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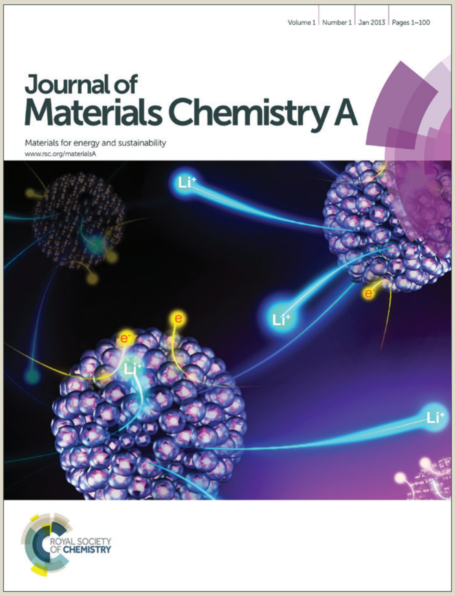

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ARTICLE

Facile synthesis of nitrogen and fluorine co-doped carbon material as efficient electrocatalyst for the oxygen reduction reaction in air-cathode microbial fuel cells

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Kai Meng,[a,b] Qin Liu,[a] Yiyin Huang[a] and Yaobing Wang[*a]

Nitrogen and fluorine co-doped carbon black (BP-NF) was prepared via direct pyrolysis of the mixture of polytetrafluoroethylene (PTFE) and BP-2000 under the ammonium atmosphere for high efficient ORR electrocatalyst in air-cathode of microbial fuel cells (MFCs). The electrocatalytic activity of BP-NF is higher than that of single nitrogen or fluorine doped carbon material (BP-N, BP-F), with an onset potential of E = 0.2V (BP-NF), E = 0.1V (BP-N), and limiting current density of I = 4.5 mA cm^{-2} (BP-NF), I = 0.31 mA cm^{-2} (BP-F), respectively. The result demonstrated that the synergistic ORR catalytic effect in N and F co-doping carbon material.The maximum power density of MFC with BP-NF as the cathode catalyst (672 mA cm^{-2}) was higher than that with commercial Pt/C (572 mA cm^{-2}).

1. Introduction

Microbial fuel cells (MFCs) have been used to wastewater treatment and electricity generation in recent years as one of green and sustainable energy resources and have attracted much attention.[1,2] The technological bottlenecks of MFCs are the development of electrocatalysts with a high price/performance ratio for oxygen reduction reactions (ORR).[3] Platinum (Pt) and its alloys have long been regarded as the best electrocatalysts for ORR at the cathode of MFCs, however, Pt-based catalysts suffer from problems, such as the high cost, poor durability and limited reserve in nature.[4-5] These problems hamper the magnification and commercialization of MFCs. Thus developing non-precious metal and metal-free electrocatalysts to replace Pt-based catalysts is an important research field in MFCs.

The heteroatom (N, B, S, P, or F) doped carbon materials, including carbon nanotubes (CNTs),[6,7] graphene,[8,9] graphitie[10,11] and activated carbon (AC),[12,13] have attracted intense attention because they demonstrate high catalytic activity, long-term durability toward the ORR and excellent anti-poisoning, and which are considered to have great potential as a rising category of potential candidates for the replacement of Pt-based catalysts.[14-17] To our best knowledge, however, only a few studies about the application of N and F co-doped carbon in MFCs have been reported so far. Single N-doped carbon nanotubes (NCNTs) and F-doped graphene exhibit high electrocatalytic activity and durability for the ORR under neutral conditions of MFCs.[6,18] However, these catalysts were based on nanostructured carbon prepared via a complex procedure, and unpractical for large-scale application.[19] Carbon black and activated carbon were the inexpensive and high surface area carbon materials that can be easily tailored to improve their performance for the desired application. F-doped carbon blacks (CB-F) exhibit superhigh ORR electrocatalytic activity and long-term operation stability in alkaline medium tests.[18,20] Meanwhile, N-doped activated carbon (AC-N) is prepared by pyrolysis of AC under NH_3 gas showed high ORR catalytic activity for MFC.[21] Surprisingly, we found that direct pyrolysis of the mixture of PTFE and BP-2000 under the ammonium atmosphere can successfully co-doped N and F atoms into carbon black and got BP-NF material. Furthermore it is a facile, green, inexpensive and easy to be scaled-up method.

