



Preparation and properties of transition metal nitrides caged in N-doped hollow porous carbon sphere for oxygen reduction reaction

Yan-juan LI<sup>1</sup>, Min WANG<sup>1</sup>, Sa LIU<sup>1</sup>, Jing-xia GAO<sup>1</sup>, Shun YANG<sup>1</sup>, Zi-hao LIU<sup>1</sup>, Xiao-yong LAI<sup>2</sup>, Xiao YAN<sup>1</sup>

1. Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials,

School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou 221116, China;

2. State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China

Received 1 June 2020; accepted 28 December 2020

Abstract: A series of transition metal nitrides ( $M_xN_y$ , M=Fe, Co, Ni) nanoparticle (NP) composites caged in N-doped hollow porous carbon sphere (NHPCS) were prepared by impregnation and heat treatment methods. These composites combine the high catalytic activity of nitrides and the high-efficiency mass transfer characteristics of NHPCS. The oxygen reduction reaction results indicate that Fe<sub>2</sub>N/NHPCS has the synergistic catalytic performance of higher onset potential (0.96 V), higher electron transfer number (~4) and higher limited current density (1.4 times as high as that of commercial Pt/C). In addition, this material is implemented as the air catalyst for zinc–air battery that exhibits considerable specific capacity (795.1 mA·h/g) comparable to that of Pt/C, higher durability and maximum power density (173.1 mW/cm<sup>2</sup>).

Key words: N-doped porous carbon; transition metal nitrides; Zn-air battery; oxygen reduction reaction; fuel cell

# **1** Introduction

Cathode oxygen reduction reaction (ORR) is a critical reaction for metal-air batteries and fuel cells that are considered as the promising electrical devices with energy efficiency and high environmental friendliness [1-6]. However, the practical application of these devices in the industry was severely hampered by the sluggish kinetics of ORR [7-9]. Pt is recognized as the most effective electrocatalyst; however, the high price and limited reserves, especially vulnerable to the toxicity of CO methanol, make it not suitable for and commercialization [10,11]. Therefore, it is of fundamental and practical importance to develop efficient electrocatalysts with inexpensive cost,

excellent durability and environmental friendliness. Numerous catalysts with high performance were explored, including metal oxides [3,12,13], metal sulfides [2,14,15], metal carbides [11,16], metal-free carbon [1,17], transition metals and nitrogen co-doped carbon as host (M—N<sub>x</sub>—C, M=Fe, Co, Ni) [18–20]. Notably, a series of M—N<sub>x</sub>—C electrocatalysts are proved, in which both M and N can be as the active sites, to exhibit higher activity, four-electron selectivity and excellent stability.

Transition metal nitrides ( $M_xN_y$ , M=Fe, Co, Ni, etc) have aroused intense attention due to their unique structural characteristics. The existence of mixture bonds (including ionic bonds, metal bonds and covalent bonds) formed between N atom and metal endows nitrides with conductivity similar to

DOI: 10.1016/S1003-6326(21)65587-5

Yan-juan LI and Min WANG contributed equally to this work

Corresponding author: Xiao YAN, Tel: +86-516-83403166, E-mail: yanxiao@jsnu.edu.cn

<sup>1003-6326/© 2021</sup> The Nonferrous Metals Society of China. Published by Elsevier Ltd & Science Press

metal, which makes it have similar performance with noble metal electrode [21–26]. Furthermore, the theoretical calculations predicted that  $M_x N_y$  is more conducive to the transportation of chargecarrier and has higher electrical conductivity than the corresponding oxides [27,28]. However, the catalytic activity and stability of nitrides for ORR are not ideal due to the lack of catalytic centers and small specific surface area. In order to overcome the above problems, it is a good strategy to combine nitrides and carbon-based material with numerous channel structures [29–32].

Nitrogen-doped hollow porous carbon sphere (NHPCS) with large specific surface area, abundant pores, and high electron conductivity can provide abundantly accessible active sites near the external surface of the catalysts to participate in the ORR, while the active sites buried in the dense carbon matrix remain inactive [29,33,34]. However, there are few studies on the application of metal nitrides ( $M_xN_y$ , M= Fe, Co, Ni) incorporated into N-doped hollow porous carbon sphere as highly efficient electrocatalyst towards ORR both in fuel cells and zinc–air batteries.

Herein, a series of  $M_x N_y$  (M=Fe, Co, Ni) nanoparticles (NPs) assembled into NHPCS  $(M_x N_y / NHPCS)$  were constructed. These materials have several merits: Firstly, metal element will preferentially combine with nitrogen in the carbon matrix and then react with NH<sub>3</sub> to form nitrides with M-N/C bond, which is more stable than the original  $M - N_x$  species and conducive to good dispersion of nitrides. Secondly, the introduction of nitride into the pore-rich structure does not destroy the large specific surface area of the carbon material carrier, which leads to the exposure of more active sites and provides an open channel for oxygen. Thirdly, the NHPCS interacting with  $M_x N_y$  NPs is beneficial to electron transfer due to its high conductivity. Such a structure gives the material excellent properties. The prepared Fe<sub>2</sub>N/NHPCS manifests outstanding catalytic activity for ORR with excellent stability and better methanol tolerance. Additionally, the prepared catalyst was implemented as the air catalyst for zinc-air battery that exhibits a comparable specific capacity of 795.1 mA·h/g and maximum power density of  $173.1 \text{ mW/cm}^2$ .

