Electronic/mass transport increased hollow porous Cu$_3$P/MoP nanospheres with strong electronic interaction for promoting oxygen reduction in Zn-air batteries

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Developing high-efficient non-noble metal-based catalysts for oxygen reduction reaction (ORR) is an inevitable way to improve Zinc-air batteries’ performance (ZAB). Herein, we report a Cu$_3$P/MoP electrocatalyst (Cu$_3$P/MoP@C) supported by hollow-porous-carbon nanospheres displaying high electrocatalytic activity and exceptional durability in alkaline media. The optimized ORR catalyst outperformed the benchmark Pt/C (20 wt%) and most recently reported Cu$_x$/Mo-based catalysts in various aspects. X-ray photoelectron spectroscopy reveals that the excellent ORR performance originates from the charge transfer between of Cu$_3$P and MoP species. Besides, the large specific surface area of Cu$_3$P/MoP@C with mesoporous structure is particularly advantageous for the inner surface contact with electrolyte to accelerate ORR kinetics. Moreover, Cu$_3$P/MoP@C also exhibits a large power density of 156 mW cm$^{-2}$, a high round-trip efficiency, and superb stability over 231 h superior to Pt/C in the ZAB. This work offers a scalable and promising approach for the rational fabrication of hollow porous structure materials.

1. Introduction

Growing energy demands and environmental deterioration issues have compelled the pursuit of renewable energy conversion-storage technologies, for instance, fuel cells and metal-air batteries [1–3]. Especially, Zinc-air batteries (ZAB) have obtained considerable attention due to their high theoretical energy density of 1086 Wh kg$^{-1}$, good safety and environmental benignity [4–6]. However, practical and large-scale commercial implementation of ZAB is lagged owing to their performance is severely affected by the sluggish kinetics of ORR [7,8]. Although Pt-based catalysts are the state-of-the-art ORR electrocatalysts to date, there is high cost, natural scarcity, poor stability, and vulnerability to methanol poisoning greatly restrict their widespread applications [9–11]. As a result, it is imperative to develop cost-effective, high-efficient and earth-abundant alternative Pt-based catalysts to living up to the high-performance requirement of ZAB and promote ORR activity.

In recent years, transition metal phosphides (TMPs) and their compounds are emerging as a promising alternative to Pt-based catalysts due to their natural abundance and cost-efficient. Importantly, previous reports have demonstrated that their ORR properties can be enhanced significantly through rational design [12–15]. However, as compared to other cathodic electrocatalysts, The ZAB of based TMPs is rarely reported because of the low specific surface area, insufficient electrical conductivity, and aggregation [16], but when TMPs such as Cu$_3$P is combined simultaneously with other carbon based substrates to form a composite material, the carbon component in the material improves conductivity; also, the synergy between various components enhances the ORR activity [17,18]. In catalytic processes, there is a consensus that electrocatalytic activity can be improved significantly by exposing more active sites [19]. In this regard, it is necessary to design and synthesize high surface area electrocatalysts with a high porosity conducive to mass transport and increase the availability of active sites, which are pivotal for enhancing the electrocatalytic performance of ORR.

In this work, we reported a rational design of the hollow porous spherical structure of Cu$_3$P/MoP@C by high-temperature phosphating using carbon spheres as support under argon flow. The optimized catalyst exhibits excellent ORR catalytic activity under alkaline...
conditions with a half-wave potential (E_{1/2}) of 0.90 V (vs. RHE) superior to commercial Pt/C (0.84 V vs. RHE) and a majority of Cu/Mo-based ORR electrocatalysts (the RHE calibration was shown in Fig. S1). Furthermore, CuP/MoP@C also demonstrates outstanding long-term stability compared to Pt/C with a slight current attenuation of 2% after 40000 s tests. The detailed characterizations indicate that the superior activity is attributed to a strong interaction between CuP and MoP species, high BET specific surface area, and porous structure facilitated mass transport. More importantly, the ZAB based on CuP/MoP@C achieves a high open-circuit voltage (OCV) of 1.51 V, a peak power density of 156 mW cm$^{-2}$, and the CuP/MoP@C + RuO$_2$ based ZAB has little decay after 231 h durability testing at a current density of 5 mA cm$^{-2}$, certifying its promising application in advanced energy conversion-storage devices.

