Cubic imidazolate frameworks-derived CoFe alloy nanoparticles-embedded N-doped graphitic carbon for discharging reaction of Zn-air battery

Ziyu Du, Peng Yu, Lei Wang^{*}, Chungui Tian, Xu Liu, Guangying Zhang and Honggang Fu^{*}

ABSTRACT The construction of transition metal-based catalysts with high activity and stability has been widely regarded as a promising method to replace the precious metal Pt for oxygen reduction reaction (ORR). Herein, we synthesized CoFe alloy nanoparticle-embedded N-doped graphitic carbon (CoFe/NC) nanostructures as ORR electrocatalysts. The ZIF-67 (zeolitic imidazolate framework, ZIF) nanocubes were first synthesized, followed by an introduction of Fe²⁺ ions to form CoFe-ZIF precursors *via* a simple ion-exchange route. Subsequently, the CoFe/NC composites were synthesized through a facile pyrolysis strategy. The ORR activity and the contents of cobalt and iron could be effectively adjusted by controlling the solution concentration of Fe²⁺ ions used for the ion exchange and the pyrolysis temperature. The CoFe/NC-0.2-900 composite (synthesized with 0.2 mmol of FeSO₄·7H₂O at a pyrolysis temperature of 900°C) exhibited ORR activity that was superior to the other samples owing to a synergistic effect of the bimetal, especially considering the extremely high limiting current density of 6.4 mA cm⁻² compared with that of Pt/C (5.1 mA cm⁻²). Rechargeable Zn-air batteries were assembled employing CoFe/NC-0.2-900 and NiFeP/NF (NiFeP supported on nickel foam (NF)) as the catalysts for the discharging and charging processes, respectively. The above materials achieved reduced discharging and charging platforms, high power density, and prolonged cycling stability compared with conventional Pt/C+RuO₂/C catalysts.

Keywords: N-doped graphitic carbon, CoFe/NC, oxygen reduction reaction, Zn-air batteries

INTRODUCTION

With the continuous development of society and the sustained increase in the population, the increasing demand for energy sources has inevitably led to the rapid

consumption of nonrenewable energy sources [1–3]. Undoubtedly, exploitation of a promising alternative to supersede traditional fossil fuels is greatly needed but challenging [4,5]. Therefore, a series of new energy systems for the future are attracting increasing attention, including overall water splitting, fuel cells, and metal-air batteries [6,7]. As one of the attractive and effective energy sources in energy storage, zinc-air batteries (ZABs) provide the advantages of high energy density (1086 W h kg⁻¹), high safety, and environmental friendliness [8]. Although ZABs have made significant progress in practical applications, it is difficult for the electrochemical performance of a prepared catalyst to satisfy the current requirements [9]. As an important discharging process, the slow kinetics of oxygen reduction reaction (ORR) limits the overall performance of ZABs by increasing polarization and decreasing energy efficiency [10]. Commercial Pt/C catalysts are recognized as benchmark catalysts for ORR, but their high price and poor selectivity and stability impede their wide applications [11,12]. Based on the above considerations, it is necessary to develop a novel and efficient ORR catalyst originating from earth-abundant and inexpensive elements as a substitute for precious metal catalysts [13]. Currently, transition metal-based catalysts (single atoms, nitrides, carbides, phosphides, etc.) exhibit good catalytic activity towards ORR, but their stability and conductivity should be further improved [14,15].

Metal-organic frameworks (MOFs) are novel crystalline porous coordination polymers with tunable pore sizes, structures and functional species, which allow them to be considered for promising applications in energy storage and conversion [16–18]. As a type of well-known MOF material, zeolitic imidazolate frameworks (ZIFs) have

Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education of the People's Republic of China, Heilongjiang University, Harbin 150080, China

^{*} Corresponding authors (emails: wanglei0525@126.com (Wang L); fuhg@vip.sina.com or fuhg@hlju.edu.cn (Fu H))

been extensively investigated as precursors to construct various porous metal-carbon hybrid catalysts [19,20]. The most prominent members are ZIF-8 and ZIF-67 derivatives with 2-methylimidazole (2-MeIM) as ligands, which have the advantages of plentiful carbon and nitrogen in the organic ligands and a high metal-ion content in each framework [21]. Thus, the pyrolysis of these precursors and their derivatives is generally considered as a low-cost and easy-to-operate strategy for the synthesis of non-precious metal catalysts [22,23]. The nitrogen-containing organic ligand in ZIF not only combines with carbon to form N-doped carbon nanostructures during the pyrolysis process, but also produces pyridine N, pyrrole N and graphite N that coordinate with metals and perform as active sites for the ORR [24,25]. ZIF-67 is always used as the template to synthesize atomic-dispersed or metal Co-N-C hybrids, which exhibit good electrocatalytic ORR performance [26]. Furthermore, the introduction of Fe^{3+} into the ZIF-8 framework could obtain Fe-N-C with single-atom or carbon-encapsulated Fe nanoparticles, enhancing the catalytic activity and stability of ORR [27]. In addition, other transition metal elements, such as Mn, Cu, Mo, and W, have also been introduced into the ZIF framework for various catalytic field applications. The electrocatalytic activity of metal-N-C structures has been systematically investigated in theory and experiments [28]. Based on their synergistic effect, bimetal-based catalyst exhibits better performance than that of a corresponding single-metal catalyst [29]. In this respect, our recent report has shown that the CoFe alloy catalyst had superior ORR activity to that of the Co or Fe-based catalyst because of the synergistic effect, as evidenced by *operando* XAFS analyses [30]. Therefore, we want to adopt an easier strategy to synthesize CoFe alloy-based ORR catalyst. Although the multi-metal composition structures derived from ZIFs have been extensively researched, few studies using the ZIF precursor for preparing CoFe alloy nanoparticles have been reported [31,32].

