Co/Co$_2$P Nanoparticles Encapsulated within Hierarchically Porous Nitrogen, Phosphorus, Sulfur Co-doped Carbon as Bifunctional Electrocatalysts for Rechargeable Zinc-Air Batteries


Developing high performance nonprecious metal-based electrocatalysts has become a critical first step towards commercial applications of metal-air batteries. Herein, nanocomposites based on Co/Co$_2$P nanoparticles encapsulated within hierarchically porous N, P, S co-doped carbon are prepared by controlled pyrolyis of zeolitic imidazolate frameworks (ZIF-67) and poly (cyclophosphazene-co-4,4’-sulfonyldiphenol) (PZS). The resulting Co/Co$_2$P@NPSC nanocomposites exhibit apparent oxygen reduction reaction (ORR) and evolution reaction (OER) catalytic performance, and are used as the reversible oxygen catalyst for zinc-air batteries (ZABs). Density functional theory (DFT) calculations exhibit that Co$_2$P could provide active sites for the ORR and promote the conversion between the adsorbed intermediates, and porous N,P,S co-doped carbon with Co$_2$P nanoparticles also improves the exposure of actives sites and endows charge transport. Liquid-state ZABs with Co/Co$_2$P@NPSC as the cathode catalysts demonstrate the greater power density of 198.1 mW cm$^{-2}$ and a long cycling life of 50 h at 10 mA cm$^{-2}$, likely due to the encapsulation of Co/Co$_2$P nanoparticles by the carbon shell. Solid-state ZABs also display a remarkable performance with a high peak power density of 74.3 mW cm$^{-2}$. Therefore, this study indicates the meaning of the design and engineering of hierarchical porous carbon nanomaterial as electrocatalyst for rechargeable metal-air batteries.

**Introduction**

Rechargeable metal-air batteries have been attracting much attention as a new effective electrochemical energy technology, owing to their high theoretical energy density, lower costs, and environment-friendly.[1,2] Of these, rechargeable ZABs with nonflammable and high ionic conductivity water electrolytes are of particular interest, thanks to their safe operation and high rate output.[3–7] Yet, the sluggish electron-transfer kinetics at the air cathode, which entails ORR during discharge and OER during charge, has been found to severely hinder the energy conversion rate and rechargeability of ZAB.[8–10] Precious metal-based nanoparticles (e.g., Pt, Pd, Ir, and Ru) have been used widely as the electrocatalysts towards ORR and OER.[11–13] However, their high costs, low natural abundance, and limited stability have rendered it challenging to achieve large-scale commercialization of the technology. Additionally, these catalysts are generally active to either ORR or OER. Therefore, it is imperative to design robust, high-efficiency bifunctional electrocatalysts for metal-air batteries.

Now Considerable efforts have been dedicated to engineer nonprecious metal-based electrocatalysts, such as, transition-metal oxides, metal-carbon nanocomposites, as well as heteroatom-doped carbon.[10,14–17] Among these, transition-metal oxides are known to show high electrocatalytic activity and good durability in metal-air batteries, but the performance is compromised by the poor electrical conductivity.[16] By contrast, porous carbon, with a high pore volume and surface area, can promote mass transport of reaction species and have emerged as a viable alternative as low-cost, high-efficiency catalysts for metal-air batteries.[19] Meanwhile, metal-carbon nanocomposites (e.g., Fe, Co, and Ni) have attracted great attention, where their high electrocatalytic activity can be gained by the dopant of heteroatom into the carbon matrix and formation of metal hybrid nanoparticles.[18,20,21] Of these, transition-metal phosphides (TMPs) have been known as hopeful oxygen electrocatalysts, as electronegative P can act as a Lewis acid and grab the electrons from metal centers to manipulate the charge distribution within the materials.[3,22–25] For instance, cobalt phosphide has demonstrated excellent electrocatalytic activity towards HER (hydrogen evolution reaction) and OER.[26–29] However, the electron transport kinetics of Co$_2$P is sluggish due to the strong binding force of surface Co atom with the
adsorbed intermediates, so their electrocatalytic activity towards ORR is limited.\textsuperscript{[30,31]} Then it is a great challenge to fine design and rationally synthesize a robust, durable and high-efficiency bi-functional Co\textsubscript{3}P-based catalyst for metal-air batteries.\textsuperscript{[32]} Significantly, the electrocatalytic activity of TMPs can be enhanced by hybridizing TMPs with porous carbon materials, due to synergistic interactions between TMPs and the carbon scaffold.\textsuperscript{[16,33–38]} and electronic modulation by the heteroatom doping (e.g., N, P, S, B, etc.) of the carbon matrix.\textsuperscript{[19,33–36]} Therefore, it is very significant to design a synergistic nanocomposite combination between Co\textsubscript{3}P materials and heteroatom-doped carbon substrates for satisfying high efficiency oxygen electrodes for metal-air batteries.

