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Article

Efficient spinel iron-cobalt oxide/nitrogen-doped ordered mesoporous carbon catalyst for rechargeable zinc-air batteries

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ABSTRACT

A robust oxygen-related electrocatalyst, composed of spinel iron-cobalt oxide and nitrogen-doped ordered mesoporous carbon (NOMC), was developed for rechargeable metal-air batteries. Electrochemical tests revealed that the optimal catalyst $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ exhibits superior activity with a half-wave potential of 0.89 V (vs. reversible hydrogen electrode) for the oxygen reduction reaction and an overpotential of 0.31 V at 10 mA cm^{-2} for the oxygen evolution reaction. For demonstration, the catalyst was used in the assembly of a rechargeable zinc-air battery, which exhibited an exceptionally high energy density of 820 Wh kg^{-1} at 100 mA cm^{-2} , a high power density of 153 mW cm^{-2} at 1.0 V, and superior cycling stability up to 432 cycles (144 h) under ambient air.

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1. Introduction

Electrochemical energy technology, including metal-air batteries and fuel cells, has been intensively investigated to tackle energy and environmental challenges [1–3]. Zinc-air batteries have attracted attention owing to their high energy density (1086 Wh kg^{-1}), low cost, and safety, making them candidates for mobile and transport power applications [4,5]. In these batteries, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) occur at the positive electrode during the discharging and charging processes, respectively [6,7]. Commercial noble metal-based catalysts, such as IrO_2 (RuO_2) and Pt/C , exhibit good electrocatalytic activity for the OER and ORR [8,9]. However, poor stability, source scarcity, and high cost seriously hamper their widespread application in Zn-air

batteries [10,11]. To address this issue, it is highly desirable to explore non-noble metal ORR/OER catalysts with high activity and stability [12–14].

Heteroatom-doped carbon has been identified as a promising electrocatalyst for the ORR [15–17]. However, carbon has rarely been applied in OER catalysts. The reasons include its intrinsically low OER activity and the inevitable carbon corrosion or structural collapse at high potentials [18]. Alternatively, loading transition metal (*e.g.* Fe, Co, Ni) oxides onto the carbon skeleton seems plausible for rationally designing a bifunctional catalyst [19–21]. Wu *et al.* [22] deposited CoO-NiO-NiCo on nitrogen-doped multi-wall carbon nanotubes as a composite electrocatalyst, which showed superior performance with an onset potential of 0.97 V (vs. RHE) for the ORR and a low overpotential of 0.27 V for the OER. Wang *et al.* [23] synthesized a

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hollow NC-Co₃O₄ catalyst by embedding hollow Co₃O₄ nanospheres in nitrogen-doped carbon nanowall arrays, which enables promising catalytic properties for both the ORR and OER. Lu *et al.* [24] reported that an atom-thin mesoporous Co₃O₄ layer, which is strongly coupled with N-rGO nanosheets and displays high performance towards the ORR/OER. In the aforementioned studies, the composite catalysts were mostly prepared in multiple steps, and the metal oxide was introduced into the pre-formed carbon frame [25,26]. As such, the loosely bound transition metal may tend to aggregate, thus degrading its electrocatalytic activity.

In this work, a precursor containing a transition metal and carbon is introduced in one step into the template of mesoporous silica. In this way, the iron-cobalt oxide has inherently intimate contact with the nitrogen-doped ordered mesoporous carbon (NOMC). A series of spinel iron-cobalt oxide-decorated NOMCs (Fe_xCo/NOMC, where *x* refers to the ratio of Fe:Co) were prepared and investigated. Physicochemical characterization revealed that Fe_xCo/NOMC features a typical structural texture of NOMC with a narrow pore size distribution and high specific surface area, and the spinel oxide nanoparticles are uniformly dispersed within the carbon frame. Electrochemical analysis revealed that Fe_{0.5}Co/NOMC exhibited the highest activity and stability toward the ORR and OER. The ORR half-wave potential was 0.89 V (vs. RHE) and the OER potential at 10 mA cm⁻² was 1.54 V, which is much lower than that of the Pt/C and IrO₂ benchmark. A rechargeable Zn-air battery assembled with Fe_{0.5}Co/NOMC in the air electrode achieved a peak power density of 230 mW cm⁻².