Herein, we propose a simple route to prepare CoFe alloy nanoparticle-embedded N-doped graphitic carbon nanostructures (CoFe/NC) by the pyrolysis of cubic CoFe-ZIF precursors. An imidazole salt skeleton of ZIF-67 nanocubes was first prepared, followed by the introduction of a small amount of Fe^{2+} ions into the ZIF-67 framework by an ion-exchange method. After pyrolysis under nitrogen ambient, CoFe/NC featured a high surface area, plentiful N content and well-dispersed CoFe alloy nanoparticles, which benefits electron/ion transfer. As expected, the catalyst displayed excellent ORR perfor-

mance, including an onset potential of (0.94 V vs. reversible hydrogen electrode (RHE)), a half-wave potential (0.82 V vs. RHE), a limiting current density (6.4 mA cm^{-2}) and a cycling stability of only 10 mV attenuation after 10,000 cycles, all of which outperform those of Pt/C catalysts. The as-prepared catalysts combined with NiFeP grown on nickel foam (NiFeP/NF) were used as air cathodes for assembling ZABs. The liquid battery exhibited a low voltage gap, long-term stability, and high power density, which were much better than those of batteries based on the commercial Pt/C+RuO₂/C catalyst. This work not only provides an effective way to develop nonprecious metal catalysts for ORR, but also inspires us to construct highly efficient sustainable energy conversion devices.

EXPERIMENTAL SECTION

Synthesis of CoFe/NC samples

Typically, 4.54 g of 2-MeIM was dispersed in 70 mL of deionized water to form a uniform solution. Then, 10 mL aqueous solution containing 1 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.014 mmol cetrimonium bromide (CTAB) was slowly poured into the above ligand solution and continually stirred for 20 min at room temperature. The resultant purple precipitate of ZIF-67 nanocubes was collected *via* centrifugation, repeatedly washed with ethanol and then dried in an oven at 60°C. The CoFe-ZIF precursor was synthesized by an ion-exchange route as follows. First, 0.2 g of ZIF-67 was uniformly dispersed into 50 mL of ethanol by ultrasonication and stirred for 0.5 h. Soon afterwards, 5 mL of ethanol solution containing 0.2 mmol of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added and continually stirred for 30 min at room temperature. Finally, the product was washed with ethanol and dried at 60°C to obtain CoFe-ZIF-0.2 nanocubes (0.2 represents the mole number of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). In the subsequent pyrolysis procedure, the above precursor was placed in a porcelain boat that was then placed into a flow-through tube furnace. Subsequently, it was heated to 900°C at a rate of 5°C min^{-1} and then maintained for 2 h under nitrogen ambient. After being naturally cooled to room temperature, the typical CoFe/NC was obtained. The sample was denoted as CoFe/NC-*M-T*, where *M* represents the mole number of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and *T* stands for the pyrolyzed temperature, so the obtained sample was denoted as CoFe/NC-0.2-900. To investigate the effect of pyrolysis temperature on the structure and performance, CoFe/NC-0.1-700, CoFe/NC-0.1-800 and CoFe/NC-0.1-1000 samples were also prepared. In addition, the mole number of FeSO_4 was

changed to 0.1 and 0.3 mmol, so CoFe/NC-0.1-900 and CoFe/NC-0.3-900 samples were also obtained. For comparison, a ZIF-67 without iron species was directly pyrolyzed at 900°C for 2 h in nitrogen ambient, and the sample was denoted as Co/NC-900.

Synthesis of NiFeP/NF as the oxygen evolution reaction (OER) catalyst for Zn-air battery

A $2 \times 3 \text{ cm}^2$ NF was ultrasonically pretreated with acetone, 1 mol L^{-1} HCl and distilled water several times to remove the oxide layer on the surface of the NF. The synthesis of NiFeP/NF was mainly divided into two simple steps, using the unique open channel and three-dimensional network of NF as an electrocatalyst substrate. In the first step, 1 mmol of $\text{Ni}(\text{NO}_3)_2$, 1 mmol of $\text{Fe}(\text{NO}_3)_3$, 8 mmol of NH_4F and 10 mmol of urea were dissolved into 40 mL deionized water to form a uniform solution. Next, the treated NF was immersed in the above solution for 1 h and then transferred into a 100 mL Teflon-lined stainless-steel autoclave, followed by heating at 120°C for 10 h. After washing and drying, the NiFe-LDH precursor was prepared. In the subsequent phosphorization process, the as-prepared NiFe-LDH and 1.0 g of NaH_2PO_2 were placed in two porcelain boats. Finally, NiFeP/NF could be synthesized after calcining at 350°C for 2 h under N_2 atmosphere.

Characterizations

The crystal structure of the samples was analyzed by X-ray diffraction (XRD, Rigaku D/max-IIIB, Bruker) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Raman spectra were obtained with the Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm with an Ar-ion laser beam. Scanning electron microscopy (SEM) for microstructures was performed using a Hitachi S-4800 instrument operating at a voltage of 5 kV. Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2100 electron microscope with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a VG Escalab MK II spectrometer with an Mg K α achromatic X-ray source. The surface area was characterized by nitrogen adsorption-desorption isotherms tested on a Micromeritics TriStar II.

Electrochemical tests

The ORR measurements of all samples were carried out on a Pine instrument (US) by a conventional three-electrode system in 0.1 mol L^{-1} KOH electrolyte at 25°C. A platinum sheet with a size of 1 cm^2 and a RHE were used as the counter electrode and reference electrode, respec-

tively. A rotating disk electrode (RDE) with a glassy carbon disk (diameter: 4 mm) was used as the working electrode. The catalyst slurry was prepared by adding 5 mg of the powder catalyst to 1.5 mL of ethanol and 0.5 mL of 0.5 wt.% Nafion solution. Next, 40 μL of catalyst was slowly dropwise added on the RDE electrode until the catalyst loading was approximately 0.1 mg cm^{-2} . In the electrochemical test process, the 0.1 mol L^{-1} KOH electrolyte had oxygen passed through for at least 0.5 h to ensure that the electrolyte was filled with adequate oxygen. The linear scan voltammetry (LSV) curves were obtained at a sweep rate of 5 mV s^{-1} with a voltage window of -0.1 – 1.1 V . The rotating ring disk electrode (RRDE) test was obtained at different speeds (from 225 to 2025 rpm) at a sweep rate of 5 mV s^{-1} . The electron transfer number (n) and kinetic current density (J_k) can be obtained by calculation based on the Koutecky-Levich (K-L) equation as follows:

$$\frac{1}{J} = \frac{1}{J_1} + \frac{1}{J_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k}, \quad (1)$$

$$B = 0.62nFC_0D_0^{2/3}v^{-1/6}, \quad (2)$$

$$J_k = nFkC_0, \quad (3)$$

where J is the current density of the test, J_k is the current density of the current limit, J_1 is the limiting current density of the diffusion, ω represents the angular velocity of the ring electrode ($\omega = 2\pi N$, where N is the linear rotation speed in rpm), n represents the number of electrons transferred during the ORR, F stands for the Faraday constant ($96,485 \text{ C mol}^{-1}$), C_0 is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_0 is the diffusion coefficient of O_2 in 0.1 mol L^{-1} KOH ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), v is the kinetic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$), and k is the electron transfer rate constant. Tafel slopes were calculated according to the Tafel equation:

$$\eta = b \log(J) + a, \quad (4)$$

where η is the overpotential, J is the measured current density and b is the Tafel slope.

