

### VP Very Important Paper

# A Composite Bifunctional Oxygen Electrocatalyst for High-Performance Rechargeable Zinc–Air Batteries

Jia-Ning Liu, Bo-Quan Li, Chang-Xin Zhao, Jia Yu, and Qiang Zhang\*<sup>[a]</sup>

Rechargeable zinc–air batteries are considered as next-generation energy storage devices because of their ultrahigh theoretical energy density of 1086 Wh kg<sup>-1</sup> (including oxygen) and inherent safety originating from the use of aqueous electrolyte. However, the cathode processes regarding oxygen reduction and evolution are sluggish in terms of kinetics, which severely limit the practical battery performances. Developing high-performance bifunctional oxygen electrocatalysts is of great significance, yet to achieve better bifunctional electrocatalytic reactivity beyond the state-of-the-art noble-metal-based electrocatalysts remains a great challenge. Herein, a composite  $Co_3O_4$ @POF (POF = framework porphyrin) bifunctional oxygen

## Introduction

The ever-growing demands for sustainable energy supplies and heavy reliance on fossil fuels that contribute to environmental concerns have stimulated the development of clean and renewable energy for the low-carbon economy.<sup>[1]</sup> Rechargeable batteries are considered a vital approach for sustainable energy storage and conversion to meet the increasing requirements of consumer electronics, electric vehicles, and the related energy industry.<sup>[2]</sup> Among the various battery configurations, rechargeable zinc-air batteries demonstrate great potential as next-generation energy storage devices because of their ultrahigh theoretical energy density of 1086 Wh kg<sup>-1</sup> (including oxygen),<sup>[3-6]</sup> inherent safety originating from the use of aqueous electrolyte,<sup>[7]</sup> and additional advantages including low cost,<sup>[8]</sup> natural abundance,<sup>[9]</sup> and environmental benignity.<sup>[10]</sup> Therefore, developing high-performance rechargeable zinc-air batteries has received extensive attention worldwide.

Typically, a rechargeable zinc-air battery is constructed from a zinc metal anode, an air cathode, and an aqueous alkaline electrolyte together with zinc salts.<sup>[11]</sup> The anode process involves the reversible plating/stripping of zinc whereas the

[a]	JN. Liu, BQ. Li, CX. Zhao, Dr. J. Yu, Prof. Q. Zhang
	Beijing Key Laboratory of Green Chemical Reaction Engineering and
	Technology, Department of Chemical Engineering
	Tsinghua University, Beijing 100084 (P. R. China)
	E-mail: zhang-qiang@mails.tsinghua.edu.cn

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This publication is part of a joint Special Issue with Batteries & Supercaps focusing on "2D Energy Storage Materials". Please visit the issue at http://doi.org/10.1002/cssc.v13.6. electrocatalyst is proposed to construct advanced air cathodes for high-performance rechargeable zinc-air batteries. The asobtained composite Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst exhibits a bifunctional electrocatalytic reactivity of  $\Delta E$ =0.74 V, which is better than the noble-metal-based Pt/C + Ir/C electrocatalyst and most of the reported bifunctional ORR/OER electrocatalysts. When applied in rechargeable zinc-air batteries, the Co<sub>3</sub>O<sub>4</sub>@POF cathode exhibits a reduced discharge-charge voltage gap of 1.0 V at 5.0 mA cm<sup>-2</sup>, high power density of 222.2 mW cm<sup>-2</sup>, and impressive cycling stability for more than 2000 cycles at 5.0 mA cm<sup>-2</sup>.

cathode reactions are the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) during charge and discharge, respectively.<sup>[12]</sup> Both ORR and OER are multi-electron reactions occurring at multi-phase boundaries and thus are heavily sluggish in kinetics, which renders large voltage gaps,<sup>[13]</sup> reduced energy efficiency,<sup>[14]</sup> and limited cycling stability.<sup>[15,16]</sup> Consequently, the poor cathode kinetics regarding ORR and OER is considered as the bottleneck that limits the practical performances of rechargeable zinc–air batteries.