## 2 Experimental

#### 2.1 Synthesis of M<sub>x</sub>N<sub>y</sub>/NHPCS

The NHPCS was obtained according to previously reported method [35]. 0.1 g of NHPCS was added into 30 mL of the aqueous solution containing 125 mg of  $Co(NO_3)_2 \cdot 6H_2O$  (or 125 mg of Ni(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O or 90 mg of Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) and stirred for 2 h. Then, the solvent was evaporated at 45 °C, and dried at 200 °C to get  $M_xO_y/NHPCS$ , and subsequently, Co<sub>2</sub>N/NHPCS was annealed at 550 °C in NH<sub>3</sub> for 2 h. For Ni<sub>3</sub>N/NHPCS, the annealed temperature in NH<sub>3</sub> is 600 °C. While for Fe<sub>2</sub>N/NHPCS, the Fe<sub>3</sub>O<sub>4</sub>/ NHPCS was heated at 750 °C for 3 h.

#### 2.2 Characterization of materials

The structural features and morphologies were characterized by powder X-ray diffractometer (XRD, D8 ADVANCE X-ray diffractometer), scanning electron microscope (SEM/EDS, S-8010) and transmission electron microscope (TEM, Tacnai G2 F20). The X-ray photoelectron spectroscopy (XPS) spectrum was harvested on a VG ESCALAB LKII instrument with Mg KR-ADES (*hv*= 1253.6 eV). The nitrogen adsorption-desorption isotherms were recorded on an Autosorb-IQ2-VP analyzer at 77 K.

#### 2.3 Electrochemical measurement

Electrochemical properties were tested using electrochemical workstation (CHI 760E). The test system adopted three-electrodes rotating disc electrode or rotating ring disc electrode (RDE or RRDE), where Pt foil  $(1 \text{ cm}^2)$  and saturated calomel electrode (SCE) were selected as counter electrode and reference electrode, respectively. The ink of all catalysts was made as follows: 5 mg of product was added into a mixture solution containing 0.75 mL of isopropanol and 50 µL of nation solution and then ultra-sonicated. The cleaned glassy carbon electrode (RDE, area:  $0.19625 \text{ cm}^2$ ) was used as work electrode and the surface was covered by certain amount of the above ink. The loading of the prepared catalysts was 637  $\mu$ g/cm<sup>2</sup>. Simultaneously, commercial Pt/C was selected as a reference with Pt loading of 25.4  $\mu$ g/cm<sup>2</sup>. The test condition was in 0.1 mol/L KOH solution with saturated N<sub>2</sub> or O<sub>2</sub> before all tests. Cyclic voltammetry (CV) and linear

sweep voltammetry (LSV) were harvested in an electrochemistry window of 0-1.2 V (vs RHE). Current density-time (*J*-*t*) curves were recorded at 0.6 V (vs RHE) in 0.1 mol/L KOH solution with 1.0 mol/L methanol.

#### 2.4 Performance of zinc-air batteries (ZABs)

A cleaned Zn plate was selected as an anode. 6 mol/L KOH was used as the electrolyte for primary ZAB. The air electrode of primary ZAB was fabricated as follows: a gas diffusion layer (GDL) attached with carbon cloth (the active area of 1 cm<sup>2</sup>) was covered by 65  $\mu$ L of catalyst ink, in which a catalyst loading of 0.5 mg/cm<sup>2</sup> was used. Afterward, the air electrode was dried at room temperature. The commercial 20%Pt/C was selected as a reference. The discharge polarization curves were obtained by LSV at a scanning rate of 1 mV/s.

## **3 Results and discussion**

## 3.1 Structural features and morphologies

 $M_xN_y/NHPCS$  was synthesized through an anion conversion from  $M_xO_y$  under ammonia atmosphere. The crystal structure of  $M_xN_y/NHPCS$ was examined by XRD (Fig. 1). Compared with the standard card, the characteristic peaks in the three products are assigned to the crystalline planes of



Fig. 1 XRD patterns of  $M_x N_v / NHPCS$ 

Fe<sub>2</sub>N (PDF No. 2-1206), Co<sub>2</sub>N (PDF No. 6-647), and Ni<sub>3</sub>N (PDF No. 10-280), respectively, showing that the  $M_xN_y/NHPCS$  materials are successfully harvested.

The typical morphologies of all catalysts are shown in Fig. 2, where well-defined spheres with diameters of 80–100 nm can be seen. The NHPCS spheres with smooth surface are dispersed well. From the SEM image of Fe<sub>2</sub>N/NHPCS, no obvious change observed indicates that the small Fe<sub>2</sub>N particles are homogenously distributed (Fig. 2(b)). While numerous small size particles are anchored on the surface of Co<sub>2</sub>N/NHPCS (Fig. 2(c)) and Ni3N/NHPCS (Fig. 2(d)), which is detrimental to the catalytic performance.



Fig. 2 SEM images of NHPCS (a), Fe<sub>2</sub>N/NHPCS (b), Co<sub>2</sub>N/NHPCS (c) and Ni<sub>3</sub>N/NHPCS (d)

1430

Taking Fe<sub>2</sub>N/NHPCS as an instance, more detailed microstructures of the nanocomposite were detected by TEM, as shown in Fig. 3. Figure 3(a) shows that the NHPCS spheres have a hollow structure with a diameter of ~100 nm, in which the size of shell is ~60 nm. The original morphology can still be maintained (Fig. 3(b)) after loading nitrides Figs. 3(b, c). In addition, the Fe<sub>2</sub>N nanoparticles with diameters of 10-20 nm are uniformly anchored in the hollow carbon, which plays three primary roles. Firstly, the carbon cladding limits the expansion and dissolution of Fe<sub>2</sub>N NPs, which significantly improves the stability of catalysts. Secondly, the hollow and mesopores structures provide enough space for mass transfer of O<sub>2</sub> and intermediate species. Thirdly, the carbon shells further enhance the electrode conductivity. Furthermore, HRTEM observations show that the Fe<sub>2</sub>N particles with a darker periphery display intelligible distance of 0.21 and 0.22 nm, which are in accordance with the (101) and (002) crystal planes of  $Fe_2N$ , respectively (Fig. 3(d)).