The number of electron transfer (n) and its hydrogen peroxide yield ($\text{H}_2\text{O}_2\%$) were calculated according to the following equation:

$$n = 4 \times \frac{I_D}{I_D + \frac{I_R}{N}}, \quad (5)$$

$$\text{H}_2\text{O}_2\% = 200 \times \frac{\frac{I_R}{N}}{I_D + \frac{I_R}{N}}, \quad (6)$$

where I_D and I_R correspond to the disk current and the

ring current, respectively. The current collection efficiency of N in a platinum ring is 0.37.

The OER performance was evaluated by a CHI660 electrochemical workstation under a three-electrode system, in which the synthesized NiFeP/NF support catalyst, a RHE, and a platinum plate were used as the working electrode, reference electrode and counter electrode, respectively. A 1 mol L⁻¹ KOH aqueous solution was used as the electrolyte. The LSV polarization curve was obtained at a sweep rate of 5 mV s⁻¹.

Assembly and test of Zn–air battery

A homemade rechargeable liquid ZAB was assembled for electrochemical measurements. A zinc foil was used as an anode and 6 mol L⁻¹ KOH + 0.2 mol L⁻¹ zinc acetate was used as the electrolyte. The air-cathode was prepared as follows: 5 mg of the catalyst was uniformly dispersed in a mixed solution of 1.5 mL ethanol and 0.5 mL of 0.5 wt.% Nafion solution, and then the catalyst slurry was added dropwise on NiFeP/NF with a loading of 1 mg cm⁻². The ZAB was tested by a LAND CT2001A model battery test system (LANHE Company, Wuhan) under air atmosphere.

RESULTS AND DISCUSSION

Morphology and structure characterization

The CoFe/NC was synthesized by pyrolysis of a cubic CoFe-ZIF precursor, as illustrated in Scheme 1. First, the ZIF-67 nanocubes were synthesized by a precipitation reaction of Co(NO₃)₂·6H₂O and 2-MeIM in an aqueous solution. Then, the CoFe-ZIF could be obtained by adding FeSO₄·7H₂O through an ion-exchange reaction [33]. Afterwards, CoFe-ZIF was prepared by pyrolysis at 900°C. The morphology and structure of the as-prepared CoFe/NC-0.2-900 were characterized by SEM and TEM. The original ZIF-67 exhibited a nanocube size of approximately 500 nm (Fig. 1a). As shown in Fig. 1b, the resultant CoFe/NC-0.2-900 still maintained the original morphology and size of the ZIF-67 nanocubes after pyrolysis. The rough surface of CoFe/NC-0.2-900 can be observed due to the shrinkage of carbon skeleton during pyrolysis. Fig. S1a suggests that the sample synthesized by direct pyrolysis of ZIF-67, namely, Co/NC, inherits the structure of the ZIF-67 nanocube precursor with a uniform size of 500 nm. The samples derived from 0.1 and 0.3 mmol FeSO₄·7H₂O, denoted as CoFe/NC-0.1-900 and CoFe/NC-0.3-900 exhibited the same morphology as that of CoFe/NC-0.2 (Fig. S1b, c). In addition, the structures of CoFe/NC-0.2-700, CoFe/NC-0.2-800 and CoFe/NC-

Scheme 1 Synthetic scheme of CoFe/NC sample.

0.2-1000 did not obviously change by tuning the pyrolysis temperature, as shown in Fig. S2. The TEM images in Fig. 1c, d demonstrate that CoFe/NC-0.2-900 is composed of CoFe alloy nanoparticle-embedded carbon nanostructures. The high-resolution TEM (HRTEM) image in Fig. 1e further shows the presence of CoFe nanoparticles encapsulated by several layers of carbon shells. Obvious lattice fringes with interplane distances of 0.20 and 0.34 nm correspond to the CoFe alloy (110) and the graphitic carbon (002) planes, respectively (Fig. 1f). The ample contact between the CoFe alloy and the graphite carbon layer was beneficial to improving the electrocatalytic activity and stability.

XRD was used to confirm the crystalline phase of the samples. As shown in Fig. S3, the CoFe-ZIF precursors exhibited similar diffraction peaks to that of ZIF-67 nanocubes and simulated ZIF-67. However, the relative negative shift of diffraction peaks for the CoFe-ZIF precursors may be caused by lattice expansion originating from the Fe²⁺ ions partially replacing the Co ions in the ZIF-67 framework [34]. Moreover, the degree of negative shift increased with an increasing dose of FeSO₄·7H₂O, indicating that the lattice size increased with increasing Fe²⁺ ion concentration [35]. The sample without iron species was also prepared for comparison, named Co/NC, which displayed the (002) plane of graphitic carbon (PDF#41-1487) at approximately 26.4°, as illustrated in Fig. 2a. The other diffraction peaks at 44.21°, 51.52° and 75.85°, corresponded to the (111), (200) and (220) phase of metal Co (PDF#15-0806), respectively [36]. In addition, the CoFe/NC-0.2-900 sample also exhibited diffraction peaks at 26.38° of the graphitic carbon (002) plane. The other two main diffraction peaks at 44.8° and 65.7° matched well with the (110) and (200) planes of a CoFe alloy (PDF#49-1568), respectively, demonstrating

Figure 1 SEM images of (a) ZIF-67 nanocubes and (b) CoFe/NC-0.2-900. TEM (c, d) and HRTEM (e, f) images of CoFe/NC-0.2-900.

