Metal-organic framework-derived Fe/Cu-substituted Co nanoparticles embedded in CNTs-grafted carbon polyhedron for Zn-air batteries

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Funding information
National Natural Science Foundation of China, Grant/Award Numbers: 51772008, 51825201; National Program for Support of Top-notch Young Professionals; Changjiang Scholar Program of Chinese Ministry of Education; National Key Research and Development Program of China, Grant/Award Number: 2017YFA0206701

Abstract
Metal-organic frameworks (MOFs) and MOF-derived materials have attracted great attention as alternatives to noble-metal based electrocatalysts owing to their intriguing structure properties, especially for high efficiency and stable oxygen reduction reaction (ORR). Herein, we employed a one-pot reaction to make a multimetal (Fe, Co, Cu, and Zn) mixed zeolitic imidazolate framework (MM-ZIF) via adopting a simple in situ redox reaction. Further pyrolysis of the target MM-ZIF, a highly porous carbon polyhedron (FC-C@NC) grafted with abundant carbon nanotubes was obtained, in which ultrasmall Co nanoparticles with partial lattice sites substituted by Fe and Cu were embedded. The obtained FC-C@NC possessed large surface area, highly porous structure, widely-spread metal active sites, and conductive carbon frameworks, contributing to outstanding ORR activity and long-term stability. It displayed superior tolerance to methanol crossover and exceeded the commercial Pt/C catalyst and most previously reported non-noble-metal catalysts. Impressively, the as-produced FC-C@NC-based zinc-air battery afforded an open-circuit potential of 1.466 V, a large specific capacity of 659.5 mAh/g, and a high gravimetric energy density of 784.3 Wh/kgzno, significantly outperforming the Pt/C-based cathode.

KEYWORDS
electrocatalysis, lattice sites substitution, metal-organic frameworks, oxygen reduction reaction, zinc-air battery

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INTRODUCTION

Proton exchange membrane fuel cells (PEMFCs), as highly efficient energy storage and conversion systems, have attracted worldwide attention in virtue of the high conversion efficiency of hydrogen energy into electricity.\(^1\) However, the sluggish kinetics of multiple electrons transfer process of oxygen reduction reaction (ORR) in PEMFCs leads to much more demand of platinum in the cathode, which hinders the wide application of PEMFCs.\(^2\) Moreover, Pt catalysts often suffer from activity degradation and even poisoning under the long-term continuous operation.\(^3\) To solve this problem, great efforts have been made to develop high-performance Pt-free catalysts including nonprecious transition metal compounds and even metal-free carbon-based catalysts.\(^4\) Among them, nitrogen-coordinated transition metals anchored on carbon nanomaterials (M-N-C), especially Fe-N-C and Co-N-C have been demonstrated promising ORR activity and selectivity approaching those of Pt.\(^7,8\)

Metal-organic frameworks (MOFs), consisting of organic ligands and metal ion/cluster centers, are promising precursors to fabricate highly porous nanomaterials for energy applications.\(^9\)–\(^12\) Using MOFs as sacrificial materials, the obtained highly controlled polyhedron carbon nanocomposites inherit the porous structures of pristine MOFs, and exhibit remarkable electrical conductivity and long-term stability.\(^13\) The derived three-dimensional ordered porous carbon matrix possesses high surface area with highly dispersed and exposed active sites, which are favorable for mass and electron transfer. Meanwhile, various heteratoms can be directly doped into the carbon matrix through the organic ligands, inducing strong charge transfer effects with adjacent C atoms and favorable chemisorption of O\(_2\). Transition metals and nitrogen codoped carbon-based catalysts (M-N-C) derived from MOFs have exhibited encouraging activity and stability. Zeolitic imidazolate frameworks (ZIFs) as a subclass of MOFs have emerged as a new platform for the synthesis of M-N-C catalysts.\(^14\)–\(^16\) In addition to the large surface area and tunable structures, the composition of the resultant M-N-C catalysts can be easily controlled by changing the metals or ligands.\(^17,18\) Although a series of Fe-N-C carbon materials have been reported, most of them are derived from Fe-doped ZIFs which are synthesized in an oxygen-free environment to avoid the oxidation of Fe\(^{2+}\) by air.\(^19,20\) In addition, some Fe-doped carbon materials are fabricated via a simple wet-chemistry impregnation method, in which Fe ions are only encapsulated within the molecular cages or absorbed on the surface of the as-prepared ZIF precursors, but not coordinated with the organic ligands.\(^21\)–\(^24\) Thus, the direct synthesis of Fe-doped ZIF by a simple method is still difficult. Besides, Cu has been theoretically proposed to have outstanding activity for ORR since it locates near the top of the "volcano plot."\(^25\) However, the inevitable aggregation will occur when synthesizing Cu-doped carbon materials via pyrolysis, which limits their electrocatalytic performances.\(^26\) In addition, the synergistic effects among bimetallic or trimetallic active sites have been proven to further enhance the ORR activity.\(^27\)–\(^29\)