2. Experimental section

2.1. Chemicals and reagents

Ethanol, formaldehyde solution (CH$_2$O), tetraethyl silicate (TEOS), resorcinol (C$_8$H$_6$O$_2$), 1,3,5-benzenetricarboxylic acid (BTC), and zinc acetate dihydrate (Zn(Ac)$_2$) were purchased from Xilong Chemical Co., Ltd. Phosphomolybdic acid hydrate (PMo$_{12}$), copper (II) acetate monohydrate (Cu(Ac)$_2$H$_2$O), and i-glutamic acid (C$_5$H$_8$NO$_4$) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai China). Ammonia solution (NH$_4$OH), potassium hydroxide and red phosphorus (P) were got from Aladdin Industrial Corporation. Nafion solution (5 wt %) and platinum on carbon (Pt/C, 20 wt%) were obtained from Alfa Aesar and Macklin Biochemical, respectively. All chemicals and reagents were of analytical grade and used directly without further purification.

2.2. Synthesis of carbon spheres

Hollow mesoporous carbon spheres were obtained according to the previously reported work with slightly modification [20]. In the protocol, 3.46 mL of TEOS was quickly added to a stirred mixture of deionized water (10 mL), ethanol (70 mL) and NH$_4$OH (3 mL). After 15 min, 3.63 mmol C$_8$H$_6$O$_2$ and 0.56 mL of CH$_2$O were added to the above mixture. The mixture was stirred vigorously at room temperature for 24 h, and centrifuged at 9000 rpm for 6 min to obtain SiO$_2$@RF nanospheres (R and F represent resorcinol and formaldehyde solution, respectively, which is a process of coating a layer of carbonaceous material on the surface of SiO$_2$ by an aldol condensation reaction). The nanospheres were washed with ethanol for several times and dried overnight in an oven at 60 °C.

The SiO$_2$@RF was placed in a clean quartz boat and transferred to a tube furnace for heating at 700 °C in a nitrogen atmosphere for 5 h with a heating rate of 5 °C min$^{-1}$ to obtain SiO$_2$@C. Carbon spheres were obtained by removing SiO$_2$ core with 3 M KOH at 60 °C.

2.3. Synthesis of CuP/MoP@C

In a synthetic procedure, a certain amount of carbon spheres were dispersed in 50 mL of deionized water containing 0.02 mmol PMO$_{12}$, 0.1 mmol Cu(Ac)$_2$H$_2$O and 0.03 mmol C$_8$H$_6$NO$_4$ and ultrasonicated for 30 min so that carbon spheres can be uniformly dispersed in the solution. After that, 50 mL of ethanol solution containing 0.1 mmol BTC was quickly added to the above solution. After vigorous stirring for 6 h, 1.82 mmol Cu$_2$O, 0.28 mL of CH$_2$O and 2 mL of NH$_4$OH were sequentially added the above mixture. After continuous stirring for 24 h under ambient conditions, the precursors were separated by centrifugation, washed with ethanol for 3 times, and dried overnight at 60 °C. 50 mg of precursor powder was ground together with 100 mg of red phosphorus, transferred to a porcelain boat, and calcined at different temperatures (800, 900, 1000 °C) for 2 h under Ar flow with a 5 °C min$^{-1}$ heating rate. Unless specifically stated, the CuP/MoP@C was obtained at 900 °C.

For comparison, the Cu doping level was first tuned by altering the Cu/Mo molar ratio (10:1, 1:1, 1:5, 1:10) during the synthesis process. Second, the mass ratio of precursor and red phosphorus was changed (1:1, 1:3, 2:1, 3:1) during the calcination process.