Figure 2 (a) XRD patterns and (b) Raman spectra of the CoFe/NC-0.2-900 and Co/NC samples.

that the CoFe/NC-0.2-900 was composed of a CoFe alloy and graphitic carbon, which was consistent with the above TEM analysis. The effective combination of a CoFe alloy can improve conductivity and increase the active sites of the electrocatalyst [37]. Raman spectroscopy was further adopted to characterize the carbon nanostructures. For the CoFe/NC-0.2-900 and Co/NC samples, the two peaks at 1361 and 1564 cm^{-1} were ascribed to the carbon D-band and G-band (Fig. 2b), respectively. The intensity ratio of the G-band and D-band can be used to evaluate the graphitic degree of carbon materials [38,39]. The I_G/I_D value of CoFe/NC was approximately 1.46, which was much higher than those of the other compared samples, including Co/NC and CoFe/NC derived from

different mole amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Fig. S4). In addition, the typical characteristic peak of graphitic carbon at 2721 cm^{-1} (2D-band) also indicated the high graphitization degree of the carbon nanostructure in the CoFe/NC sample [40]. It was demonstrated that the CoFe/NC-0.2-900 had outstanding conductivity, which could be favorable for electron transfer.

XPS was used to detect the surface structure and chemical valence of the samples. From the wide spectra of XPS in Fig. 3a, it can be seen that the CoFe/NC-0.2-900 was composed of Fe, Co, C, N, and O elements, whereas the Co/NC sample contained Co, C, N, and O elements. The high-resolution C 1s spectrum in Fig. 3b revealed the presence of four types of C-atom bonding in the CoFe/

Figure 3 Wide-scan XPS spectra of (a) CoFe/NC-0.2-900 and Co/NC samples. High-resolution XPS spectra of (b) C 1s, (c) N 1s, (e) Co 2p and (f) Fe 2p for the CoFe/NC-0.2-900 sample. Contents of different N-doping types for (d) CoFe/NC-0.2-900 and Co/NC samples.

NC-0.2-900, namely, C–C (284.62 eV), C–N (285.72 eV), C=O (287.61 eV) and π – π^* (289.60 eV) bonds. The presence of a C–N bond proved that N atoms were successfully doped into the carbon skeleton [41]. As illustrated in Fig. 3c, the high-resolution N 1s spectrum of the CoFe/NC-0.2-900 sample was mainly deconvoluted into pyridine N (396.88 eV), pyrrole N (399.03 eV) and graphitic N (402.03 eV). It can be concluded that the main forms of nitrogen in CoFe/NC-0.2-900 was pyridinic N and graphitic N (approximately 70 wt.% of total nitrogen content) (Fig. 3d), and they were considered to be the main contributor to the catalytic activity of ORR [42].

The high-resolution Co 2p XPS spectrum of CoFe/NC-

0.2-900 in Fig. 3e shows that Co 2p_{3/2} can be deconvoluted into three different peaks of 780.12 eV (Co⁰), 781.64 eV (high-valence state Co) and 787.08 eV (shakeup satellite peaks), which can act as electrocatalytic active sites for ORR. Similarly, the three peaks in Co 2p_{1/2} corresponded to the Co⁰, high-valence state Co and shakeup satellite peaks. High-valence state Co could provide evidence of Co–N, further indicating the interaction between Co and N [43]. The high-resolution Fe 2p XPS spectrum is shown in Fig. 3f. The main peaks at 716.91 and 706.89 eV were attributed to zero-valence metallic Fe, while the peaks at 725.18 and 714.46 eV with shakeup satellite peaks at 720.36 and 711.34 eV were assigned to the Fe 2p_{1/2} and Fe 2p_{3/2} of Fe²⁺, respectively.

The XPS spectra of Fe 2p and Co 2p also confirmed the presence of Fe–N and Co–N groups as well as Fe and Co metals. The high-resolution XPS spectra of N 1s, C 1s and Co 2p for Co/NC are shown in Fig. S5, which demonstrates the existence of C–N and Co–N bonds. The nitrogen adsorption-desorption isotherms are displayed in Fig. S6. It was demonstrated that the Brunauer-Emmett-Teller (BET) specific surface area of CoFe/NC-0.2-900. The BET specific surface area for CoFe/NC-0.1-900 was approximately $602.98 \text{ m}^2 \text{ g}^{-1}$, which was much higher than that of the Co/NC ($196.92 \text{ m}^2 \text{ g}^{-1}$), CoFe/NC-0.2-900 ($573.91 \text{ m}^2 \text{ g}^{-1}$) and CoFe/NC-0.3-900 ($384.75 \text{ m}^2 \text{ g}^{-1}$). A large surface area can promote the surface oxygen and electrolyte transport, thus enhancing ORR activity [44].

Electrocatalytic activity

Based on the special structure of CoFe/NC-0.2-900, the ORR performance was tested in an O_2 -saturated 0.1 mol L^{-1} KOH electrolyte by using a RDE at a scanning rate of 5 mV s^{-1} with a rotating speed of 1600 rpm. The most important criteria for evaluating ORR performance is the onset potential (E_{onset}) and the half-wave potential ($E_{1/2}$). As displayed in Fig. 4a, both the E_{onset} of 0.94 V and $E_{1/2}$ of 0.82 V for CoFe/NC-0.2-900 showed a much higher positive shift compared with that of the Co/NC catalyst ($E_{\text{onset}}=0.89 \text{ V}$, $E_{1/2}=0.75 \text{ V}$), and these values were slightly lower than that of the commercial Pt/C ($E_{\text{onset}}=0.99 \text{ V}$, $E_{1/2}=0.83 \text{ V}$). The results indicated that the presence of a bimetal FeCo alloy could indeed enhance ORR activity owing to the synergistic effect [45]. In addition, the performance of CoFe/NC-0.2-900 was better than that of CoFe/NC-0.1-900 ($E_{\text{onset}}=0.92 \text{ V}$, $E_{1/2}=0.78 \text{ V}$) and CoFe/NC-0.3-900 ($E_{\text{onset}}=0.91 \text{ V}$, $E_{1/2}=0.76 \text{ V}$), implying the optimal performance was achieved by CoFe/NC-0.2-900 due to the moderate metal and N-dopant contents and the high BET surface area (Fig. S7). In addition, the present catalyst exhibited much higher ORR activity than those of most of the reported CoFe-based nonprecious metal catalysts, especially in E_{onset} , $E_{1/2}$ and J_L (Table S1).