In this study, we employed a one-pot reaction to make a multimetal (Fe, Co, Cu, and Zn) mixed zeolitic imidazolate framework (MM-ZIF) via adopting a simple redox reaction (2Fe\(^{3+}\) + Cu\(\rightarrow\) Cu\(^{2+}\) + 2Fe\(^{2+}\)) during the growth of CoZn-ZIF in the ambient atmosphere, which could not only avoid the oxidation of Fe\(^{2+}\) during the MOF-growth but also could introduce the highly active Cu species. By using this ZIF as the precursor, a carbon matrix-supported Co nanoparticles with partial lattice sites substituted by Fe and Cu was obtained (FC-C@NC). In addition, the evaporative Zn in the framework could assist the formation of a highly porous structure and avoid the agglomeration of large metal particles. The homogeneous distribution of Fe and Cu within Co nanoparticles, as well as the highly porous carbon matrix, gave rise to good performance with long-term stability as the ORR catalyst in both alkaline and acidic media. To further apply this catalyst for practical applications, a primary zinc-air battery was constructed by using FC-C@NC as the cathode. It could deliver an open-circuit potential of 1.466 V, a large specific capacity of 659.5 mA h g\(^{-1}\), a high gravimetric energy density of 784.3 Wh kg\(^{-1}\)Zn, and a peak power density of 118.2 mW cm\(^{-2}\) with excellent stability. The results suggested its potential application in energy storage and conversion process.

EXPERIMENTAL SECTION

2.1 Preparation of multimetal (Fe, Co, Cu, and Zn) MM-ZIF

MM-ZIF was prepared in methanol at room temperature. Typically, 412.2 mg of Zn(NO\(_3\))\(_2\)-6H\(_2\)O, 44.8 mg of Co(NO\(_3\))\(_2\)-6H\(_2\)O, and 124.0 mg of Fe(NO\(_3\))\(_3\)-9H\(_2\)O were dissolved in 30 mL of methanol under continuous magnetic stirring at room temperature to obtain solution A. Then, three pieces of copper foil (2 \(\times\) 2 cm\(^2\)), which were freshly etched and cleaned by 3 M HCl, deionized water, and ethanol, were immersed into solution A followed by sonication until the solution color turned to light green. In this process, all Fe\(^{3+}\) were converted to Fe\(^{2+}\) in the presence of Cu. Subsequently, 1314.0 mg of 2-methylimidazole was dissolved in 30 mL of methanol to form a clear solution B. These two solutions were mixed together and aged for 24 hours with constant stirring. Finally, the obtained lilac
precipitates were collected by centrifugation and washed with methanol for four times. The final product was then dried in a vacuum oven at 70°C overnight.

To illustrate the role of Fe and Cu in modulating the catalytic performance, Cu-CoZn-ZIF and CoZn-ZIF were also synthesized with the same method except for using Zn(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Cu(NO$_3$)$_2$·3H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·6H$_2$O as the metal sources. By tuning the raw material mol ratio between Co (NO$_3$)$_2$·6H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O, a series of catalysts with different ratio of Co/Fe/Cu were obtained, which were used to investigate the effects of metal contents on catalytic performance.

### 2.2 Preparation of FC-C@NC

FC-C@NC was obtained by directly annealing MM-ZIF under Ar atmosphere in a tube furnace at 900°C for 3 hours with a heating rate of 5°C/min. Then it was naturally cooled down to room temperature. The obtained material was directly used without further treatments.