In this study, we report a facile method, by directly pyrolyzing the polytetrafluoroethylene (PTFE) mixed BP-2000 in the presence of the ammonium atmosphere, for preparation of N and F co-doped carbon black catalyst. The structure and morphology of the BP-NF was characterized by the TEM, BET and XPS. The catalytic activity of BP-NF in neutral medium was examined by electrochemical measurements and compared with single N or F doped carbon catalyst. Finally, the performance of BP-NF in MFCs was evaluated and compared with commercial Pt/C.

2. Experimental

2.1 Materials

Preparation of N, F co-doped carbon black (BP-2000) material

The synthesis of BP-NF was based on one-step procedure with BP-2000 (Black Pearls 2000, Cabot Corporation carbon blacks), polytetrafluoroethylene (PTFE, 60 wt%, DuPont, USA) as initial materials. The mixture of BP-2000 and PTFE in a quartz tube furnace were pyrolyzed at 950 °C with a rate of 7.5 °C min^{-1} under the ammonium atmosphere, and maintained at the target temperature for 1 h, after cooling down to room temperature and collected the black product. For comparison, the BP-2000, BP-F or BP-N was also obtained in a way without or with ammonium or PTFE by the thermal annealing of BP-2000 at 950 °C.

Characterization of the N, F co-doped carbon black material

Transmission electron microscope (TEM) image was performed on (JEM-2010) with an acceleration voltage of 200 kV. X-ray photoelectron spectrum (XPS, VG ESCALAB 250) was tested on a 1487 eV X-ray photoelectron spectrometer using Al K_α radiation exciting source. The Brunauer-Emmett-Teller (BET) measurement was determined by using ASAP 2010 at 77 K through nitrogen adsorption apparatus. The pore size distributions (PSD) were acquired from the N_2 sorption isotherms based on Density Function Theory (DFT) model.

2.2 Electrochemical measurements

All electrochemical measurements were performed with a CHI660e electrochemical working station (CH Instrument Inc.), with a three-electrode cell comprising an Ag/AgCl electrode (saturated with KCl, 0.197 V vs. SHE) as reference electrode, Pt electrode as counter and a glassy carbon (GC) disk with a diameter of 5 mm was used as the working electrode. The activity for the oxygen reduction reaction (ORR) was evaluated from voltammetry by the nitrogen and fluorine co-doped carbon materials as electrodes. Cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements were carried out in the O_2-saturated 50 mM PBS solution (pH 7.0 and conductivity 6.533 mS cm^{-1}) at room temperature. In the preparation of electrode, 10 mg of catalyst and 50 μL of Nafion solution were dispersed into 1.95 mL of isopropanol. Then, 4 μL of catalyst dispersion was transferred onto GC electrode and dried for the following test.

This cubic sing-chamber air-cathode MFCs configuration was constructed in accordance with a previously reported method.[22-24]

The cell voltage across the external resistor was measured using a battery test system equipped with a data acquisition system (LANHE, CT2001A, Wuhan, China). Polarization and power density curves were measured by varying the external resistance from 1500 Ω to 200 Ω, with each resistor used for a complete cycle. Current density (mA cm^{-2}) was calculated from I = U/(RA), and power density (mA cm^{-2}) was calculated from P = UI/A, where U (V) is the cell voltage, and A (cm^2) is the projected area of the air-cathode (7 cm^2). All experiments were conducted at room temperature (30 ± 1 °C).

The electron transfer numbers (n) were calculated from the slopes of the Koutecky-Levich (K-L) plots using

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}$$

$$B = 0.62 n F C_0 (D_0)^{2/3} v^{-1/6}$$

where J is the measured current; ω is the electrode rotationrate in rad s^{-1}; F is the Faraday constant (96485 C mol^{-1}); C_0 is the concentration of O_2 (1.26×10^{-6} mol cm^{-3}); D_0 is the diffusion coefficient of O_2 (2.7×10^{-5} cm^2 s^{-1}) and v is the kinematic viscosity of the electrolyte (0.01 cm^2 s^{-1}).

