Electronic Supplementary Information (ESI) for

**ZIF-8-derived Fe/P/N-co-doped Carbon as Efficient Electrocatalysts for Oxygen Reduction Reaction and Zinc-air Batteries**

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**EXPERIMENTAL SECTION**

**Materials.** All chemicals were used as received without any further purification. Zinc nitrate hexahydrate (Zn(NO3)2·6H2O) (≥99 %), 2-Methylimidazole (2-MIM) (98 %), Methanol (99.5 %), 1,1'-Bis (diphenylphosphino) ferrocene (DPPF) (98%), N, N-Dimethylformamide (DMF) (≥99.5 %), Potassium hydroxide (KOH) (≥99 %) were purchased from bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Commercial 20% Pt/C was purchased from Suzhou Yilongsheng Energy Technology Co., Ltd.

**Synthesis of ZIF-8 and N-C.** ZIF-8 was synthesized following a method described in the literature with a little modification. Typically, 2-methylimidazole with a mass of 11.2 g was added into 50 mL methanol, 50 mL methanol containing 4 g Zn(NO3)2·6H2O was poured into the above solution with stirring for 24 h at room temperature. The product was separated by centrifugation and washed with methanol, and dried. N-C was synthesized by annealing the ZIF-8 precursor at 950 ℃ for 2 h.

**Synthesis of Fe-N/P-C and Fe-N-C.** The Fe-N/P-C catalyst was synthesized by a facile method as follow: the synthesized ZIF-8 precursor with a mass of 1 g was added to 50 mL of DMF and sonicated for 30 minutes to disperse it. Then 0.2 g DPPF was added and stirred for 12 hours. The product was separated by centrifuge, wash, filter and dry overnight at 80 ℃. Finally, the white powder was annealed at 950 ℃ for 2 h, the final product was labeled as Fe-P/N-C. For the synthesize of Fe-N-C, DPPF was replaced by ferrocene.

**Material characterization.** The morphology of the samples was examined by scanning electron microscopy (SEM; Hitachi S-4800), transmission electron microscopy (TEM; Tecnai G2 F20 S-Twin TMP), high-resolution TEM (HRTEM; Tecnai G2 F20 S-Twin TMP), and scanning transmission electron microscopy (STEM; Tecnai G2 F20 S-Twin TMP). The chemical composition and crystalline structure were tested with XRD (Bruker D8 Advance diffractometer, Cu kα), XPS (Ultima IV, Al Kα X-ray radiation of 1486.6 eV). Raman Spectroscopy (Lab RAM HR Evolution, Horiba, Japan) with an electron excitation wave length of 532 nm. Nitrogen adsorption−desorption isotherms and pore size distribution were characterized with a Micrometrics ASAP2460 analyzer at 77 K.

**Electrochemical measurements.** The electrochemical measurements were carried out using the Gamry Reference 600 + electrochemical workstation in a general three-electrode system, in which Hg/HgO (1 M KOH) was regarded as the reference electrode, carbon electrode as the counter electrode, and 0.1 M KOH aqueous solution as electrolyte. All the potentials in this work were converted to the reversible hydrogen electrode (RHE) according to the Nernst equation (ERHE = E (Hg/HgO) + 0.0591 × pH + 0.095). Working electrodes were prepared by dispersing 5 mg of catalyst powder with 1 mL ethanol-Nafion (5 wt%) (v/ v = 18/2) mixed solvent by sonication for at least 30 min. The loading amounts of all the catalysts including commercial Pt/C (20 wt%) were 0.4 mg cm–2. The cyclic voltammetry (CV) tests were conducted in N2- and O2-saturated electrolyte solutions at 50 mV s–1 scan rate. The linear sweep voltammetry (LSV) tests were performed in O2-saturated electrolyte solutions at different rotating speeds from 400 to 2025 rpm with a scan rate of 10 mV s–1. Durability was investigated by chronoamperometry at 0.7 V vs. RHE in O2-saturated electrolyte with a rotation speed of 1600 rpm. The methanol crossover measurements were also recorded by chronoamperometry at 0.7 V vs. RHE with a rotation speed of 1600 rpm with the addition of 3 M methanol into of 0.1 M KOH electrolyte at around 300 s.

**Construction of Zn-air batteries.** A zinc-air battery was constructed with a Zn foil anode, air electrode and an electrolyte of 6 M KOH solution mixed with 0.2 M zinc acetate. Fe-P/N-C and Pt/C were coated on carbon papers as cathodes. All the loading amount of the catalyst was 1 mg cm-2. The preparation method of the catalyst ink was the same as that used for electrochemical testing. The batteries were discharged at a current density of 10 mA cm-2. The test was measured by CHI 660 testing system.



Fig. S1 SEM results: (a-c)ZIF-8, (d-f)Fe-P/N-C.



Fig. S2 XRD patterns of ZIF-8 and DPPF@ZIF-8.



Fig. S3 (a) Fe 2p, (b) N 1s and (c) N species content of Fe-N-C and Fe-P/N-C.



Fig. S4 CV curves of N-C, Fe-N-C and Fe-P/N-C in O2-saturated 0.1 M KOH solution.



Fig. S5 CV curve of 20 wt% Pt/C in O2-saturated 0.1 M KOH solution.



Fig. S6 Polarization curves at different rotation speeds and K-L plots of Pt/C at different electrode potentials.



Fig. S7 SEM morphology after 18 h discharge in Zn-air battery.



Fig. S8 XPS results after 18 h discharge in Zn-air battery. (a) Fe 2p; (b) P 2p; (c) N 1s; (d) C 1s.

Table S1 Estimated percent of Fe, N and P obtained by the XPS spectra of Fe-N-C and Fe-P/N-C.

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| Elements atom content (at%) | Fe | N | P |
| Fe-N-C | 0.18 | 2.61 | / |
| Fe-P/N-C | 0.22 | 2.55 | 1.32 |