2.4. Synthesis of CuP@C and MoP@C

The CuP@C and MoP@C were synthesized using a similar method as CuP/MoP@C mentioned above, except that only PMO$_{12}$ or Cu (Ac)$_2$H$_2$O are added during the synthesis.

2.5. Zn-air batteries (ZAB) fabrication and test

The catalyst slurry was prepared by ultrasonically dispersing 2 mg of catalyst and 5 μL of 5 wt % Nafion into a mixed solution of 150 μL of water and 50 μL of isopropanol, coating the obtained slurry on hydro-
phobic carbon paper (loading: 1 mg cm$^{-2}$) and dried at room temperature to be used as the air cathode. Zinc foil was employed as the anode, and the 6.0 M KOH solution containing 0.2 M Zn(Ac)$_2$ was served as the electrolyte to assemble the Zinc-Air battery. Since Cu$_3$P/MoP@C showed a poor OER performance (Fig. S2), a Cu$_3$P/MoP@C + RuO$_2$ (mass ratio = 1:1) was used as an air cathode during the stability test by applying the same preparation method as above. For comparison, Pt/C (mass ratio = 1:1) was used as a phosphorus source does not generate toxic PH$_3$ gas at high temperature compared with NaH$_2$PO$_2$ approach.

The crystalline characteristics of the as-prepared catalysts were elucidated by X-ray diffraction (XRD) patterns (Fig. 1b). In addition to the broad peaks at around 24.8$^\circ$ and 43.3$^\circ$ belonging to (002) and (101) facets of graphitic carbon [22, 23], and diffraction peaks at around 36.2$^\circ$, 39.3$^\circ$, 41.7$^\circ$, 45.1$^\circ$, and 46.3$^\circ$ can be assigned to the (112), (202), (211), (300) and (113) lattice planes of hexagonal Cu$_3$P (JCPDS: 02–1263), respectively [17, 24]. Because the diffraction peaks of MoP are not prominent, it is likely to have a low crystallinity. The content of Mo loading onto the Cu$_3$P/MoP@C is up to 12.85 wt% measured by inductively coupled plasma mass spectroscopy (ICP-MS) (Table S1). The above results demonstrate Cu$_3$P/MoP has been successfully fabricated on the carbon matrix. Furthermore, the intensity ratio of the D band and G band (I_D/I_G), an evaluation index of carbon disorders, were given in the Raman spectra (Fig. 1c). For Cu$_3$P/MoP@C, the I_D/I_G was 0.93, which is roughly consistent with Cu$_3$P@C (0.91) and MoP@C (0.92), indicating that the surface disorder caused by loading metal is approximately the same [25, 26]. Raman spectroscopy was shown in Fig. S3. The graphitization degree can be adjusted by changing the calcination temperature and copper and phosphorus contents during the synthesis process. The N$_2$ adsorption-desorption isotherm was illustrated in Fig. 1d, which presented reversible type IV isotherm with a remarkable hysteresis loop confirming the presence of mesoporous [22, 27]. The Brunauer–Emmett–Teller (BET) specific surface area and average pore size of Cu$_3$P/MoP@C were calculated to be 428.6 m$^2$ g$^{-1}$ and ~7 nm, which were important factors to improve electrocatalytic activity due to increase the maximum utilization of active sites and promote mass transport [28].

