Supporting Information

F-Doped Carbon Blacks: Highly Efficient Metal-free Electrocatalysts for Oxygen Reduction Reaction

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SI Materials and Methods

1. Materials and Methods

Chemicals. The carbon black BP2000 (BP) was purchased from Asian-Pacific Specialty Chemicals Kuala Lumpur, Vulcan XC-72 and Pt/C (20 wt.% & 60 wt.%) were purchased from E-TEK Com. USA. Ammonium fluoride (NH4F) was purchased from Beijing Chemical Works, China, Potassium hydroxide (KOH) was purchased from Beijing Chemical Works, and Nafion solution (5 wt %) were obtained from Sigma-Aldrich. All the chemicals were used as delivered without further treatment. Ultrapure water with the specific resistance of 18.23 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration. Synthesis and characterization of catalysts. In a typical synthesis, a given amount of NH4F and BP were firstly dispersed in 10 ml H2O. The mixture was sonicated for about 2 h and then stirred overnight. The resulting suspension was dried under vacuum at 40°C and then pyrolyzed at 1000°C for 1h under argon atmosphere with flow rate of 80 ml/min. After that, the sample was cooled down to room temperature and collected from the quartz tube. For comparison, the BP without F doping was treated in a similar way and denoted as BP. In this work, the mass ratio of NH4F and BP are 10, 18 and 20. As a result, the F doped samples are denoted as BP-10F, BP-18F and BP-20F, respectively. For F doped Vulcan XC-72, all the processes are the same as that F doped BP, except that Vulcan XC-72 was used instead of BP. The obtained products were denoted as Vulcan XC-15F, Vulcan XC-18F, and Vulcan XC-20F. The transmission electron microscopy (TEM) images were obtained on a JEM-2100F microscopy with an accelerating voltage of 200 kV. Photoelectron spectroscopic (XPS) measurements were performed on a AXIS Ultra DLD (Kratos company) using a monochromatic Al X-ray source. The Brunauer-Emmett-Teller (BET) surface areas obtained from 77 K N2 sorption isotherms using ASAP 2020 instrument. The Raman spectroscopy was performed using a with a laser source of 633 nm.

2. Electrochemical Measurements and Fuel Cell Test

The activity for the oxygen reduction reaction (ORR) was evaluated by voltamperometry by BP-F as electrodes. Fabrication of the working electrodes was done by mixing 5 mg of BP, BP-F catalysts, 50.0 µL of a 5 wt % Nafion solution in alcohol, and 950.0 µL of ethanol under ultra-sonication. A 10-µL
aliquote of the ink was dropped on the surface of the glassy carbon rotating disk electrode, yielding an approximate catalyst loading of 0.05 mg. For comparison, a commercially available platinum/carbon catalyst (20 wt % Pt on carbon black from E-TEK) ink was obtained by mixing 1 mg catalyst, 50 µL of a 5 wt % Nafion solution in alcohol, 950µL of ethanol. Then, a 15-µL aliquot of the platinum ink was dropped on the glassy carbon rotating disk electrode, yielding an approximate loading of 0.12 mg cm\(^{-2}\) Pt/C or 24ug cm\(^{2}\). The electrochemical performance was conducted in 0.1 M KOH solution; the counter and the reference electrodes were a platinum wire and a SCE electrode, respectively. The potential of the electrode was controlled by a CHI 750E system (CH Instrument Co., USA). Rotating ring disk electrode (RRDE) tests were conducted on RRDE-3A apparatus (ALS Company, Japan) with the Glassy Carbon disk and Pt ring electrode (the diameter is 4 mm for disk). Cyclic voltammetry (CVs) were performed from 0.2 to -1.2 V at 50 mV s\(^{-1}\) after purging the electrolyte with O\(_2\) or N\(_2\) gas for 30 min. Voltamperometry measurements were performed by using the rotating ring-disk electrode (RRDE) at different rotating speeds from 225 to 1600 rpm in an O\(_2\)-saturated electrolyte from 0.2 to -1.2 V (vs. SCE) at a sweep rate of 5 mV/s in O\(_2\) saturated 0.1 M KOH solution. Koutecky-Levich equation was used for analyzing the transferred electron number (n) during the ORR with disk currents.

\[
\frac{1}{j} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}
\]

\[
B = 0.2nFC_{O_2}D_{O_2}^{1/2}\nu^{-1/6}
\]

Where \(j\) is the overall current density, \(J_L\) is the diffusion-limiting current density, \(J_K\) is the kinetic current density, \(\omega\) is the rotation speed, \(F\) is the Faraday constant (96485 C mol\(^{-1}\)), \(C_{O_2}\) is the bulk concentration of O\(_2\) (1.2 x10\(^{-6}\) mol cm\(^{-3}\)), \(D_{O_2}\) is the diffusion coefficient of O\(_2\) (1.9 x 10\(^{-5}\) cm\(^{2}\) s\(^{-1}\)), \(\nu\) is the kinematics viscosity of the electrolyte (0.01 cm\(^{2}\) s\(^{-1}\)) and \(n\) is the transferred electron numbers in the ORR. The constant 0.2 is adopted when the rotation speed is expressed in rpm.