 $N_2$  adsorption-desorption was employed to investigate the textural structure of samples. The results are shown in Fig. 4. All isotherms present Type IV, indicating that there are a large number of mesopores in all catalysts [36,37], which contribute to the high surface area and provide more active adsorption sites. The NHPCS has a high specific surface area of 1024.25 m<sup>2</sup>/g, large pore volume of 0.78 cm<sup>3</sup>/g, and pore size of 3.94 nm. For  $M_x N_y$ / NHPCS, the specific surface area and pore volume decrease, indicating that the  $M_x N_y$  is successfully loaded. For Fe<sub>2</sub>N/NHPCS, two new pores centered at 6.0 and 13.1 nm appear due to non-compact packed Fe<sub>2</sub>N particles, which lead to larger pore volume  $(0.84 \text{ cm}^3/\text{g})$  (Table 1). Furthermore, the curves sharply increase in the relative pressure range of 0.9-1.0, confirming the existence of stacked macropores, which not only offer a propagation path for the ORR centers to capture active species and electrons but also enhance the diffusion rate of O<sub>2</sub>. In conclusion, the synergistic effect of the above results will accelerate the catalytic reaction.

X-ray photoemission spectroscopy (XPS) was used to further study the surface chemistry of all samples. N element can be detected in NHPCS (Fig. 5(a)), suggesting successfully doping of heteroatoms into carbon matrix. The nitrogen deconvolution shows three major forms of N doping in the NHPCS at 397.9, 399.8 and 401.6 eV [38,39] with contents of 33.76% pyridinic



Fig. 3 TEM/HRTEM images of NHPCS (a) and Fe<sub>2</sub>N/NHPCS (b-d)



**Fig. 4**  $N_2$  adsorption–desorption isotherms and pore size distribution of NHPCS (a),  $Fe_2N/NHPCS$  (b),  $Co_2N/NHPCS$  (c) and  $Ni_3N/NHPCS$  (d) (*V* and *d* in inserts are volume and diameter of pores, respectively)

from adsorption-desorption isotherm								
Sample	Specific surface area/ $(m^2 \cdot g^{-1})$	Pore volume/ $(cm^3 \cdot g^{-1})$	Pore size/nm					
NHPCS	1024.25	0.78	3.94					
Fe <sub>2</sub> N/NHPCS	656.55	0.84	3.97, 6.0, 13.1					
Co <sub>2</sub> N/NHPCS	549.42	0.44	3.92					
Ni <sub>3</sub> N/NHPCS	870.99	0.55	3.90					

 Table 1 Texture parameters of all composites obtained

 from adsorption-desorption isotherm

N, 43.97% pyrrolic N and 22.27% graphitic N, respectively. Each spectrum can be divided into four peaks for all  $M_xN_y/NHPCS$  catalysts. According to previous reports [40,41], the doped N in the form of pyridinic N and graphitic N, especially the former, is considered to be more active for catalysis in comparison to pyrrolic N. In particular, the total content of pyridinic N and graphitic N in Fe<sub>2</sub>N/NHPCS and Ni<sub>3</sub>N/NHPCS catalysts is up to 63%, respectively (Table 2), which enhances the catalytic performance. Furthermore, the addition peaks situated at 399.6, 397.6 and

397.5 eV in Figs. 5(b–d) are contributed to Fe—N, Co—N and Ni—N bonds, respectively, suggesting that the metal nitrides are successfully harvested. Generally, the N atoms in carbon matrix can enhance conductivity and capture metal atoms, and nitrides provide catalytic active sites. The synergistic effect of the two is conducive to improve catalytic performance.

#### 3.2 ORR performance

Cyclic voltammograms (CVs) were first carried out to detect the catalytic activities in 0.1 mol/L KOH solution with saturated  $O_2$  and  $N_2$ (Fig. 6(a)). The non-characteristic is observed from the CV curve under  $N_2$  condition, while all the prepared catalysts exhibit a certain redox peak under  $O_2$ -saturated condition. The difference of current density and potential between oxygen and nitrogen can indicate the catalytic performance for ORR and the values order from high to low as follows: Fe<sub>2</sub>N/NHPCS > Ni<sub>3</sub>N/NHPCS > Co<sub>2</sub>N/ NHPCS > NHPCS, indicating that Fe<sub>2</sub>N/NHPCS processes the best catalytic activity.



Fig. 5 N 1s XPS spectra of NHPCS (a), Fe<sub>2</sub>N/NHPCS (b), Co<sub>2</sub>N/NHPCS (c) and Ni<sub>3</sub>N/NHPCS (d)



Fig. 6 CV curves of catalysts in  $O_2$  (red lines) and  $N_2$  (black lines) saturated 0.1 mol/L KOH solution at 50 mV/s (a) and LSV curves of catalysts at scan rate of 10 mV/s and rotating speed of 1600 r/min (b)

Table 2 Contents of C, O	, M and different nitrogen spe	cies in all electrocatalysts (wt.%)