The morphology of samples was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The surface of SiO$_2$@RF nanospheres was smooth, whereas the surface of hollow nanospheres obtained after removing the SiO$_2$ core was rough and cracked (Figs. 2a-b and S4a–c), demonstrating the formation of pores, which was in good accordance with BET test results and its shell was approximately 6 nm thick. The porous carbon sphere maintained complete after Cu$_3$P/MoP was supported on carbon spheres, except that the shell was increased to 10 nm thick (Figs. 2c–e and S5). The lattice fringes of Cu$_3$P/MoP@C were observed from high-resolution TEM (HR-

![Fig. 2. (a) SEM and (b) TEM images of carbon spheres. (c) SEM, (d, e) TEM, (f) HR-TEM, and (g) HAADF-STEM images and the corresponding elemental mappings of Cu$_3$P/MoP@C.](image-url)
TEM) images, of which 0.209 nm and 0.201 nm were consistent with the (101) crystal plane of MoP and the (300) crystal plane of Cu₃P, respectively (Fig. 2f) [29]. As shown in Figs. 2g and S6, the hollow porous structure was further reaffirmed by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), as well the corresponding energy-dispersive X-ray spectroscopy (EDS) mappings confirmed the uniform dispersion of C, O, P, Cu, and Mo on the Cu₃P/MoP@C structure. The results obtained further supported XRD analysis to evidence the successful formation of Cu₃P/MoP on the carbon spheres.

XPS spectra probed the chemical states and composition of elements. The survey XPS spectra (Fig. S7) show that Mo, Cu, C, P, and O elements are dominant in the catalysts. For Cu₃P/MoP@C, the high-resolution C 1s spectrum is deconvoluted into four peaks at \( \approx 284.8 \text{(C–C)} \), 286.1 \((\text{C–O})\) and 289.1 eV \((\text{C–O})\) (Fig. S8) [30,31]. The Mo 3d XPS spectrum of Cu₃P/MoP@C shows peaks at around 228.5 and 231.7 eV are indexed to Mo\(^{2+}\) species \((0 < \delta < 4)\) in MoP [32–34]. The other two peaks located at 232.2 eV and 235.3 eV coincide with Mo \((\text{VI})\) \(3d_{3/2}\) and \(3d_{5/2}\) of MoO₃, respectively, which might arise from the surface oxidation of MoP. Compared with MoP@C, the binding energies of Mo-P are negatively shifted by 0.2 eV (Fig. 3a). Moreover, the Cu 2p XPS spectrum of Cu₃P/MoP@C was fitted into three peaks assigned to Cu-P \((933.1 \text{ eV})\), Cu-O \((935.2 \text{ eV})\) and one satellite peak \((942.1 \text{ eV})\) [17,35], respectively, the presence of Cu-O bond is unavoidable due to the surface oxidation of Cu₃P. Contrary to Mo 3d, the binding energies of Cu-P are positively shifted at 0.2 eV than Cu₃P@C (Fig. 3b). Meanwhile, the P 2p region of

![Fig. 3. High-resolution XPS spectra of (a) Mo 3d, (b) Cu 2p, and (c) P 2p regions in Cu₃P/MoP@C, Cu₃P@C, MoP@C, respectively.](image)

Fig. 4. Electrochemical performance of different catalysts. (a) CV curves in N₂ or O₂-saturated 0.1 M KOH solutions. (b) LSV polarization curves in O₂-purged 0.1 M KOH electrolyte and (c) the corresponding half-wave potential \((E_{1/2})\) and kinetic current density \((J_k)\) at 0.9 V. (d) Polarization curves of Cu₃P/MoP@C with various rotating speeds from 400 to 2025 rpm and the corresponding K-L plots (inset). (e) Tafel plots and (f) \(\text{H}_2\text{O}_2\) yield (%) and electron transfer number (n) from various catalysts.
Cu$_3$P/MoP@C is deconvoluted into three peaks at 129.4, 130.3, and 133.7 eV (Fig. 3c), and ascribed to 2p$_{3/2}$ and 2p$_{1/2}$ of Mo–P or Cu–P, and P–O bonds due to surface oxidation caused by phosphorus [17,32, 36]. The C–P bonds was not found in the C 1s and P 2p spectra indicating no P-doping on the carbon frame (Figs. 3c and S7) [37]. It is worth noting that the positive shift on Cu–P and the negative shift on Mo–P no P-doping on the carbon frame (Figs. 3c and S7) [37]. Overall, as expected, XPS analysis further confirmed that the Cu–P to the MoP, interpreting the strong electronic interaction between Cu$_3$P and MoP species [33,38]. Moreover, the high-resolution N 1s spectrum shows a small amount of nitrogen that exists in the form of pyridinic N (398.0 eV) and pyrrolic N (400.6 eV) (Fig. S9) [39], indicating N-doping in the carbon frame result of the ammonia treatment during the synthesis. However, the contribution of the N-doping to ORR performance is not discussed separately since it is the common step for all the catalysts. Overall, as expected, XPS analysis further confirmed that the Cu$_3$P/MoP was successfully synthesized on the carbon spheres, which is consistent with TEM and XRD analysis.