2. Experimental

2.1. Materials preparation

2.1.1. Synthesis of the silica templates (SBA-15)

The synthesis process of SBA-15 is referenced to our previous work [25,27]. Typically, 4.0 g of Pluronic P123 was completely dissolved in 126.0 mL of deionized (DI) water, and 20.0 mL of concentrated HCl (37.0 wt%). Then, 9.20 mL of TEOS was added into the above solution and stirred for 20 h in a water bath at 35 °C. The above slurry was hydrothermally reacted at 100 °C for 24 h. The suspended solid was filtered, washed with DI water and dried. Finally, the obtained powders were pyrolyzed in air at 550 °C for 6 h to remove the organic template.

2.1.2. Synthesis of Fe_xCo/NOMC, Fe/NOMC and Co/NOMC

First, 0.60 g of 1,10-phenanthroline monohydrate (3.0 mmol, Phen), 0.097 g of iron(II) acetate (0.50 mmol) and 0.249 g of the cobalt(II) acetate tetrahydrate (1.0 mmol) were dissolved in a solution containing 20.0 mL ethanol and 20.0 mL DI water. Second, 0.50 g of silica template SBA-15 was dispersed in the above solution by ultrasonic stirring for 6 h at room temperature. Then, the solvent was evaporated at 100 °C, and the obtained powders were calcined at 900 °C for 3 h under argon (99.999%). Finally, the precursor materials were washed with 10.0 mol L⁻¹ NaOH solution at 120 °C for 24 h to remove SBA-15. The resultant material is designated as Fe_xCo/NOMC,

where *x* refers to the molar ratio of Fe:Co. For *x* = 0.5, 1 and 2, the feeding molar ratios of Fe:Co:Phen are 0.5:1:3, 0.75:0.75:3 and 1:0.5:3, respectively.

For comparison, we also prepared monometallic materials, viz. Fe decorated NOMC (Fe/NOMC) and Co decorated NOMC (Co/NOMC). The synthesis was similar to that of Fe_xCo/NOMC, except for the metal precursor used.

2.1.3. Electrochemical characterization

The electrochemical evaluation of ORR and OER was performed in a standard three-electrode system using CHI630e electrochemical workstation at room temperature, in which rotating disk electrode (Glassy carbon disk: 5.0 mm in diameter, RDE) as working electrode, saturated calomel electrode (SCE for the ORR) and Hg/HgO electrode (for the OER) as reference electrode, gold gauze as counter electrode and 0.10 M KOH (ORR) or 1.0 M KOH (OER) as electrolyte, respectively.

The thin-film electrode on the disk was prepared as follows. 10 mg of powder were dispersed in 1.0 mL of Nafion/ethanol (0.84 wt% Nafion) by sonication for 1 h to obtain a homogeneous dispersion solution. Then, the ink was dropped on the RDE with a loading of 10.0 μL (0.5 mg cm⁻²). For comparison, the electrocatalytic activity of the commercial 40 wt% Pt/C (HiSPEC4000, Johnson Matthey) for the ORR and the commercial IrO₂ (P40V030, Premetek Co.) for the OER was evaluated with a metal loading of 20.0 and 500.0 μg cm⁻², respectively.

For the electrochemical test, the electrolyte solution was bubbled with either argon or oxygen for 1 h. The cyclic voltammograms (CVs) were recorded at 30 mV s⁻¹ between 0 and 1.05 V (vs. reversible hydrogen electrode, RHE) for 30 cycles. The linear sweep voltammograms (LSVs) were recorded by scanning the disk potential from 1.05 down to 0 V for the ORR and from 1.0 to 1.8 V for the OER, respectively, at a rate of 5 mV s⁻¹ under 1600 rpm.