To introduce a high-performance ORR/OER bifunctional electrocatalyst constitutes a reasonable strategy to address the kinetic issue of the air cathode, where bifunctional electrocatalytic reactivity for both ORR and OER is required to promote rechargeable zinc-air batteries.[17-19] Generally, the ORR/OER bifunctional electrocatalytic reactivity is evaluated by the voltage gap ( $\Delta E$ ) between the half-wave potential ( $E_{1/2}$ ) for ORR and the OER potential required to reach the current density of 10.0 mA cm<sup>-2</sup> ( $E_{10}$ ).<sup>[20]</sup> Currently, noble-metal-based electrocatalysts exhibit the state-of-the-art performances (Pt/C and Ir/C for ORR and OER, respectively).<sup>[21,22]</sup> However, disadvantages such as high cost, scarcity, and poor durability retard their widespread application in rechargeable zinc-air batteries.<sup>[23]</sup> Consequently, developing high-performance noble-metal-free bifunctional ORR/OER electrocatalysts is of great significance for application in rechargeable zinc-air batteries.

Tremendous efforts have been devoted to exploring bifunctional ORR/OER electrocatalysts including transition-metal compounds,<sup>[24-29]</sup> metal–organic frameworks,<sup>[30-37]</sup> and heteroatomdoped nanocarbon.<sup>[38-44]</sup> Nevertheless, their bifunctional electrocatalytic performances remain unsatisfactory with single active site. Actually, ORR and OER go through different path-

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ways with distinct rate-determining steps<sup>[45]</sup> and therefore require different active sites for an optimized configuration. A single active site can hardly satisfy both ORR and OER simultaneously. To this end, rational design of a composite electrocatalyst that integrates advanced ORR and OER active sites is in high demand for the construction of high-performance bifunctional electrocatalysts.

The composite strategy for bifunctional oxygen electrocatalysis has been demonstrated to be effective in many cases.<sup>[46-54]</sup> For instance, Chen et al. reported a composite of manganese dioxide and nitrogen-doped carbon nanotubes with high bifunctional electrocatalytic reactivity.<sup>[55]</sup> The composite of NiFe layered double hydroxides with Co, N co-doped carbon nanoframes was also proved to be effective for bifunctional oxygen electrocatalysis.<sup>[56]</sup> Nevertheless, the selection of ORR/OER active sites remains delicate yet insufficient with the bifunctional reactivity inferior to the noble-metal-based electrocatalysts in most cases.<sup>[57–59]</sup> Rational design strategies to integrate ORR/OER active sites within a composite electrocatalyst are highly desired to construct advanced bifunctional electrocatalysts for high-performance rechargeable zinc–air batteries.

In this contribution, a composite bifunctional oxygen electrocatalyst is proposed to construct advanced air cathodes for high-performance rechargeable zinc-air batteries. Atomic Co-N-C is selected as the ORR active site<sup>[60,61]</sup> whereas Co<sub>3</sub>O<sub>4</sub> serves as the OER electrocatalyst, owing to their high intrinsic

reactivity and compatibility.<sup>[62,63]</sup> The composite electrocatalyst (named as Co<sub>3</sub>O<sub>4</sub>@POF) is fabricated in situ with Co<sub>3</sub>O<sub>4</sub> nanoparticles hybridized on the surface of cobalt-coordinated framework porphyrin. The as-obtained composite Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst exhibits a bifunctional electrocatalytic reactivity of  $\Delta E = 0.74$  V, which is better than that for the noble-metalbased Pt/C + Ir/C electrocatalyst ( $\Delta E = 0.77$  V) and most reported bifunctional ORR/OER electrocatalysts. When applied in rechargeable zinc-air batteries, the Co<sub>3</sub>O<sub>4</sub>@POF cathode exhibits a reduced discharge-charge voltage gap of 1.0 V at 5.0 mA cm<sup>-2</sup>, high power density of 222.2 mW cm<sup>-2</sup>, and impressive cycling stability for more than 2000 cycles at 5.0 mA cm<sup>-2</sup>.