3.2. ORR activities of electrocatalysts in alkaline medium

The ORR performance was measured by rotating disk electrode (RDE) and rotating ring disk electrodes (RRDE) techniques in 0.1 M KOH solution. The optimized calcination temperature and the doping content, and the corresponding performance parameters are shown in Figs. S10–12. The ORR polarization curves of all samples were recorded in O$_2$-saturated 0.1 M KOH. The resulting onset potential ($E_{\text{onset}}$) and half-wave potential ($E_{1/2}$) are listed in Table S2. In general, the higher the onset potential shows better electrocatalytic activity in the LSV polarization curve [40,41]. The results showed that the best catalyst, designated as Cu$_3$P/MoP@C, was obtained when the molar ratio of Cu/Mo was 5/1, the mass ratio of P with precursor was 2/1 together with an annealing temperature was 900 °C. Therefore, if not explicitly stated, the optimized catalyst here is the target catalyst discussed below.

Cyclic voltammetry (CV) were recorded in O$_2$-saturated 0.1 M KOH solution. As displayed in Fig. 4a, the distinct cathodic peaks were observed in all samples under O$_2$-saturated electrolyte compared to N$_2$-saturated solution, indicating an efficient ORR process. The linear sweep voltammetry (LSV) were tests in O$_2$-saturated 0.1 M KOH are presented in Fig. 4b, the Cu$_3$P/MoP@C exhibits an incremental $E_{\text{onset}}$ (1.03 V) and $E_{1/2}$ (0.90 V) in contrast to those of carbon spheres (0.94 V, 0.77 V) and Cu$_3$P@C (1.02 V, 0.90 V), MoP@C (1.00 V, 84 V) and commercial Pt/C (1.02 V, 0.84 V). Meanwhile, the kinetic current density ($J_0$) of Cu$_3$P/MoP@C reaches 5.08 mA cm$^{-2}$ at 0.9 V, which outperforms those of carbon spheres (0.29 mA cm$^{-2}$), Cu$_3$P@C (4.60 mA cm$^{-2}$), MoP@C (1.41 mA cm$^{-2}$) and commercial Pt/C (2.04 mA cm$^{-2}$) (Fig. 4c). The LSV curves are obtained at the same rotational speed (1600 rpm) to minimize the effect of the mass transfer process. Nevertheless, the current density of Cu$_3$P/MoP@C (5.13 mA cm$^{-2}$) is 19 % and 28 % higher than those of Cu$_3$P@C (4.30 mA cm$^{-2}$) and MoP@C (4.00 mA cm$^{-2}$) at 0.4 V (vs. RHE). Moreover, the number is 19 % and 42 % higher at 0.6 V (vs. RHE), respectively, which is much more pronounceable than the similar studies reported in the literature under the same voltages suggesting the synergy between the Cu$_3$P and MoP species resulted by the charge transfer [42,43]. All the data suggested that the Cu$_3$P/MoP@C catalyst possesses the highest ORR electrocatalytic activity and Cu$_3$P@C is the main activity center. The outstanding ORR performance of Cu$_3$P/MoP@C is ascribed to the strong synergistic interaction between Cu$_3$P and MoP. Besides, LSV curves were also obtained at varying rotational speeds from 400 to 2025 rpm (Fig. 4d), and the resulted Koutech-Levich (K-L) plots possess an excellent linear relationship (inset), which reveals first-order reaction kinetics related to the concentration of dissolved oxygen [44]. The average number of electron transfer number ($n$) is estimated to be ~3.7 based on the K-L plots at various potentials, corroborating that oxygen can be reduced through the direct four-electron pathway. To demonstrate that the rapid ORR kinetics of the as-prepared catalysts, Fig. 4e illustrates the corresponding Tafel slopes of Cu$_3$P/MoP@C, carbon spheres, Cu$_3$P@C, MoP@C, and commercial Pt/C are calculated to be 77.2, 93.1, 84.1, 87.8, and 96.5 mV dec$^{-1}$, respectively. Simultaneously, the electrochemical impedance spectroscopy (EIS) was tested shown in Fig. S13; the Cu$_3$P/MoP@C shows a smaller charge transfer resistance ($R_{ct}$, 66 Ω) than other catalysts, which further proves that the high charge transport...
kinetics of Cu$_3$P/MoP@C \cite{45,46}. To further interrogate the mechanism of Cu$_3$P/MoP@C promote ORR activity, the RRDE technique was executed to verify $n$ close to 4, consistent with the value based on the K-L plots. The calculated H$_2$O$_2$ yield is 20 \% or less on the potential range of 0.2--0.8 V vs. RHE, implying that the reduced product exhibits superior selectivity (Fig. 4f). These excellent performances reveal that the ORR activity of Cu$_3$P/MoP@C catalyst not just surpasses commercial Pt/C but compares favorably with the majority of recently reported advanced Cu-/Mo-based ORR electrocatalysts (Table S3).