11.00

Sample	Content/wt.%			Fract	Fraction in N 1s spectrum/%		
	С	0	М	Ν	Pyridinic N	Pyrrolic N	Graphitic N
NHPCS	92.42	4.18	0	3.4	33.76	43.97	22.27
Fe <sub>2</sub> N/NHPCS	84.12	7.03	5.2	3.65	45.05	25.24	18.22
Co <sub>2</sub> N/NHPCS	89.9	5.48	2.88	1.74	32.67	35.19	26.22
Ni <sub>3</sub> N/NHPCS	81.35	7.14	7.44	4.07	46.16	29.10	17.05

further estimate To the electrocatalytic properties of all samples, LSV curves on RDE are presented in Fig. 6(b). Compared with other prepared samples, Fe<sub>2</sub>N/NHPCS exhibits the highest electrocatalytic activity towards ORR with an onset potential of 0.96 V (vs RHE) and a half-wave potential ( $\varphi_{1/2}$ ) of 0.81 V (vs RHE), which are slightly lower than those of Pt/C (0.98 and 0.86 V (vs RHE), respectively). However, the limited current density of Fe<sub>2</sub>N/NHPCS is 7.68 mA/cm<sup>2</sup> and 1.4 times as high as that of Pt/C, exceeding the theoretical diffusion limited current density  $(5.7 \text{ mA/cm}^2)$  calculated by Levich's equation, which is ascribed to the unique porous architectural structure characterized by TEM observation and N<sub>2</sub> adsorption-desorption isotherm. The unique porous structure facilitates the rapid mass transfer by shortening the diffusion pathways, in which the macroporous frameworks can serve as reactant buffering reservoirs and mesoporous frameworks can ensure a large specific surface area that is favorable to the exposure of active sites, and multi-electron transport channels [34,42,43]. According to the TEM image (Fig. 3(c)) and  $N_2$ adsorption-desorption isotherm (Fig. 4(b)), the Fe<sub>2</sub>N

is not solid particle and new pores appear at 6.0 and 13.1 nm, which might facilitate the mass transport, resulting in abnormally high limited current density.

In order to investigate the effect of catalyst load on properties of the electrode, the LSV curves with different loads from 159 to 796  $\mu$ g/cm<sup>2</sup> are displayed in Fig. 7(a). The one with a load of 637  $\mu$ g/cm<sup>2</sup> manifests the highest activity and sequentially all the electrodes discussed are with the same loading.

RDE measurements with different electrode rotation speeds and catalyst loads were performed to further understand the ORR kinetics and the catalytic pathway of the resulted catalysts. The results are shown in Fig. 7(b). Generally, the direct four-electron reduction of  $O_2$  which can deliver higher energy efficiency is desirable. All LSV curves exhibit well limiting current density with the catalyst loading of 637 µg/cm<sup>2</sup> and constant onset potential, indicating that the catalytic behaviour is display good linearity and near parallelism, indicating that the electron transfer numbers of all samples are similar.

According to the K-L equation (Eq. (1)), the



**Fig.** 7 LSV curves of  $Fe_2N/NHPCS$  with different loads at 1600 r/min (a), LSV curves of  $Fe_2N/NHPCS$  at various speeds and insert showing K–L plots (b), electron transfer number of  $Fe_2N/NHPCS$  by RRDE (c), yield of  $H_2O_2$  (d) and Tafel plots (e) of  $Fe_2N/NHPCS$  and Pt/C catalysts obtained from LSV curves

electron transfer number (*n*) is in the range of 3.80-4.10, suggesting the conversion reaction from  $O_2$  to  $H_2O$  is a quasi-four electron process. According to K–L equation, *n* can also be acquired by RRDE as shown in Fig. 7(c), and the results are well consistent with that obtained from K–L equation. Furthermore, the amount of the ORR intermediate, peroxide ( $H_2O_2$ ) is also quantified (Fig. 7(d)) and the average  $H_2O_2$  yield is ~5.8% at 0.45 V (vs RHE) according to Eq. (2). The Tafel plots of ORR on Fe<sub>2</sub>N/NHPCS and Pt/C catalysts are shown in Fig. 7(e). The Tafel slope of Fe<sub>2</sub>N/NHPCS is apparently smaller than that of Pt/C, which indicates the high intrinsic catalytic activity of Fe<sub>2</sub>N/NHPCS.

$$\frac{1}{J} = \frac{1}{J_{k}} + \frac{1}{J_{d}} = \frac{1}{J_{k}} + \frac{1}{B\omega^{0.5}} = \frac{1}{nkFC_{0}} + \frac{1}{0.62nFD_{0}^{2/3}\upsilon^{-1/6}C_{0}\omega^{0.5}}$$
(1)

where J represents the measured current density,  $J_k$  is the kinetic current density at a constant potential,

 $J_{\rm d}$  represents the diffusion-limited current density,  $\varpi$  is angular velocity of the disk, *n* represents total number of electrons transferred during the ORR test, *k* is the electron transfer rate constant, *F* is the Faraday constant (96485 C/mol),  $D_0$  represents the diffusion coefficient of O<sub>2</sub> in 0.1 mol/L KOH solution ( $1.9 \times 10^{-5}$  cm<sup>2</sup>/s), *v* is kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup>/s), and  $C_0$  is saturation concentration of O<sub>2</sub> in 0.1 mol/L KOH solution ( $1.2 \times 10^{-6}$  mol/cm<sup>3</sup>) [44,45].

$$\eta = 200 \times \frac{I_{\rm R}/N}{I_{\rm D} + I_{\rm R}/N} \times 100\%$$
<sup>(2)</sup>

where  $\eta$  is the yield of H<sub>2</sub>O<sub>2</sub>,  $I_R$  and  $I_D$  represent the diffusion-limited current and disk current, respectively, and the value of N is 0.424 (the collection efficiency of ring electrode) [46].

