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Development of high performance of Co/Fe/N/CNT nanocatalyst for oxygen reduction in microbial fuel cells

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ABSTRACT

In this paper, we synthesized a unique cathode catalyst Co/Fe/N/CNTs with high performance oxygen reduction. Through the π-stacking force, the cobalt porphyrins (CoTMPP) and iron phthanlocyanine (FePc) were deposited to the carbon nanotubes (CNTs) sidewall. The CoTMPP/FePc functionalized CNTs were used as the precursor to prepare the Co/Fe/N/CNTs based oxygen reduction nanocatalyst through high-temperature pyrolysis. The as-prepared catalyst exhibited higher electrocatalytic activity for the reduction of dioxygen than that of the Co/Fe/N/graphite and commercial Pt/C. The high electrocatalytic activity and good stability for dioxygen reduction made the Co/Fe/N/CNT as a potential candidate for the efficient cathode material in microbial fuel cells (MFCs). The maximum power of the MFC using the Co/Fe/N/CNT as cathode catalyst is 751 mW m^{-2}, which was 1.5 times larger than the MFC with the commercial Pt/C catalyst under the same condition. Such an approach is useful for the improvement of the cathode performance and to provide the basis for the development of the efficient MFC cathodes.

1. Introduction

Microbial fuel cells (MFCs), which convert biochemical energy to electrical energy, are a cost-effective, sustainable energy process [1,2]. MFCs could be used in biomass-based energy production, but many technical challenges must be overcome before they will be practical for renewable energy production. The most immediate need for an MFC-based technology is to scale up in a cost-effective manner [3]. To date, platinum is extensively utilized to catalyze the oxygen reduction reaction (ORR) in MFCs. Because platinum is rare and expensive, alternative catalyst materials with a high catalytic activity toward the ORR and sufficient chemical stability is of a high priority. It has been known for several years that N_4-metal macrocycles (tetraazaannulenes, porphyrins, and phthalocyanines) with metal Fe or Co, adsorbed on carbon and heat-treated range from 600 to 1000 °C, are good catalysts for the reduction of O_2 [4–6]. In contrast to the platinum, the better oxygen reduction performance of the pyrolyzed N_4-metal macrocycles in neutral pH condition makes them attractive in the MFC application [7]. Catalyst support materials such as Vulcan XC-72R, Black Pearl, Ketjenblack and other carbon materials are commonly used [6,8–10], but these supports are known to be weakly active toward the electroreduction of oxygen. Because of the unique and useful electrical and mechanical properties, carbon nanotubes (CNTs) exhibit promising potential ability to promote electron transfer reaction when used as electrode materials in electrochemical reaction [11,12]. The CNTs modified with N_4-macrocycles have been increasingly investigated because these flat, planar aromatic structures are ideal for π-stacking interactions with the sidewalls of CNTs [12,13]. Take the advantage of CNTs as the carbon support, the electrocatalytic performance of heat-treated N_4-metal macrocycles could be more efficient. In this paper, using CNTs as the carbon support, we prepared the Co/Fe/N/CNT oxygen reduction catalyst. Rotating disk electrode (RDE) voltammetry and rotating ring-disk electrode (RRDE) voltammetry demonstrated that the Co/Fe/N/CNT can catalyze an almost four-electron reduction of O_2 to H_2O in neutral pH condition. We have studied noble-metal free Co/Fe/N/CNT catalyst in comparison with platinum and Co/Fe/N/graphite by means of galvanodynamic, poteniostatic and MFC experiments. The Co/Fe/N/CNT catalyst exhibited slightly higher current density and better power output compared with the Co/Fe/N/graphite and commercial Pt/carbon electrode. The high electrocatalytic activity and good stability for dioxygen reduction made the Co/Fe/N/CNT nanocatalyst attractive as a potential candidate for the efficient cathode material in MFCs.