The RRDE test was performed to measure the electron transfer number (*n*), as calculated by the following equation.

$$n = 4 \times \frac{I_{\text{disk}}}{\left(\frac{I_{\text{ring}}}{N}\right) + I_{\text{disk}}}$$

where *I*_{disk} is the disk current (A), *I*_{ring} is the ring current (A), and *N* (20.5%) is the current collection efficiency of Pt ring.

2.1.4. Assembly of rechargeable zinc-air battery

Catalyst ink was prepared by dispersing the catalyst and Nafion (5.0 wt% in EtOH) with a weight ratio of 9:1 in water (20.0 mL) and EtOH (20.0 mL). Then, the catalyst ink was uniformly brushed onto the gas diffusion layer at 70 °C. The catalyst loading was 1.0 ± 0.1 mg cm⁻² for Fe_{0.5}Co/NOMC and 0.50 ± 0.05 mg cm⁻² for Pt/C+IrO₂, respectively.

A home-made zinc-air battery was used to evaluate the polarization performance and cycling stability. A polished zinc plate (2.0 × 1.0 cm²) and the air electrode were used as the negative and positive electrode, respectively. The area of the cathode exposed to the air was about 0.785 cm². The electrolyte used in the zinc-air battery system was 6.0 M KOH + 0.20 M zinc acetate solution. The cycling test was performed at 25 °C

using the double-pulse method, in which one cycle (5.0 mA cm^{-2} for 20 min) consisted of an initial discharging step (5.0 mA cm^{-2} for 10 min) and a consequent charging step with the same current density and duration time.

3. Results and discussion

All the materials show nitrogen adsorption and desorption isotherms (Fig. 1(b)) that are similar in shape. The curves are typical type-IV isotherms associated with an H3 hysteresis loop, which implies a mesoporous structure [28]. As shown in Table S1, it was found that all the samples possess a high specific surface area (S_{BET}), which is consistent with previous reports [29]. Moreover, all the samples show a narrow pore size distribution in the range of 2–7 nm (Fig. S1). High specific surface area and mesoporous structure are believed to favor electrocatalysis, as discussed below.

Fig. 1(c) presents the X-ray diffraction (XRD) patterns of the catalysts. All of the catalysts show a broad and strong peak located at approximately 26.4° , which is assigned to the (002) plane of graphitic carbon. It was further found that the crystalline phase of the metal oxide evolves with the composition. First, Fe/NOMC presents the characteristic crystal phase of Fe_3O_4 (PDF#75-0033). Second, the incorporation of Co has a remarkable effect on the diffraction pattern, and the diffraction peaks show a positive shift for FeCo/NOMC and $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$. Such an evolution is understandable because the incorporated cobalt randomly occupies the tetrahedral/octahedral sites in spinel Fe_3O_4 , generating a new spinel phase, $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ [30–32]. When the Co content is further increased, it can be seen that $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ includes two spinel phases, viz. $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ and Co_3O_4 (PDF#42-1467) [33,34]. Finally, Co/NOMC shows the characteristic spinel phase of Co_3O_4 (PDF#42-1467).