In this work, we developed an exquisite hybrid composite based on Co/Co\textsubscript{3}P nanoparticles encapsulated within N,P,S co-doped porous carbon by controlled pyrolysis of a cobalt-containing ZIF-67 and PZS. Electrochemical measurements showed enhanced ORR activity and long-term durability compared with commercial Pt/C, whereas the OER activity and stability was comparable to that of RuO\textsubscript{2}. With the Co/Co\textsubscript{3}P@NPSC composite as the oxygen catalysts, a rechargeable ZAB in liquid electrolyte was fabricated, which demonstrated a high peak power density of 198.1 mW cm\textsuperscript{-2}, a specific capacity of 890.5 mAh g\textsuperscript{-1}, low discharge and charge of polarization, and a long cycling life of 50 h at 10 mA cm\textsuperscript{-2}. Similarly remarkable performance was observed with a solid-state ZAB, containing ZIF-67 and PZS. Electrochemical measurements depicted in Figure 2e, all Co/Co\textsubscript{3}P@NPSC samples exhibited a hollow-sphere structure of 250–300 nm in diameter. The corresponding XRD patterns to those of Co-NC. Yet at increasing PZS to ZIF-67 alone, three major diffraction peaks can be identified at 2\texttheta = 44.2°, 51.5° and 75.9°, which are readily attributed to the characteristic (111), (200) and (220) reflections of metallic cobalt (JCPDS No. 15-0806), suggesting the formation Co nanoparticles in the sample. With the coating of PZS onto ZIF-67 prior to pyrolysis, Co/Co\textsubscript{3}P@NPSC-1 (Table S1) exhibited almost identical XRD patterns to those of Co-NC. Yet at increasing PZS to ZIF feed ratio, additional diffraction peaks emerged. For instance, Co/Co\textsubscript{3}P@NPSC-2 exhibited a peak at 2\texttheta = 40.9°, which was assigned to the (121) facet of Co\textsubscript{3}P (JCPDS No. 32-0306), suggestive of the formation of Co\textsubscript{3}P.\textsuperscript{[33]} This peak became intensified with Co/Co\textsubscript{3}P@NPSC-3 and Co/Co\textsubscript{3}P@NPSC-4, whereas for Co/Co\textsubscript{3}P@NPSC-5, more peaks appeared at 2\texttheta = 31.5°, 36.3°, 48.1°, and 56.7°, due to the (011), (111), (211), and (301) reflections of CoP (JCPDS No. 29-0497), respectively.\textsuperscript{[40]}