The permeation of methanol from anodic to cathodic and the failure of catalyst during long-time utilization are also the key indicators to evaluate the performance of fuel cells. The methanol tolerance of Fe<sub>2</sub>N/NHPCS and Pt/C (Fig. 8(a)) was estimated



**Fig. 8** Chronoamperometric responses of  $Fe_2N/NHPCS$  and Pt/C with 1 mol/L methanol added at around 50 s and potential of 0.6 V (vs RHE) (a), LSV curves of  $Fe_2N/NHPCS$  (b) and Pt/C (c) before and after 5000 cycles and TEM/HRTEM images of  $Fe_2N/NHPCS$  after 5000 cycles (d)

by chronoamperometry measurement. There is no obvious response observed in J-t curve for Fe<sub>2</sub>N/NHPCS electrode after adding 1 mol/L methanol at about 50 s, which suggests that Fe<sub>2</sub>N/NHPCS has good anti-crossover effect ability. While for Pt/C, the current density increases significantly. Durability is another indicator to measure the performance, and the LSV curves of catalysts before and after 5000 cycles are represented in Figs. 8(b, c). For Fe<sub>2</sub>N/NHPCS, almost no change can be observed at the onset potential and half-wave potential ( $\varphi_{1/2}$ ) except for a very slow attenuation in the limited current density. But for Pt/C, onset potential and  $\varphi_{1/2}$  both negatively shift more significantly (34 and 39 mV, respectively), and the current density drops sharply, which is just 87.8% of the original one. The excellent performance of Fe2N/NHPCS may be due to the maintenance of the structure (Fig. 8(d)). The above results confirm that Fe2N/NHPCS has potential application in fuel cell.

#### **3.3 ZABs performance**

The home-made primary zinc-air batteries (ZABs) were assembled (Fig. 9(a)), using zinc plate as anode and Fe<sub>2</sub>N/NHPCS as the air electrode catalyst, which were inspired by high ORR activities of Fe<sub>2</sub>N/NHPCS and Pt/C. A string of red-LEDs can be lighted by two Fe<sub>2</sub>N/NHPCS-based ZABs in series. As represented in Fig. 9(b), the open-circuit voltage (OCV) of Fe2N/NHPCS-based ZAB is 1.30 V, which is slightly higher than 1.19 V of Pt/C-based ZAB. The typical discharge curves for Fe<sub>2</sub>N/NHPCS and Pt/C at a current density of 20 mA/cm<sup>2</sup> display a similar voltage plateaus. However, the Fe<sub>2</sub>N/NHPCS manifests better durability. The discharge polarization curves are shown in Fig. 9(c). The maximum power density of Fe<sub>2</sub>N/NHPCS-based ZAB is  $173.1 \text{ mW/cm}^2$ , about 1.14 times that of the Pt/C-based ZAB  $(152.3 \text{ mW/cm}^2)$ , which illustrates that the prepared Fe<sub>2</sub>N/NHPCS possesses the highly electrochemical performance.



**Fig. 9** Photograph of home-made solid-state device of Zn–air batteries (a), open-circle voltage curves (b), specific capacities of zinc–air batteries (normalized to mass of consumed Zn) (c) and current density–voltage and current density–power density curves of zinc–air batteries using  $Fe_2N/NHPCS$  and Pt/C catalysts (d)

## **4** Conclusions

(1) A series of  $M_x N_y$  (M=Fe, Co, Ni) composite caged into N-doped hollow porous carbon sphere (NHPCS) for the oxygen reduction reaction were successfully harvested.

(2) For ORR, the prepared  $Fe_2N/NHPCS$  catalyst shows comparable performances in terms of onset potential, half-wave potential and high limited current density. Additionally,  $Fe_2N/NHPCS$  also has outstanding methanol resistance and superior durability compared with Pt/C catalyst.

(3) Fe<sub>2</sub>N/NHPCS as the air catalyst for zinc–air battery displays high durability, specific capacity (795.1 mA·h/g), and maximum power density of 173.1 mW/cm<sup>2</sup>.

## Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Nos. 51702137, 51802128), the Natural Science Foundation of Jiangsu Province, China (No. BK20181013), the Priority Academic Program Development of Jiangsu Higher Education Institutions, China (No. 18KJB430013), and the Foundation of State Key Laboratory of High-Efficiency Utilization of Coal and Green Chemical Engineering, China (No. 2020-KF-20).

## References

- ZHANG Jin-tao, ZHAO Zheng-hang, XIA Zhen-hai, DAI Li-ming. A metal-free bifunctional electrocatalyst for oxygen reduction and oxygen evolution reactions [J]. Nature Nanotechnology, 2015, 10: 444–452.
- [2] WANG Jun-ren, LU Hui-min, HONG Qing-shui, CAO Yuan, LI Xu-dong, BAI Jun-jie. Porous N, S-codoped carbon architectures with bimetallic sulphide nanoparticles encapsulated in graphitic layers: Highly active and robust electrocatalysts for the oxygen reduction reaction in Al-air batteries [J]. Chemical Engineering Journal, 2017, 330: 1342–1350.
- [3] ZHANG Han-ming, ZHAO Yong, ZHANG Yi-jie, ZHANG Ming-hui, CHENG Meng-si, YU Jia-li, LIU Hui-chao, JI Mu-wei, ZHU Cai-zhen, XU Jian. Fe<sub>3</sub>O<sub>4</sub> encapsulated in porous carbon nanobowls as efficient oxygen reduction reaction catalyst for Zn–air batteries [J]. Chemical Engineering Journal, 2019, 375: 122058.
- [4] WU Qiu-mei, RUAN Jian-ming, ZHOU Zhong-cheng, SANG Shang-bin. Effect of preparation routes on activity of Ag-MnO<sub>x</sub>/C as electrocatalysts for oxygen reduction reaction in alkaline media [J]. Transactions of Nonferrous

Metals Society of China, 2015, 25: 510-519.