A ^{57}Fe Mössbauer spectrum was recorded to study the spinel structure (Fig. 1(d), Table S2). $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ shows a typical sextet curve, which can be well fitted with one quadrupole doublet and two sextets. The quadrupole doublet component, where $\delta = 0.43 \text{ mm s}^{-1}$ and $\Delta E_{\text{Q}} = 0.79 \text{ mm s}^{-1}$, is assigned to a superparamagnetic iron species [35,36]. The two sextets arise from spinel iron oxide species in tetrahedral (A) and octahedral (B) sites [37]. Peaks belonging to either iron nitride or carbide species were not detected [38], indicating that iron exists solely in the spinel oxide phase. The contents of Fe and Co were further measured by inductively coupled plasma optical emission spectrometry (ICP-OES); the results are summarized in Table S3. These results match well with the feed ratios. Based on the above discussion, it was inferred that the metal oxide of $\text{Fe}_x\text{Co}/\text{NOMC}$ is in the spinel phase of CoFe_2O_4 , $\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_4$, and $\text{Co}_x\text{Fe}_{3-x}\text{O}_4/(2-x) \text{Co}_3\text{O}_4$ ($1.5 < x < 2$).

Scanning electron microscopy (SEM) images (Fig. S2) show that all the materials exhibit rod-like structures. Transmission electron microscopy (TEM) images (Figs. 2(a) and S3) reveal their ordered mesoporous structures, on which the metal oxide nanoparticles are uniformly dispersed. The average diameters of the metal oxide particles are 3.5, 7.5, 13.7, 15.1 and 17.5 nm for Fe/NOMC, $\text{Fe}_2\text{Co}/\text{NOMC}$, FeCo/NOMC, $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$, and Co/NOMC, respectively. Therefore, the incorporation of cobalt dramatically increases the particle size of the metal oxide, as discovered previously [39,40]. The energy dispersive spectroscopy (EDS) results are shown in Fig. S4, indicating that the weight ratios of Fe:Co are 2.01, 1.15, and 0.45 for $\text{Fe}_2\text{Co}/\text{NOMC}$, FeCo/NOMC, and $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$, respectively. In addition, the elemental mapping images (Figs. 2(d)–(f)) show that both Fe and Co are uniformly distributed on the carbon.

The surface composition and chemical state were investigated using X-ray photoelectron spectroscopy (XPS). The survey and high-resolution spectra are shown in Figs. 3–5, S6 and

Fig. 1. (a) Schematic illustration of the synthesis protocol of $\text{Fe}_x\text{Co}/\text{NOMC}$; (b) Nitrogen ad/de-sorption isotherms and (c) XRD patterns of all the samples; (d) Mössbauer spectroscopy of $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$.

Fig. 2. (a) TEM image and (b) corresponding particle size distribution diagram of $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$; (c) Size distribution of all the samples; (d–f) Elemental mapping images of $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$.

S7. The elemental compositions were quantified and are listed in Table 1. The molar ratios of Fe:Co were 1.82, 0.78, and 0.53 for $\text{Fe}_2\text{Co}/\text{NOMC}$, FeCo/NOMC , and $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$, respectively. The molar ratio on the surface, measured by XPS, deviates from that of the bulk measured by ICP-OES and EDS. For the former two samples, the surface shows a slightly smaller ratio than the bulk; in comparison, for $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$, the molar ratio of the surface is much larger than that of the bulk. This may be due to the evolution of the crystalline structure, as shown by XRD. The surface composition likely has a significant effect on electrocatalytic activity, as discussed later.

The curve fitting result of the high-resolution C 1s peak is shown in Fig. S6. The fraction of nitrogen-activated carbon, which acts as the ORR active site [27,41], increases from 12.27% to 14.93% with increasing Co content (Table S4) for $\text{Fe}_x\text{Co}/\text{NOMC}$.

The Fe 2p XPS spectra (Fig. 4) show peaks at 710.9, 714.7, 724.3 and 728.6 eV, which correspond to $\text{Fe}^{2+} 2p_{3/2}$, $\text{Fe}^{3+} 2p_{3/2}$, $\text{Fe}^{2+} 2p_{1/2}$, and $\text{Fe}^{3+} 2p_{1/2}$, respectively [42]. Similarly, the peaks in Fig. 5 at 780.9 and 796.2 eV can be assigned to $\text{Co}^{3+} 2p_{3/2}$ and $\text{Co}^{3+} 2p_{1/2}$, respectively. These results confirm the coexistence of two valence states in $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ [43]. The contents of each iron and cobalt component are summarized in Table S6. It can be seen that the molar ratio of $\text{Fe}^{3+}:\text{Fe}^{2+}$ remarkably increases with the increase in Co content; in comparison, the

molar ratio of $\text{Co}^{3+}:\text{Co}^{2+}$ decreases in a mild trend. This result indicates that there is a strong electronic interaction between the two transition metals, which results in a significant effect on the electrocatalysis.