3. Results and discussion

3.1 Physical characterization

The structure and morphology of BP-NF electrocatalyst were investigated by transmission electron microscopy (TEM) as shown in Fig. 1. The micro-region in Fig. 1a exhibits that there are abundant nanoparticles with an outer diameter of about ~20 nm stacked together. The elemental mapping images in Fig.1b~e indicated that the N and F elements were uniformly distributed on the carbon black, which suggested the successful formation of N and F co-doped carbon black. Furthermore, the EDX spectra of the as-prepared sample indicate that the atomic ratios of N and F were about 0.67 at% and 0.16 at% in BP-NF (Supplementary Fig. S1). The Brunauer–Emmett–Teller (BET) specific surface area of BP-NF was characterized through the nitrogen sorption technique. The BET specific surface area for BP-NF was calculated to be 1515.41 m^2 g^{-1}. The steep increase in nitrogen adsorption-desorption isotherms of BP-NF display small hysteresis loops at the pressure region (P/P_0 = 0.9) clearly suggest that the pore volume is mainly contributed by mesopores (Fig. 2a). For comparison, the surface areas of BP-2000, BP-N and BP-F were estimated to be 1378.57, 1350.04 and 1403.64 m^2 g^{-1}, respectively, which is slightly lower than that of BP-NF (Supplementary Fig. S2). The derived pore size distribution of BP-NF is plotted in Fig. 2b, the corresponding pore size distribution plot demonstrated the well-defined mesopores about 1.5-2 nm existed in BP-NF, which is similar with the single N or F doped carbon black. These results demonstrated that the N and F atoms co-doped in carbon black slightly varied the carbon black surface properties, but mainly introduced the catalytic active sites into carbon black.

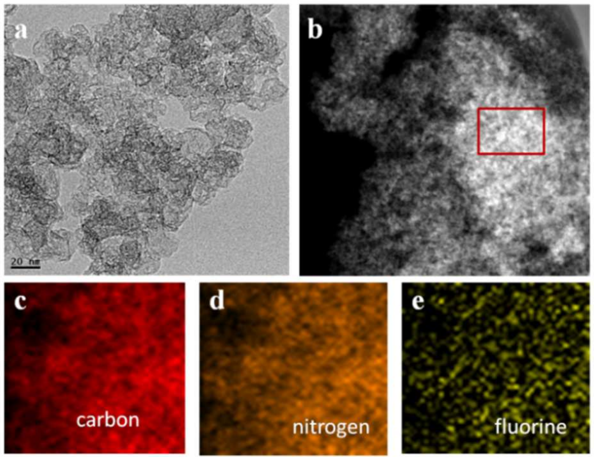

Fig. 1 (a) High-magnification TEM image of BP-NF and (b) EDX element distribution maps of C (c), N (d) and F (e).

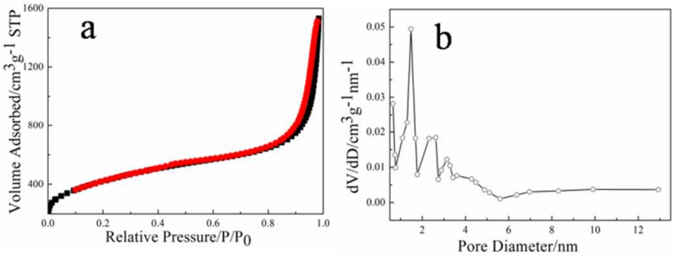

Fig. 2 (a) N_2 sorption isotherms and (b) pore size distributions of BP-NF.

XPS was performed to further study the N, F elements contents and their states of bonding with carbon black. In the synthesized BP-NF, the atomic ratios of N and F were about 0.53 at% and 0.17 at%, respectively, which is agree with the result of the EDX. The N1s XPS spectrum of BP-NF, as shown in Fig. 3a, is located at 397-402 eV, which can be split into two peaks corresponding to pyridinic-N (398.4 eV) and pyrrolic-N (400.3 eV), both of which have positive effects on electrochemical performance of carbon catalyst.[24-26] Fig. 3b showed the high-resolution XPS spectra of F 1s for BP-NF with a single peak at 684.6 eV, which could be attributed to an ionic C–F bond.[18] Since it has been found that the ionic C–F bond is more active than covalent C–F bond,[27] the high catalytic activity of BP-NF could be attributed in part to the content of F in the form of the ionic state.

