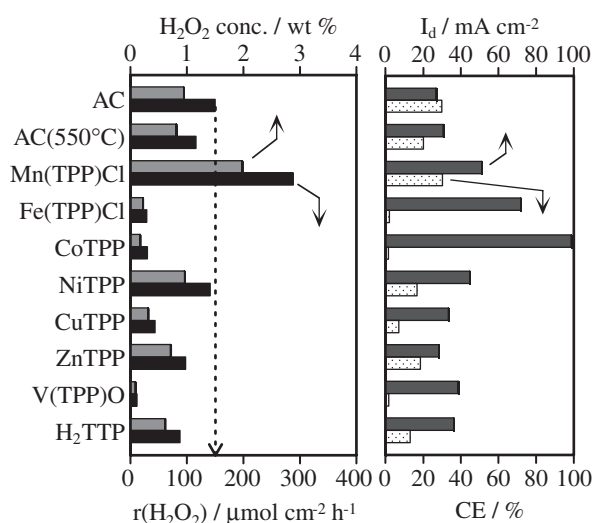

Figure 1. Electrocatalytic activities of metal–porphyrins supported on AC for the H$_2$O$_2$ formation by the H$_2$/O$_2$ fuel cell method at 25 °C.

efficiency (CE) for H$_2$O$_2$ formation was calculated as 2e$^-$ reduction, which was corresponding to a H$_2$O$_2$ selectivity based on H$_2$.

Figure 1 shows electrocatalytic activities of various M–Por/AC (550 °C) for the H$_2$O$_2$ formation at 25 °C. All metal–porphyrins loadings were 0.5 wt % based on metal. As mentioned above, AC functioned as electrocatalyst for the H$_2$O$_2$ synthesis in acid electrolyte.[6] As you can see clearly, the formation rate of H$_2$O$_2$ over the Mn(TPP)Cl/AC (550 °C) was twice higher than that over the AC. A concentration of H$_2$O$_2$ was 2.0 wt % at 2 h with 30% CE. Fe(TPP)Cl/AC (550 °C) and Co(TPP)Cl/ AC (550 °C) were active for the reduction of O$_2$ but not for the H$_2$O$_2$ formation which was corresponding to the previous reports.[9] Other metal–porphyrin did not show significant electrocatalysis for the reduction of O$_2$. The activated Mn(TPP)Cl/AC (550 °C) shows particular electrocatalysis for the H$_2$O$_2$ formation.

Various Mn compound[10]/AC (550 °C, 0.5 wt % Mn loading) electrocatalysts were examined for the H$_2$O$_2$ synthesis. The Mn loadings on the cathodes were 2.0 μmol cm^{-2}. Order of electrocatalytic activities was Mn(OEP)Cl (356 μmol cm^{-2} h^{-1}) > Mn(TPP)Cl (290) > Mn(TPPS)Cl (265) > Mn(TMPyP)Cl (180) > AC (116) > Mn(salen) (110), Mn(Pc)Cl (99), Mn(acac)$_3$ (87). N$_4$-ligand, porphyrin ring was effective for the H$_2$O$_2$ synthesis, but phthalocyanine ring was not. Mn(OEP)Cl/AC was the most active electrocatalyst (178 TON h^{-1}) for the H$_2$O$_2$ synthesis in H$_2$SO$_4$ electrolyte (0.5 mol L^{-1}) among the Mn compounds though the CE of 35% was not enough.
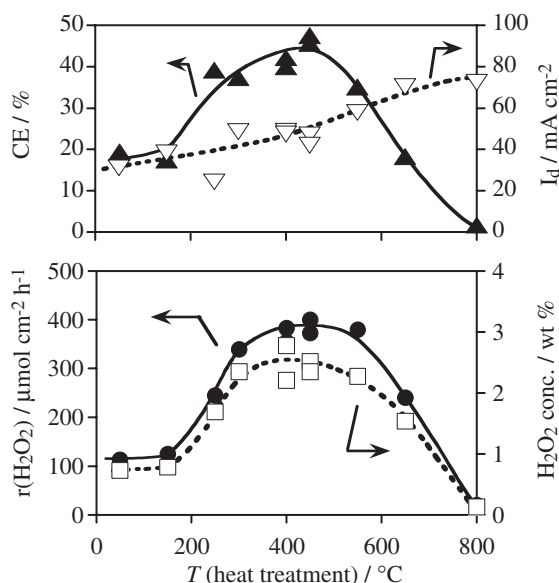
Figure 2. Effects of heat-treatment temperature of Mn(OEP)Cl/AC on the H_2O_2 formation by the H_2/O_2 fuel cell method at 25 °C.

