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Interfacing Manganese Oxide and Cobalt in Porous Graphitic Carbon

Polyhedrons Boosts Oxygen Electrocatalysis for Zn-air Batteries

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Abstract

Rational design and synthesis of highly active and robust bifunctional non-noble electrocatalysts for both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are urgently required for efficient rechargeable metal-air batteries. Herein, abundant MnO/Co heterointerfaces are engineered in porous graphitic carbon (MnO/Co/PGC) polyhedrons via a facial hydrothermal-calcination route with a bimetal-organic framework as the precursor. The in situ generated Co nanocrystals not only create well-defined heterointerfaces with high conductivity to overcome the poor OER activity but also promote the formation of robust graphitic carbon. Owing to the desired composition and formation of heterostructure, the resulting MnO/Co/PGC exhibits superior activity and stability towards both OER and ORR, which makes it an efficient air cathode for the rechargeable Zn-air battery. Importantly, the homemade Zn-air battery is able to deliver excellent performance including a peak power density of 172 mW cm^{-2} and a specific capacity of 872 mAh g^{-1} , as well as excellent cycling stability (350 cycles), outperforming the mixed commercial Pt/C||RuO₂ catalysts. This work highlights the synergy from heterointerfaces in oxygen electrocatalysis, thus providing a promising approach for advanced metal-air cathode materials.

Keywords: MnO/Co heterointerface; graphitic carbon; synergetic effect; bifunctional electrocatalyst; Zn-air batteries

Urgent demands on green and sustainable energy have promoted intensive investigations on highly efficient and environment-friendly energy storage or conversion technologies, such as fuel cells, water electrolyzers and metal-air batteries.^[1,2] Among various energy storage and conversion technologies, rechargeable zinc-air batteries (ZABs) have attracted increasing attentions because of their high theoretical energy density, low cost, environmental friendliness and high safety.^[3-5] ZABs are driven by the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) during discharging and charging processes respectively. However, the sluggish kinetics for ORR and OER at the air cathode greatly impedes their commercial application.^[4,6] Therefore, Pt, Ru and Ir-based noble metal materials have been widely used. Unfortunately, the reserve scarcity, high cost, mono-function, and poor durability of these noble-metal catalysts hinder their large-scale practical application.^[7,8] Therefore, rational design and synthesis of highly efficient bifunctional non-noble metal based electrocatalysts towards ORR and OER is still of great significance for development of these renewable energy technologies.

Transition-metal compounds (TMCs) represent a class of potential alternative due to their low price, abundant resources, and environmental friendliness.^[7,9] In particular, manganese oxide (MnO_x) has drawn considerable interest for oxygen electrocatalysis due to its multiple 3d electron configurations and various morphologies and phases.^[10-12] Intensive research has demonstrated that MnO_x can effectively assist the charge transfer to adsorb oxygen on the surface of catalysts, facilitating the HO_2^- decomposition.^[13,14] However, its poor durability and low electrical conductivity prohibit its wide application in oxygen electrocatalysis, especially OER.^[15,16] It is worth noting that Co-based hybrids can greatly improve the OER performance of materials due to their moderate catalytic activity and good resistance under alkaline solution.^[17-19] Furthermore, recent studies show that hybrid electrocatalysts composed of metal/metal oxide heterointerfaces and carbonaceous materials exhibit enhanced catalytic activity and stability owing to fast interfacial electron transfer and the synergistic effect originated from the chemical coupling between metal/metal oxide and

carbon support.^[20-23] However, most of these metal/metal oxide systems are based on the same metal elements or randomly dispersed on the surface of carbon via a complicated and time-consuming process. Therefore, construction of well-defined heterointerfaces in complex compositions and structures is very challenging but desirable to prepare highly efficient bifunctional electrocatalysts.