To further study the underlying electrocatalytic mechanism for ORR, the corresponding Tafel plots based on the LSV curves are presented in Fig. 4b. The Tafel plot of CoFe/NC-0.2-900 (73 mV dec^{-1}) was close to that of Pt/C (70 mV dec^{-1}), and much smaller than that of CoFe/NC-0.1-900 (98 mV dec^{-1}), CoFe/NC-0.3-900 (106 mV dec^{-1}) and Co/NC (112 mV dec^{-1}), which indicated the fast kinetics process of the CoFe/NC-0.2-900 catalyst and that the protonation process of oxygen was the rate determining step of the ORR. Moreover, the catalysts derived from different pyrolysis temperatures were also

tested as listed in Fig. S8. It can be concluded that the catalyst synthesized at 900°C exhibited the best ORR performance. Fig. 4c suggests that the limiting current density increased with increasing rotation speed. The corresponding K-L plots in the inset that were calculated at 0.3, 0.4, 0.5 and 0.6 V showed a linear relationship, and the calculated electron transfer number (n) was approximately 3.91. Fig. 4d displays the LSV curves of the CoFe/NC-0.2-900 and Pt/C catalysts obtained from the RRDE test. The electron transfer number (n) and the yields of hydrogen peroxide ($\text{H}_2\text{O}_2\%$) were further analyzed (Fig. 4e). On the basis of the ring current and the disk current, the electron transfer number was approximately 3.91, and the hydrogen peroxide yield was less than 5.0% between 0.2 and 0.7 V, which were close to the results of the Pt/C catalyst (Fig. S9), demonstrating a four-electron process. Long-term stability tests were also performed for the CoFe/NC-0.2-900 and Pt/C catalysts, as illustrated in Fig. 4f and Fig. S10. After 10,000 cycles, the $E_{1/2}$ of CoFe/NC-0.2-900 only experienced a negative shift of 10 mV, while the negative shift of Pt/C was approximately 36 mV. It was further confirmed that the stability of the CoFe/NC-0.2-900 catalyst was much better than that of the Pt/C catalyst.

The excellent ORR activity of CoFe/NC-0.2-900 was further confirmed by measuring the electrochemical active surface area (ECSA), which can be obtained from the C_{dl} calculated on the basis of the CV curves (Fig. S11). The CoFe/NC-0.2-900 exhibited a higher C_{dl} of approximately 29.32 mF cm^{-2} than that of Co/NC (25.15 mF cm^{-2}), implying that there are sufficient active sites present in CoFe/NC-0.2-900 compared with the number in Co/NC (25.15 mF cm^{-2}). [46]. The Nyquist plots in terms of electrochemical impedance spectroscopy (EIS) were provided to study the electrode kinetics. As shown in Fig. S12, the Nyquist plots demonstrated that the charge-transfer resistance for CoFe/NC-0.2-900 was smaller than that of Co/NC, indicating a faster charge transfer process with CoFe/NC-0.2-900.

The OER is the charging reaction of rechargeable ZABs, which is as important as the ORR. In order to assemble a ZAB by using CoFe/NC-0.2-900 as the ORR catalyst, we synthesized the NiFeP/NF (NiFeP nanoflowers grown on NF through a facile hydrothermal reaction followed by a phosphorization process) as the OER catalyst. The characteristic diffraction peaks of the XRD pattern were located between Ni_2P and Fe_2P (Fig. S13), revealing the formation of NiFeP on the NF [47]. The SEM image in Fig. S14 indicates the NiFeP has a diameter of approximately 7–10 μm . As shown in Fig. S15, NiFeP/NF ex-

Figure 4 Electrocatalytic ORR performance tested in O_2 -saturated 0.1 mol L^{-1} KOH electrolyte. (a) LSV curves tested at 1600 rpm with a scanning sweep of 5 mV s^{-1} of the CoFe/NC-0.2-900, Co/NC and Pt/C catalysts. (b) Tafel plots of CoFe/NC-0.2-900, Co/NC and Pt/C catalysts. (c) LSV curves of CoFe/NC-0.2-900 at different rotation rates and corresponding K-L plots (inset). (d) RRDE voltammograms at 1600 rpm with a scanning sweep of 5 mV s^{-1} . (e) H_2O_2 yield (blue) and electron transfer number (n) (red) of CoFe/NC-0.2-900 and Pt/C that were calculated based on (e). (f) LSV curves of CoFe/NC-0.2-900 before and after 10,000 cycles.

hibited a very low overpotential of 190 mV at 50 mA cm^{-2} , which was significantly higher than those of many reported RuO_2 catalysts [48].

Zn-air battery performance

A schematic diagram of a rechargeable ZAB is shown in

Fig. 5a. A home-made rechargeable ZAB was assembled by using CoFe/NC-0.2-900@NiFeP/NF (CoFe/NC-0.2-900 loaded on NiFeP/NF with a content of 1 mg cm^{-2}) as an air-cathode, 6 mol L^{-1} KOH + 0.2 mol L^{-1} zinc acetate as the electrolyte, and a zinc foil as the anode. During the discharge process, the oxygen at the cathode was reduced

Figure 5 Rechargeable ZAB performance. (a) Structural scheme of a home-made liquid ZAB. (b) Discharge curves of ZABs and the corresponding power density plots. (c) Discharge profiles of the liquid ZAB assembled using CoFe/NC-0.2-900@NiFeP/NF as an air-cathode at current densities of 2, 5, 10 and 20 mA cm⁻² for 20 h. (d) Long-term galvanostatic charge-discharge plots at 10 mA cm⁻². (e) Photograph of a blue light-emitting diode illuminated by three liquid batteries in series.

to hydroxide ions, and the zinc at the anode was oxidized to zincate ions and spontaneously converted to zinc oxide [49]. Fig. 5b shows the polarization and power density curve of the ZABs constructed with the CoFe/NC-0.2-900@NiFeP/NF and Pt/C+RuO₂/C catalysts. A higher peak power density of 173 mW cm⁻² for CoFe/NC-0.2-900@NiFeP/NF was obtained at 260 mA cm⁻², which exceeded those of the reported M-N-C structure catalysts, such as FeN_x/C (36 mW cm⁻² at 80 mA cm⁻²) [50] and Cu@Fe-N-C (92 mW cm⁻² at 130 mA cm⁻²) [51]. The open circuit voltage of the reversible ZAB was 1.423 V (Fig. S16). The galvanostatic discharge experiments at different current densities from 2 to 20 mA cm⁻² for 20 h are shown in Fig. 5c.