- [5] LI Yan-qiang, CUI Ming, YIN Ze-hao, CHEN Si-ru, MA Ting-li. Metal-organic framework based bifunctional oxygen electrocatalysts for rechargeable zinc-air batteries: Current progress and prospects [J]. Chemical Science, 2020, 11: 11646–11671.
- [6] ZHANG Ming, XU Qiang, SANG Lin, DING Fei, LIU Xing-jiang, JIAO Li-fang. α-MnO<sub>2</sub> nanoneedle-based hollow microspheres coated with Pd nanoparticles as a novel catalyst for rechargeable lithium-air batteries [J]. Transactions of Nonferrous Metals Society of China, 2014, 24: 164–170.
- [7] KUMAR R, KHAN A A P, KHAN A, ASIRI A M, HAMID Y. Preparation and characterization of polyvinylchloride membrane embedded with Cu nanoparticles for electrochemical oxidation in direct methanol fuel cell [J]. Transactions of Nonferrous Metals Society of China, 2020, 30: 2207–2216.
- [8] FENG Yan, LEI Ge, HE Yu-qing, WANG Ri-chu, WANG Xiao-feng. Discharge performance of Mg–Al–Pb–La anode for Mg–air battery [J]. Transactions of Nonferrous Metals Society of China, 2018, 28: 2274–2286.
- [9] SONG Yan-yan, DUAN Dong, SHI Wen-yu, WANG Hai-yang, SUN Zhan-bo. Facile synthesis of 3D nanoporous Pd/Co<sub>2</sub>O<sub>3</sub> composites with enhanced catalytic performance for methanol oxidation [J]. Transactions of Nonferrous Metals Society of China, 2018, 28: 676–686.
- [10] ZHANG Yu, LIU Li-huai, LIU Sa, WANG Min, YANG Shun, YANG Zhi-lin, YAN Xiao, LI Yan-juan. Coral-like cobaltous sulfide/N, S-codoped carbon with hierarchical pores as highly efficient noble metal-free electrocatalyst for oxygen reduction reactions [J]. Journal of Alloys and Compounds, 2018, 769: 801–807.
- [11] KONG Ai-guo, MAO Cheng-yu, LIN Qi-pu, WEI Xiao, BU Xian-hui, FENG Ping-yun. From cage-in-cage MOF to N-doped and Co-nanoparticle-embedded carbon for oxygen reduction reaction [J]. Dalton Transactions, 2015, 44: 6748–6754.
- [12] CHEN Xiao-wen, WANG Si, WANG Yan, YANG Zheng, LIU Sa, GAO Jing-xia, SU Zi-qian, ZHU Ping, ZHAO Xin-sheng, WANG Guo-xiang. Nitrogen-doped mesoporous carbon layer with embedded Co/CoO<sub>x</sub> nanoparticles coated on CNTs for oxygen reduction reaction in Zn–air battery [J]. Electrocatalysis, 2019, 10: 277–286.
- [13] LI Yan-qiang, HUANG Hui-yong, CHEN Si-ru, YU Xin, WANG Chao, MA Ting-li. 2D nanoplate assembled nitrogen doped hollow carbon sphere decorated with Fe<sub>3</sub>O<sub>4</sub> as an efficient electrocatalyst for oxygen reduction reaction and Zn-air batteries [J]. Nano Research, 2019, 12: 2774–2780.
- [14] LI Yan-juan, LI Nan, YANAGISAWA K, DING Xiang, LI Xiao-tian, WEI Ying-jin, YAN Xiao. Spherical Rh<sub>17</sub>S<sub>15</sub>@C and Rh@C core-shell nanocomposites: Synthesis, growth mechanism and methanol tolerance in oxygen reduction reaction [J]. Chemical Engineering Journal, 2013, 228: 45–53.
- [15] LI Yan-juan, LI Nan, YAN Xiao, LI Xiao-tian, WANG Run-wei, ZHANG Xiao-ting. Watermelon-like Rh<sub>x</sub>S<sub>y</sub>@C nanospheres: Phase evolution and its influence on the

electrocatalytic performance for oxygen reduction reaction [J]. Journal of Materials Science, 2017, 52: 11402–11412.