Recently, pyrolysis of metal-organic frameworks (MOFs) provides us a simple and effective strategy to prepare nanoparticle catalysts with controllable size and uniform distribution in carbon support.^[24-26] The unique features of high porosity and multiple metallic species in MOFs offer more opportunities to fabricate well-defined nanoparticles with complex compositions within porous carbon matrix.^[27] With above considerations, herein a bimetal-organic framework containing cobalt and manganese (named Co/Mn-MIL-100) was first prepared via a hydrothermal method. Due to the huge difference of reduction potential of these two metals, the calcined product composed of MnO/Co hybrid with porous graphitic carbon (MnO/Co/PGC) polyhedrons possess abundant desired MnO/Co heterointerfaces instead of conventional bimetal oxides.^[28] The in situ generated Co nanocrystals not only create well-defined heterointerfaces with high conductivity to overcome the poor OER activity but also promote the formation of robust graphitic carbon. Benefiting from the advantages of structure and composition, including heterointerface and porous graphite carbon, the as-prepared MnO/Co/PGC exhibits excellent bifunctional oxygen electrocatalytic performance with a small overpotential gap, rapid kinetics with reduced Tafel slopes, and long-term durability. Consequently, an aqueous rechargeable Zn-air battery using the MnO/Co/PGC cathode affords a higher power density (172 mW cm^{-2}) and specific capacity (872 mAh g^{-1}), as well as excellent cycling stability (350 cycles) over the noble-metal-based cathode.

We first synthesized unique Mn-MIL-100 and Co/Mn-MIL-100 (MIL stands for Material from Institut Lavoisier) octahedrons as precursors via a solvothermal method (see Supporting Information for details). The field-emission scanning electron microscopy (FESEM) images show that these MIL octahedrons are uniform with an average size of about 730 nm for Mn-MIL-100 (**Figure 1a**; Figure

S1a,c, Supporting Information) and 780 nm for Co/Mn-MIL-100 (Figure 1c; Figure S1b,d, Supporting Information). The transmission electron microscopy (TEM) images verify that these octahedrons are well-defined solid with a smooth surface (Figure 1b,d). X-ray diffraction (XRD) patterns (Figure S1e, Supporting Information) and Fourier-transform infrared (FTIR) spectra (Figure S1f, Supporting Information) demonstrate that these MILs share the same crystal structure and constituent units, which are in good accordance with the previous report.^[29,30] The unique morphology and crystalline nature of the structure make them suitable for obtaining desired electrocatalysts possessing abundant active sites and robust structure.

We then employed these MILs octahedrons as precursors to obtain desired electrocatalysts towards OER and ORR. Based on the thermogravimetric analysis (TGA) curves (Figure S2, Supporting Information), we use 800 °C as the target temperature to make sure the complete decomposition of these MILs and obtain stable catalysts with high crystallinity. Particularly, the lower decomposition temperature and residual mass for Co/Mn-MIL-100 than those for Mn-MIL-100 suggest the higher graphitization degree and more oxygen vacancies in derived MnO/Co/PGC due to the high catalytic ability of metallic cobalt. As shown in Figure 1e,g, the carbonization products retain the polyhedral shape of their precursors with a smaller diameter (Figure S3, Supporting Information) and rough surface due to the decomposition of organic chains and formation of metal/metal oxide nanoparticles during calcination. As revealed by TEM images (Figure 1f; Figure S4a, Supporting Information), the as-synthesized MnO nanoparticles are uniformly embedded in porous amorphous carbon polyhedrons (MnO/PAC). The high-resolution TEM (HRTEM) image (Figure S4b, Supporting Information) shows the presence of ultrafine nanoparticles with ~ 5 nm in size. The clear lattice fringe with an inter-planar spacing of 0.22 nm is assigned to the (200) plane of MnO (Figure S4c,d, Supporting Information).^[23] Compared with MnO/PAC, the surface of MnO/Co/PGC is much rougher (Figure 1g). TEM and HRTEM images (Figure 1h-j) show the closely packed metal oxide and metal nanoparticles and characteristic graphitic carbon layer, resulting in abundant robust