In SEM measurements (Figure S1), Co-NC can be seen to display a rough, solid morphology, whereas the Co/Co\textsubscript{3}P@NPSC samples all possessed a porous, hollow structure. Then BET was used to evaluate the porosity of the Co/Co\textsubscript{3}P@NPSC samples. As depicted in Figure 2e, all Co/Co\textsubscript{3}P@NPSC samples exhibited a type IV isotherm, implying the formation of micro- and mesoporous structure; yet the BET specific surface area varied. For instance, the BET specific surface area was about 399.1 m\textsuperscript{2} g\textsuperscript{-1} for the Co-NC sample, with the pore size mainly between 3 and 5 nm (Figure 2f), and decreased to 275.6 m\textsuperscript{2} g\textsuperscript{-1}

![Figure 1. Schematic diagram of the preparation of Co/Co\textsubscript{3}P@NPSC nanocomposites.](image-url)
Figure 2. SEM images of ZIF-67 (a), NPSC (b), and Co/Co$_2$P@NPSC-3 (c). XRD patterns (d), $N_2$ adsorption/desorption isotherms of Co/Co$_2$P@NPSC nano-composites (e) and BJH pore-size distributions of the series of samples (f).

Figure 3. Typical TEM images of Co/Co$_2$P@NPSC-3 (a–c). Representative HAADF-STEM of Co/Co$_2$P@NPSC-3 (d), and the elemental mapping of Co (e), C (f), N (g), P (h) and S (i).
for Co/CoP@NPSC-1, likely due to the formation of the NPSC shell that blocked some of the surface pores. Yet for Co/CoP@NPSC-2, it increased slightly to 281.7 m² g⁻¹, due to the existence of a hollow structure. With a further increasing feed of PZS, the hollow interior expanded accordingly, and the surface area increased to 337.2 m² g⁻¹ for Co/CoP@NPSC-3, 347.7 m² g⁻¹ for Co/CoP@NPSC-4 and 420.1 m² g⁻¹ Co/CoP@NPSC-5. Note that the porous structure (Figure 2f) is conducive to mass transfer of electrocatalytic reactions.⁴¹⁻⁴³

Consistent results were also confirmed in HRTEM images. As illustrated in Figure 3(a, b), the Co/CoP@NPSC-3 sample exhibited a number of nanoparticles encapsulated in a carbon shell; and the thickness of carbon shell increased with the increasing feed of PZS. In fact, from Figure S2, the NPSC
thickness was estimated to be 1.4 ~ 2.7 nm for Co/Co$_2$P@NPSC-1, 5 ~ 6 nm for Co/Co$_2$P@NPSC-2, 9.0 ~ 11.2 nm for Co/Co$_2$P@NPSC-3, ca. 21.3 nm for Co/Co$_2$P@NPSC-4, and ca. 32.4 nm for Co/Co$_2$P@NPSC-5 (Table S1). In addition, the nanoparticles displayed well-defined lattice fringes (Figure 3c), which included three interplanar distances, 0.350, 0.222, and 0.201 nm, corresponding to the carbon (002), Co$_2$P (121) and Co (111) planes, respectively, in consistent with results from the XRD patterns (Figure 2d).}

Furthermore, the elemental mapping analysis based on HAADF-STEM measurements (Figure 3d–i) demonstrated that the C, N, P and S elements were well distributed on the Co/Co$_2$P@NPSC-3 sample, whereas Co was concentrated at the nanoparticles.

