ACS Catalysis

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Fluorine-Doped Carbon Blacks: Highly Efficient Metal-Free Electrocatalysts for Oxygen Reduction Reaction

Xiujuan Sun,[†,‡,§] Yuwei Zhang,[†,‡] Ping Song,[†,‡] Jing Pan,[⊥] Lin Zhuang,[⊥] Weilin Xu,*[,†,‡] and Wei Xing*[,†,‡]

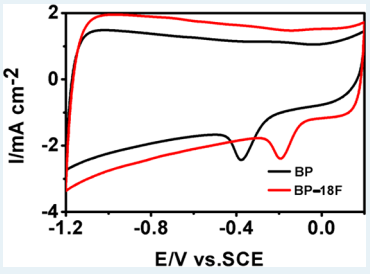
[†]State Key Laboratory of Electroanalytical Chemistry, [‡]Jilin Province Key Laboratory of Low Carbon Chemical Power, Changchun Institute of Applied Chemistry, Chinese Academy of Science, 5625 Renmin Street, Changchun 130022, People's Republic of China

[§]Graduate University of Chinese Academy of Science, Beijing, 100049, People's Republic of China

[⊥]College of Chemistry and Molecular Sciences, Hubei Key Lab of Electrochemical Power Sources, Wuhan University, Wuhan 430072, People's Republic of China

Supporting Information

ABSTRACT: For the goal of practical industrial development of fuel cells, inexpensive, sustainable, and high performance electrocatalysts for oxygen reduction reactions (ORR) are highly desirable alternatives to platinum (Pt) and other rare materials. In this work, sustainable fluorine (F)-doped carbon blacks (CB-F) as metal-free, low-cost, and high-performance electrocatalysts for ORR were synthesized for the first time. The performance (electrocatalytic activity, long-term operation stability, and tolerance to poisons) of the best one (BP-18F, based on Black Pearls 2000 (BP)) is on the same level as Pt-based or other best non-Pt-based catalysts in alkaline medium. The maximum power density of alkaline direct methanol fuel cell with BP-18F as the cathode (3 mg/cm^2) is ~15.56 mW/cm^2 at 60 °C, compared with a maximum of 9.44 mW/cm^2 for commercial Pt/C (3 mg_{Pt}/cm^2). All these results unambiguously demonstrate that these sustainable CB-F catalysts are the most promising alternatives to Pt in an alkaline fuel cell. Since sustainable carbon blacks are 10 000 times less expensive and much more abundant than Pt or other rare materials, these CB-F electrocatalysts possess the best price/performance ratio for ORR to date.



KEYWORDS: *oxygen reduction reaction, metal-free electrocatalyst, fuel cell, fluorine, energy*

As a result of the energy crisis in the world, fuel cells are attractive as clean and sustainable energy conversion devices because they can help address the ever increasing global energy demand.[1] One of the technological bottlenecks for the industrial development of fuel cells is the development of electrocatalysts with a high price/performance ratio for oxygen reduction reactions (ORR).[2,3] To date, Pt-based materials are the most widely used electrocatalysts for ORR;[4−6] however, Pt-based catalysts suffer from problems, such as sluggish oxygen reduction at any pH, durability, very limited reserves, high cost, and inactivation by carbon monoxide (CO) poisoning.[3,7,8] These obstacles hamper the commercial application of fuel cells.[1] Consequently, tremendous efforts are aimed at developing nonprecious metal[2,8−11] and metal-free electrocatalysts[3,12] to rival Pt-based catalysts. Recently, heteroatom (N, B, S, P, Fe, or Co)-doped carbon materials, such as carbon nanotubes (CNTs),[13,14] graphene,[15−21] graphitic arrays[12] and amorphous carbon,[22−24] were found to exhibit excellent electrocatalytic performance for ORR. Among these carbon-based non-Pt and metal-free catalysts, very few are on a competitive level with platinum.[3,8] The best of these catalysts, such as vertically aligned CNTs (VA-CNTs), CNT−graphene complexes, and amorphous carbon derivatives, are as expensive or rare, if not more so, as Pt. Of the carbon materials, carbon blacks are the least expensive and most sustainable and can have important implications for the commercialization of fuel cells in the future.[22,25]

On the other hand, at present, almost all the non-Pt-based ORR electrocatalysts with performance comparable with Pt are dependent on the doping of heteroatom nitrogen (N),[3,8,11] which has been known to be critically important for the formation of active sites for ORR process.[8] So, a question arises: Are there any other elements that could take a role as important as N in this case? Here, by exploring several different nonmetal heteroatoms (such as P, S, B, and F) doping alone on inexpensive carbon blacks systematically, for the first time, we luckily found the doping of fluorine (F) alone on inexpensive carbon blacks can induce superior high ORR electrocatalytic performance that is competitive with Pt or other best non-Pt catalysts.[8,11,26] Because of the low cost and abundance of carbon blacks, these CB-F electrocatalysts possess the best price/performance ratio ever for ORR.