The ORR activity was evaluated by recording linear sweep voltammograms (LSVs) using the rotating disk electrode (RDE) method, as shown in Fig. 6(a). It can be seen that $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ exhibits the highest ORR performance among the five samples. The half-wave potential ($E_{1/2}$) of $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ reaches 0.89 V vs. RHE, implying that it outperforms the non-precious metal catalysts reported in the literature (Table S7). The remarkable activity originates from both the composition and structure of the catalyst. First, it has been claimed that the ORR activity is positively correlated with the content of nitrogen-activated carbon (C-N). As mentioned in the XPS analysis, $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$

Fig. 3. XPS survey spectra of Fe/NOMC , $\text{Fe}_2\text{Co}/\text{NOMC}$, FeCo/NOMC , $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ and Co/NOMC .

Table 1

Elemental composition (at. %) measured by XPS.

Sample	C	N	O	Fe	Co	Fe:Co
Fe/NOMC	81.14	1.75	15.25	1.86	0	—
$\text{Fe}_2\text{Co}/\text{NOMC}$	82.42	1.76	13.16	1.72	0.94	1.83
FeCo/NOMC	83.36	1.79	12.52	1.08	1.25	0.78
$\text{Fe}_{0.5}\text{Co}/\text{NOMC}$	82.41	1.82	13.39	0.82	1.56	0.53
Co/NOMC	81.01	1.50	15.76	0	1.73	—

Fig. 4. High-resolution XPS spectra of Fe 2p peak and peak fitting result of (a) Fe/NOMC, (b) Fe₂Co/NOMC, (c) FeCo/NOMC, (d) Fe_{0.5}Co/NOMC.

has the highest C-N fraction and thus exhibits the best electrocatalytic activity. Second, the ordered mesoporous structure is known to favor both the mass transfer of active species and exposure of the active sites. Finally, the electron transfer number (n), which was measured by the rotating ring-disk electrode (RRDE) method, reveals that the ORR occurs via a 4-electron pathway on the investigated catalysts (Fig. 6(c)).

Fig. 6(d) shows the LSVs of the OER without iR correction. It can be seen that the activity follows the order of Fe_{0.5}Co/NOMC > FeCo/NOMC > Fe₂Co/NOMC > IrO₂ > Co/NOMC > Fe/NOMC. For clearer viewing, the overpotential at 10 mA cm⁻² was extracted and plotted in Fig. 6(e). Fe_{0.5}Co/NOMC exhibited the lowest overpotentials of 0.31 V at 10 mA cm⁻² and 0.42 V at 100 mA cm⁻². The good activity can be attributed to both the

Fig. 5. High-resolution XPS spectra of Co 2p peak and peak fitting result of (a) Fe₂Co/NOMC, (b) FeCo/NOMC, (c) Fe_{0.5}Co/NOMC, (d) Co/NOMC.

surface composition and the synergistic effect between Co and Fe in Fe_{0.5}Co/NOMC. In addition, the ordered mesoporous structure exposes the active sites and extends the catalyst-electrolyte interface, which benefits the electrocatalysis and mass transfer for the OER [44–46]. Finally, it is worth noting that for the OER, the activity of Fe_{0.5}Co/NOMC is on par with most catalysts reported in the literature (Table S8).