The valence state and elemental composition of the series of samples were then investigated by XPS spectra. As depicted in Figure S3, the Co, C, N, P and S elements can be clearly discerned for the samples, and their contents were displayed in Table S2. The deconvoluted scans of the C 1s electrons are displayed in Figure S4a, where three major components can be resolved at 284.8, 285.8, 287.6 and 289.1 eV, due to C–C, C–N/ C–S/C–P, C=O/C=N and O–C=O, respectively. Note that the constituent of C–N/C–S/C–P suggests successful doping of N and S into the porous carbon matrix.\cite{44,45} Figure S4b shows the deconvoluted N 1s spectra of the samples, and deconvolution yields four peaks at 398.6 eV, 399.6 eV, 403.5 eV, and 409.1 eV, which should be ascribed to pyridinic N, pyrrolic N, graphitic N and oxidized N, respectively.\cite{39} The contents of these N species in the series of samples are summarized in Table S3, where Co$_2$P@NPSC-3 exhibited the highest content of pyridinic N (3.23 at%).\cite{35} In Figure 4a, a doublet can be found at 129.2 eV for P–Co (P 2p$_{3/2}$) and 130.2 eV for P–Co (P 2p$_{1/2}$) in the high-resolution P 2p spectra, due to P in CoP/Co$_2$P; whereas the peak at 132.3 eV indicates the formation of P–C bond, and that at 133.3 eV due to the P–O bond, suggesting the doping of P into the C shell.\cite{47} Figure 4b shows the high-resolution Co 2p spectra, where the Co-NC sample exhibited two doublets at 778.5/793.0 eV and 780.2/796.2 eV, due to the 2p$_{3/2}$ and 2p$_{1/2}$ electrons of metallic Co and Co$^{2+}$/3$^+$/4$^+$ (the latter most likely arose from surface oxidation), respectively.\cite{19,48} For the Co/Co$_2$P@NPSC samples, in addition to the Co$^{2+}$/3$^+$/4$^+$ doublet at 780.2/796.2 eV, another peak can be resolved at 781.6 eV, consistent with the formation of CoP and CoP nanoparticles (Table S3).\cite{35} In addition, the binding energy of Co 2p$_{3/2}$ (778.5 eV) can be seen to show a positive shift, whereas that of P 2p$_{3/2}$ (129.2 eV) demonstrates a negative-shift, in comparison to those of metallic Cobalt (about 778.1–778.2 eV) and P (130.2 eV), indicating the transfer of electrons from Co to P.\cite{31,49} The S 2p spectra (Figure S4c) can be deconvoluted into three peaks at 163.8, 165.2 and 168.5 eV, due to the 2p$_{3/2}$ and 2p$_{1/2}$ electrons of C–S/C and the oxidized S, respectively.\cite{39} These results are consistent with those from the above XRD, BET and HR-TEM measurements, confirming the doping of heteroatoms (N, P and S) into the carbon matrix and incorporation of Co species in the samples, which facilitate the catalytic activity toward both OER and ORR (\textit{vide infra}).\cite{49}
Notably, the series of Co/Co$_2$P@NPSC nanocomposites demonstrated high electrocatalytic activity towards ORR in alkaline solution. From the LSV tests at 1600 rpm, it could be observed that the electrocatalytic performance varied apparently among the series of Co/Co$_2$P@NPSC samples. As illustrated in Figure S5, the onset potential ($E_{\text{onset}}$) and half-wave potential ($E_{1/2}$) could be estimated to be +0.93 and +0.80 V for Co/Co$_2$P@NPSC-1, +0.95 V and +0.82 V for Co/Co$_2$P@NPSC-2, +0.99 V and +0.84 V for Co/Co$_2$P@NPSC-3, +0.89 V and +0.79 V for Co/Co$_2$P@NPSC-4, and +0.88 V and +0.78 V for Co/Co$_2$P@NPSC-5. In other words, the Co/Co$_2$P@NPSC-3 sample performed as the best ORR electrocatalyst among the series, likely due to the combined contributions of both the Co and Co$_2$P nanoparticles and doped carbon scaffold.

The ORR performance of Co/Co$_2$P@NPSC-3 was further investigated by CV measurements in both nitrogen and oxygen-saturated 0.1 M KOH aqueous solution, at the side of Pt/C. As depicted in Figure 5a, while there was no apparent cathodic peak in the voltammetric profiles in the N$_2$-saturated solution, a clearly reduction peak appeared at +0.85 V in O$_2$-saturated solution, suggesting effective reduction of oxygen; and the peak potential was more positive than that of Pt/C (+0.84 V), implying a better catalytic performance of Co/Co$_2$P@NPSC-3. To further explore the ORR performance, LSV curves were collected in 0.1 M KOH (O$_2$-saturated) solution at 10 mV s$^{-1}$, and the results are consistent with the CV data (Figure 5b). Co/Co$_2$P@NPSC-3 demonstrates $E_{\text{onset}}$ of +1.00 V and $E_{1/2}$ of +0.86 V, markedly higher than those of Co-NC (+0.85 and +0.77 V), NPSC (+0.87 and +0.78 V) and Pt/C catalysts (+0.98 and +0.83 V), further confirming that Co/Co$_2$P@NPSC possessed the best electrocatalytic activity for ORR within the present experimental context.