2. Experimental

2.1. Catalyst preparation

Iron(II) phthanlocyanine (FePc) and cobalt tetramethoxyphenylporphyrin (CoTMPP) were synthesized in our

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lab. Multiwalled carbon nanotubes (MWNTs) (95%, 20–50 nm) purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China) were first shortened and functionalized by sonicating in a mixture of concentrated 16 mol L^{-1} HNO_3 and 18 mol L^{-1} H_2SO_4 (1:3, v/v) for 6 h followed by extensive washing in deionized water until the filtrate was neutral. Then the pH was adjusted to 8.0 to achieve net negatively charged carboxylate anions. The negatively charged CNTs were centrifuged at 10,000 rpm for 30 min to remove the supernatant and dried in a vacuum. Varying amounts of CoTMPP and FePc were dissolved in THF. This mixture was added to a dispersion of CNT in THF and was treated with ultrasonic for 30 min. The THF was removed by the rotary evaporator and the CoTMPP/FePc/CNT composite was dried at 80 °C overnight. Subsequently, the impregnated CNT was heat-treated 750 °C for 2 h with heating rate of 2 °C/min under N_2 gas. The catalyst was allowed to cool down to room temperature before it was exposed to air. Then this catalyst was ball-milled for 1 h. The Co/Fe/N/graphite was synthesized under the same procedure with graphite instead of the CNT. The catalyst was mixed with 0.5% Nafion (Aldrich) in a ratio of 50 μL Nafion solution to 1 mg catalysts in an ultrasonic bath. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 EM with an accelerating voltage of 200 kV.

2.2. Electrochemical characterization

Electrochemical experiments were performed with EG&G 273A (Princeton Applied Research) and carried out in a conventional three electrode arrangement using Nafion and catalyst mixture modified glass carbon (GC 3-mm diameter) as the working electrode, twisted platinum wire as the auxiliary electrode and an Ag/AgCl (saturated KCL) as reference electrode. An EG&PARCmodel 636 rotating ring-disk electrode (RRDE) system and an EG&PARC model 366 bipotentiostat were used for RDE and RRDE voltammetry experiments. A rotating GC disk platinum ring electrode was used as a working electrode. The collection efficiency (*N*) of the ring electrode obtained by reducing ferricyanide at a disk electrode was 0.193.

2.3. MFC test system setup

MFC tests were conducted using a single chamber cubic reactor as previously described [2] with electrode geometric areas of 3 cm^2. The electrode spacing was 2 cm, with a total reactor volume of 6 mL. MFCs were inoculated with *E. coli* K12. Details on the bacteria growth and activation can be found in previous study [2]. The solution in the chamber was 200 mM phosphate buffer solution (PBS pH 7.0) with glucose 1 g L^{-1}. The Toray carbon paper (without wet proofing; E-Tek) was used as the MFC anode electrode. Cathodes were (wet-proofed type B carbon cloth; E-Tek) coated with four poly(tetrafluoroethylene) (60% dispersion solution from Aldrich) diffusion layers on the side exposed to air [14]. The catalyst was casted on the side of the carbon cloth exposed to solution with catalyst loading of 1 mg cm^{-2}. The MFC operated with a 200 Ω external resistor except as noted.

3. Results and discussion

It was reported that the mixture of the CoTMPP and FePc has better stability and higher electroactivity towards the mono-component catalysts [15], here we applied these two N_4-metal macrocycles together with the CNT to synthesis the oxygen reduction catalysts. The CoTMPP and FePc can attach to the CNT surface by π-stacking interactions [13]. The formation of this nanohybrid was characterized by XPS as shown in Fig. 1. The XPS spectrum of the Co/Fe/N/CNT exhibited the Fe 2p binding energies peak at 711.6. While the Co 2p peaks was at 779.8 eV, which are typically characteristic of Co. The oxygen reduction activity of Co/Fe/N/CNT composite, Co/Fe/N/graphite and a commercial Pt/carbon catalyst were compared using galvanodynamic linear sweep polarization measurements (Fig. 2) in oxygen saturated 0.2 M PBS (pH 7.0). The Co/Fe/N/CNT composite modified electrode showed the highest open circuit potential (473 mV), followed by Co/Fe/N/graphite and a commercial Pt/carbon with 376 mV and 330 mV, respectively. In contrast to conventional carbon supported electrocatalysts, the higher electrochemical activity could be attributed to the higher catalytical active surface in the presence of the CNTs. At the same time, the CNTs played an additional role in the dioxygen reduction process, which might make the electron transfer through the films easier and decrease the oxygen reduction overpotential. That is to say that the electron transfer barrier was lower in this system that included short CNTs as connectors. In virtue of the excellent performance of CNTs in this catalyst, the oxygen reaction was more efficient than the conventional carbon material based catalyst. The molar ratio between the CoTMPP and FePc was optimized, the best stability and highest current of this catalyst was found to be 1:1 between CoTMPP and FePc. This result was consistent with the previous reports [15]. To increase the concentration of catalytic centers, the loading of CoTMPP/FePc onto the CNTs was gradu-