#### **Results and Discussion**

The fabrication of  $Co_3O_4@POF$  followed a two-step synthetic route in which the cobalt-coordinated framework porphyrin (named as POF) was first fabricated and then hybridized in situ with  $Co_3O_4$  nanoparticles (Figure 1 a). Concretely, POF was facilely synthesized by condensation of benzene-1,4-dialdehyde (BDA) and pyrrole with additional cobalt acetate as the cobalt source to generate the Co-N-C active sites. Also, graphene (G) was employed as the template for framework porphyrin hybridization to fully expose the active sites through morphology regulation as well as to enhance the electronic conductivity of the composite electrocatalyst.<sup>[64]</sup>



**Figure 1.** Synthesis and characterization of the composite  $Co_3O_4@POF$  electrocatalyst. (a) Scheme of the synthetic route of  $Co_3O_4@POF$ . (b) SEM, (c) TEM, and (d) high-resolution TEM images of  $Co_3O_4@POF$ . (e) XRD patterns of  $Co_3O_4@POF$ . High-resolution (f) N 1s and (g)  $Co_2p$  XPS spectra of  $Co_3O_4@POF$ .



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The fabrication of POF was comprehensively evaluated by morphology and structural characterizations. Transmission electron microscopy (TEM) images exhibit the similar sheet morphology of POF as G (Figures S1 and S2 in the Supporting Information), indicating conformal growth of the POF layers on the surface of G without self-aggregation. The structure of POF was elucidated by X-ray diffraction (XRD) techniques. Bare G demonstrates two broad diffraction peaks at 26° and 42° afforded by G (002) and (100) lattice faces, respectively (Figure S3). In comparison, the distinct diffraction peak at 13° of POF is indexed to the characteristic signal of framework porphyrin with intrinsic ordered structure.<sup>[65]</sup>

Elemental analysis was performed by using X-ray photoelectron spectroscopy (XPS) measurements. POF exhibits a reasonable nitrogen content of 5.7 at% and a cobalt content of 0.6 at %, whereas neither nitrogen nor cobalt signals are recorded for G (Figure S4 and Table S1). Considering the nitrogen and cobalt contents exclusively originate from cobalt-coordinated framework porphyrin, the XPS results unambiguously indicate the fabrication of POF. The cobalt content was further analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES), which reveals a detectable cobalt content of 0.50 wt% for POF whereas no cobalt signal was detected in G (Table S2). In addition, the high-resolution N1s XPS spectrum reveals deconvoluted signals of dominant pyrrole N at 400.1 eV (72 at %) and Co-N at 398.5 eV (28 at %),<sup>[66,67]</sup> thus proving the coordination of cobalt within the porphyrin units (Figure S5 and Table S3). Consequently, cobalt-coordinated framework porphyrin was successfully fabricated on the surface of G to render the POF electrocatalyst with Co-N-C active sites for ORR electrocatalysis.

To add composite OER active sites for bifunctional oxygen electrocatalysis, Co<sub>3</sub>O<sub>4</sub> was hybridized in situ with POF through co-precipitation to obtain the composite Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst. Scanning electron microscopy (SEM) images (Figure 1 b and Figure S6) demonstrate a rod-like morphology of the Co<sub>3</sub>O<sub>4</sub> nanoparticles. Further TEM images indicate that the Co<sub>3</sub>O<sub>4</sub> nanoparticles are approximately 10 nm in diameter and hybridized on the surface of POF (Figure 1c and Figure S7). The nanosized morphology of the Co<sub>3</sub>O<sub>4</sub> particles guarantees full exposure of the surface-active sites for OER electrocatalysis. High-resolution TEM images reveal lattice fringes of the nanoparticles with the spacing of 0.465 nm, which is identified to be the (111) lattice face of the standard Co<sub>3</sub>O<sub>4</sub> phase (Figure 1 d). The existence of crystalline Co<sub>3</sub>O<sub>4</sub> nanoparticles is further confirmed by XRD characterization. Co3O4@POF exhibits six intensive diffraction peaks at 19°, 31°, 37°, 44°, 59°, and  $65^{\circ}$ , respectively, in correspondence with the (111), (220), (311), (400), (440), and (511) lattice faces of the standard Co<sub>3</sub>O<sub>4</sub> phase (PDF 71-0816; Figure 1e), which indicate the desired structure.[62]