The ORR kinetics was then evaluated by Koutecky-Levich (K-L) analysis, [Eqs. (1–3)]:

\[
J = \frac{1}{J_k} + \frac{1}{J_L} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k} \tag{1}
\]

\[
B = 0.62 nF_{C_0}D_0^{2/3}\nu^{-1/6} \tag{2}
\]

\[
J_k = nF_{C_0} \tag{3}
\]

where $J$ represents the experimental current density, the kinetic and diffusion-limited current density are denoted as $J_k$ and $J_L$, respectively, stands for the rotation rate, $n$ is on behalf of the number of electron transfer, $F$ is Faradaic constant (96485 C mol$^{-1}$), $C_0$ is the dissolved O$_2$ bulk concentration, $D_0$ is the coefficient of diffusion of O$_2$ in 0.1 M KOH solution, $\nu$ is the

![Figure 7. a) Free energy diagram of ORR on C and C–Co$_2$P cluster model; b, c) DOS of C–Co$_2$P cluster. Calculated charge density differences for C–Co$_2$P cluster (d), adsorbates OOH$^*$ (e), O$^*$ (f), and (g) OH$^*$ on the model.](image-url)
kinetic viscosity of KOH solution, and $k$ is the constant of electron transfer rate. From Figure 5c, $n$ was calculated to be about 3.85–4.00 for Co/Co$_2$P@NPSC-3 in the potential range of 0.45–0.70 V, which is higher than those of Co-NC (3.4–3.7) and NPSC (3.3–3.93), and similar to that of Pt/C (3.90–3.95), implying that ORR on Co/Co$_2$P@NPSC proceeded via the 4-electron pathway. Meanwhile, the K–L plots (Figure 5d and e) of Co/Co$_2$P@NPSC-3 can be seen to exhibit good linearity with a same slope at different potentials, confirming that the ORR process conformed to the first-order reaction of kinetics with reference to the dissolved O$_2$ concentration.$^{[50,51]}$ Consistent behaviors were shown for other samples, as manifested in Figure S6 and S7.

The Tafel plots are demonstrated in Figure 5f, where the Tafel slope was found to be 55.9 mV dec$^{-1}$ for Co-NC, 69.4 mV dec$^{-1}$ for NPSC, 77.4 mV dec$^{-1}$ for Co/Co$_2$P@NPSC-3, and 66.8 mV dec$^{-1}$ for Pt/C in the low-overpotential regime, indicating that the reaction kinetics for ORR was largely determined by a pseudo 2-electron reaction. In the high overpotential region, the Tafel slope was 90.2 mV dec$^{-1}$ for Co-NC, 102.6 mV dec$^{-1}$ for NPSC, 102.0 mV dec$^{-1}$ for Co/Co$_2$P@NPSC-3, and 105.7 mV dec$^{-1}$ for Pt/C ($< +0.85$ V), suggesting that the first electron transfer to O$_2$ might be the ORR rate-determining step.$^{[52,53]}$