Impressively, the home-made liquid ZAB provided a higher voltage of 1.15 V even at 20 mA cm⁻² because of its excellent ORR activity. To further characterize the stability, long-term galvanostatic discharge and charge curves at 10 mA cm⁻² (charging for 10 min and discharging for 10 min) are displayed in Fig. 5d. The discharging and charging platforms of CoFe/NC-0.2-900@NiFeP/NF were approximately 1.09 and 1.93 V, respectively. Slightly attenuation was exhibited after 230 h (approximately 690 cycles) of the test, whereas an obvious performance de-

gradation for Pt/C+RuO₂/C could be observed. It is further explained that CoFe/NC-0.2-900@NiFeP/NF had better battery durability than the Pt/C+RuO₂/C. Furthermore, three ZABs connected in series can drive a 3.0 V blue light-emitting diode with good stability. Additionally, to explain the difference between the integrated electrode and the separated electrode for conventional electrochemical testing, the galvanostatic charge-discharge plots of the ZAB by using CoFe/NC-0.2-900 as the air-cathode was also examined. As shown in Fig. S17, the battery assembled by using CoFe/NC-0.2-900 as the air-cathode exhibited a higher discharging voltage of 2.15 V, which was attributed to the nonideal OER activity of CoFe/NC-0.2-900.

CONCLUSIONS

In conclusion, the CoFe/NC composed of CoFe alloy nanoparticle-embedded N-doped graphitic carbon nanostructures was successfully synthesized by the pyrolysis of a cubic CoFe-ZIF precursor. This catalyst possessed the merits of high surface area, plentiful N content and well-dispersed CoFe alloy nanoparticles, all of which benefit the electron/ion transfer during the electrocatalytic reaction. As a nonprecious metal electrocatalyst toward the

ORR, the catalyst exhibited an E_{onset} of 0.94 V, an $E_{1/2}$ of 0.82 V, a limiting current density of 6.4 mA cm^{-2} and long-term stability (only 10 mV attenuation after 10,000 cycles) in an alkaline electrolyte; these values surpassed those of the state-of-the-art Pt/C catalyst. When used as an ORR catalyst for ZABs, the assembled liquid battery showed a lower voltage gap, better durability, and higher power density compared with the commercial Pt/C + RuO₂/C catalysts. This simple synthesis method can be used for the construction of other functional materials derived from MOFs, which opens up a new way for the development of highly active electrocatalysts.

Received 9 August 2019; accepted 20 September 2019;
published online 6 November 2019