Fluorine doping has been investigated in functionalization carbon materials[27−29] or glass,[30] but nobody had reported any application of it in ORR electrocatalysts. In the present work, on the basis of inexpensive carbon blacks (such as Black Pearls 2000 (BP)), NH_4F and a simple procedure (see the Supporting Information (SI)), we successfully fabricated a family of F-doped inexpensive carbon-based electrocatalysts (BP-F) for

Received: May 20, 2013
Revised: July 2, 2013
Published: July 3, 2013

   dx.doi.org/10.1021/cs400374k | ACS Catal. 2013, 3, 1726−1729

ORR in alkaline medium. By varying the initial mass ratio between NH_4F and BP in the order of 0 (BP), 10 (BP-10F), 18 (BP-18F) and 20 (BP-20F) to tune the F content and BET surface area of the catalyst (Figure 1A, 1B), then the ORR

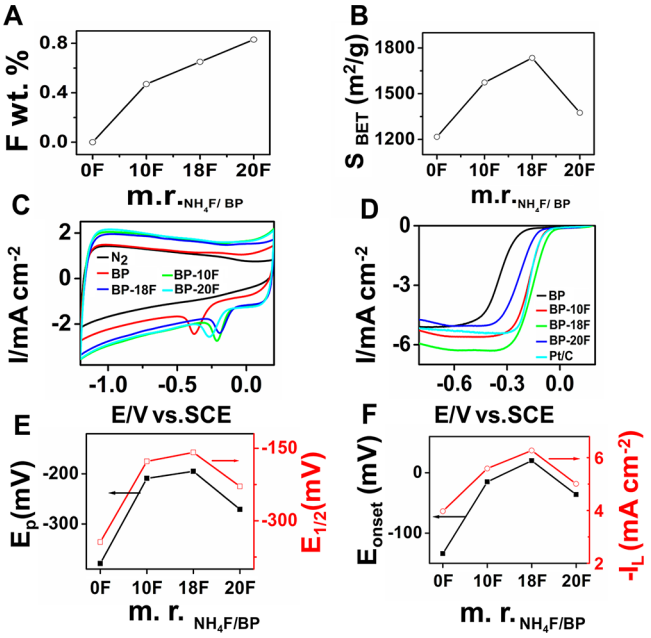


Figure 1. The optimization of BP-F catalysts. (A) Tuning of the F content in the catalysts by varying the initial mass ratio between NH_4F and BP. (B) The dependence of BET surface area on the F doping. (C) CV curves of BP-F catalysts in 0.1 M KOH with or without O_2. (D) Linear sweep curves of different BP-F catalysts and 20 wt % Pt in O_2-saturated 0.1 M KOH with a rotation rate of 1600 rpm and a scan rate of 5 mV/s. The catalyst loading is 0.39 mg cm^{-2} for doped carbon catalysts and 0.12 mg cm^{-2} for commercial Pt/C. (E, F) Volcano-shaped dependences of E_p, $E_{1/2}$, E_{onset}, and I_l on F doping.

electrocatalytic activities of BP-F catalysts were tuned in a wide range evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in O_2-saturated 0.1 M KOH on a rotating ring disk electrode (RRDE) (Figure 1C, 1D). From CVs or LSVs, we can tell clearly the distinct effect of F doping on the catalytic activity of carbon. Volcano-shaped dependences of four key parameters (peak potential (E_p) from CV, half-wave potential ($E_{1/2}$), onset potential (E_{onset}), and diffusion-limiting current (I_l) from LSV) on the F content are shown in Figure 1E, F. All these volcano-shaped dependences coincidently show the catalytic activity of BP-F increases first with the F content, then reaches a maximum at an optimal F content (0.65 wt % for BP-18F), and finally decreases at higher F content (0.83 wt % for BP-20F). Interestingly, these four volcano shapes are coincident with the F content dependence of the BET surface area of these catalysts, as shown in Figure 1B, indicating the larger the BET surface area is, the better the performance of BP-F catalyst is. The volcano-shaped dependence of BET surface area on the F content (Figure 1B) probably is due to the etching of some micropores at high NH_4F content.