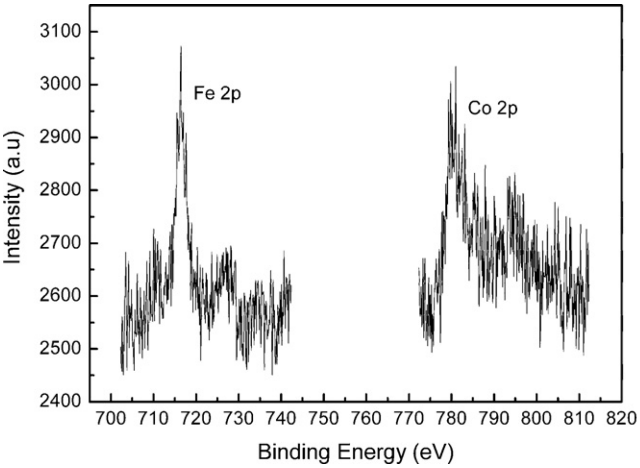

Fig. 1. X-ray photoelectron spectra of Co and Fe energy levels of Co/Fe/N/CNT nanohybrids.

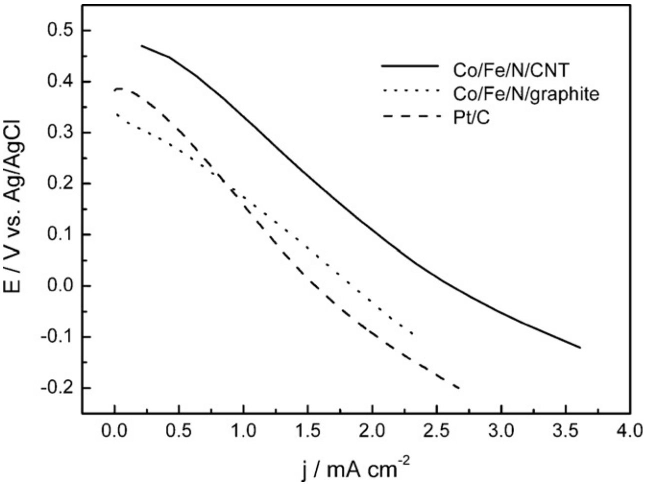

Fig. 2. Galvanodynamic polarization plots of the electrocatalytic oxygen reduction at Co/Fe/N/CNT (solid line), Co/Fe/N/graphite (dot line) and Pt/C (dash line) modified GC electrode. The scan rate was 10^{-5} A s^{-1}.