The potential gap ($\Delta E = E_{\text{OER}@10} - E_{1/2}$) between the OER potential at 10 mA cm⁻² and the ORR half-wave potential was used to evaluate the electrochemical reversibility of the oxygen-related electrode, where lower ΔE implies higher reversibility and better ORR/OER activity [47]. As shown in Figs. 6(f) and S8, Fe_{0.5}Co/NOMC exhibits the lowest ΔE of 0.66 V, demonstrating its superior ORR/OER activity.

Fig. 6. (a) ORR's polarization curves (scanning rate: 10 mV s⁻¹, rotating rate: 1600 rpm, O₂-saturated 0.10 M KOH solution), (b) the corresponding current density at 0.90 V, and (c) electron transfer number (n) of all the catalysts; (d) OER's polarization curves (scanning rate: 5 mV s⁻¹, rotating rate: 1600 rpm, O₂-saturated 1.0 M KOH solution), and (e) OER's overpotential at 10 mA cm⁻² of all the catalysts; (f) Full-potential-window polarization curve of Fe_{0.5}Co/NOMC.

Fig. 7. (a) Discharging and charging polarization curves, and (b) power density diagram of Zn-air battery assembled with $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ and $\text{IrO}_2+\text{Pt}/\text{C}$, respectively; (c) Specific capacity and (d) specific energy density diagrams at 100 mA cm^{-2} , and (e) cycling performance at 5 mA cm^{-2} for 10 min discharging and 10 min charging of Zn-air battery assembled with $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$; (f) Schematic of the rechargeable Zn-air battery; (g) Photo of thirty-eight LEDs powered by two rechargeable Zn-air batteries. Photo of 38 LEDs powered by two rechargeable Zn-air batteries.

The best-performing catalyst, viz. $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$, was used to fabricate the air electrode and assemble a zinc-air battery. Typical discharging/charging polarization curves are shown in Fig. 7(a). The voltage at 50 mA cm^{-2} of $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ was 1.09 V, which is significantly lower than that of $\text{IrO}_2 + \text{Pt}/\text{C}$ (1.27 V). The discharging polarization curve and the corresponding power density curve are plotted in Fig. 7(b). The $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ catalyst yielded a power density of 153.2 mW cm^{-2} at 1.0 V, which is three times higher than that of the noble metal catalyst ($\text{IrO}_2 + \text{Pt}/\text{C}$). The peak power density was found to be 230.4 mW cm^{-2} , which is among the highest of those reported in the literature (Table S9). Figs. 7(c) and (d) shows the specific capacity and energy density at a constant discharging current density of 100 mA cm^{-2} , which reached 770 mAh g^{-1} and 820 Wh kg^{-1} , respectively. The cycling stability of the battery is shown in Fig. 7(e). The initial charging/discharging voltage was 1.97/1.20 V at 5 mA cm^{-2} with a voltage gap of 0.77 V. Notably, the battery was stable during 432 cycles (144 h) of continuous testing with no serious degradation identified. In comparison,

the battery using commercial $\text{IrO}_2 + \text{Pt}/\text{C}$ produced a significantly larger voltage gap and unstable cycling curves under the same test conditions (Fig. S11). To demonstrate its practical usage, a prototype zinc-air battery was assembled with $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$, as shown in Figs. 7(f)–(g). Two rechargeable batteries connected in series were effective to continuously power 38 parallel LEDs in an array displaying SCUT (South China University of Technology).