The samples also exhibited efficient catalytic activity towards OER. Among the series of samples, Co/Co$_2$P@NPSC-3 demonstrates the smallest overpotential, again standing out as the best sample (Figure 6a). From Figure 6b and c, the Co/Co$_2$P@NPSC-3 sample can be seen to display a higher specific current and much lower onset potential than those of Co-NC, NPSC, RuO$_2$ and Pt/C. Specifically, Co/Co$_2$P@NPSC-3 exhibited an overpotential ($\eta_{OER}$) of about 325 mV at the current density of 10 mA cm$^{-2}$, which was lower than those of Co-NC (429 mV), NPSC (418 mV), RuO$_2$ (387 mV) and Pt/C (545 mV), indicating that Co/Co$_2$P@NPSC-3 possessed the best electrocatalytic activity for OER. Meanwhile, the Tafel plots were depicted in Figure 6d, and the Tafel slope was estimated to be 78.9 mV dec$^{-1}$ for Co/Co$_2$P@NPSC-3, which was also lower than those of Co-NC (108.6 mV dec$^{-1}$), NPSC (98.1 mV dec$^{-1}$), RuO$_2$ (120.1 mV dec$^{-1}$), and Pt/C (148.7 mV dec$^{-1}$), implying the fastest reaction kinetics.$^{[54,55]}$ This is also consistent with the trend of the aforementioned overpotential values.

The high electrocatalytic performance of Co/Co$_2$P@NPSC-3 may be attributed to the interactions between Co/Co$_2$P nanoparticles and NPSC. First of all, the high specific surface area of
the NPSC shell allowed ready access to the catalytic active sites and the high porosity facilitated mass transport of important species in the electrocatalytic reactions, such as $\text{O}_2$, $\text{H}_\text{2}$, $\text{OH}$, and $\text{H}_\text{2}O$.[56,57] Secondly, the interfacial charge transfer between the metal core and the NPSC carbon shell that handle the electronic interactions between the intermediates and catalysts surface could promote the catalytic activities. The NPSC carbon shell can also prevent the aggregation and the corrosion of metal core, leading to excellent stability.[58] Thirdly, the N, P and S dopants in the porous carbon shell could induce charge redistribution of the carbon scaffold and the formation of the electrocatalytic active sites towards ORR and OER.[25,53,59,60] For instance, N doping can modulate the electron-neutrality of neighboring carbon atoms and improve the adsorption of $\text{O}_2$ species.[61,62] As reported in previous studies,[21,29] DFT calculations showed that the reverse electronegativity between P and S dopants in the porous carbon shell could induce charge redistribution of the carbon scaffold and the formation of the electrocatalytic active sites towards ORR and OER.[25,53,59,60] The presence of metallic cobalt as a conductive electrocatalytic material provided more active sites, and Co$_2$P played a key role in optimizing the catalytic active site towards ORR, where charge transfer between P and Co led to activation of the encapsulated carbon shell, as observed previously.[19,33]

To further study the ORR activity of Co$_2$P, DFT calculations were conducted by clusters model. Two models were constructed (Figure S8) including C and C–Co$_2$P based on the results of XPS and XRD. The optimized configurations with the adsorbates OOH*, O*, and OH* as depicted in Figure S8. Based on the typical ORR reaction pathway of $\text{O}_2$→$^\ast\text{O}_2$→$^\ast\text{OOH}$→$^\ast\text{O}$→$^\ast\text{OH}$→$\text{H}_\text{2}\text{O}$, the free energy diagram at the equilibrium potential ($U_{\text{RHE}} = 0 \, \text{V}$) is displayed in Figure a. The Gibbs free energy diagram of the $^\ast\text{O}_2$→$^\ast\text{OOH}$ on graphene is uphill process, but all the process of C–Co$_2$P is downhill process, indicating that Co$_2$P could significantly promote the ORR. From the calculated density of states (DOS) in Figure b–c and Figure S9, one can see that the highest d orbit density of Co at Fermi level also confirmed that d orbit electrons effectively enhance the activity in ORR reaction. Meanwhile, the charge density difference further confirmed the above results in Figure 7(d–g). Additionally, Co$_2$P heterojunction model was also conducted to evaluate the electrocatalytic performance of Co$_2$P as observed in Figure S10, but the heterojunction model is far less reasonable and sufficient than the cluster model. In sum, DFT calculations exhibit that Co$_2$P could provide active sites for ORR and promote the conversion between the adsorbed intermediates, and N,P,S co-doped carbon with Co$_2$P nanoparticles also improve the exposure of actives sites and endow charge transport.