heterointerfaces. The joint lattice fringes as marked in Figure 1j show the heterointerfaces, which may provide the synergetic effect for the enhanced electrochemical performance. The clear interplanar spacing of 0.18 nm and 0.22 nm can be readily assigned to the (200) plane of Co and MnO, respectively (Figure 1k-n). Elemental mapping images show the homogenous distribution of C, O, Mn and Co elements in MnO/Co/PGC (Figure 1o). The mapping image of Co element shows the obvious graininess and its larger color area suggests some MnO/Co core-shell structures, further implying the formation of heterointerfaces. As comparison, we also prepared Co nanoparticles embedded in porous graphitic carbon (Co/PGC) polyhedrons (Figure S5, Supporting Information) by dissolving MnO in MnO/PAC combined with a reduction of Co^{2+} and calcination process (see Supporting Information for details).

XRD analysis (**Figure 2a**) indicates that the primary crystalline phases are MnO (JCPDS No. 07-0230) and Co (JCPDS No. 15-0806) in the derivative from Mn/Co-MIL-100, while only MnO in the derivative from Mn-MIL-100. Only Co nanoparticles exist in the comparative sample Co/PGC, suggesting the complete dissolution of MnO. More information about carbon species in the resultant samples is provided by Raman spectra (Figure 2b). The higher intensity ratio of peak G to peak D indicates that more sp^2 -hybridized graphitic carbon atoms are present in MnO/Co/PGC and Co/PGC, which may be beneficial for accelerating the charge transfer rate and stabilizing the metal oxide/metal heterointerfaces.^[31,32] The peak at 650 cm^{-1} is attributed to the Co-Co stretching mode.^[33,34] The TGA curves under air atmosphere show that MnO/Co/PGC has enhanced thermal stability and a slower weight loss rate, indicating better antioxidant capacity of PGC and the presence of metallic cobalt (Figure S6, Supporting Information). The energy-dispersive X-ray spectroscopy (EDX) results (Figure 2c) also confirm the purity of the resultant samples, specially the existence of only C, O, Mn and Co elements in MnO/Co/PGC is consistent with the result of elemental mapping. Nitrogen sorption curves (Figure S7, Supporting Information) reveal that all the derivatives possess high specific surface area with a value of $126\text{ m}^2\text{ g}^{-1}$ for MnO/PAC, $127\text{ m}^2\text{ g}^{-1}$ for MnO/Co/PGC, and 228

$\text{m}^2 \text{g}^{-1}$ for Co/PGC. X-ray photoelectron spectroscopy (XPS) study was carried out to further analyse and compare the surface chemical state of the three samples. The survey spectra (Figure S8a, Supporting Information) also show the purity of the three samples. In the high-resolution XPS spectra of Mn 2p (Figure 2d), compared with the peak for MnO/PAC at 641.45 eV assigned to Mn (II) $2p_{3/2}$, the negative shift of binding energy for MnO/Co/PGC implies the strong interaction between MnO and Co.^[15,19,35] Additionally, the multiplet splitting energy for Mn 3s is reported to increase linearly as the valence of Mn element decreases.^[35,36] The increase multiplet splitting energy furtherly confirms the transfer of electron from O to Mn, resulting in a lower valence of Mn in MnO/Co/PGC (Figure S8b, Supporting Information). Compared to the Co 2p for Co/PGC, the half width of MnO/Co/PGC is obviously wider, suggesting the existence of other valences. The fitting data of Co 2p in Figure 2e show that except for a pair of peaks assigned to metallic Co at 780.07 eV for $2p_{3/2}$ and 796.03 eV for $2p_{1/2}$, there is another pair of peaks at higher binding energy assigned to Co-O-Mn.^[19,37,38] This obvious shift of binding energy for Mn 2p, Mn 3s and Co 2p confirms the strong electronic interactions induced by MnO/Co heterointerfaces, which may facilitate the adsorption/desorption of intermediate products during oxygen electrolysis process. The O 1s XPS spectra (Figure 2f) can be simulated by the combination of three features at 529.92, 531.59 and 533.27 eV, ascribed to oxygen species of metal-oxygen, oxygen vacancy and surface adsorbed oxygen, respectively.^[39,40] The plentiful oxygen vacancies induced by non-stoichiometric oxygen generated by high-temperature calcination in Ar/H₂ can well tune the electronic structure and surface properties, thereby inducing more active sites for catalytic reactions.^[41,42]