For the calculation of yields of H\(_2\)O\(_2\) on different catalysts, based on both ring and disk currents from RRDE, the percentage of HO\(_2\)\(^{-}\) generated from ORR and the electron transfer number (n) were estimated by the following equations 38:

\[
(1) \quad HO_2%^{\circ} % = 200 \times \frac{i_R/N}{i_D+i_R/N}
\]

\[
(2) \quad n = 4 \times \frac{i_D}{i_D+i_R/N}
\]

Where \(i_D\) is the disk current density, \(i_R\) is the ring current density and \(N\) is the current collection efficiency of the Pt ring disk. \(N\) was 0.37 from the reduction of K\(_3\)Fe[CN]\(_6\).

All the current densities have already been normalized to the electrode surface area.

**Membrane assembly electrode (MEA) preparation and fuel cell tests**

In this work, a self-cross linked alkaline solid polymer electrolyte (xQAPS) (1) was used to prepare anion-exchange membrane with thickness of about 40 um for alkaline direct methanol fuel cells tested here. Before fabrication of MEA, the membrane was soaked in 2 M KOH for at least one week to change it to OH\(^{-}\). The membrane was then rinsed and stored in Millipore water two days before later use. Carbon supported Pt (20 or 60 wt % on Vulcan XR72, E-TEK, USA) or BP-18F was used to prepare the catalyst ink. Inks were made by mixing the catalysts powder, ethanol and 5% Nafion (Aldrich, USA) suspension. The catalyst layer was prepared on non-wet-proofed Toray 90 carbon paper (E-TEK, USA). After the desired amount of catalyst loading was achieved, the anode, cathode and membrane were sandwiched together and pressed at 130 kg/cm\(^2\) for 5 min at room temperature.

A stainless steel cell consisting of two compartments with 2 mm parallel channel flow field for methanol and oxygen flow was employed in this work. The active cross-section area of the cell was 6.25
cm². The fuel used was 2 M methanol in 2 M KOH at an operation temperature of 60°C, unless otherwise specified. A peristaltic pump (Watson Marlow, UK) was used to supply methanol to anode. The pure dry oxygen was supplied to the cathode with a flow rate of 100 mL/min. An in-house-made water bath and temperature controller was used to maintain the temperature at 60°C. All the cell polarization data were obtained after 24 h of cell conditioning.

3. The structure and morphology of BP-18F electrocatalysts

The structure and morphology of BP-18F electrocatalysts were investigated by transmission electron microscopy (TEM) as shown in Figure S1A. Large amount of BP-18F thin sheet packed together and the mesopore structures can be clearly seen. Figure S1B shows the typical N₂ adsorption-desorption curve of BP-18F, a type IV curve with a hysteresis loop (P/P₀ > 0.4), which means that the catalysts are mesoporous materials.

![Figure S1](image.png)

Figure S1. (A) TEM images and (B) N₂ sorption curve for BP-18F catalysts.

4. Electrocatalytic characterization of commercial Pt/C.

![Figure S2](image.png)

Figure S2. Linear sweep curves of 20 wt% Pt/C catalysts at different rotation rates when the scan rate is 5 mV/s in O₂-saturated 0.1 M KOH solution (Insert: the K-L plots under different potentials).

From the above Figure S2, the number of transferred electrons per oxygen molecule calculated from K-L equation for commercial Pt/C is about 4, indicating a four-electron pathway of ORR on Pt/C with water as the main product.

![Raman spectrum](image)

Figure S3. Raman spectrum for BP and BP-18F catalysts. These two were obtained under the heat-treatment of 1000°C. The inset is the magnification of the black line for BP.

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 D- and G-bands increased greatly, indicating that F-doping process created many defect sites and increased the content of graphitic carbon in the sample.

From Figure 4(b-d) we can see the F-doping clearly. In some cases, ammonia could be used as nitrogen-precursor for some N-doping by flowing ammonia in the whole doping process at high temperature (2). Herein, as shown in Figure 4d, no nitrogen was detected in the high resolution XPS, indicating the catalysts were only F-doped. The reason why there is no N-doping probably is that the doping process in our case was done under argon (rather than ammonia) atmosphere with flow rate of 80 mL/min.

6. The performance of XC-72 carbon-based CB-F catalysts

The RRDE measurements of F doped Vulcan XC-72 for ORR is shown in Figure S4. As shown in panels a, b and c, linear relationships between I and w0.5 were clearly seen for F doped Vulcan XC-72 with different F doped. The ring current density and the disk current density obtained from RRDE for Vulcan XC-15F, Vulcan XC-18F, Vulcan XC-20F and Pt/C are shown in Figure S4d. The ring current density was to estimate the amount of generated hydrogen peroxide ions. As can be seen, the generation of hydrogen peroxide ions on Vulcan XC-15F and Vulcan XC-18F are very close to the Pt/C catalysts. The compare of the disk current density of Vulcan XC-15F, Vulcan XC-18F, Vulcan XC-20F and Pt/C when the scan rate is 5 mV/s and the rotation rate is 1600 rpm suggested that the onset potential of F doped Vulcan XC is close to Pt/C.
**Figure S4.** ORR polarization curves for Vulcan XC-15F(a), Vulcan XC-18F (b), Vulcan XC-20F(c) catalysts obtained in O_2 saturated 0.1M KOH solution with a sweep rate of 5 mV/s. (d) the ring current density and disk current density of Vulcan XC-15F, Vulcan XC-18F, Vulcan XC-20F and Pt/C catalysts obtained from the RRDE in O_2 saturated 0.1 M KOH solution with a sweep rate of 5 mV/s and rotation rate of 1600 rpm.