The other pyrolyzed samples (C-C@NC and C@NC) were obtained by the same procedure, using Cu-CoZn-ZIF and CoZn-ZIF as precursors, respectively.

### 2.3 Characterization

The crystallographic structures of the materials were obtained using a Rigaku SmartLab 9 kW diffractometer with Cu Kα radiation (λ = 1.5406 Å). The surface characterization of elemental electronic states was measured by an X-ray photoelectron spectrometer (XPS; Axis Ultra imaging photoelectron spectrometer with the monochromatic Al Kα line). The nitrogen isotherms of the materials were measured at 77 K using a Quantachrome Autosorb-IQ instrument. Applying Brunauer-Emmett-Teller (BET) model to these isotherms, specific areas and pore size distributions were determined for each material. The microstructure and morphology were examined by using a scanning electron microscope (SEM; Hitachi S-4800 microscope). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were collected by Tecnai F30 microscope. High-angle annular dark-field scanning TEM (HAADF-STEM) images and the corresponding electron energy loss spectroscopy (EELS) mapping images were obtained by JEM-ARM-200F (JEOL, Tokyo, Japan) instrument equipped with cold field-emission gun and double spherical aberration (Cs) correctors operating at 200 kV. Raman analysis was performed on a Renishaw RM 1000 spectromicroscopy system (~2 μm spot size) with a ×20 objective optical microscope. An Ar laser with a 488 nm wavelength was used for the excitation of the Raman signal with a total power of 10 mW. The elemental contents were estimated by an inductively coupled plasma atomic emission spectroscopy (ICP-AES; Leeman).

### 2.4 Electrochemical measurements

Electrochemical measurements were carried out using an electrochemical workstation (CHI 760e) coupled with a rotating ring disk electrode (RRDE; PINE) in a three-electrode cell. The graphite rod and the Ag/AgCl (saturated KCl) electrode were used as the counter electrode and the reference electrode, respectively. The RRDE with a disk diameter of 5 mm covered by a thin film of the catalyst was used as the working electrode. To prepare the working electrode, 4 mg of as-prepared catalyst was ultrasonically dispersed in a 1 mL mixture of ethanol, deionized water, and Nafion (5 wt%) solution to form an ink. Then the ink was drop-casted onto the disk electrode with a mass loading of 0.2 mg/cm$^2$ and dried at room temperature to yield a thin-film electrode. Commercial 20 wt% Pt/C was measured for comparison. The catalyst-coated working electrode was subjected to cyclic voltammetry (CV) in Ar- or O$_2$-saturated electrolyte with a scan rate of 50 mV/s to activate the catalysts. The electrocatalytic activity for ORR was tested from 1.1 to 0 V vs reversible hydrogen electrode (RHE) in O$_2$-saturated electrolyte with a rotation rate of 1600 rpm. Four-electron selectivity during ORR was determined by measuring the ring current for calculating H$_2$O$_2$ yield. The electron-transfer number (n) and H$_2$O$_2$ yield percentage were determined by the following equations:

$$\text{HO}_2^\% = 200 \times \frac{I_R/N}{I_R + I_R/N},$$  \hspace{1cm} (1)

$$n = 4 \times \frac{I_D}{I_D + I_R/N},$$ \hspace{1cm} (2)

### 2.5 Primary zinc-air battery tests

The air electrode was fabricated by slowly dropping a certain volume of FC-C@NC catalyst inks onto a carbon paper substrate to achieve a catalyst loading of 1.0 mg/cm$^2$, and then dried the electrode overnight in a vacuum oven at 70°C. In our measurements, the values of specific capacity and energy density were all normalized to the consumed Zn mass during the galvanostatic discharge process.$^{30,31}$ A battery equipped with commercial Pt/C-cathode was also assembled and tested under the same measurement conditions.
conditions for comparison purposes. The batteries’ performances were measured by LAND-CT2001A testing devices.

3 | RESULTS AND DISCUSSION

The fabrication process of FC-C@NC is schematically depicted in Figure 1. In brief, to fabricate MM-ZIF, the copper foil was dipped into the solution containing Co²⁺, Zn²⁺, and Fe³⁺ to produce Fe²⁺ and Cu²⁺ (according to the reaction: 2Fe³⁺ + Cu → 2Fe²⁺ + Cu²⁺). Then, the resulting solution was mixed with a solution containing ligand. A subsequent pyrolysis process in the inert atmosphere was performed to form FC-C@NC. By using this method, not only Fe²⁺ could be introduced into the MOF skeleton to coordinate with the ligands without being oxidized, but also highly active Cu species could be involved. On the contrary, it was unable to directly synthesize Fe-CoZn-ZIF in the ambient atmosphere via the co-precipitation between the solution containing Fe²⁺ and the ligand solution (Figure S1).