To investigate the interface effect for oxygen electrolysis, the OER performance of the three samples together with commercial RuO₂ as comparison is first evaluated in an alkaline solution (1.0 M KOH) by a standard three-electrode system. **Figure 3a** shows the linear sweep voltammetry (LSV) curves with *iR*-compensation of RuO₂, MnO/PAC, Co/PGC and MnO/Co/PGC. To reach a current density of 10 mA cm^{-2} , which is a common criterion to evaluate OER activity, MnO/Co/PGC needs

a potential (E_{j10}) of only 1.537 mV, which is 47 and 114 mV lower potentials required for Co/PGC and MnO/PAC. The corresponding overpotential is only 307 mV, which is also smaller than those of many other Mn-based OER electrocatalysts (Table S1, Supporting Information) and even comparable with the commercial RuO₂ (301 mV), proving the superior OER performance of MnO/Co/PGC. The excellent OER catalytic activity is further evidenced by the analysis of Tafel slopes (Figure 3b). The Co/PGC possesses the lowest Tafel slope of 63 mV dec⁻¹. After the introduction of Co nanoparticles, the MnO/Co/PGC exhibits a lower Tafel slope (77 mV dec⁻¹) than that of the MnO/PAC (99 mV dec⁻¹), implying the favourable OER kinetics of MnO/Co/PGC. The promotional effect of Co on OER can also be seen from its rapid rising current density in the LSV curve at high potentials. The lower Tafel slope of MnO/Co/PGC than that of MnO/PAC indicates the interfacial electron transfer for water oxidation on the heterointerfaces, which is evidenced by the electrochemical impedance spectroscopy (EIS) results in Figure 3c. The smallest diameter of the semicircle for Co/PGC in the Nyquist plot indicates the high conductivity of metal cobalt, leading to the lower charge-transfer resistance in MnO/Co/PGC than that in MnO/PAC and RuO₂. The Nyquist plots were fitted with an equivalent circuit (Figure S10, Supporting Information). The electrochemically active surface area (ECSA) is further evaluated through the electrochemical double-layer capacitance measured by cyclic voltammetry (CV) curves (Figure S11, Supporting Information).^[43,44] The highest value of MnO/Co/PGC (35.7 mF cm⁻²) indicates that more active sites can be exposed in MnO/Co/PGC, in line with the more excellent OER performance. Chronopotentiometric response measurement (Figure 3e) shows that the MnO/PAC, Co/PGC and MnO/Co/PGC stably run over 12 h at a current density of 10 mA cm⁻² without obvious amplification in potential, while there is a big amplification in potential for RuO₂, demonstrating the important role of carbon for stability. Stability testing at a high current density of 50 mA cm⁻² and the corresponding FESEM images after stability test (Figure S12, Supporting Information) further show the advantage of graphitic carbon to amorphous carbon, which may be due to the better oxidation and corrosion resistance of graphitic carbon.^[45]