- Huang ZF, Song J, Li K, *et al.* Hollow cobalt-based bimetallic sulfide polyhedra for efficient all-pH-value electrochemical and photocatalytic hydrogen evolution. *J Am Chem Soc*, 2016, 138: 1359–1365
- Wang X, Yu L, Guan BY, *et al.* Metal-organic framework hybrid-assisted formation of Co₃O₄/Co-Fe oxide double-shelled nanoboxes for enhanced oxygen evolution. *Adv Mater*, 2018, 30: 1801211
- Jiao C, Wang Z, Zhao X, *et al.* Triple-shelled manganese-cobalt oxide hollow dodecahedra with highly enhanced performance for rechargeable alkaline batteries. *Angew Chem Int Ed*, 2019, 58: 996–1001
- Liu Q, Wang L, Liu X, *et al.* N-doped carbon-coated Co₃O₄ nanosheet array/carbon cloth for stable rechargeable Zn-air batteries. *Sci China Mater*, 2019, 62: 624–632
- Wang G, Chen J, Cai P, *et al.* A self-supported Ni-Co perselenide nanorod array as a high-activity bifunctional electrode for a hydrogen-producing hydrazine fuel cell. *J Mater Chem A*, 2018, 6: 17763–17770
- Lu Z, Wang B, Hu Y, *et al.* An isolated zinc-cobalt atomic pair for highly active and durable oxygen reduction. *Angew Chem Int Ed*, 2019, 58: 2622–2626
- Xu H, Ci S, Ding Y, *et al.* Recent advances in precious metal-free bifunctional catalysts for electrochemical conversion systems. *J Mater Chem A*, 2019, 7: 8006–8029
- Wang J, Liu W, Luo G, *et al.* Synergistic effect of well-defined dual sites boosting the oxygen reduction reaction. *Energy Environ Sci*, 2018, 11: 3375–3379
- Amiin IS, Pu Z, Liu X, *et al.* Multifunctional Mo-N/C@MoS₂ electrocatalysts for HER, OER, ORR, and Zn-air batteries. *Adv Funct Mater*, 2017, 27: 1702300
- Qiao Y, Yuan P, Hu Y, *et al.* Sulfuration of an Fe-N-C catalyst containing Fe_xC/Fe species to enhance the catalysis of oxygen reduction in acidic media and for use in flexible Zn-Air batteries. *Adv Mater*, 2018, 30: 1804504
- Bai Z, Heng J, Zhang Q, *et al.* Rational design of dodecahedral MnCo₂O_{4.5} hollowed-out nanocages as efficient bifunctional electrocatalysts for oxygen reduction and evolution. *Adv Energy Mater*, 2018, 8: 1802390
- Xiao Y, Tian C, Tian M, *et al.* Cobalt-vanadium bimetal-based nanoplates for efficient overall water splitting. *Sci China Mater*, 2018, 61: 80–90
- Li J, Chen M, Cullen DA, *et al.* Atomically dispersed manganese catalysts for oxygen reduction in proton-exchange membrane fuel cells. *Nat Catal*, 2018, 1: 935–945
- Liu J, Jin Z, Wang X, *et al.* Recent advances in active sites identification and regulation of M-N/C electro-catalysts towards ORR. *Sci China Chem*, 2019, 62: 669–683
- Du H, Kong RM, Guo X, *et al.* Recent progress in transition metal phosphides with enhanced electrocatalysis for hydrogen evolution. *Nanoscale*, 2018, 10: 21617–21624
- Zou L, Hou CC, Liu Z, *et al.* Superlong single-crystal metal-organic framework nanotubes. *J Am Chem Soc*, 2018, 140: 15393–15401
- Zhang W, Wu ZY, Jiang HL, *et al.* Nanowire-directed templating synthesis of metal-organic framework nanofibers and their derived porous doped carbon nanofibers for enhanced electrocatalysis. *J Am Chem Soc*, 2014, 136: 14385–14388
- Liang Q, Jin H, Wang Z, *et al.* Metal-organic frameworks derived reverse-encapsulation Co-NC@Mo₂C complex for efficient overall water splitting. *Nano Energy*, 2019, 57: 746–752
- Liu S, Wang Z, Zhou S, *et al.* Metal-organic-framework-derived hybrid carbon nanocages as a bifunctional electrocatalyst for oxygen reduction and evolution. *Adv Mater*, 2017, 29: 1700874
- Amiin IS, Liu X, Pu Z, *et al.* From 3D ZIF nanocrystals to Co-N_x/C nanorod array electrocatalysts for ORR, OER, and Zn-air batteries. *Adv Funct Mater*, 2018, 28: 1704638
- Meng J, Niu C, Xu L, *et al.* General oriented formation of carbon nanotubes from metal-organic frameworks. *J Am Chem Soc*, 2017, 139: 8212–8221
- Wu HB, Xia BY, Yu L, *et al.* Porous molybdenum carbide nanooctahedrons synthesized *via* confined carburization in metal-organic frameworks for efficient hydrogen production. *Nat Commun*, 2015, 6: 6512
- Wang T, Kou Z, Mu S, *et al.* 2D dual-metal zeolitic-imidazolate-framework-(ZIF)-derived bifunctional air electrodes with ultrahigh electrochemical properties for rechargeable zinc-air batteries. *Adv Funct Mater*, 2018, 28: 1705048
- Xia BY, Yan Y, Li N, *et al.* A metal-organic framework-derived bifunctional oxygen electrocatalyst. *Nat Energy*, 2016, 1: 15006
- Cai P, Peng X, Huang J, *et al.* Covalent organic frameworks derived hollow structured N-doped noble carbon for asymmetric-electrolyte Zn-air battery. *Sci China Chem*, 2019, 62: 385–392
- Yu P, Wang L, Sun F, *et al.* Co nanoislands rooted on Co-N-C nanosheets as efficient oxygen electrocatalyst for Zn-air batteries. *Adv Mater*, 2019, 10: 1901666
- Guan BY, Lu Y, Wang Y, *et al.* Porous iron-cobalt alloy/nitrogen-doped carbon cages synthesized *via* pyrolysis of complex metal-organic framework hybrids for oxygen reduction. *Adv Funct Mater*, 2018, 28: 1706738
- Chen Y, Ji S, Wang Y, *et al.* Isolated single iron atoms anchored on N-doped porous carbon as an efficient electrocatalyst for the oxygen reduction reaction. *Angew Chem Int Ed*, 2017, 56: 6937–6941
- Fu Y, Yu HY, Jiang C, *et al.* NiCo alloy nanoparticles decorated on N-doped carbon nanofibers as highly active and durable oxygen electrocatalyst. *Adv Funct Mater*, 2018, 28: 1705094
- Liu X, Wang L, Yu P, *et al.* A stable bifunctional catalyst for rechargeable zinc-air batteries: iron-cobalt nanoparticles embedded in a nitrogen-doped 3D carbon matrix. *Angew Chem Int Ed*, 2018, 57: 16166–16170