The morphology of MM-ZIF and FC-C@NC were characterized by SEM and TEM. As shown in Figure 2A, MM-ZIF had a uniform rhombododecahedral shape with an average size of 600 nm, which was similar to the morphology of CoZn-ZIF (Figure S2). After the thermal treatment, the shape of FC-C@NC was maintained as the ZIF precursor, but the size was shrunken a little bit (Figure 2B). The introduction of Zn into ZIF precursor could assist the formation of highly porous structures and create open channels due to the evaporation of Zn during the calcination. As a result, it could be clearly seen that the porous carbon matrix was formed with small metal nanoparticles distributing within it (Figure 2C,D). More interestingly, many carbon nanotubes (CNTs) whose sizes were tens of nanometers with metal nanoparticles on their tips could be observed on the surfaces of FC-C@NC. The HRTEM image of FC-C@NC further indicated that Co nanoparticles were encapsulated in graphitic carbon shells with lattice spacings determined to be 2.04 and 3.45 Å, corresponding to the (111) plane of Co nanoparticles and (002) plane of graphitic carbon (Figure 2E,F). Elemental mapping images of FC-C@NC showed that Co, Fe, Cu, C, and N were distributed throughout the structure, and Co, Fe, and Cu also accumulated to form the dispersed nanoparticles (Figure S3). To further verify the substitution of Fe and Cu, aberration-corrected HAADF-STEM and EELS elemental mapping analysis were performed. The elemental mapping of metal nanoparticles within the carbon matrix showed that the Co, Fe, and Cu homogeneously distributed throughout the whole particle (Figure 2G). Simultaneously, the metal nanoparticles within the tips of CNTs were also confirmed to consist of Co, Fe, and Cu (Figure 2H), which were demonstrated to play an important role in catalyzing the formation of graphitic carbon/CNTs. Furthermore, the average atomic ratio of Co:Fe:Cu in FC-C@NC was estimated to be 83:6:11 based on ICP-AES results, indicating that 17% of the Co sites were substituted by Fe and Cu.

X-ray diffraction (XRD) was then carried out to study the composition and structure of MM-ZIF and FC-C@NC. Figure 3A showed that all the reflected peaks in the XRD pattern of MM-ZIF were matched well with the simulation pattern, indicating its good crystallinity and the same structures. The XRD pattern of FC-C@NC (Figure 3B) displayed a broad peak around 26.5°, assigning to the (002) plane of the graphitic carbon. The other three peaks located at 44.2°, 51.5°, and 75.8° were identical to the characteristic peaks of Co (JCPDS 15-0806), without any other peaks belonging to Fe or Cu, suggesting that the Co sites in Co nanoparticles were partially substituted by Fe and Cu. Raman spectra of FC-C@NC, Cu-CoZn-ZIF derived carbon composite (C-C@NC), and CoZn-ZIF-derived carbon composite
(C@NC) further verified the formation of graphitic carbon with a G-band at 1572 cm\(^{-1}\) and the presence of defect carbon with a D-band at 1352 cm\(^{-1}\) (Figure 3C).\(^{34}\) The peak intensity ratio \((I_D/I_G)\) of FC-C@NC was 1.13, which was higher than that of C-C@NC (1.10) and C@NC (1.06). The results indicated that FC-C@NC had more defects in structure and composition, which could enhance the ORR performance.\(^{35}\) In addition, \(N_2\) adsorption-desorption measurement was performed to investigate the surface area and porosity of FC-C@NC. Significantly, the as-prepared FC-C@NC exhibited typical I isotherms, with a sharp increase in the volume of adsorbed \(N_2\) with the pressure increasing at around \(P/P_0 = 0\), suggesting the formation of micropores within this catalyst (Figure 3D).\(^{36}\) The BET surface area of FC-C@NC was 702 m\(^2\)/g, and the detailed pore size distribution suggested the existence of abundant micropores with the pore size of about 0.85 and 1.10 nm and a small quantity of mesopores with the pore size of about 2.20 nm. This highly porous structure was favorable for the interaction with the electrolyte and mass transport in the heterogeneous oxygen electrocatalysis.\(^{37}\)

