ABSTRACT: The design and synthesis of MnCo2O4 anchored on P-doped hierarchical porous carbon (MCO/P-HPC) is reported. Without harsh oxidative treatment, creating anchoring sites for MnCo2O4 on the surface of carbon is realized by P-doping in carbon. The chemical coupling between P-HPC and MCO induced by P-doping provides pathways for fast charge transport. This hybrid with a hierarchical porous structure favors efficient electrolyte penetration, oxygen transport, and effective accommodation of insoluble discharge product Li2O2. When employed as an electrocatalyst in rechargeable Li−O2 batteries, the MCO/P-HPC hybrid delivers a high discharge capacity (13 150 mAh g−1 at 200 mA g−1), excellent rate capability (7028 mAh g−1 at 1000 mA g−1), and long cycle stability (200 cycles at a capacity of 1000 mAh g−1 under 200 mA g−1).

KEYWORDS: Li−O2 battery, electrocatalyst, MnCo2O4, P-doped carbon, chemical coupling
common strategies to solve this problem are to support spinel oxides onto a conductive carbon substrate. On the basis of their strongly coupled hybrid approach, Dai and co-workers prepared MnCo$_2$O$_4$/graphene hybrid, which delivered a capacity of $\sim 3784$ mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$ when used as a cathode electrocatalyst for rechargeable Li$-\text{O}_2$ batteries.$^{12}$ As is well-known, to ensure an intimate contact between metal oxide and carbon substrate, carbon is usually pretreated with harsh oxidative agents to have sufficient functional groups to coordinate the metal ions. However, excessive oxidation of carbon will inevitably destroy the sp$^2$ structure of carbon and therefore decrease the electronic conductivity of carbon. This requires the oxidation degree of carbon to be carefully controlled to balance the surface functional groups and the electronic conductivity of carbon.$^{15}$ This makes the process control of metal oxide/carbon hybrid complicated. Therefore, other method for functionalizing the surface of carbon for anchoring metal oxides needs to be explored. Recently, phosphorus (P) doping has been reported to be an effective way to improve the electronic conductivity of carbon. Moreover, P doping induces not only structural changes of carbon (like high plane edge exposure) but also charge redistribution of carbon, creating charge sites of C$^{-}\text{Li}^+$.$^{16-19}$ Therefore, it can be expected that doping of P in carbon could provide nucleation sites for metal oxides while improving the electronic conductivity of carbon.

To further boost the performance of Li$-\text{O}_2$ batteries, the morphology of electrocatalysts is considered to be important for the air electrode design. Specifically, the hierarchical porous structure not only facilitates the electrolyte immersion, electron and Li$^+$ transport but also provides an effective space for O$_2$ diffusion and O$_2$/Li$_2$O$_2$ conversion,$^{20-25}$ which are beneficial for the rate capability and cycling capability of the Li$-\text{O}_2$ batteries.

Herein, we design and construct a hybrid of MnCo$_2$O$_4$ and P-doped hierarchical porous carbon (MCO/P-HPC) for the first time. P-doped hierarchical porous carbon is first synthesized using a template method coupled with an electrostatic attraction process. Then MnCo$_2$O$_4$ is supported on the as-synthesized P-doped hierarchical porous carbon with a hydrothermal method. Without harsh oxidative treatment, creating anchoring sites for MnCo$_2$O$_4$ on the surface of carbon is realized by P-doping in carbon. Meanwhile the chemical coupling forms between MnCo$_2$O$_4$ and P-doped carbon. This MCO/P-HPC hybrid favors the transport of electron, Li$^+$ as well as O$_2^*$, and also effectively accommodates insoluble discharge product Li$_2$O$_2$ (Scheme 1). With this MCO/P-HPC hybrid catalyst, the Li$-\text{O}_2$ battery exhibits a high specific capacity, excellent rate capability and cycling performance.

### EXPERIMENTAL SECTION

**Sample Preparation. Synthesis of SiO$_2$ Templates.**

1. SiO$_2$ with a diameter of 400 nm, 14.7 mL of ultrapure water, 65 mL of alcohol, and 80 mL of NH$_3$·H$_2$O were mixed to be a transparent solution. Subsequently, 6.94 mL of tetraethyl orthosilicate (TEOS) was added into the mixture followed by continuous stirring for 4 h. Then the precipitate was collected and washed with water and alcohol for several times. The obtained white powder was dried at 60 °C for at least 24 h.