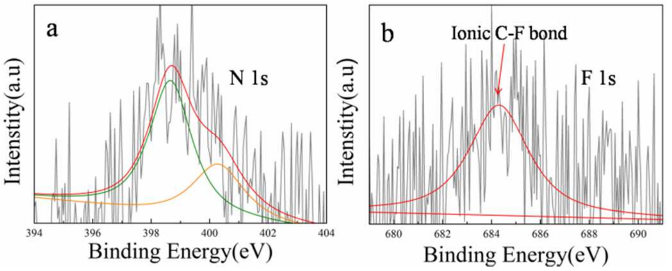

Fig. 3 High-resolution N 1s (a) and F1s (b) XPS spectra of BP-NF.

3.2 Electrochemical characterization

The electrocatalytic activity of BP-NF for ORR was examined by cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements. As shown in Fig. 4a, the CV curves present the electrocatalytic activity of BP-2000, BP-F, BP-N and BP-NF in O_2-saturated 50 mM PBS. BP-NF exhibited the cathodic peak at a more positive potential of 0.04 V for ORR, compared with that of BP-2000 (-0.18 V), BP-F (-0.12 V), and BP-N (-0.09 V). Linear sweep voltammetry (LSV) curves as shown in Fig. 4b were measured on the rotating-disk electrode (RDE) at a rotation rate of 1600 rpm to further investigate the ORR activity. It can be observed that the onset potential of BP-NF was 0.20 V, which was not as excellent as Pt/C (0.24 V), but was greatly improved compared to the BP-N (0.1V). The limiting current density for BP-NF was 4.5 mA cm^{-2}, which is substantially higher than 4 mA cm^{-2}, 3.6 mA cm^{-2} and 3.1 mA cm^{-2} of the Pt/C, BP-N and BP-F catalysts, respectively. The above results indicate that the BP-NF catalyst shows higher electrocatalytic activity than BP-N, BP-F catalysts, and it is comparable with commercial Pt/C catalyst. This may be caused by the new active sites resulted from the nitrogen and fluorine co-doping. As presented in Fig 4c, the current density of BP-NF increased from 1.8 mA cm^{-2} to 4.5 mA cm^{-2} as the rotation rate increased from 200 to 1600 rpm. The Koutecky-Levich (K-L) plots at the potential of -0.2, -0.3 and -0.4 V were obtained and displayed good linearity. The n value for BP-NF was calculated to be 3.8, for comparison, K-L plots of BP-2000, BP-N and BP-F showed the low or similar electron transfer number of 2.7, 3.6 and 3.8, respectively (Supplementary Fig S3), indicating a pathway of 4e- for BP-NF. Whereas the n value for Pt/C was 3.74, which was lower than that for BP-NF. These results were in agreement with the CV results.

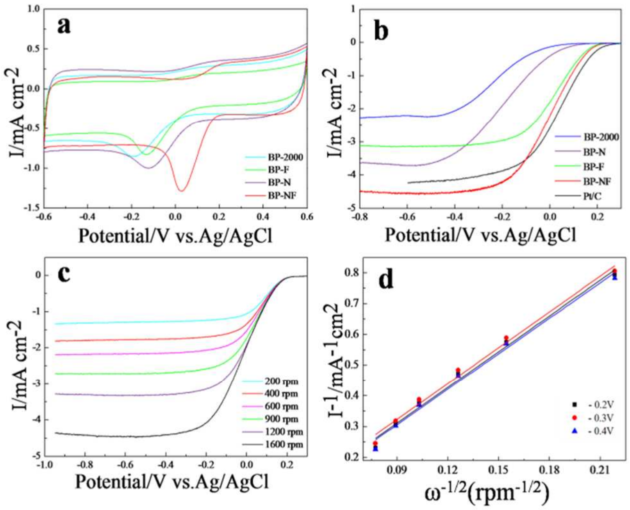

Fig.4 (a) CV of BP-2000, BP-F, BP-N, BP-NF in O_2-saturated 50 mM PBS; (b) LSVs for BP-2000, BP-F, BP-N, BP-NF and Pt/C in O_2-saturated PBS at a rotation rate of 1600 rpm; (c) LSVs for BP-NF at different rotation rates; (d) K-L plots for BP-NF at -0.2, -0.3 and -0.4 V.