The role of F doping in these carbon catalysts for ORR was very clear, as shown in Figure 1C. For pure BP, CV shows the E_p was about −0.38 V, whereas after F doping, the E_p positively shifted hugely up to −0.19 V for BP-18F, which is slightly higher than that on commercial Pt/C. Such a huge positive shift (~0.2 V) with F doping indicates that the doped F affected the electronic structure of the carbon materials and created new active sites for the ORR process on the catalysts. This role also can be observed from the polarization curves for the ORR on these electrocatalysts. As displayed in Figure 1D, the pure BP catalyst shows poor ORR activity with very low E_{onset} (~−134 mV), $E_{1/2}$ (~−344 mV) and small diffusion-limiting current (I_l ~ 5.1 mA/cm^2). With the doping of F, all three parameters—onset potential, half-wave potential and diffusion-limiting current—for the optimal BP-18F catalyst exhibited a huge positive shift, up to 30 mV, −158 mV, and 6.1 mA/cm^2, respectively, indicating pronounced electrocatalytic activity for ORR. For comparison, the performance of commercial Pt/C is also shown (cyan line in Figure 1D), which is almost the same as the performance of BP-10F, although the best catalyst obtained here (BP-18F, green curve in Figure 1D) is slightly better than that of commercial Pt/C and on the same level as that of the best non-Pt ORR catalysts ever reported.[3,8]

As an example, the BP-based optimal catalyst BP-18F is introduced in detail as the following: The morphology of it was investigated by means of transmission electron microscopy (TEM). As shown in SI Figure S1A, the BP-18F particles are amorphous with many mesopores. The porous nature of BP-18N was assessed with nitrogen adsorption−desorption analysis (SI Figure S1B). A type IV curve with a hysteresis loop was obtained, indicating that the catalyst is mesoporous.

To elucidate the mechanism of ORR on these BP-F catalysts, polarization curves for ORR on BP-18F were recorded from 225 to 1600 rpm on a RRED electrode, as shown in Figure 2A.

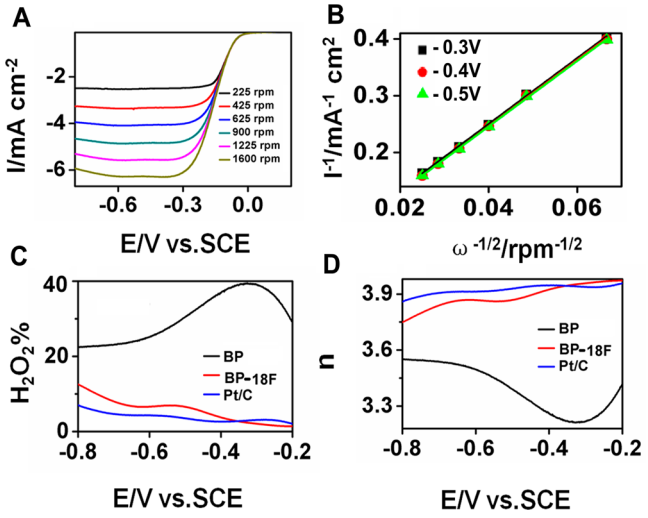


Figure 2. The ORR mechanism study. (A)Poralization curves of BP-18F catalysts in O_2-saturated 0.1 M KOH at a scan rate of 5 mV/s. (B) Koutecky−Levich plots for BP-18F catalysts at different potentials. (C) The H_2O_2 yield during the ORR process on different catalysts obtained from RRDE electrode. (D) The number of electrons transferred for each O_2 during the ORR process on different catalysts.

The disk current shows a typical increase in the rotation rate due to the shortened diffusion layer.[31] The linearity of the Kouteckey−Levich (K−L) plots and almost overlapped linear fitting lines indicate that the ORR on the BP-18F catalyst was a first-order reaction related only to the dissolved oxygen concentration in the potential range from −0.3 to −0.5 V (Figure 2B), the same as that on Pt/C (SI Figure S2). The number of transferred electrons per oxygen molecule calculated from the K−L equation is 3.96, indicating a four-electron

dx.doi.org/10.1021/cs400374k | ACS Catal. 2013, 3, 1726−1729

pathway of ORR on BP-18F with water as the main product. To consider the effect of F doping on the yield of H_2O_2, we further analyzed the ring-disk currents for different catalysts. Figure 2C, D shows the F doping can greatly inhibit the two-electron (or H_2O_2) pathway compared with pure BP and make water the main product (four-electron pathway) in the whole wide potential window for BP-18F, just like commercial Pt/C does.

