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Dual Catalysts System Based on Nano-manganese Oxide and Multiwall Carbon Nanotube for Four-electron Oxygen Reduction

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The dual catalysts system, in which nano-manganese oxide (nano-MnOx) is electrodeposited on multiwall carbon nanotube (MWCNT) modified glassy carbon (GC) electrode, efficiently catalyzes 4-electron O_2 reduction in alkaline media through the redox-mediation of O_2 to O_2^- (superoxide ion) by functional quinone groups on the MWCNT surface and the subsequent disproportionations of O_2^- to O_2 and HO_2^- (hydrogen peroxide) and further HO_2^- to O_2 and OH^- catalyzed by nano-MnOx.

The catalysts for 4-electron reduction of oxygen (O_2) with a low over-potential have been much focused in the development of air electrode used in energy conversion technologies, such as fuel cell and metal–air batteries in recent two decades. In addition to Pt and Pt-based alloys, non-Pt catalysts such as a variety of transition metal-based materials (porphyrins, oxides, carbides, nitrides, and chalcogenides) have been proposed for this purpose.[1] Recently, chemically and electrochemically prepared manganese oxides having a catalytic activity toward 4-electron reduction of O_2 have been reported.[2] Carbon nanotubes (CNTs) have become of great interest as electrode material, because of their high surface area and electronic conductivity. By oxidation treatment in acidic media, CNTs are functionalized with functional groups such as carbonyl ($>C{=}O$), carboxyl (–COOH), and hydroxy (–OH),[3] and consequently their surfaces become hydrophilic and more accessible to the aqueous solution of metal precursor or deposits.[4] Therefore, CNTs have been expected as catalysts or new supports for metal nanoparticles and enzyme catalysts toward O_2 reduction.[5]

Here, in order to develop non-platinum-based alkaline air electrode for 4-electron O_2 reduction with a low over-potential, we will propose a combined use of dual functional catalysts of MWCNT and nano-MnOx for redox-mediating O_2 reduction and for sequentially disproportionating the reduction intermediates into hydrogen peroxide (HO_2^-) and finally into OH^-.

MWCNT (outer diameter: 60–100 nm, inner diameter: 5–10 nm, length: 0.5–500 µm, Aldrich) was oxidized by refluxing in a concentrated H_2SO_4–HNO_3 mixture (1:1 v/v ratio) for 6 h at 80 °C. The reaction mixture was then diluted with Milli-Q water and stirred for 14 h, cooled down to room temperature and filtered with 5C filter paper and a pump, finally dried under vacuum at 50 °C for several hours.[6] By such an oxidation treatment, the quinone groups were formed on the surface of MWCNT, which could be proved by the cyclic voltammogram with a reversible redox response at -0.43 V vs Ag/AgCl (KCl-saturated) (as its formal potential $E^{0'}$) in N_2-saturated 0.1 M KOH solution, being expected for quinone compounds.[7]

MWCNT-modified GC electrode (Nafion-MWCNT/GC) and Pt nanoparticle-modified GC electrode (Nafion-Pt/GC) were prepared by coating aliquots of ethanol suspension solutions containing MWCNT + 0.05% Nafion and carbon-supported Pt nanoparticles (their average diameter is 2.3 nm, with a mass ratio of 46.3% Pt and 53.7% carbon, Tanaka Kikinzoku, Japan) + 0.05% Nafion, respectively. The surface coverages of MWCNT and Pt nanoparticle are 0.21 mg cm^{-2} and 56 µg cm^{-2}, respectively, on the surface of the cleaned GC disk electrode. Nano-MnOx electrodeposited GC and Nafion-MWCNT/GC disk electrodes (abbreviated as nano-MnOx/GC and nano-MnOx/Nafion-MWCNT/GC, respectively) were prepared by repeating 45 times the potential scan at 20 mV s^{-1} between 0 and 0.4 V in 0.1 M sodium sulfate solution containing 0.1 M manganese(II) acetate. The amount of Mn on the electrode surface was estimated to be 37 µg cm^{-2} using an inductively coupled plasma optical emission spectroscopy (JEOL).