2. SiO$_2$ with a diameter of 20 nm, 139 g of ultrapure water, 10.88 g of C$_{12}$H$_{25}$O, and 0.146 g of lysine were mixed, and
11.51 mL of TEOS was added to the mixture followed by continuous stirring for 20 h at 60 °C. Then the mixture was kept static at 100 °C for another 20 h. Finally, the mixture was dried at 100 °C, and the obtained powder was annealed at 600 °C for 3 h to remove the organic component.

**Synthesis of P-Doped Hierarchical Carbon (P-HPC).** Initially, 1.2 g of C6H5PBr was added into 25 mL of ethanol to form a transparent solution. One gram of SiO2 with a diameter of 400 nm, 0.1 g of SiO2 with a diameter of 20 nm, and 5 mL of ultrapure water were added, and the mixture was stirred for 2 h. Then the mixture was dried with a slow rate at 45 °C. The obtained white powder was annealed at 800 °C for 2 h under an inert atmosphere. Then 6 M NaOH solution was used to remove SiO2 templates.

**Synthesis of MnCo2O4 Anchored on P-Doped Hierarchical Carbon Hybrid (MCO/P-HPC).** In the first step, 12.62 mg of C2H4CoO4·4H2O and 6.21 mg of C2H4MnO4·4H2O were added into 17 mL of alcohol to form a pink solution. Ten milligrams of as-obtained P-HPC, 0.5 mL of ultrapure water, and 0.5 mL of NH3·H2O were added, and the mixture was stirred for 10 h at 80 °C. Then the mixture was transferred to an autoclave and kept at 150 °C for 3 h. After washing and drying, the MCO/P-HPC catalyst was obtained.

The synthesis of free MCO is similar to that of MCO/P-HPC only without adding P-HPC.

**Electrochemical Measurements.** The MCO/P-HPC (MCO or P-HPC), conductive carbon (acetylene black), and PVDF were mixed with a mass ratio of 45:45:10. MnCo2O4, conductive carbon (acetylene black), and PVDF were mixed with a mass ratio of 45:45:10. The LiTFSI and a wall thickness of 10 nm. It retains the morphology of P-HPC hybrid due to the uniform distribution of MnCo2O4 nanoparticles on the surface of P-HPC (Figure 1b,c). In the high-resolution TEM (HRTEM, Figure 1d), the spacings between adjacent fringes are 0.48 and 0.29 nm, which are in conformity with the (111) and (220) lattice spacings of spinel MnCo2O4, respectively. The elemental mapping images of C, P, Co, Mn, and O are shown in Figure 1e, indicating the uniformly doping of P in carbon and uniformly distribution of Co, Mn, and O on the surface of P-HPC. The P content in P-HPC is calculated to be about 8.3 nm by the Scherrer formula.
experiments, as shown in Figure S4b. A type-IV isotherm clearly demonstrates the presence of mesopores. From the pore size distribution, mesopores with a diameter of 5.6–12 nm and 20–40 nm can be clearly observed, which come from the templating of silica colloid (~20 nm in diameter) and the voids between macropores, respectively. The MCO/P-HPC possesses a surface area of 134.8 m² g⁻¹ and a total pore volume of 0.31 cm³ g⁻¹. The macropores could store discharge products, and the mesopores are favorable for electrolyte penetration into the electrode and O₂ transport. This hierarchical macromesoporous structure also promotes the diffusion of Li⁺, and the P-doped carbon network itself facilitates the transport of electron, providing an efficient triple-phase region for ORR and OER during discharge and charge process.

In order to obtain the cation oxidation state and the surface chemical composition of the MCO/P-HPC hybrid, X-ray photoelectron spectroscopy (XPS) measurements were conducted. In the high-resolution spectra of Mn 2p in MCO (Figure 2a), the asymmetric peaks of Mn 2p3/2 and Mn 2p1/2 can be fitted to two peaks, respectively. The two fitted peaks at 641.9 and 653.2 eV are ascribed to Mn²⁺, and another two fitted two peaks at 643.3 and 654.7 eV are ascribed to Mn³⁺. A positive shift of 0.4 and 0.6 eV toward a high binding energy exists in the peak of Mn 2p3/2 and Mn 2p1/2, respectively, for MCO/P-HPC, as compared to MCO (Figure 2a). A positive peak shift can also be observed for the peak of Co 2p (Figure 2b). The positive shifts in Mn 2p and Co 2p indicate the electron transfer from Mn and Co atoms to the neighbor atom in the hybrid.

In the XPS spectra of P 2p in P-HPC, two deconvolved contributions at 133.9 and 132.5 eV refer to surface oxidized P species (i.e., P=P=O bonding) and P−C bonding (Figure 2c). The results along with the XPS spectra of C 1s (Figure S5) reveal that P atom has been incorporated into the carbon lattice.