Figure 2 shows effect of the heat-treatment temperatures for Mn(OEP)Cl/AC on the H_2O_2 formation at 25 °C. The formation rates of H_2O_2 over the Mn(OEP)Cl/AC electrocatalyst treated below 150 °C were as low as that over the AC. We could not observe the heat-treatment effect blow 150 °C. The formation rate of H_2O_2 remarkably increased with increasing heat-treatment temperature above 200 °C. The maximum formation rate of H_2O_2 (400 μmol cm^{-2} h^{-1}) was obtained by the heat-treatment at 450 °C, and a H_2O_2 concentration was 2.3% in 2 h. The CE of H_2O_2 showed a similar dependence of the formation rate. The maximum CE was 47% at the heat-treatment temperature of 450 °C. When the heat-treatment temperatures increase over 550 °C, the formation rate of H_2O_2 remarkably decreased, 20 μmol cm^{-2} h^{-1} at 800 °C, but the current densities increased. In other words, the O_2 reduction paths to H_2O_2 (2e$^-$ reduction) and H_2O (4e$^-$ reduction) were drastically changed with the heat-treatment temperatures. This significant influence of the heat treatment is very interesting.

Effects of the Mn(OEP)Cl loading over AC were studied on the H_2O_2 formation. The formation rate of H_2O_2 increased with the Mn(OEP)Cl loading and the maximum formation rate of 450 μmol cm^{-2} h^{-1} was obtained at 0.3 wt % loading based on Mn which turnover number was over 850 in 1 h. The CE of H_2O_2 jumped from 23% (AC) to 45–50% at 0.1–0.6 wt % Mn(OEP)Cl loadings. Excess loadings above 0.6 wt % decrease the formation rate and the CE. When the reaction time was expanded for the H_2O_2 formation over 0.3 wt % Mn–OEP–Cl/AC (450 °C), the H_2O_2 concentration gradually increased from 2.5 wt % at 2 h to an upper limit of 3.5 wt % after 4 h. The total H_2O_2 yield linearly increased with a constant current density of 45 mA cm^{-2} after 4 h. An apparent upper limit of the H_2O_2 concentration was due to an increase of catholyte volume during the reduction of O_2.[7] Therefore, we can perform steady production of 3.5 wt % H_2O_2 solutions.

The most important point is active site structure of heat-treated Mn(OEP)Cl/AC and what reactions occur during the heat-treatment. We attempted characterizations of the heat-treated Mn(OEP)Cl/AC by XAFS, FT-IR, and CV, but these data are not clear. We have to do more detailed and careful characterization studies to clarify active site structure. However, we observed very interesting spectra of temperature-programmed desorption (TPD) over the Mn(OEP)Cl/AC with 10 °C min^{-1} from 150 to 800 °C. Desorpiton products directly monitored by an on-line mass spectrometer (Anelva MS-GA200-DM) were CO ($m/e = 28$), CO_2 (44), CH_4 (16), H_2 (2), HCl (36), and Cl (35). Differences in TPD spectra of CO, CO_2, CH_4, and H_2 were not observed for Mn(OEP)Cl/AC and AC. This result suggests that CO, CO_2, CH_4, and H_2 were produced by decomposition of functional groups on the AC surface. On the other hand, HCl and Cl were observed for the Mn(OEP)Cl/AC from 250 °C, to the maximum at 350 °C, and stopped at 550 °C. They were not observed for AC. This dependence of HCl and Cl desorption on temperature (TPD) is very similar to that of the formation rate of H_2O_2 in Figure 2. This result suggests that desorption of Cl from Mn(OEP)Cl/AC is essential process for generation of the active site forming H_2O_2. It is able to speculate that Mn(OEP) species with no Cl axial ligand would strongly interact with the AC surface and that an open site generates on Mn(OEP)/AC. At higher heat-treatment temperatures over 600 °C, porphyrin ring structure of Mn(OEP)/AC would decompose,[9] and electrocatalysis of Mn site changed from the 2e$^-$ reduction to 4e$^-$ reduction. As mentioned above, detailed structure of Mn site has not been clarified yet.

The Mn(OEP)/AC(450) cathode can reuse for the H_2O_2 synthesis several times. The formation rate and the CE of H_2O_2 gradually increased with reuse numbers. The maximum TON(Mn) for the H_2O_2 formation was over 1000 in 1 h at 25 °C.

References and Notes
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8   VGCF: vapor grown carbon fiber, 13 m^2 g^{-1}, Show Denko Co, XC72: carbon black, Cabot Co, AC: active carbon, Wako Chem. Co., 800 m^2 g^{-1}, PTFE: poly(tetrafluoroethylene).
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10 TPP: tetraphenylporphyrin, OEP: octaethylporphyrin, TPPS: tetraphenylporphyrinsulfonate, TMPyP: tetramethylpyridinyl-porphyrin.
11 Cathodes (1.34 cm^{-2}) were prepared from catalysts, VGCF, PTFE powders by kneading, rolling, and shaping to a round thin sheet.
12 The cell was divided to two parts (1.18 mL each) by a Nafion-117, in order to prevent the diffusion of H_2O_2 from the cathode to the anode. Pure O_2 and H_2 were separately supplied (20 mL min^{-1}).