SEM images of Nafion-MWCNT/GC electrode are given in Figures 1a and 1b with different magnifications, showing that MWCNTs are relatively uniformly distributed over the whole surface. Figures 1c and 1d show the SEM images of nano-MnOx electrodeposited Nafion-MWCNT/GC electrode. The nano-MnOx is composed of nanorods with a diameter of ca. 20 to 30 nm and a length of ca. 75 to 100 nm attached on the wall surfaces of MWCNT. The MnOx obtained is similar in shape to that electrodeposited directly on GC substrate, but the nano-MnOx is more densely electrodeposited on the surface of MWCNT than on the GC surface. This result indicates that the oxidation-treated MWCNT is favorable for a dense electrodeposition of nano-MnOx.

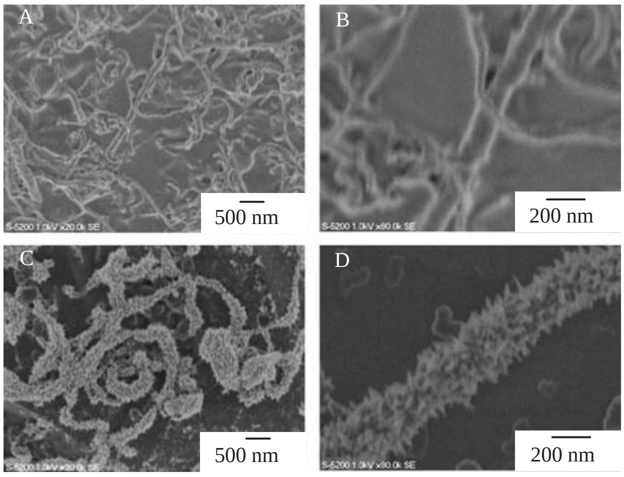

Figure 1. SEM images for Nafion-WMCNT (A and B) and nano-MnOx/Nafion-WMCNT (C and D).

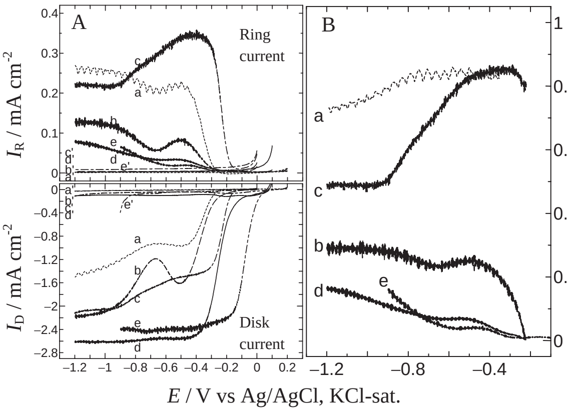

Figure 2. (A) RRDE voltammograms obtained at GC (a and a′), nano-MnOx/GC (b and b′), Nafion-MWCNT/GC (c and c′), nano-MnOx/Nafion-MWCNT/GC (d and d′) disk and Nafion-Pt/GC (e and e′) disk and Pt ring electrodes in N_2 saturated (a′, b′, c′, d′, and e′) and O_2 saturated (a, b, c, d, and e) 0.1 M KOH solutions. Rotation rate: 400 rpm. Potential scan rate: 10 mV s^{-1}. The ring electrode potential was kept at 0.5 V. (B) Plots of fraction of H_2O_2 formation (X) vs potential obtained from Figure 2a.