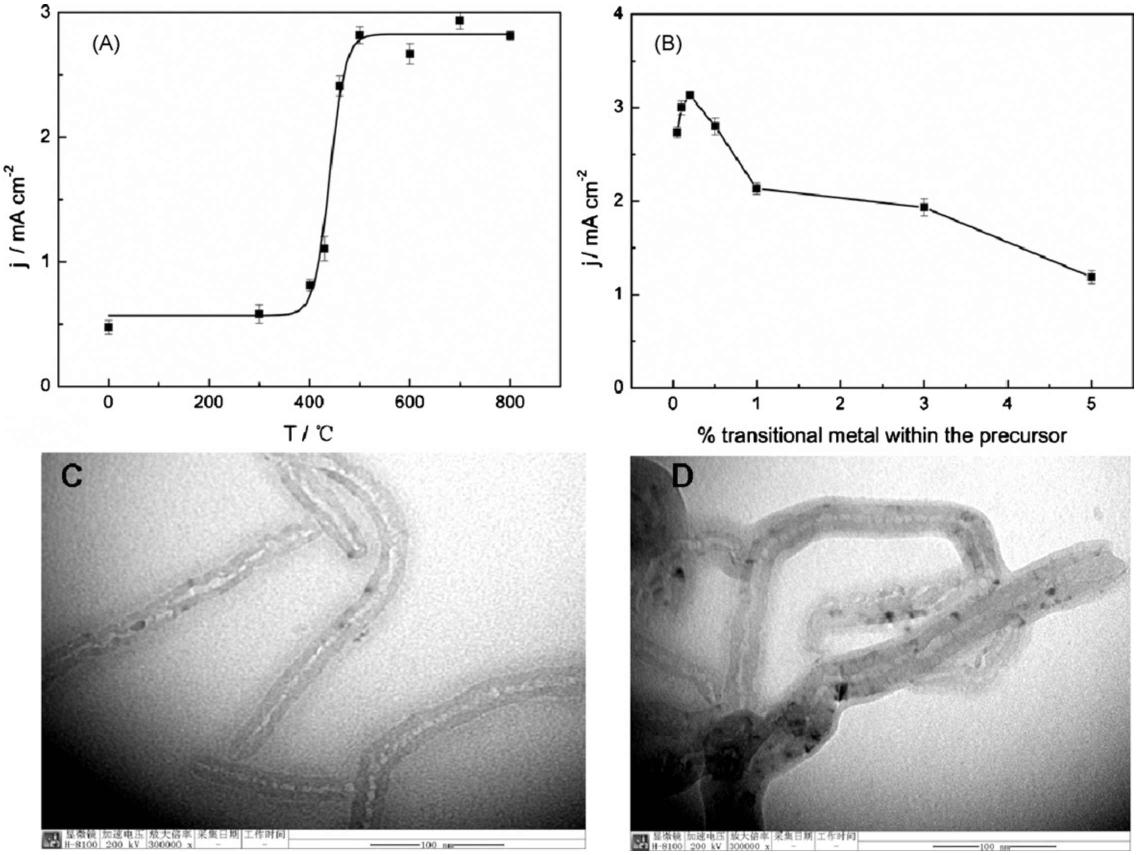

Fig. 3. (A) Current density of oxygen reduction obtained at 0.0 V vs. Ag/AgCl (saturated with KCl) of pyrolysed CoTMPP/FePc/CNTs plotted vs. the final heat treatment temperature. (B) Current density of oxygen reduction obtained at 0.0 V vs. Ag/AgCl (saturated with KCl) of pyrolysed CoTMPP/FePc/CNTs plotted vs. the TM-macrocycles content in the precursor mixture. TEM images of heat-treated Co/Fe/CNTs loaded with 0.2% CoTMPP/FePc (C) and 6% CoTMPP/FePc (D).

ally raised. Surprisingly, the electrochemical activity in the oxygen reduction reaction (ORR) decreased with increasing amounts of CoTMPP/FePc (Fig. 3B). Fig. 3C and D showed TEM images of a sample loaded with 0.2% and 6 wt% CoTMPP/FePc, respectively. In the latter case the single particles was found to stick together within a CNT, which was obviously formed during the pyrolysis of CoTMPP/FePC. With higher load of TM-macrocycles, the metal was supposed to form metal particles not to bind with nitrogen in the active sites. Those dense particles had no noteworthy electrochemical activity [9]. Fig. 3A showed the current density at 0.0 V in dependence on the temperature of the heat treatment. Compared to the small electrochemical activity of the untreated precursor mixture, a drastic enhancement of the current density was achieved by the heat treatment between 350 and 800 °C. The sharp increase around 400 °C could be ascribed to the macrocycles melting and then the catalytic active site formed on the MWNT surface. The structure of these centers was assumed to be very similar to the metal N_4-chelate structure of the precursor. All results described in the following were carried out employing 0.1% CoTMPP/0.1% FePC/CNT heat treated at 750 °C.

We had investigated the electrocatalytic activity of the Co/Fe/N/CNT composite for dioxygen reduction in detail. To quantify the stoichiometry of the catalytic reduction of O_2, voltammetric measurements at a RDE had been performed (Fig. 4). Savéant and coworkers [16] have described the kinetics process of the catalytic reaction at the modified electrodes using the following equation, when the mass-transport process in the solution and the catalytic reaction become dominant:

$$\frac{1}{i_l} = \frac{1}{0.62} nFAc_0 D^{2/3} \nu^{-1/6} \omega^{1/2} + \frac{1}{n} FAc_0 k\Gamma, \quad i_K = nFAc_0 k\Gamma \tag{1}$$

where n, A, c_0, D, ν, ω, k and Γ represent the number of electrons transferred, the electrode area, the bulk concentration of O_2 in the solution, the O_2 diffusion coefficient, the kinematics viscosity, the rotation rate, the reaction rate constant, and the surface concentration of the catalyst, respectively. The other symbols have their usual meanings. The Koutecky–Levich plots obtained from the current–potential curves of O_2 reduction in air-saturated PBS at Co/Fe/N/CNT composite modified rotating GC disk electrode. The calculated number of electrons involved in the reduction of O_2