- 31 Li S, Chen W, Pan H, *et al.* FeCo alloy nanoparticles coated by an ultrathin N-doped carbon layer and encapsulated in carbon nanotubes as a highly efficient bifunctional air electrode for rechargeable Zn-air batteries. *ACS Sustain Chem Eng*, 2019, 7: 8530–8541
- 32 Qu Y, Li Z, Chen W, *et al.* Direct transformation of bulk copper into copper single sites *via* emitting and trapping of atoms. *Nat Catal*, 2018, 1: 781–786
- 33 Wang J, Huang Z, Liu W, *et al.* Design of N-coordinated dual-metal sites: a stable and active Pt-free catalyst for acidic oxygen reduction reaction. *J Am Chem Soc*, 2017, 139: 17281–17284
- 34 Kuang M, Wang Q, Han P, *et al.* Cu, Co-embedded N-enriched mesoporous carbon for efficient oxygen reduction and hydrogen evolution reactions. *Adv Energy Mater*, 2017, 7: 1700193
- 35 Hu Z, Guo Z, Zhang Z, *et al.* Bimetal zeolitic imidazolate framework-derived iron-, cobalt- and nitrogen-codoped carbon nanopolyhedra electrocatalyst for efficient oxygen reduction. *ACS Appl Mater Interfaces*, 2018, 10: 12651–12658
- 36 Wei L, Qiu L, Liu Y, *et al.* Mn-doped Co–N–C dodecahedron as a bifunctional electrocatalyst for highly efficient Zn–air batteries. *ACS Sustain Chem Eng*, 2019, 7: 14180–14188
- 37 Li C, Wu M, Liu R. High-performance bifunctional oxygen electrocatalysts for zinc-air batteries over mesoporous Fe/Co–N–C nanofibers with embedding FeCo alloy nanoparticles. *Appl Catal B-Environ*, 2019, 244: 150–158
- 38 Zhao Y, Lai Q, Zhu J, *et al.* Controllable construction of core-shell polymer@zeolitic imidazolate frameworks fiber derived heteroatom-doped carbon nanofiber network for efficient oxygen electrocatalysis. *Small*, 2018, 14: 1704207
- 39 Chen H, Shen K, Mao Q, *et al.* Nanoreactor of MOF-derived yolk-shell Co@C–N: precisely controllable structure and enhanced catalytic activity. *ACS Catal*, 2018, 8: 1417–1426
- 40 Wu Q, Liang J, Yi JD, *et al.* Porous nitrogen/halogen dual-doped nanocarbons derived from imidazolium functionalized cationic metal-organic frameworks for highly efficient oxygen reduction reaction. *Sci China Mater*, 2019, 62: 671–680
- 41 Jin Q, Ren B, Chen J, *et al.* A facile method to conduct 3D self-supporting Co-FeCo/N-doped graphene-like carbon bifunctional electrocatalysts for flexible solid-state zinc air battery. *Appl Catal B-Environ*, 2019, 256: 117887
- 42 Zhu C, Shi Q, Xu BZ, *et al.* Hierarchically porous M–N–C (M = Co and Fe) single-atom electrocatalysts with robust MN_x active moieties enable enhanced ORR performance. *Adv Energy Mater*, 2018, 8: 1801956
- 43 Peera SG, Balamurugan J, Kim NH, *et al.* Sustainable synthesis of Co@NC core shell nanostructures from metal organic frameworks *via* mechanochemical coordination self-assembly: an efficient electrocatalyst for oxygen reduction reaction. *Small*, 2018, 14: 1800441
- 44 Niu Q, Chen B, Guo J, *et al.* Flexible, porous, and metal-heteroatom-doped carbon nanofibers as efficient ORR electrocatalysts for Zn–air battery. *Nano-Micro Lett*, 2019, 11: 8
- 45 Sultan S, Tiwari JN, Jang JH, *et al.* Highly efficient oxygen reduction reaction activity of graphitic tube encapsulating nitrated Co_xFe_y alloy. *Adv Energy Mater*, 2018, 8: 1801002
- 46 Pu Z, Zhao J, Amiin IS, *et al.* A universal synthesis strategy for P-rich noble metal diphosphide-based electrocatalysts for the hydrogen evolution reaction. *Energy Environ Sci*, 2019, 12: 952–957
- 47 Wu Y, Tao X, Qing Y, *et al.* Cr-doped FeNi–P nanoparticles encapsulated into N-doped carbon nanotube as a robust bifunctional catalyst for efficient overall water splitting. *Adv Mater*, 2019, 31: 1900178
- 48 Li M, Zhu Y, Wang H, *et al.* Ni strongly coupled with Mo₂C encapsulated in nitrogen-doped carbon nanofibers as robust bifunctional catalyst for overall water splitting. *Adv Energy Mater*, 2019, 9: 1803185
- 49 Wang Q, Shang L, Shi R, *et al.* NiFe layered double hydroxide nanoparticles on Co,N-codoped carbon nanoframes as efficient bifunctional catalysts for rechargeable zinc-air batteries. *Adv Energy Mater*, 2017, 7: 1700467
- 50 Han S, Hu X, Wang J, *et al.* Novel route to Fe-based cathode as an efficient bifunctional catalysts for rechargeable Zn-air battery. *Adv Energy Mater*, 2018, 8: 1800955
- 51 Wang Z, Jin H, Meng T, *et al.* Fe, Cu-coordinated ZIF-derived carbon framework for efficient oxygen reduction reaction and zinc-air batteries. *Adv Funct Mater*, 2018, 28: 1802596

Acknowledgements We gratefully acknowledge the support of the National Natural Science Foundation of China (21771059, 21631004 and 21571054), the Natural Science Foundation of Heilongjiang Province (JJ2019YX0122), Heilongjiang Provincial Postdoctoral Science Foundation (LBH-Q16194) and the excellent Youth Foundation of Heilongjiang University (JC201706).

Author contributions Du Z designed and performed the experiments; Yu P, Tian C and Liu X discussed partial experimental data. Wang L and Fu H wrote the paper. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information XRD, SEM, TEM, XPS and performance data for comparing the samples are available in the online version of the paper.

Ziyu Du is currently a MSc candidate in inorganic chemistry under the supervision of assistant professor Lei Wang and Prof. Honggang Fu at Heilongjiang University. Her research centers on developing the excellent catalytic materials of electrocatalysts for energy conversion devices.

Lei Wang received her BSc degree in 2007 and MSc degree in 2010 from Heilongjiang University, China. In 2013, she received her PhD degree from Jilin University, China. Then, she joined Heilongjiang University as a lecturer. She became an assistant professor in 2015. Her interests focus on the carbon-based nanomaterials for Li-ion batteries, supercapacitors, fuel cells, metal-air batteries, and electrocatalysis.

Honggang Fu received his BSc degree in 1984 and MSc degree in 1987 from Jilin University, China. He joined Heilongjiang University as an assistant professor in 1988. In 1999, he received his PhD degree from Harbin Institute of Technology, China. He became a full professor in 2000. Currently, he is Cheung Kong Scholar Professor. His interests focus on the oxide-based nanomaterials for solar energy conversion and photocatalysis, the carbon-based nanomaterials for energy conversion and storage, and electrocatalysis.

立方体咪唑骨架衍生CoFe合金纳米粒子嵌入N-掺杂石墨化碳中用于锌空气电池放电反应

杜梓毓, 于鹏, 王蕾*, 田春贵, 刘旭, 张光颖, 付宏刚*

摘要 目前, 贵金属铂被认为是性能最优异的氧还原催化剂, 但是其昂贵的价格、有限的储量制约了其大规模应用, 因此制备具有高催化活性和稳定性的过渡金属基催化剂迫在眉睫. 在本工作中, 我们构筑了一种CoFe合金纳米颗粒嵌入到N-掺杂石墨化碳纳米结构中的复合材料(CoFe/NC)作为氧还原催化剂. 我们首先制备了ZIF-67纳米立方体, 再利用离子交换法在其骨架中引入 Fe^{2+} 形成CoFe-ZIF前驱体. 通过在惰性气氛下煅烧得到CoFe/NC催化剂. 由于钴、铁及氮掺杂的协同作用, CoFe/NC-0.2-900催化剂(在 900°C 下煅烧掺杂 0.2 mmol 硫酸亚铁的CoFe/NC)表现出优异的氧还原性能, 尤其是极限电流密度(6.4 mA cm^{-2})远高于Pt/C(5.1 mA cm^{-2}). 采用CoFe/NC-0.2-900和NiFeP/NF(负载在泡沫镍上的NiFeP)分别作为放电和充电反应催化剂组装的可充电锌空气电池, 与传统的Pt/C+ RuO_2 /C催化剂组装的电池相比, 具有较低的充放电电压差、较大的功率密度和更优异的循环稳定性.