Remarkably, a positive shift of about 0.7 eV in the binding energy of P 2p in MCO/P-HPC with respect to P-HPC is observed, which most likely results from the chemical coupling between metal atom and oxidized phosphorus, such as the M−O=P (M=Mn, Co) bond. Note that the surface amount of P in P-HPC is 1.96 at. % as calculated from the XPS data by measuring the ratio of C 1s to P 2p intensities (integrated peak area) normalized by their respective sensitivity factors. It is very close to the bulk content obtained from the EDX (2.01 at. %) and ICP-AES (2.13 at. %). The shift of the binding energy in Co 2p, Mn 2p as well as P 2p reveals the covalent coupling between MCO and P-HPC in MCO/P-HPC. This covalent...
bonding provides pathways for charge transport through the interface and thus promotes the electrochemical catalytic activity. Furthermore, P-doping induces charge redistribution in the carbon atom and structure defects, which are favorable for O₂ adsorption and facilitate the ORR process. 26, 31, 32

The above results indicate that P-doping in carbon is an effective way for the modification of carbon to be favorable for anchoring metal oxides on carbon. This process does not involve pretreatment with harsh oxidation and thus avoid the possible conductivity decreasing or the architecture of carbon support destroying. 24 Moreover, it is worth noting that optimized P-doping in carbon can increase the electrical conductivity of carbon based on our previous study. 17 When P is doped in carbon, P is positively charged, and C is negatively charged due to the smaller electronegativity of P than C. Meanwhile, the P bonded to C is partially oxidized, as confirmed by the high resolution P 2p spectrum (Figure 2c). The O atom bonded to P is also negatively charged. 33 Therefore, positively charged metal ions, such as Co²⁺ and Mn²⁺, are facile to be absorbed on the surface of carbon due to the electrostatic interaction during the hydrothermal process (Scheme 1).

**Electrochemical Performance of MCO/P-HPC.** The electrocatalytic activity of MCO/P-HPC air electrode was evaluated in a Li−O₂ cell. MCO and P-HPC were also tested for comparison in which 1 M LiTFSI/TEGDME was used as the electrolyte. The current density and specific capacity are normalized to the total mass of catalyst (MCO/P-HPC, P-HPC, MCO), binder, and carbon black (acetylene black). The weight of carbon paper is not considered in the calculation of the discharge/charge capacity because the capacity of the same Torray carbon paper alone has been reported to be very limited (90 mAh g⁻¹ at most) by other researchers. 34, 25 Therefore, the contribution of the carbon paper is negligible. The discharge and charge measurements were performed in the voltage between 2.2 and 4.4 V. Figure 3a shows the discharge curves of MCO/P-HPC catalysts at different current densities. At a current density of 200 mA g⁻¹, the discharge capacity is about 13150 mAh g⁻¹. With increasing current density, the discharge capacity decreases. But even at a high current density of 1000 mA g⁻¹, the discharge capacity is still about 7028 mAh g⁻¹, suggesting excellent rate capability of MCO/P-HPC catalysts.

As shown in Figure 3b, the MCO/P-HPC hybrid catalysts exhibit excellent cycling stability with a cutoff capacity of 1000 mAh g⁻¹ at a current density of 200 mA g⁻¹. In the first cycle, the discharge platform is about 2.75 V, and charge platform is lower than 4.00 V. Note that the charge profiles of MCO/P-HPC exhibit two apparent plateaus, which is similar to previous reports. 34, 35−37 The lower charge plateau corresponds to the surface delithiation of Li₂O₂ or surface nonstoichiometric Li₁₋ₓO₂, while the higher charge plateau corresponds to the bulk oxidation of Li₂O₂. 35 With increasing cycling numbers, no severe deterioration can be seen. Even in the 200th cycle, the discharge platform is still higher than 2.60 V, and the charge platform is lower than 4.40 V. The cycling performance of MCO/P-HPC catalysts is superior to that of MCO, P-HPC, and acetylene black (Figure S6), respectively. As shown in Figure S6, in the 70th cycle, the discharge platform of MCO, P-HPC, and acetylene black are 2.52, 2.63, and 2.45 V, respectively, and the charge platform of MCO, P-HPC, and acetylene black are 4.76, 4.70, and 4.87 V, respectively. Note that the Li−O₂ batteries with MCO/P-HPC catalysts show excellent cyclability over 200 cycles, much longer than the MCO-based cathodes reported early. 12, 26 The MCO/P-HPC...
The cathode was also tested by full charge/discharge between 2.2 and 4.4 V, as shown in Figure 3c. The initial discharge capacity reaches about 13 150 mA g⁻¹ and it is still about 9 803 mA g⁻¹ in the fourth cycle. When the mass of discharge products Li₂O₂ is included, the initial discharge capacity is about 10 700 mA g⁻¹, which is close to the theoretical capacity of Li-O₂ battery (11 655 mA h g⁻¹). Meanwhile, the Coulombic efficiency of the MCO/P-HPC cathode is almost 100% at the first four cycles (Figure S7).