RRDE voltammetry has been used to study the catalytic activity of the dual catalysts system for O_2 reduction. The RRDE voltammograms obtained at bare GC, Nafion-MWCNT/GC, nano-MnOx/GC and nano-MnOx/Nafion-MWCNT/GC disk electrodes together with Nafion-Pt/GC disk electrode in 0.1 M KOH solution are shown in Figure 2a. The potential of the Pt ring electrode (E_R) was kept at 0.5 V vs Ag/AgCl to detect the reduction intermediate (HO_2^-) produced at the disk electrodes. O_2 reduction at Nafion-MWCNT/GC disk electrode (curve c) shows two reduction steps similarly to that at the bare GC disk electrode (curve a). However, the limiting current for the first reduction step is larger than that at the bare GC electrode and the half-wave potential shifts by ca. 130 mV to the positive direction of potential compared with that at the GC disk electrode, and the ring current during the first reduction step is larger than that at the bare GC electrode. These results may suggest that the quinone functional groups produced on the surface of MWCNT by the acid oxidation treatment mediate the one-electron reduction of O_2 to O_2^-, just as in the case of the mediated O_2 reduction by quinone-like functional groups on the GC electrode surface.[2a,8]

The favourable electrodeposition of nano-MnOx on the Nafion-MWCNT/GC electrode clearly resulted in a much smaller ring current for HO_2^- oxidation and a larger disk current for O_2 reduction, indicating that nano-MnOx can catalyze efficiently the disproportionations of the O_2 reduction intermediate (O_2^-) into O_2 and HO_2^- and further HO_2^- into O_2 and OH^-, and substantially enables a four-electron reduction of O_2.[2a] The magnitude of the ring current and disk current for the nano-MnOx/Nafion-MWCNT/GC electrode is almost the same as that at the Nafion-Pt/GC electrode (see curves d and e). Therefore, the dual catalysts system composed of MWCNT and nano-MnOx possesses a high electrocatalytic activity toward 4-electron O_2 reduction through the redox-mediation of O_2 to O_2^- by functional quinone groups on the surface of MWCNT and the subsequent disproportionations of O_2^- to O_2 and HO_2^- and further HO_2^- into O_2 and OH^- catalyzed by nano-MnOx, although the half-wave potential for O_2 reduction at the nano-MnOx/Nafion- MWCNT/GC electrode is by ca. 0.15 V more negative than at the Nafion-Pt/GC electrode. The electrocatalytic activity of the present dual catalysts system for O_2 reduction can further be evidenced from the plots of fraction of HO_2^- formation[9] ($X = 2I_R/(NI_D + I_R)$) vs electrode potential as shown in Figure 2b. The collection efficiency value (N) at Nafion-coated GC disk and Pt ring electrodes used in this study was estimated to be 0.34 for the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox couple in 0.1 M Na_2SO_4 solution. That is, the values of X obtained for both nano-MnOx/Nafion-MWCNT/GC and Nafion-Pt/GC disk electrodes are almost the same in the potential range of −0.1–−0.75 V and are much smaller than those obtained for the GC and Nafion-MWCNT/GC disk electrodes. In addition, at more negative potential than −0.75 V, the X value at the dual catalysts electrode is smaller than at the Nafion-Pt/GC electrode and thus it should be noted that the dual catalysts system is more efficient for 4-electron O_2 reduction than the Pt nano-particles system. Further, we can see that the catalytic activity of nano-MnOx electrodeposited on the Nafion-MWCNT for 4-electron O_2 reduction is higher than that electrodeposited on the GC electrode (see Figure 2b curves b and d).

In summary, the present results demonstrate that the dual catalysts system composed of MWCNT and nano-MnOx possesses a bifunctional catalytic activity for the redox-mediating reduction of O_2 to O_2^- and sequentially disproportionating O_2^- into HO_2^- and finally into OH^-, and consequently enables an apparent 4-electron reduction of O_2 in alkaline media. The catalytic activity for O_2 reduction at the dual catalysts electrode was greatly improved in comparison with the electrodes modified with either of the dual catalysts: its performance is not far from that of a Pt-nanoparticle electrode.

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