The elemental contents of  $Co_3O_4@POF$  were evaluated by using XPS and ICP-OES methods.  $Co_3O_4@POF$  demonstrates a decreased nitrogen content of 3.0 at % and an increased cobalt content of 11.3 at % compared with POF based on the XPS survey spectrum (Figure S8 and Table S1), which is in agreement with  $Co_3O_4$  hybridization. The ICP-OES results also afford an increased cobalt content of 44.39 wt% (Table S2). The chemical environments of the cobalt content in Co<sub>3</sub>O<sub>4</sub>@POF was further evaluated by XPS measurements. The signal of Co-N interactions can be identified in the high-resolution N1s XPS spectrum (Figure 1 f) with a portion of 29.4 at % in comparison with pyrrolic N of 70.6 at % (Table S3). The Co-N interactions in Co<sub>3</sub>O<sub>4</sub>@POF suggest the Co-N-C active sites are preserved from POF to serve as the ORR active sites. Meanwhile, the high-resolution Co2p XPS spectrum reveals deconvoluted signals at 780.5 and 798.0 eV ascribed to the  $Co^{2+} 2p^{3/2}$  and  $2p^{1/2}$  spin–orbit peaks and signals at 779.5 and 795.0 eV ascribed to the  $Co^{3+} 2p^{3/2}$  and  $2p^{1/2}$  spin–orbit peaks, respectively (Figure 1g).<sup>[62]</sup> The cobalt content exists with oxidation states of both +2 and +3, which is consistent with the Co<sub>3</sub>O<sub>4</sub> phase. Overall, Co<sub>3</sub>O<sub>4</sub> nanoparticles are sufficiently hybridized on the surface of POF to afford Co<sub>3</sub>O<sub>4</sub>@POF as the composite electrocatalysts with ORR and OER active sites for bifunctional oxygen electrocatalysis.

The ORR and OER bifunctional electrocatalytic reactivity was evaluated by using a three-electrode system. The electrolyte was oxygen-saturated 0.10 M KOH aqueous solution and the areal mass loading of the electrocatalysts was controlled to be 0.25 mg cm<sup>-2</sup> in all cases. The ORR half-wave potential ( $E_{1/2}$ ) defined as the potential to reach half of the limiting current density (3.0 mA cm<sup>-2</sup> in this work) and potential to reach an OER current density of 10 mA cm<sup>-2</sup> ( $E_{10}$ ) are employed as the descriptors to evaluate the ORR and OER electrocatalytic reactivity, respectively. The bifunctional reactivity ( $\Delta E$ ) is defined as the potential gap between  $E_{1/2}$  and  $E_{10}$ . All potentials were calibrated to the reversible hydrogen electrode (RHE).

Figure 2a demonstrates the 95% iR-compensated linear sweep voltammetry (LSV) profile of the composite  $Co_3O_4@POF$ electrocatalyst and the noble-metal-based Pt/C+Ir/C electrocatalyst serving as the benchmark. The mass ratio of Pt/C and Ir/ C was controlled to be 1:1. The  $E_{1/2}$  and  $E_{10}$  of the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst are 0.82 and 1.56 V (vs. RHE), respectively, to render the  $\Delta E$  of 0.74 V. In contrast, the benchmark noblemetal-based Pt/C + Ir/C electrocatalyst affords the  $E_{1/2}$  and  $E_{10}$ values of 0.85 and 1.62 V (vs. RHE), respectively, to render the  $\Delta E$  of 0.77 V. Therefore, the composite Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst explicitly demonstrates superior bifunctional oxygen electrocatalytic reactivity to the noble-metal-based Pt/C+Ir/C electrocatalyst, which demonstrates the efficiency of the composite strategy. The corresponding Tafel plots additionally reveal the kinetic advantages of the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst over the Pt/C+Ir/C electrocatalyst. Lower Tafel slopes of  $38 \text{ mV} \text{dec}^{-1}$  for ORR and  $66 \text{ mV} \text{dec}^{-1}$  for OER are realized on the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst whereas the Tafel slopes of the Pt/C + Ir/C electrocatalyst are 86 and 74 mV dec<sup>-1</sup> for ORR and OER, respectively (Figure 2b). Moreover, the composite Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst exhibits higher bifunctional oxygen electrocatalytic reactivity than most reported noble-metal-free electrocatalysts with reduced  $\Delta E$  (Figure 2 c and Table S4). The bifunctional ORR/OER electrocatalytic reactivity is therefore validated to exceed the noble-metal-based electrocatalyst and indeed is among the best.





Figure 2. Bifunctional oxygen electrocatalytic reactivity evaluation. (a) ORR/OER LSV profiles and (b) corresponding Tafel plots of the  $Co_3O_4@POF$  and Pt/C + Ir/C electrocatalysts. (c) Comparison of the bifunctional oxygen electrocatalytic reactivity of  $Co_3O_4@POF$ , Pt/C + Ir/C, and other reported noble-metal-free electrocatalysts.