4. Conclusions

In this work, we prepared a spinel Fe-Co oxide/nitrogen-doped ordered mesoporous carbon ($\text{Fe}_x\text{Co}/\text{NOMC}$) composite catalyst using a one-step method. The feed ratio of Fe:Co has a significant effect on both the surface composition and electronic structure of the catalyst; therefore, the oxygen-related electrocatalysis can be tuned effectively in this way. The optimal catalyst, viz. $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$, exhibits electrocatalytic activity superior to its commercial counterpart ($\text{IrO}_2 + \text{Pt}/\text{C}$) and is one of the most effective catalysts found in the literature. For demonstration, a catalyst-assembled rechargeable Zn-air battery exhibits superior power density and long-term stability, which can be used as an efficient oxygen-related catalyst in practice.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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Efficient spinel iron-cobalt oxide/nitrogen-doped ordered mesoporous carbon catalyst for rechargeable zinc-air batteries

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A robust ORR/OER oxygen-related catalyst was synthesized via a one-step method. A rechargeable zinc-air battery assembled using the optimal catalyst, viz. Fe_{0.5}Co/NOMC, exhibits a power density of 153 mW cm⁻² at 1.0 V and superior cycling stability.

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高效的尖晶石铁钴氧/氮掺杂有序介孔碳催化剂应用于可充电锌-空气电池

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摘要: 以电催化为核心的新能源储存和转换技术为缓解能源与环境问题提供了有效手段。可充电锌空气电池因其理论能量密度($1086 \text{ Wh}\cdot\text{kg}^{-1}$)高、成本效益显著、安全系数高、环境友好及放电平稳等优点被认为是一种具有前景的能源存储/转换装置, 有望在新能源汽车、便携式电源等领域广泛应用。氧还原反应(ORR)和氧析出反应(OER)是锌-空气电池中的核心反应, 目前, 虽然贵金属催化剂对上述反应表现出一定的电催化活性, 但由于其稀缺性、高昂价格和低稳定性因素严重阻碍了它们在锌-空气电池中的广泛应用。而非贵金属催化剂所面临的瓶颈在于ORR/OER反应动力学缓慢, 导致其在实际应用过程中存在电压效率低和催化剂腐蚀等问题。因此, 为了推进锌-空气电池商业化进程, 研制低成本、高效、稳定的非贵金属催化剂迫在眉睫。

本文通过一步法将双金属前驱体嵌入氮掺杂有序介孔碳(NOMC)中, 合成了具有尖晶石型铁钴氧化物的高性能非贵金属电催化剂($\text{Fe}_x\text{Co}/\text{NOMC}$, x 代表铁钴的摩尔比)。实验结果表明, 在 $x = 0.5$ 时, 所制备的催化剂具有最佳的催化活性, 与商业贵金属催化剂相比, 该催化剂展现更优的电催化活性和稳定性。电化学测试结果表明, 其ORR的半波电位为 0.89 V (vs. RHE), 当OER电流密度为 $10 \text{ mA}\cdot\text{cm}^{-2}$ 时, 过电势仅为 0.31 V , 且电流-时间曲线测试结果表明催化剂表现出较好的稳定性。通过X射线光电子能谱(XPS)、穆斯堡尔谱(Mössbauer)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和拉曼光谱(Raman)等表征手段对电催化剂的物化性质进行表征, 结果表明该材料优异的氧电催化性能归因于双金属氧化物的电子调控作用、NOMC的介孔结构、高导电性和高比表面积, 其ORR与OER的催化活性位点分别是氮活化的碳(N-C)和双金属氧化物。以优化的 $\text{Fe}_{0.5}\text{Co}/\text{NOMC}$ 为正极组装可充电锌-空气电池, 该电池在空气环境下展现出优良的充放电性能, 其在电流密度为 $100 \text{ mA}\cdot\text{cm}^{-2}$ 条件下操作时能量密度达到 $820 \text{ Wh}\cdot\text{kg}^{-1}$, 在 1.0 V 时功率密度达到 $153 \text{ mW}\cdot\text{cm}^{-2}$, 它还表现出较好的稳定性, 经过 144 h 的循环实验, 活性没有明显下降。本文不仅制备了一种有前景的尖晶石型氧化物碳基氧电催化材料, 还为高效氧电催化剂的合理开发与构筑提供了一条新的思路。

关键词: 氧相关催化剂; 氧析出反应; 氧还原反应; 尖晶石氧化物; 锌空气电池

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