The electrochemical active surface area (ECSA) was evaluated by the double-layer capacitance ($C_{dl}$) to explain the intrinsic ORR activity further. The ECSA has a positive correlation with $C_{dl}$, and $C_{dl}$ is calculated according to the CV curve in the non-faradic region at different scan rates (Fig. S14) \cite{47–49}. As shown in Fig. 5a, the Cu$_3$P/MoP@C presents a $C_{dl}$ value of 33.8 m F cm$^{-2}$, being beyond that of Cu$_3$P@C (25.1 m F cm$^{-2}$) and MoP@C (10.9 m F cm$^{-2}$), indicating Cu$_3$P/MoP@C has a higher ECSA, which can expose more active sites and promote ORR activity. Subsequently, ECSA was further reaffirmed by testing CV at different sweep speeds in the mixed solution of 0.5 mM K$_3$[Fe(CN)$_6$] and 0.1 M KCl (Fig. S15). A pair of prominent redox peaks were observed in all samples’ CV curves, and the corresponding CV fitting curves are shown in Fig. 5b, which are consistent with $C_{dl}$ trends, indicating Cu$_3$P/MoP@C has a higher ECSA compared with other catalysts \cite{39}. The chronoaomperometric response was measured in O$_2$-saturated 0.1 M KOH at a rotation rate of 1600 rpm to assess stability and methanol tolerance. As depicted in Fig. 5c and d, the Cu$_3$P/MoP@C seemed to be immune and maintain a constant current density after 3 M methanol was rapidly injected into electrolyte at 200 s, whereas the Pt/C current density drops sharply. Furthermore, the current density of Cu$_3$P/MoP@C retained 98 \% of its initial value after approximately 40000 s, which was significantly higher than the commercial Pt/C (66 \%). The results indicated that Cu$_3$P/MoP@C was endowed with good durability and a subtle methanol crossover effect, attributing to the porous carbon skeleton structure and the strong synergistic effect Cu$_3$P and MoP species \cite{50}. These properties are critical to the practical application of Cu$_3$P/MoP@C electrocatalyst.