To investigate the origin of the excellent bifunctional ORR/ OER electrocatalytic reactivity of the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst, an electrocatalytic evaluation was performed on the control samples with only ORR or OER active sites to validate the composite strategy. The POF with only Co-N-C sites and Co<sub>3</sub>O<sub>4</sub> nanoparticles hybridized on bare G (named as Co<sub>3</sub>O<sub>4</sub>) served as the control samples with only the ORR or OER active sites, respectively. The Co<sub>3</sub>O<sub>4</sub> electrocatalyst was synthesized under otherwise identical procedures as Co<sub>3</sub>O<sub>4</sub>@POF except using the same amount of G instead of POF. The Co<sub>3</sub>O<sub>4</sub> electrocatalyst demonstrates analogous morphologies as the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst with Co<sub>3</sub>O<sub>4</sub> nanoparticles hybridized on the surface of G (Figure S9). XRD patterns and the XPS survey spectrum further confirm the existence of the  $Co_3O_4$  phase and reasonable cobalt component (Figures S10 and S11). The cobalt content of the Co<sub>3</sub>O<sub>4</sub> and the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst is comparable (Table S2).

The ORR and OER electrocatalytic reactivity of the control POF and  $Co_3O_4$  electrocatalysts were evaluated by using identical methods as the  $Co_3O_4$ @POF electrocatalyst. The  $E_{1/2}$  of the POF electrocatalyst is 0.79 V (vs. RHE), which is close to that of the  $Co_3O_4$ @POF electrocatalyst of 0.82 V (vs. RHE) but much higher than the  $Co_3O_4$  electrocatalyst of 0.64 V (vs. RHE; Figure 3a). In contrast, the  $E_{10}$  of the  $Co_3O_4$  electrocatalyst is 1.61 V (vs. RHE), which is comparable with the  $Co_3O_4$ @POF electrocatalyst of 1.56 V (vs. RHE) but distinctly reduced compared with the POF electrocatalyst of 1.74 V (vs. RHE; Figure 3b). Correspondingly, the bifunctional electrocatalytic reac-

tivity of the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst is the highest among all the samples. In addition, the above tendency remains the same for the kinetic evaluation based on the Tafel plots, in which the POF and Co<sub>3</sub>O<sub>4</sub>@POF electrocatalysts exhibit similarly reduced ORR Tafel slopes whereas the Co<sub>3</sub>O<sub>4</sub> and the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalysts exhibit similarly reduced OER Tafel slopes (Figure S12). Based on the above discussion, it is concluded that POF with Co-N-C active sites and Co<sub>3</sub>O<sub>4</sub> nanoparticles afford the ORR and OER electrocatalytic reactivity, respectively. The composite Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst that integrates both ORR and OER active sites affords promoted bifunctional oxygen electrocatalytic reactivity.

Notably, the ORR and OER electrocatalytic reactivity of the  $\mathsf{Co}_3\mathsf{O}_4@\mathsf{POF}$  electrocatalyst is better than that of the POF and Co<sub>3</sub>O<sub>4</sub> electrocatalysts on each side, respectively. Such improved electrocatalytic reactivity suggests possible synergistic effects between POF and Co<sub>3</sub>O<sub>4</sub> to render further promoted performances. Electrochemically active surface area (ECSA) analysis and electrochemical impedance spectroscopy (EIS) measurements were performed on the electrocatalysts to provide more information. The Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst exhibits the largest ECSA manifested by the highest double-layer capacity (Figure 3 c) and the lowest charge transfer resistance indicated by the reduced semicircle in the high frequency range of the Nyquist plot (Figure 3d). Considering the similar morphology and structure of the electrocatalysts, the improved ECSA and reduced resistance are suggested to be attributed to the synergistic effect between POF and Co<sub>3</sub>O<sub>4</sub> nanoparticles,



**Figure 3.** Mechanistic investigation of the origin of the bifunctional electrocatalytic reactivity. (a) ORR and (b) OER LSV profiles of the POF,  $Co_3O_4$ , and  $Co_3O_4@POF$  electrocatalysts. (c) ECSA and (d) EIS spectra of the POF,  $Co_3O_4$ , and  $Co_3O_4@POF$  electrocatalysts.

which is beneficial to improve the bifunctional electrocatalytic reactivity.