Motivated by the remarkable activity of Co/Co$_2$P@NPSC-3 toward both ORR and OER, it was then used as bifunctional electrocatalysts to construct rechargeable ZABs (Figure 8a). As illustrated in Figure 8b, the ZAB demonstrated a peak power density of 198.1 mW cm$^{-2}$, much higher than that of a mixed commercial Pt/C and RuO$_2$ catalysts based ZAB (183.8 mW cm$^{-2}$). Then the corresponding discharge and charge polarization curves of ZABs are shown in Figure 8c, and the ZAB with Co/Co$_2$P@NPSC-3 demonstrated a smaller voltage gap
 Additionally, the cycle life of the air-cathode was investigated by the charge-discharge measurements at 10 mA cm\(^{-2}\) in a short period (10 min), as displayed in Figure 8d and e. Obviously, the ZAB with Co/Co\(_{P}\)@NPSC-3 displayed superior cycling stability for more than 300 cycles (or 50 h equivalent), much better than that of Pt/C + RuO\(_2\) (only 141 cycles, or 23.5 h). As illustrated in Figure 8e, the initial voltage gap was 0.85 and 0.83 V for Co/Co\(_{P}\)@NPSC-3 and Pt/C + RuO\(_2\), respectively. Notably, it increased to 1.80 V after 23.5 h for Pt/C + RuO\(_2\), but remained virtually unchanged at 0.88 V for Co/Co\(_{P}\)@NPSC-3. The round-trip efficiency of Pt/C + RuO\(_2\) decreased significantly from 57.2% to 30.1% after a 23.5 h charging-discharging cycle test, in contrast to a slight decrease from 58.5% to 57.7% for Co/Co\(_{P}\)@NPSC-3. In fact, the battery charging-discharging cycles of Co/Co\(_{P}\)@NPSC-3 remained stable and only decayed to 50.4% at 50 h, further implying the excellent stability of Co/Co\(_{P}\)@NPSC-3, which actually outperformed a number of catalysts reported previously (Table S4). The long time discharge curves of ZAB with Co/Co\(_{P}\)@NPSC-3 at different current density of 10, 20 and 50 mA cm\(^{-2}\) are displayed in Figure 8f, and the specific capacity normalized to the loss efficiency and voltage gap changed from 56.8% to 46.1% and 23.5 h). As illustrated in Figure 8e, the initial voltage gap was about 1.24 V (Figure 9c), implying a stable charge and discharge performance. As depicted in Figure 9d, the round-trip efficiency and voltage gap changed from 56.8% to 30.1% after a 23.5 h discharge-charge cycling test for 10 h (10 min per cycle). A red LED was lit by three all-solid-state ZABs with Co/Co\(_{P}\)@NPSC-3 as the air-cathode catalysts in series (Figure 9e).

Conclusions

In this work, nanocomposites based on Co/Co\(_{P}\) nanoparticles encapsulated within hierarchically porous NPS-doped carbon are prepared by ZIF-67 and PZS. The resulting Co/Co\(_{P}\)@NPSC demonstrate apparent catalytic activity towards both ORR and OER, and are used as the reversible oxygen catalyst for ZABs, which exhibited markedly enhanced activity and durability in both liquid and solid electrolytes, as compared to that based on commercial benchmarks of Pt/C and RuO\(_2\). Therefore, this work demonstrates a promising strategy for the synthesis of efficient catalysts based on cobalt phosphide nanoparticles and carbon scaffolds for flexible power sources in wearable electronics applications.

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Conflict of Interest

The authors declare no conflict of interest.

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