The tolerance of BP-18F to CO or methanol was assessed with LSV in O_2-saturated 0.1 M KOH with methanol (3 M) or CO. For comparison, commercial Pt/C catalyst was also tested under the same conditions. As shown in Figure 3A, BP-18F did

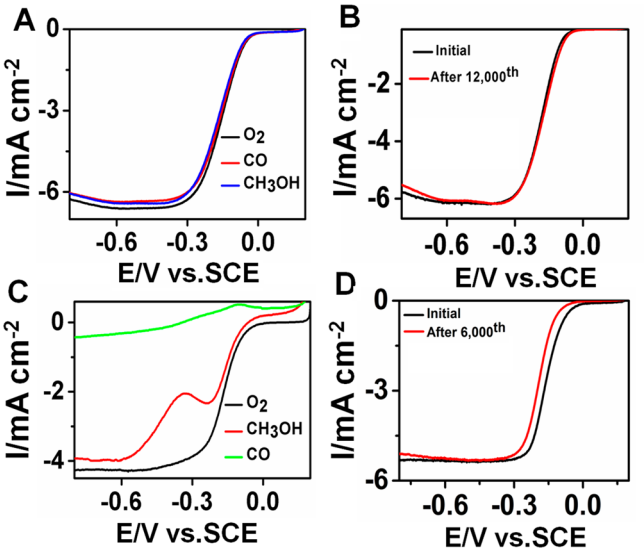


Figure 3. The tolerance and stability of BP-18F and Pt/C. (A, C)The response of BP-18F (A) and Pt/C (C) to methanol and CO. (B, D) The long-term operation stability of BP-18F (B) and Pt/C (D) in oxygen-saturated 0.1 M KOH.

not show any response to the addition of methanol or CO into the system, and the characteristic peaks of ORR are maintained. In contrast, the obvious electrooxidation of methanol or CO on commercial Pt/C seriously retards the ORR process on it (Figure 3C), as indicated by the disappearance of the oxygen reduction peak. This fact indicates that the as-prepared BP-18F is a nice alternative to Pt for alkaline direct methanol fuel cells as a cathode catalyst.

On the basis of the U.S. Department of Energy's accelerated durability test protocol, we assessed the long-term operation stabilities of BP-18F and Pt/C toward ORR by cycling the catalysts between −1.2 and 0.2 V at 200 mV/s in oxygen-saturated 0.1 M KOH.[11] As shown in Figure 3B, after 12 000 continuous cycles, the $E_{1/2}$ from LSV for BP-18F negatively shifted almost 0 mV, and there is almost no change on E_{onset}, although for commercial Pt/C, a 32 mV negative shift of $E_{1/2}$ and 40 mV negative shift of E_{onset} occurred on it (Figure 3D). All these data exhibited excellent long-term operation stability of the optimal BP-18F during the ORR process.

Fuel cell tests are more persuasive for us to assess the performance of new catalysts. Here, with the same anodes based on commercial Pt/C and a self-cross-linked alkaline solid polymer electrolyte (xQAPS),[32] we assembled alkaline direct methanol fuel cells (ADMFCs) with the optimal BP-18F and Pt/C as cathode catalysts, respectively. As shown in Figure 4A, the fuel cell with BP-18F as cathode can discharge up to 140