### 3.3. Test for performance of assembled Zinc-air batteries (ZAB)

Considering the outstanding ORR performance of Cu$_3$P/MoP@C, we assembled a ZAB to evaluate the application potential of Cu$_3$P/MoP@C in real energy conversion equipment. Pt/C is also tested under the same conditions as the benchmark. The schematic diagram of ZAB is presented in Fig. 6a. The open-circuit voltage (OCV) of ZAB is 1.51 V, slightly larger than Pt/C (1.48 V) (Fig. 6b). Additionally, the maximum power density of Cu$_3$P/MoP@C is 156 mW cm$^{-2}$ at 245 mA cm$^{-2}$, greatly exceeding commercial Pt/C (131 mW cm$^{-2}$ at 170 mA cm$^{-2}$) and others recently reported catalysts (Fig. 6c, f), which implied that Cu$_3$P/MoP@C has better performance. The specific-capacity was calculated based on the normalized mass of consumed Zinc. As shown in Fig. 6d,
the ZAB of based Cu3P/MoP@C yield slight higher specific capacity (704 mAh g⁻¹ ~87.8 % utilization of the theoretical capacity of 820 mAh g⁻¹) relative to commercial Pt/C (699 mAh g⁻¹, 85.2 % utilization of the theoretical capacity of 820 mAh g⁻¹) [51]. The two ZAB connected in-series can provide enough voltage to illuminate a LED (~3.0 V) (inset). Subsequently, Fig. 6e presents discharge curves at different current densities, when the current density returned to 2 mA cm⁻² with only a voltage loss rate of 0.8 %, indicating that the Cu3P/MoP@C possesses excellent rate performance [52]. Galvanostatic cycling tests showed that the Cu3P/MoP@C + RuO2-based ZAB could continuously keep working for over 231 h, and the voltage gap (ΔE) between charge and discharge is negligible. By contrast, the ZAB of based Pt/C + RuO2 is capable of operating steadily for only ~157 h with a significant ΔE (Fig. 6g), suggesting the former had a higher round-trip efficiency. Taken together, it demonstrated that Cu3P/MoP@C has excellent ORR activity and has the potential for practical application in Zn-air batteries. Based on the above experimental results, the Cu3P/MoP@C shows outstanding ORR activity and stability compared to Cu3P@C and MoP@C, indicating that the strong electronic interaction of Cu3P and MoP species reduce the charge transfer impedance and enhance ORR kinetics, which has been affirmed by XPS analysis and EIS results [53]. Apart from that, the hollow mesoporous Cu3P/MoP@C with a large specific surface area, which is beneficial to expose more active sites and provide high contact area with electrolytes to expedite electron and mass transport efficiently [54–56]. These excellent properties endow the Cu3P/MoP@C one of the most promising ORR electrocatalysts.

4. Conclusions

To summarize, we have innovatively adopted carbon spheres as a template, combined with impregnation and high-temperature pyrolysis to co-anchor Cu3P and MoP on a hollow porous carbon support. The resulting Cu3P/MoP@C exhibit outstanding ORR activity in alkaline solution compared with monometallic phosphate. XPS and BET analysis showed that high ORR activity is due to the strong synergistic effect between Cu3P and MoP and the porous structure with a large specific surface area. The aqueous ZAB was assembled with Cu3P/MoP@C as an air cathode due to its remarkable electrocatalytic performance. The ZAB achieved a high power density of 156 mW cm⁻², a specific capacity of 704 mAh g⁻¹, and a high round-trip efficiency demonstrated by the lower charge-discharge voltage gap and robust stability for over 231 h superior to the ZAB based on Pt/C + RuO2 and most currently reported advanced electrocatalysts. Our synthetic strategy of preparing bimetallic phosphate can be extended to the design and synthesis of other hollow porous electrocatalysts for sustainable energy conversion and storage devices.

CRediT authorship contribution statement


Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

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References