Herein we presented some reasons to explain the mechanism for high electrocatalytic activity of the BP-NF from XPS. As shown in Fig. 3, we can find some clues, for N-doping, certain types of N-containing functional groups, such as pyridinic and pyrrolyic groups, especially those at carbon surface sites, have been claimed to be responsible for the high ORR activity, such as the high limiting current density.[28,29] For the F-doping, the high activity of BP-NF could also be partially attributed to the content of ionic C-F bond, which is more activity than covalent C-F bond.[18,27] That maybe why the BP-NF exhibits high activity in neutral medium, especially the high onset potential. More importantly, both N and F atoms are electron receptor toward C atom, probably leading to a synergistic catalytic enhancement in ORR, which reflected by the electrochemical performance of BP-NF compared with BP-F, BP-N as shown in Fig.4.

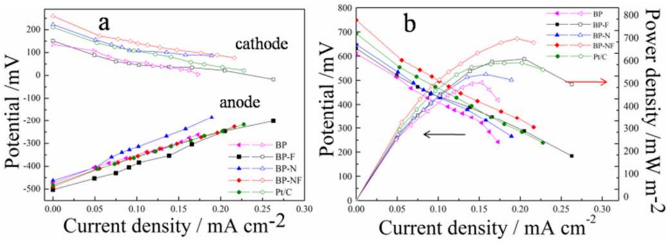

Fig. 5 (a) electrode potentials curves of MFCs with different catalysts (b) Polarization curves and power density curves of different catalysts.

Furthermore, we conducted single chamber air-cathode MFCs tests in optimum condition with different samples as cathode catalysts. As shown in Fig. 5a, the potential of the anodes in different MFCs were controlled almost the same. The polarization and power density curves revealed that BP-NF as cathode for the MFC exhibited very good stability and activity. The open circuit voltage of BP-NF was 749 mV, higher than that of commercial Pt/C (693 mV) and BP-2000 (610mV). The maximum power density with BP-NF was 672 mW m^{-2}, which was higher than 572 mW m^{-2} of commercial Pt/C and 490 mW m^{-2} of BP-2000. In addition, the open circuit voltage and peak power density of 655 mV, 588 mW m^{-2} and 645 mV, 524 mW m^{-2} were achieved on the single cell with BP-F and BP-N catalysts, respectively, which were remarkably lower than that of the cell with BP-NF, suggesting that nitrogen and fluorine co-doping plays a key role in the improvement of the catalytic activity than single nitrogen or fluorine doping, as shown in Fig. 5b. The results demonstrate N, F co-doping can effectively improve electrocatalytic activity in neutral medium of MFCs.

4. Conclusions

In summary, N and F co-doped carbon material was successfully prepared by direct pyrolysis the mixture of PTFE and BP-2000 under the ammonium atmosphere. BP-NF catalyst exhibited better catalytic performance (high onset potential and limiting current density) than that of single N or F doped carbon material, our result demonstrated that the synergetic ORR electrocatalytic effect of N and F co-doped in carbon material. The MFCs with BP-NF as the cathode catalyst generated a high maximum power density of 672 mW m^{-2} and the open circuit voltage of 749 mV, which was higher than that with commercial Pt/C catalyst (572 mW m^{-2}, 693 mV), and also higher than the BP-N (588 mW m^{-2}, 655 mV) and BP-F (524 mW m^{-2}, 645 mV), respectively. Finally, the raw materials are commercial and can be available at low cost, and the preparation method is facile and easy to be scaled-up. This study provides a facile method and new concept for preparation of highly efficient ORR catalyst for MFCs.

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[a] *State Key Laboratory of Structural Chemistry; Key Laboratory of design and assembly of functional nanostructures Chinese Academy of Sciences, YangQiao West Road 155#, Fuzhou, 350002, P. R. China.*
E-mail: wangyb@fjirsm.ac.cn.
[b] *Sichuan Agricultural University, College of Agricultural Sciences, Chengdu 611130China.*

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