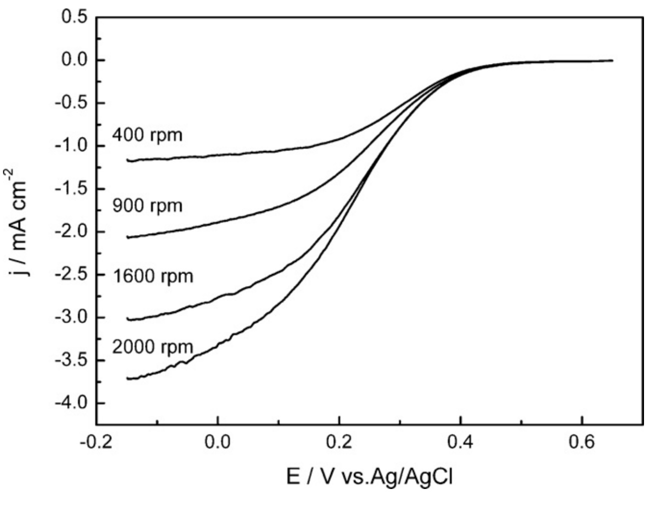

Fig. 4. Current–potential curves of dioxygen reduction at a RDE modified with Co/Fe/N/CNTs with different rotating rates.

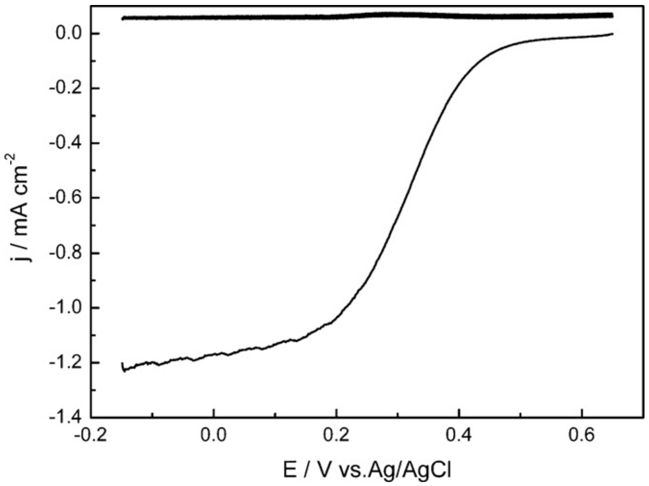

Fig. 5. RRDE voltammograms of the GC modified with Co/Fe/CNT (disk scan rate, 20 mV s^{-1}; ω 100 rpm). The potential of the platinum ring electrode was set to 1.0 V to oxidize H_2O_2 to O_2 completely. All electrochemical experiment carried out in oxygen saturated solution (0.2 M PBS, pH 7.0).

was found to be 3.75. A RRDE was employed to determine the quantity of H_2O_2 (Fig. 5). The ratio of the ring to disk current, i_R/i_D, was 0.019. The electrons involved in the reduction of O_2 was found to be 3.81, according to the equation $n = 4 - 2(i_R/i_D N)$, which was almost identical to that acquired from the Koutecky–Levich plot. While taking account of the rates of H_2O_2 and H_2O production are i_R/N and $i_D - i_R/N$, respectively, the formation efficiency of H_2O for the Co/Fe/N/CNT composite amounted to 82%, according to $P_{(H_2O)} = (N(i_D/i_R) - 1)/(N(i_D/i_R) + 1)$. This result indicated that the reduction of dioxygen at the Co/Fe/N/CNT composite electrode mainly supported the four-electron pathway to produce a low yield of H_2O_2. There was no observable decrease in the catalytic current of dioxygen reduction of Co/Fe/N/CNT nanocomposite after continuous scanning for 2 h. The good stability of the Co/Fe/N/CNT nanocatalyst was very useful in cathode material of MFCs.