The chemical state and molecular environment of FC-C@NC and other composites were further characterized by XPS. The survey spectrum (Figure S4) of FC-C@NC clearly showed the peaks of Co, Fe, Cu, C, N,
and O. The high-resolution Co 2p3/2 spectrum could be deconvoluted into three peaks (Figure S5A), corresponding to metallic Co peak at 776.5 eV, Co-Nx peak at 781.5 eV, and satellite peak at 786.2 eV, respectively.\textsuperscript{38–40} The high-resolution N 1s spectrum (Figure S5B) could be deconvoluted into five peaks centered at 398.1, 399.1, 399.8, 401.2, and 403.1 eV, respectively, corresponding to pyridinic-N, Co-Nx, pyrrolic N, graphitic-N, and oxidized graphitic-N.\textsuperscript{41,42} Compared with C-C@NC (without Fe substitution) and C@NC (without Fe and Cu substitution), FC-C@NC exhibited energy shifts in binding energies in Co 2p and N 1s spectra (a positive shift of about 0.6 eV for Co 2p and a negative shift of about 0.6 eV for N 1s, as shown in Figure 3E,F), indicating Fe and Cu substitution into Co sites had a little influence on the chemical states of Co and N. In addition, FC-C@NC contained higher N content (10.8%), and the content of pyridinic N and graphitic-N was 60% of the total N content, which was supposed to be beneficial for ORR process.\textsuperscript{43}

The electrocatalytic activities of all samples for ORR were first evaluated using a three-electrode configuration cell in alkaline solution (0.1 M KOH) at room temperature. As shown in Figure S6, no redox peak was observed for FC-C@NC in Ar-saturated KOH solution, while a well-defined cathodic peak (0.65 V vs RHE and all the potentials in this study were compared with RHE) was observed in O2-saturated KOH solution, predicting its effective ORR catalytic activity. Linear sweep voltammetry (LSV) curve of FC-C@NC displayed that FC-C@NC possessed a more positive onset potential ($E_{\text{onset}}$) of 1.02 V, a half-wave potential ($E_{1/2}$) of 0.85 V, and a diffusion-limited current density ($J_{dl}$) of −4.66 mA/cm², which were comparable to those of commercial 20 wt% Pt/C (0.973 V, 0.813 V, and −4.88 mA/cm²) (Figure 4A). In contrast, C-C@NC and C@NC exhibited an inferior ORR performance, suggesting Fe, Cu co-substitution played an important role in the ORR process. The effects of different ratio of Co/Fe/Cu on the ORR performance were also investigated by tuning the raw material mol ratio between Co(NO3)2·6H2O and Zn(NO3)2·6H2O. As shown in Figure S7, the catalyst with a ratio of Co/Zn = 1:9 possessed the best activity in comparison with other catalysts.

LSV measurements were further conducted at various rotation speeds from 400 to 2025 rpm to gain insight into the reaction mechanism of FC-C@NC. As expected, the current densities increased as the rotation rate increased, but the onset of potentials kept constant under different rotation rates (Figure 4B). The linear Koutecky-Levich plots indicated the first-order reaction kinetics toward the concentration of dissolved oxygen, and the same transferred electron number per oxygen molecule under different potentials (Figure 4C).\textsuperscript{28} The electron-transfer number ($n$) was calculated to be ~3.7, indicating a four-electron oxygen reduction process. RRDE measurements were also carried out to monitor the formation of peroxide (HO2⁻) during the ORR
From 0.15 to 0.9 V, the HO$_2^−$ yields of FC‐C@NC remained below 7%, which was close to that of Pt/C. And the average electron‐transfer number ($n$) of FC‐C@NC was determined to be $\sim$4, indicating FC‐C@NC exhibited a direct four‐electron reduction pathway with high catalytic efficiency (Figure 4D). In addition, the Tafel slope of FC‐C@NC, which reflected the kinetic properties, was calculated to be 90.3 mV/dec, lower than that of Pt/C and the other catalysts (Figure S8). This demonstrated that FC‐C@NC possessed a much favorable catalytic reaction kinetics.