Considering the outstanding ORR/OER bifunctional reactivity, the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst was further employed as the cathode electrocatalyst to construct the air cathode of rechargeable zinc–air batteries. The rechargeable zinc–air batteries were assembled with a stack-type cell configuration.<sup>[68]</sup> A zinc metal foil with the diameter of 19.0 mm and thickness of 0.25 mm served as the anode, and the electrolyte was 6.0 m KOH aqueous solution containing 0.20 M Zn(OAc)<sub>2</sub>. The air cathode was fabricated with a hydrophobic gas diffusion layer and a hydrophilic layer where the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalysts were loaded. The areal mass loading of the electrocatalysts within the air cathode was controlled to be 0.50 mg cm<sup>-2</sup> in all cases. An air cathode with the same amount of the noblemetal-based Pt/C + Ir/C electrocatalyst was also prepared as a comparison.

Figure 4a shows the polarization profiles of the cells with the  $Co_3O_4@POF$  or the Pt/C + Ir/C cathode. The  $Co_3O_4@POF$  affords higher discharge voltages and lower charge voltages to render reduced polarization, indicating the higher electrocatalytic reactivity of the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst. In addition, the Co<sub>3</sub>O<sub>4</sub>@POF cathode renders a higher peak power density of 222.2  $mW\,cm^{-2}\!,$  clearly outperforming the Pt/C+Ir/C cathode of 110.7  $\rm mW\,cm^{-2}$ . The rate performance was evaluated by comparing the discharge voltages at varied discharge current densities. The Co<sub>3</sub>O<sub>4</sub>@POF cathode exhibits higher discharge voltages corresponding to reduced polarization compared with the Pt/C + Ir/C cathode at all the current densities (Figure 4b). Specifically, the average discharge voltages of the Co<sub>3</sub>O<sub>4</sub>@POF cathode are 1.25, 1.20, 1.16, 1.10, and 0.89 V at the current densities of 2.0, 5.0, 10, 25, and 50 mA cm<sup>-2</sup>, respectively. In contrast, the average discharge voltages reduce to 1.19, 1.12, 1.03, 0.80, and 0.65 V on the Pt/C+Ir/C cathode accordingly (Figure S13). When the discharge current density reduces, the discharge voltages of the Co<sub>3</sub>O<sub>4</sub>@POF cathode recover rapidly without attenuation whereas the Pt/C + Ir/C cathode exhibits a clear voltage hysteresis. Consequently, the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst exhibits better rate performances in rechargeable zinc-air batteries than the noble-metal-based Pt/C + Ir/C electrocatalyst.

The cycling stability of the Co<sub>3</sub>O<sub>4</sub>@POF cathode was evaluated by following a galvanostatic discharge-charge method with each galvanostatic cycle undergoing a 5.0 min discharge and a 5.0 min charge. The electrolyte was intermittently replaced to eliminate the obstruction from electrolyte deterioration and to reveal the actual stability of the air cathode. At the current density of 2.0 mA cm<sup>-2</sup>, the initial discharge-charge voltage gaps of the Co<sub>3</sub>O<sub>4</sub>@POF and the Pt/C+Ir/C cathodes are similar, around 0.8 V (Figure S14). However, the discharge-charge voltage gap increases significantly after 400 cycles with the Pt/ C+Ir/C cathode to render the failure of the zinc-air battery. In comparison, the Co<sub>3</sub>O<sub>4</sub>@POF cathode affords stable cycling for more than 2000 cycles with stable discharge-charge voltage gaps. At the higher current density of  $5.0 \text{ mA cm}^{-2}$ , the Co<sub>3</sub>O<sub>4</sub>@POF cathode affords an even longer cycling stability of 2250 cycles corresponding to 375 h with the discharge-charge voltages gaps maintained around 1.0 V (Figure 4 c), whereas the Pt/C + Ir/C cathode failed after only 400 cycles (Figure S15). Such outstanding cycling stability exceeds most of the reported cathode electrocatalysts for rechargeable zinc-air batteries (Table S5) to indicate the composite Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst is highly promising to realize high-performance rechargeable zinc-air batteries. When the current density is further increased to 10 mA  $\rm cm^{-2}$ , the cycling stability advantages are still present for 365 cycles for the Co<sub>3</sub>O<sub>4</sub>@POF cathode or 280 cycles for the Pt/C + Ir/C cathode (Figure 4 d). Overall, the  $Co_3O_4@POF$  electrocatalyst demonstrates extraordinary rechargeable zinc-air