- [16] KO A R, LEE Y W, MOON J S, HAN S B, CAO G Z, PARK K W. Ordered mesoporous tungsten carbide nanoplates as non-Pt catalysts for oxygen reduction reaction [J]. Applied Catalysis A: General, 2014, 477: 102–108.
- [17] GENG Dong-sheng, DING Ning, ANDY HOR T S, LIU Zhao-lin, SUN Xue-liang, ZONG Yun. Potential of metal-free "graphene alloy" as electrocatalysts for oxygen reduction reaction [J]. Journal of Materials Chemistry A, 2015, 3: 1795–1810.
- [18] KAMIYA K, HASHIMOTO K, NAKANISHI S. Instantaneous one-pot synthesis of Fe–N-modified graphene as an efficient electrocatalyst for the oxygen reduction reaction in acidic solutions [J]. Chemical Communications, 2012, 48: 10213–10215.
- [19] WANG Ying, CUI Xiao-qiang, ZHAO Jing-xiang, JIA Guang-ri, GU Lin, ZHANG Qing-hua, MENG Ling-kun, SHI Zhan, ZHENG Li-rong, WANG Chun-yu. Rational design of Fe–N/C hybrid for enhanced nitrogen reduction electrocatalysis under ambient conditions in aqueous solution [J]. ACS Catalysis, 2018, 9: 336–344.
- [20] LIU Xiao, LIU Hong, CHEN Chi, ZOU Liang-liang, LI Yuan, ZHANG Qing, YANG Bo, ZOU Zhi-qing, YANG Hui. Fe<sub>2</sub>N nanoparticles boosting  $FeN_x$  moieties for highly efficient oxygen reduction reaction in Fe–N–C porous catalyst [J]. Nano Research, 2019, 12: 1651–1657.
- [21] YE Chao, JIAO Yan, JIN Huan-yu, SLATTERY A D, DAVEY K, WANG Hai-hui, QIAO Shi-zhang. 2D MoN–VN heterostructure to regulate polysulfides for highly efficient lithium-sulfur batteries [J]. Angewandte Chemie International Edition, 2018, 57: 16703–16707.
- [22] LI Xing-xing, GAO Biao, HUANG Xian, GUO Zhi-jun, LI Qing-wei, ZHANG Xu-ming, CHU P K, HUO Kai-fu. Conductive mesoporous niobium nitride microspheres/ nitrogen-doped graphene hybrid with efficient polysulfide anchoring and catalytic conversion for high-performance lithium-sulfur batteries [J]. ACS Applied Materials & Interfaces, 2019, 11: 2961–2969.
- [23] XIAO Mei-ling, ZHANG Hao, CHEN Yong-ting, ZHU Jian-bing, GAO Li-qin, JIN Zhao, GE Jun-jie, JIANG Zheng, CHEN Sheng-li, LIU Chang-peng, XING Wei. Identification of binuclear Co<sub>2</sub>N<sub>5</sub> active sites for oxygen reduction reaction with more than one magnitude higher activity than single atom CoN<sub>4</sub> site [J]. Nano Energy, 2018, 46: 396–403.
- [24] CHEN Zhao-yang, LI Ya-nan, LEI Ling-li, BAO Shu-juan, WANG Min-qiang, ZHAO Zhi-liang, XU Mao-wen. Investigation of Fe<sub>2</sub>N@carbon encapsulated in N-doped graphene-like carbon as a catalyst in sustainable zinc-air batteries [J]. Catalysis Science & Technology, 2017, 7: 5670-5676.
- [25] ZHANG Jie, CHEN Jin-wei, LUO Yan, CHEN Yi-han, KIANI M, WEI Xiao-yang, LUO Rui, WANG Gang, WANG Rui-lin. Controllable synthesis of two-dimensional tungsten nitride nanosheets as electrocatalysts for oxygen reduction reaction [J]. Science China (Materials), 2018, 61: 1567–1574.
- [26] FRITZ K E, YAN Yi-chen, SUNTIVICH J. Influence of 3D transition-metal substitution on the oxygen reduction

reaction electrocatalysis of ternary nitrides in acid [J]. Nano Research, 2019, 12: 2307–2312.

- [27] JIA Xiao-dan, ZHAO Yu-fei, CHEN Guang-bo, SHANG Lu, SHI Run, KANG Xiao-feng, WATERHOUSE G I N, WU Li-zhu, TUNG C H, ZHANG Tie-rui. Ni<sub>3</sub>FeN nanoparticles derived from ultrathin NiFe-layered double hydroxide nanosheets: An efficient overall water splitting electrocatalyst [J]. Advanced Energy Materials, 2016, 6: 1502585.
- [28] CHI Yi-min, MISHRA M, CHIN T K, LIU W S, PERNG T P. Fabrication of macroporous/mesoporous titanium nitride structure and its application as catalyst support for proton exchange membrane fuel cell [J]. ACS Applied Energy Materials, 2019, 2: 398–405.
- [29] SAAD A, CHENG Zhi-xing, ZHANG Xu-yang, LIU Si-qi, SHEN Hang-jia, THOMAS T, WANG Jia-cheng, YANG Ming-hui. Ordered mesoporous cobalt–nickel nitride prepared by nanocasting for oxygen evolution reaction electrocatalysis [J]. Advanced Materials Interfaces, 2019, 6: 1900960.
- [30] WANG Qing-hong, ZHANG Wen-chao, GUO Can, LIU Ya-jie, WANG Chao, GUO Zai-ping. In situ construction of 3D interconnected FeS@Fe<sub>3</sub>C@graphitic carbon networks for high-performance sodium-ion batteries [J]. Advanced Functional Materials, 2017, 27: 1703390.
- [31] GAO Tao-tao, JIN Zhao-yu, ZHANG Ya-jie, TAN Guangqun, YUAN Hong-yan, XIAO Dan. Coupling cobalt-iron bimetallic nitrides and N-doped multi-walled carbon nanotubes as high-performance bifunctional catalysts for oxygen evolution and reduction reaction [J]. Electrochimica Acta, 2017, 258: 51–60.
- [32] LI Zhen-jiang, WANG Xue-hua, LIU Jing, GAO Cheng-hai, JIANG Lu-hua, LIN Yu-sheng, MENG A-lan. 3D Honeycomb nanostructure comprised of mesoporous N-doped carbon nanosheets encapsulating isolated cobalt and vanadium nitride nanoparticles as a highly efficient electrocatalyst for the oxygen reduction reaction [J]. ACS Sustainable Chemistry & Engineering, 2020, 8: 3291–3301.
- [33] HU Yu-xiang, LUO Bin, YE De-lai, ZHU Xiao-bo, LYU Miao-qiang, WANG Lian-zhou. An innovative freeze-dried reduced graphene oxide supported SnS<sub>2</sub> cathode active material for aluminum-ion batteries [J]. Advanced Materials, 2017, 29: 1606132.
- [34] PAMPEL J, FELLINGER T P. Opening of bottleneck pores for the improvement of nitrogen doped carbon electrocatalysts [J]. Advanced Energy Materials, 2016, 6: 1502389.
- [35] XU Fei, TANG Zhi-wei, HUANG Si-qi, CHEN Lu-yi, LIANG Ye-ru, MAI Wei-cong, ZHONG Hui, FU Ruo-wen, WU Ding-cai. Facile synthesis of ultrahigh-surface-area hollow carbon nanospheres for enhanced adsorption and energy storage [J]. Nature Communications, 2015, 6: 7221.
- [36] LI Yan-juan, YU Liang-min, LI Nan, YAN Wen-fu, LI Xiao-tian. Heterostructures of Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub> mesoporous spheres with highly efficient visible light photocatalytic activity [J]. Journal of Colloid and Interface Science, 2015, 450: 246–253.
- [37] CHEN Si-ru, HUANG Hui-yong, LI Yan-qiang, MA Ting-li. A facile and general procedure to hyperporous carbons:

Yan-juan LI, et al/Trans. Nonferrous Met. Soc. China 31(2021) 1427-1438

Carbonization of organic zinc salts [J]. Materials Today Energy, 2020, 17: 100446.

- [38] GUO D H, SHIBUYA R, AKIBA C, SAJI S, KONDO T, NAKAMURA J. Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts [J]. Science, 2016, 351: 361–365.
- [39] DONG Yi-fan, WANG Bing-liang, ZHAO Kang-ning, YU Yan-hao, WANG Xu-dong, MAI Li-qiang, JIN Song. Air-stable porous Fe<sub>2</sub>N encapsulated in carbon microboxes with high volumetric lithium storage capacity and a long cycle life [J]. Nano Letters, 2017, 17: 5740–5746.
- [40] GONG Kuan-ping, DU Feng, XIA Zhen-hai, DURSTOCK M, DAI Li-ming. Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction [J]. Science, 2009, 323: 760–764.
- [41] REDDY A L M, SRIVASTAVA A, GOWDA S R, GULLAPALLI H, DUBEY M, AJAYAN P M. Synthesis of nitrogen-doped graphene films for lithium battery application [J]. ACS Nano, 2010, 4: 6337–6342.
- [42] ZHOU Xue-jun, TANG Sheng, YIN Yan, SUN Shui-hui, QIAO Jin-li. Hierarchical porous N-doped graphene foams with superior oxygen reduction reactivity for polymer electrolyte membrane fuel cells [J]. Applied Energy, 2016, 175: 459–467.

- [43] QIU Kai-pei, CHAI Guo-liang, JIANG Chao-ran, LING Min, TANG Jun-wang, GUO Zheng-xiao. Highly efficient oxygen reduction catalysts by rational synthesis of nanoconfined maghemite in a nitrogen-doped graphene framework [J]. ACS Catalysis, 2016, 6: 3558–3568.
- [44] LIU Sa, WANG Yan, LIU Li-wen, LI Meng-li, LV Wen-jie, ZHAO Xin-sheng, QIN Zheng-long, ZHU Ping, WANG Guo-xiang, LONG Zhou-yang. One-pot synthesis of Pd@ PtNi core-shell nanoflowers supported on the multi-walled carbon nanotubes with boosting activity toward oxygen reduction in alkaline electrolyte [J]. Journal of Power Sources, 2017, 365: 26–33.
- [45] YU Hui-jun, SHANG Lu, BIAN Tong, SHI Run, WATERHOUSE G I N, ZHAO Yu-fei, ZHOU Chao, WU Li-zhu, TUNG C H, ZHANG Tie-rui. Nitrogen-doped porous carbon nanosheets templated from g-C<sub>3</sub>N<sub>4</sub> as metal-free electrocatalysts for efficient oxygen reduction reaction [J]. Advanced Materials, 2016, 28: 5080–5086.
- [46] LIU Sa, YANG Zheng, LI Meng-li, LIU Li-wen, WANG Yan, LV Wen-jie, QIN Zheng-long, ZHAO Xin-sheng, ZHU Ping, WANG Guo-xiang. FeS-decorated hierarchical porous N, S-dual-doped carbon derived from silica-ionogel as an efficient catalyst for oxygen reduction reaction in alkaline media [J]. Electrochimica Acta, 2018, 265: 221–231.

# 用于氧还原反应的氮掺杂空心多孔碳球封装的 过渡金属氮化物的制备和性能

李彦娟1, 王 敏1, 刘 飒1, 高京夏1, 杨 舜1, 刘子豪1, 赖小勇2, 闫 霄1

江苏师范大学 化学与材料科学学院 江苏省功能材料绿色合成化学重点实验室, 徐州 221116;
 宁夏大学 化学化工学院 煤炭高效利用与绿色化工国家重点实验室, 银川 750021

摘 要:通过浸渍和热处理方法制备一系列氮掺杂空心多孔碳球(NHPCS)封装的过渡金属氮化物(M<sub>x</sub>N<sub>y</sub>, M=Fe, Co, Ni)纳米颗粒复合材料。此纳米复合材料兼具氮化物的高催化活性和氮掺杂多孔碳球的高效传质特性。氧气还原反应结果表明,Fe<sub>2</sub>N/NHPCS表现出优异的催化性能,其具有较高的起始电位(0.96 V)、电子转移数(~4)和极限电流密度(为工业 Pt/C 的 1.4 倍)。此外,该材料作为锌-空气电池的空气催化剂,表现出与 Pt/C 相媲美的比容量(795.1 mA·h/g)、更优的耐久性和最大的功率密度(173.1 mW/cm<sup>2</sup>)。

关键词: 氮掺杂多孔碳; 过渡金属氮化物; 锌-空气电池; 氧还原反应; 燃料电池

(Edited by Wei-ping CHEN)

1438