Besides the remarkable catalytic activity, FC‐C@NC also showed outstanding stability. The stability test was operated through chronoamperometric measurement at a constant voltage of 0.767 V. As shown in Figure 4E, FC‐C@NC displayed superior durability with 87% current retention over 30 000 seconds of continuous operation, while Pt/C suffered from a fast current loss with only $\sim$30% retention, indicating better stability of FC‐C@NC without obvious activity decay. Meanwhile, the accelerated durability tests (ADTs) were conducted in a potential range from 0.567 to 1.167 V for 5000 cycles. By comparing the LSV curves measured before and after CV cycles, FC‐C@NC behaved highly stable, with a negative shift of only 3 mV in the $E_{1/2}$ value and a slight increase in the $J_d$. In contrast, Pt/C showed inferior stability under the same condition with a 26 mV negative shift in the $E_{1/2}$ value. In addition, a methanol crossover test was conducted to evaluate the catalytic selectivity against fuel oxidation. No noticeable disturbance of current density was observed for FC‐C@NC after the addition of methanol into the electrolyte, whereas Pt/C presented a sharp disturbance and a subsequent decrease in the current density (Figure S9). The above results manifested that FC‐C@NC had better long‐term stability and stronger resistance to methanol poisoning, which made it promising as a Pt‐free catalyst in practical applications.

Besides, the ORR performance was also investigated in acidic electrolyte. Notably, FC‐C@NC achieved high activity and superior stability toward ORR under the similar operation as well, which was always a challenge for noble‐metal‐free electrocatalysts. A distinct oxygen reduction peak for ORR was observed for FC‐C@NC in O$_2$‐saturated 0.5 M H$_2$SO$_4$ solution, while no peak appeared in Ar‐saturated 0.5 M H$_2$SO$_4$ (Figure S10). As shown in Figure 4F, the $E_{onset}$ and $E_{1/2}$ of FC‐C@NC were 0.845 and 0.741 V. The $E_{1/2}$ approached that of Pt/C with a gap of 9 mV, and the RRDE analysis demonstrated a high average $n$ ($n > 3.9$) and a low HO$_2^−$ yields achieved by FC‐C@NC in the tested potential range (Figure 4G).
Tafel plots showed a much smaller slope of 80.7 mV/dec of FC-C@NC, indicating superior reaction kinetics (Figure S11). Normally, the catalysts synthesized from the pyrolysis of precursors are etched by acid before testing. Therefore, the catalysts were further treated by acid leaching (3 M H$_2$SO$_4$, 80°C, 12 hours) and the performance was compared before and after the acid leaching process. As shown in Figure S12, the performance became worse in both 0.1 M KOH and 0.5 M H$_2$SO$_4$ after acid leaching, which should be contributed to the loss of the catalytically active metal sites. In addition, the fabricated FC-C@NC exhibited outstanding long-term stability after ADT tests. As displayed in Figure 4H, no decay but a little enhancement in $E_{1/2}$ with a slight decrease in $J_d$ of FC-C@NC was observed after 5000 continuous cycles. After continuous operation for 20 000 seconds, FC-C@NC exhibited a 65% retention of the initial current density. In comparison, Pt/C showed obvious deterioration with retention of only 35%. When methanol was injected into the electrolyte, only a small impact was observed on the current density of FC-C@NC during the testing (Figure S13). The above results indicated that FC-C@NC possessed outstanding electrocatalytic stability.