**Figure 4.** Rechargeable zinc–air battery performances of the  $Co_3O_4@POF$  cathode. (a) Discharge–charge polarization curves and corresponding discharge power density of the  $Co_3O_4@POF$  and Pt/C + Ir/C cathodes. (b) Rate performances of the  $Co_3O_4@POF$  and Pt/C + Ir/C cathodes. Galvanostatic discharge–charge profiles at the current density of (c) 5.0 mA cm<sup>-2</sup> of the  $Co_3O_4@POF$  cathode and (d) 10 mA cm<sup>-2</sup> of the  $Co_3O_4@POF$  and Pt/C + Ir/C cathodes.

battery performance advantages regarding reduced polarization, improved rate responses, and long-term cycling stability over the noble-metal-based electrocatalyst.

To further evaluate the structural stability of the composite Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst under working zinc-air battery conditions, morphology characterization and elemental analysis were performed on the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst after cycling at 5.0 mA cm<sup>-2</sup>. The cycled Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst demonstrates the morphology of Co<sub>3</sub>O<sub>4</sub> nanoparticles composited on the surface of POF without significant difference from the pristine sample (Figure S16). Further elemental mapping affords distinct signal of carbon, nitrogen, oxygen, and cobalt with uniform spatial distribution in correspondence with the corresponding TEM image (Figure S17). Meanwhile, the elemental content of the cycled Co3O4@POF electrocatalyst remains stable with a relatively low zinc content of 1.2 at %, indicating excellent chemical stability and limited influence of the electrolyte on the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst (Figure S18). Therefore, the Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst exhibits structural stability regarding the preserved morphology and maintained elemental content after long-term cycling, further validating the advances of the composite  $Co_3O_4@POF$  bifunctional oxygen electrocatalyst to construct high-performance rechargeable zinc–air batteries.

High-performance bifunctional oxygen electrocatalysts are of great significance for rechargeable metal-air batteries, where the bifunctional ORR/OER electrocatalytic reactivity plays a determining role that influences the battery performances. To essentially break the limitation of the benchmark noble-metal-based electrocatalyst has been the pursuit for decades and has recently been realized by advanced electrocatalysts. To construct a composite electrocatalyst constitutes a highly effective strategy, where rational integration of distinguished ORR and OER active sites into one composite electrocatalyst remains a main challenge. The integration of different active sites requires an optimized balance, and synergistic effects can further improve the bifunctional electrocatalytic reactivity. Besides the selection of the active sites, morphology,



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conductivity, and the structural stability shall also be seriously considered. The composite  $Co_3O_4$ @POF electrocatalyst reported herein affords an example to inspire further design and fabrication of advanced composite multi-functional electrocatalysts. The success of the  $Co_3O_4$ @POF cathode highlights the board potential of rechargeable zinc–air batteries for sustainable energy storage and supply.

#### Conclusions

A composite Co<sub>3</sub>O<sub>4</sub>@POF bifunctional oxygen electrocatalyst was rationally designed and fabricated to construct advanced air cathodes for high-performance rechargeable zinc–air batteries. The Co<sub>3</sub>O<sub>4</sub>@POF electrocatalyst exhibits a bifunctional electrocatalytic reactivity of  $\Delta E = 0.74$  V, which exceeds the noblemetal-based Pt/C + lr/C electrocatalyst and most of the reported noble-metal-free bifunctional electrocatalysts. When applied as the cathode electrocatalyst, the rechargeable zinc–air batteries afford a high peak power density of 222.2 mW cm<sup>-2</sup>, decreased discharge–charge voltage gaps, and extraordinary cycling stability for more than 2000 cycles at the current density of 5.0 mA cm<sup>-2</sup>. This work affords an advanced bifunctional oxygen electrocatalyst with outstanding performances and further inspires the rational integration of different active sites for multi-functional electrocatalysis in energy-related applications.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** electrocatalysis • framework porphyrin • noblemetal-free electrocatalysts • oxygen reduction reaction • rechargeable zinc-air batteries

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