To demonstrate such a possibility, the MFC tests were conducted using this catalyst. With the Co/Fe/N/CNT as the cathode catalyst, the performance of cell at a constant external load of 200 Ω was recorded over time (Fig. 6). As shown in Fig. 7, the open circuit potential of the Co/Fe/N/CNT composite cathode based MFCs were 0.76 V. The maximum power output of the Co/Fe/N/CNT based MFC was 751 mW m^{-2} at the cell potential 480 mV. The maximum power output of the Co/Fe/N/graphite and Pt/carbon based MFC were 618 and 498 mW m^{-2}, respectively (data not show). In this investigation, the power density was increased by 21% compared with using Co/Fe/N/graphite as the cathode catalysts. Both MFCs with non-Pt cathodes showed higher power output than the commercial available E-Tek Pt/C cathode. These results suggested that Co/Fe/N/CNT is a suitable material for the preparation of MFCs. The CNT as the support material facilitated the increase in active surface; while the electrons may be transferred to the electrode easily via conductivity paths assembled by CNTs. The stability of the MFC was examined at the load resistance of 200 Ω as a function of time. The power output did not change obviously after 2 months.

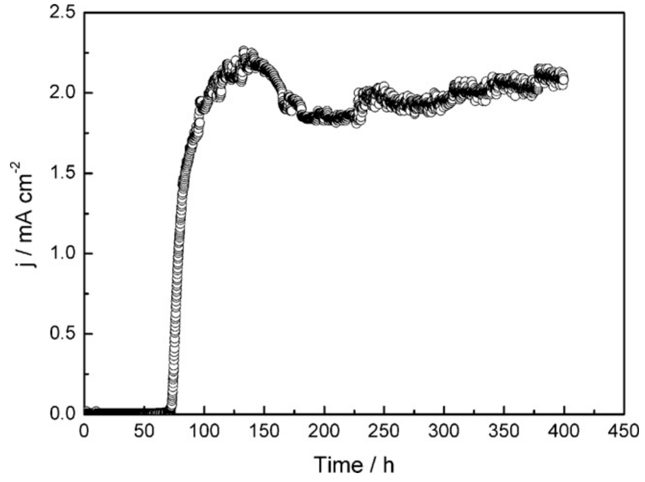

Fig. 6. Current generation over time of the assembled MFC.

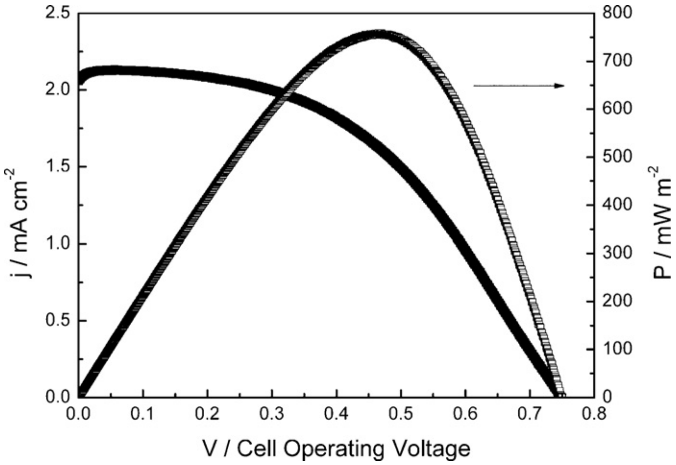

Fig. 7. Power generation as a function of current density and polarization curve of the assembled MFC.

4. Conclusion

In this paper, we prepared the cathode oxygen catalyst Co/Fe/N/CNT from the CoTMPP and FePc with molar ratio 1:1 functionalized CNT. This noble-metal free Co/Fe/N/CNT catalyst exhibited higher current density and better power output compared with the Co/Fe/N/graphite and commercial Pt/carbon electrode. The introduction of CNTs could facilitate the oxygen reduction reaction with less activation overpotential and increased the performance of the MFC accordingly. The maximum power of the MFC with the Co/Fe/N/CNT as cathode catalyst is 751 mW m^{-2}, which was 1.5 times larger than the MFC with the commercial Pt/C catalyst under the same condition. The high electrocatalytic activity and good stability for dioxygen reduction made the Co/Fe/N/CNT nanocatalyst as an attractive potential candidate for efficient cathode material in MFCs. It was reported that the MFC cathode performance could be improved with the cathode catalyst layers prepared by ink spraying rather than paste painting in this investigation. Further work is necessary to study the mechanisms of the oxygen reduction at the Co/Fe/N/CNT nanocatalysts more in detail and to optimize the performance of the system.

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