The prominent ORR activity and stability of FC-C@NC motivated us to explore its feasibility in practical energy conversion applications. As shown in Figure 5A, a homemade primary zinc-air battery was assembled, which comprised an FC-C@NC air cathode, alkaline electrolyte (6 M KOH + 0.2 M Zn(Ac)$_2$), and a Zn foil anode. A comparative study for commercial battery with Pt/C air cathode was also conducted under the same measurement conditions. The as-prepared FC-C@NC-based primary zinc-air battery afforded an open-circuit potential of 1.466 V (Figure 5B), which was much larger than that of commercial battery (1.371 V; Figure S14). The FC-C@NC-based battery delivered a much larger specific capacity of 659.5 mAh/g and a higher gravimetric energy density of 784.3 Wh/kg$_{Zn}$, greater than those of Pt/C-based counterpart (specific capacity of 614.7 mAh/g and energy density of 694.6 Wh/kg$_{Zn}$; Figure 5C). Furthermore, the discharge polarization and power density curves clearly showed that FC-C@NC cathode presented a higher current density and a higher peak power density than those of commercial battery (Figure 5D). Remarkably, the FC-C@NC-based battery achieved a maximum power density of 118.2 mW/cm$^2$ at 120.0 mA/cm$^2$, which was much larger than that of commercial one (58.3 mW/cm$^2$ at 100.0 mA/cm$^2$). The potential plains of FC-C@NC-based battery at different current densities (ranging from 2 to 40 mA/cm$^2$) in the galvanostatic discharge process were also higher than those of the commercial counterpart (Figure 5E), making it highly promising for both high-energy-density and high-power-capability applications. Also, a commercial light-emitting diode (LED) device could be easily illuminated without brightness decay for over 2 hours by
connecting two FC-C@NC-based primary zinc-air batteries in series, indicating the excellent operation stability (Figure 5F). Overall, the above results confirmed that the proposed FC-C@NC catalyst was feasible in practical zinc-air batteries under ambient conditions.

In our experimental results, the excellent electrocatalytic performance and stability of the as-synthesized FC-C@NC have been proven. These values are also comparable or even superior to those of the previously reported catalysts (Tables S1 and S2). We believe that the outstanding activities were attributed to the following reasons. First of all, the highly porous carbon frameworks with open structures could effectively expose the active sites. These structural advantages could facilitate mass transportation and gas diffusion, enlarging the electrolyte/catalyst contact area and thus promoted the ORR process. Besides, the high degree of graphitization of FC-C@NC could be expected to enhance the electrical conductivity. Meanwhile, abundant CNTs in situ catalyzed by the metal particles could boost electron transfer as well. Moreover, the strong affinity between metal particles and carbon supports induced by high-temperature pyrolysis not only guaranteed the uniform dispersion of active metal sites but also contributed to the superior stability. In addition, the high fraction of pyridinic-N and graphitic-N in carbon frameworks was beneficial to the adsorption of O₂ due to the optimization of C electronic structure by N-doping, which could further promote the electrical conductivity and hydrophilicity. Furthermore, the introduction of Fe and Cu into Co nanoparticles to partially substitute Co lattice sites could produce a little influence on the chemical states of Co and N, thus synergistically improved the electrocatalytic performances. All the above profitable features rendered FC-C@NC a promising electrocatalyst with reinforced activity and durability.

4 | CONCLUSIONS

In summary, we adopted a simple redox reaction (2Fe³⁺ + Cu = Cu²⁺ + 2Fe²⁺) during the growth of CoZn-ZIF in the ambient atmosphere to fabricate MM-ZIF, which not only avoided the oxidation of Fe²⁺ during the MOF-growth but also introduced the highly active Cu species. Subsequently, Fe, Cu-substituted Co nanoparticles embedded within the highly porous carbon matrix were obtained by high-temperature pyrolysis. Benefiting from the architectural and composition merits, the obtained FC-C@NC exhibited excellent ORR performance with impressive E onset and E 1/2, high long-term stability, and superior tolerance to methanol crossover, outperforming those of commercial Pt/C catalyst. The primary zinc-air battery based on FC-C@NC air cathode delivered a large specific capacity of 659.5 mAh/g and a high gravimetric energy density of 784.3 Wh/kg Zn₂, as well as excellent durability. This study develops a cost-effective and high-performance electrocatalyst as an alternative to Pt for energy conversion and storage applications.

ACKNOWLEDGMENTS

This study was financially supported by the Natural Science Foundation of China (Grant no. 51825201 and 51772008), the National Key Research and Development Program of China (Grant no. 2017YFA0206701), National Program for Support of Top-notch Young Professionals, and Changjiang Scholar Program.

CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section.

**How to cite this article:** Zhang K, Zhang Y, Zhang Q, et al. Metal-organic framework-derived Fe/Cu-substituted Co nanoparticles embedded in CNTs-grafted carbon polyhedron for Zn-air batteries. *Carbon Energy*. 2020;1–11. 
https://doi.org/10.1002/cey2.35