The comparison between the charge/discharge capacity of MCO/P-HPC with that of MCO, P-HPC, and acetylene black (Figure 3d) clearly shows that the capacity of the former is much higher than that of MCO and P-HPC as well as that of acetylene black. Note that P-doped carbon delivers higher discharge capacity (4 626 mA h g⁻¹) and charge capacity (4 259 mA h g⁻¹) than acetylene black (Figure 3d), which is similar to the effect of S-doping in increasing the discharge (4 300 mA h g⁻¹) and charge capacity (4 100 mA h g⁻¹) of carbon reported elsewhere (38, 39). It is worth mentioning that the discharge platform of MCO (2.65 V) has been increased by 50 mV, and the charge platform (4.24 V) has been decreased by 120 mV after coupling with P-HPC. This indicates that the MCO/P-HPC hybrid efficiently decreases the overpotential of both ORR and OER and offers high catalytic activity toward these two reactions.

The high capacity, enhanced rate capability, and excellent cycling stability with low overpotential of MCO/P-HPC could be attributed to superior ORR and OER catalytic activity of strongly coupled MCO/P-HPC and the hierarchical porous structure of the MCO/P-HPC electrode, which can conserve Li₂O₂ in its macropores and transfer electrolyte, oxygen, and Li ions through its mesopores. In addition, P-HPC can provide an efficient electron conductive network. The results suggest that engineering the chemical coupling between metal oxides and carbon via P-doping is an efficient way for enhancing the activity of metal oxide electrocatalysts.

To gain insight into the discharge and charge process of MCO/P-HPC catalysts, the XRD patterns of the MCO/P-HPC cathodes discharged to 2.2 V and charged to 4.4 V were analyzed as shown in Figure 4. It can be seen from Figure 4 that the diffraction pattern of the electrode discharged to 2.2 V show that the discharged product is Li₂O₂. After it is charged to 4.4 V, the disappearance of the Li₂O₂ pattern provides the evidence of complete decomposition of discharged product Li₂O₂ (i.e., successful charging). The formation of Li₂CO₃ after discharge might result from the side reaction between Li₂O₂ and the MCO/P-HPC catalyst, the decomposition of electrolyte, or the direct reaction between oxygen anion radicals and cathode catalyst, which requires further study in the future. The accumulation of Li₂CO₃ will lead eventually to the failure of the Li–O₂ battery. The morphology of the MCO/P-HPC cathodes at different charge/discharge stages of Li–O₂ batteries was monitored by SEM image as shown in Figure 5.
of hierarchical porous structure of this hybrid toward both ORR and OER during the discharge and charge process.

### CONCLUSIONS

In conclusion, we successfully synthesized MCO/P-HPC hybrid by growing MnCo2O4 on P-doped hierarchical porous carbon. P-doping in carbon offers an efficient strategy for anchoring metal oxides on carbon. When employed as an electrocatalyst in rechargeable Li–O2 batteries, the MCO/P-HPC hybrid delivers a high discharge capacity of 13 150 mAh g−1 at a current density of 200 mA g−1 with low overpotentials under 200 mA g−1. The enhanced performance of Li–O2 batteries is attributed to the chemical and electrical coupling between MnCo2O4 and P-doped carbon as well as the hierarchical macroporous-structure of the MCO/P-HPC electrode. Engineering the chemical and electrical coupling between MnCo2O4 and carbon via P-doping is an effective way for enhancing the electrocatalytic activity of MnCo2O4. This work provides an alternative approach for the design of cathode electrocatalysts used in rechargeable Li–O2 batteries.

### ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00494.

SEM and TEM images of P-HPC, EDX spectrum of MCO/P-HPC, TGA of MCO/P-HPC, XRD pattern, BET surface area and pore size distribution of MCO/P-HPC, high-resolution C 1s spectra of MCO/P-HPC and P-HPC, Coulombic efficiency of MCO/P-HPC for the first four cycles (PDF)

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Notes

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