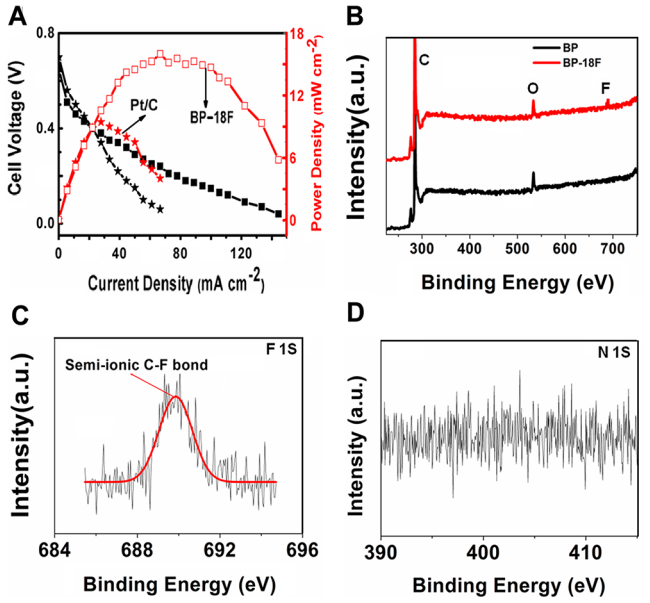


Figure 4. ADMFC performance and XPS characterization of BP-18F. (A) The voltages and power densities of ADMFCs at 60 °C with (square) BP-18F (3 mg/cm^2) and (star) Pt/C (60 wt %, 3 mg_{Pt}/cm^2) as cathodes, respectively. Anode: Pt/C (60 wt %, 3 mg_{Pt}/cm^2) with 2 M methanol in 2 M KOH with a flow rate of 5 mL/min. Cathode: dry oxygen with flow rate of 100 mL/min. (B) Survey scans of BP and BP-18F. (C) High-resolution XPS spectrum of F 1s. (D) High resolution XPS spectrum of N 1s for BP-18F.

mA/cm^2, which is much higher than the 60 mA/cm^2 for the commercial Pt/C-based fuel cell. The maximum power density for a fuel cell based on BP-18F reached 15.6 mW/cm^2 at 60 °C, compared with 9.5 mW/cm^2 for commercial Pt/C. The fuel cell performance with the BP-18F catalyst unambiguously indicates that the BP-18F is an excellent alternative to Pt as a cathode catalyst for ORR in alkaline fuel cells.

Some clues about the mechanism for the high electrocatalytic activity of BP-F catalysts can be obtained from XPS and Raman spectra of the catalysts. As shown in Figure 4B, the XPS survey scan spectrum for the BP-18F clearly shows the existence of F in addition to the original carbon and oxygen. No nitrogen (N) was detected (Figure 4D). Figure 4C shows the high-resolution XPS spectra of F 1s for BP-18F with a single peak at 289.8 eV, which could be attributed to a semiionic C−F bond.[33] Since it has been found that the semiionic C−F bond is more active than covalent C−F bond,[34] the high catalytic activity of BP-F could be attributed in part to the high content of F in the form of the semiionic state. Raman spectroscopy also gives some clue to the high electrocatalytic activity of BP-F. SI Figure S3 shows the Raman spectrum of pristine BP (black line) and BP-18F (red line) catalysts. With the F doping on BP, the intensities of both the D- and G-bands increased greatly,[29] indicating that the F doping process created many defect sites and increased the content of graphitic carbon in sample. Obviously, the high ORR activity of BP-F could be attributed in part to these two components, which have been known to play critical roles in the ORR electrocatalytic process.[29]

Furthermore, we found that our synthesis protocol can be generalized to other inexpensive carbon blacks to get high-performance CB-F catalysts for ORR. For example, in addition to BP-F, the other metal-free high-performance ORR catalysts (XC-F) were also obtained by doping Vulcan XC-72 with F

dx.doi.org/10.1021/cs400374k | ACS Catal. 2013, 3, 1726−1729

atoms in the same way. They show a similar high performance in alkaline medium (SI Figure S4).

In summary, CB-F catalysts with superhigh ORR electrocatalytic activity in alkaline medium were synthesized by simple pyrolysis of CB and NH_4F for the first time. The doped F atoms have great influence on the electronic properties of CB-F, which greatly promotes the ORR process on catalysts. Electrochemical measurements indicate that the optimal BP-18F exhibits higher ORR activity, long-term operation stability, and tolerance than commercial Pt/C catalysts. All these observations have been further validated by ADMFC tests. The maximum power density of ADMFC with BP-18F as the cathode outperforms the ADMFC with commercial Pt/C as the cathode. These novel metal-free electrocatalysts are the most promising alternatives with the best price/performance ratio to Pt for the application in alkaline fuel cells as a result of their superlow cost and superhigh performance. The discovery of the critical role of doped F alone for ORR electrocatalysts indicates the opening of a new research field for us to explore.

■ ASSOCIATED CONTENT

Supporting Information

Materials and methods; experimental details; control experiments. This information is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: weilinxu@ciac.jl.cn, xingwei@ciac.jl.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the "Hundred Talents Project" of the Chinese Academy of Sciences (110000PP65), the "Recruitment Program of Global youth Experts" of China, National Natural Science Foundation of China (21273220, 21073180, 20933004), and the National Basic Research Program of China (973 Program, 2012CB215500).

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