Aside from the fascinating OER performance, the synthesized MnO/Co/PGC also affords satisfactory ORR performance, as shown in **Figure 4**. Figure 4a shows the LSV curves at 1600 revolutions per minute (rpm) of commercial 20 wt% Pt/C, MnO/PAC, Co/PGC and MnO/Co/PGC in O₂-saturated 0.1 M KOH solution. The higher onset potential (0.95 V versus reversible hydrogen electrode (vs RHE)), half-wave potential ($E_{1/2}$, 0.78 V vs RHE), and larger limited current density (6.0 mA cm⁻²) in comparison with those of MnO/PAC and Co/PGC suggests that heterointerface of MnO/Co can significantly enhance the ORR performance. Moreover, the Tafel slope of MnO/Co/PGC (69 mV dec⁻¹) in Figure 4b derived from the LSV curves and Koutecky-Levich plots (K-L plots) in Figure 4c based on the polarization curves at different rotation speeds (Figure S13, Supporting Information) further highlights the favorable ORR kinetics with a direct four-electron transfer. The excellent ORR performance of MnO/Co/PGC is comparable to the benchmarking commercial Pt/C and even rivals with many other Mn-based oxides reported so far (Table S2, Supporting Information). The excellent ORR activity of MnO/Co/PGC mainly originates from the PGC-supported MnO species since the Co/PGC alone shows a relatively poor activity towards ORR. However, to some extent, the addition of Co can reduce the resistance of MnO/Co/PGC due to its high electrical conductivity, thus facilitating the electron transfer, as already verified by the EIS spectra (Figure 3c). Regarding the superior ORR performance, the overall polarization curve towards ORR and OER was recorded within a potential range of 0.3-2.0 V vs RHE in O₂-saturated 0.1 M KOH (Figure 4d). The catalyst hybrid of commercial Pt/C and RuO₂ with a mass ratio of 1/1 (Pt/C||RuO₂) was also measured as comparison. As known, the smaller value of ΔE ($\Delta E = E_{j10} - E_{1/2}$) reflects the better bifunctional oxygen electrocatalysis performance.^[3,4] Clearly, the MnO/Co/PGC exhibits the significantly smallest value of only 0.82 V among the synthesized catalysts (Inset in Figure 4d), which is comparable to the value of Pt/C||RuO₂ (0.72 V) and recently reported advanced bifunctional electrocatalysts (Table S3, Supporting Information). The stability towards ORR is also evaluated by the chronoamperometry curves at 0.68 V vs RHE in O₂-saturated 0.1 M KOH solution

(Figure 4e). Remarkably, the MnO/PGC and MnO/Co/PGC maintain 83% and 89% of their initial current density after 20000 s, while a large current loss is observed for Co/PGC (27%) and Pt/C (31%) catalysts. The better stability of MnO/PAC and MnO/Co/PGC may be due to the robust chemical and mechanical stability of metal/metal oxide nanoparticles in situ derived from MOFs, which have better resistance to aggregation and dissolution during the stability test.^[46-48]

The outstanding bifunctional OER/ORR properties of MnO/Co/PGC inspire us to evaluate its application in practical ZABs. A homemade aqueous rechargeable Zn-air battery was assembled, which consists of carbon fiber paper-supported MnO/Co/PGC as the air cathode, Zn plate as the anode, and 6.0 M KOH + 0.2 M Zn(CH₃COO)₂·2H₂O as the electrolyte (**Figure 5a**; Figure S14, S15, Supporting Information). As can be seen in Figure 5b, the ZAB driven by MnO/Co/PGC exhibits a stable open-circuit voltage (OCV) of 1.52 V, higher than that of ZAB driven by Pt/C||RuO₂ (1.42 V). A light emitting diode (LED) screen can be powered by two ZABs connected in series (Inset in Figure 5b), manifesting its promising application in energy storage. Figure 5c depicts the discharge polarization curves and the corresponding power density curves. The ZAB driven by MnO/Co/PGC exhibits a peak power density of 172 mW cm⁻², exceeding that of the ZABs driven by Pt/C||RuO₂ (150 mW cm⁻²) and many other reported bifunctional electrocatalysts (Table S4, Supporting Information). The specific capacity reaches up to 873 mAh g_{Zn}⁻¹ at a current density of 5 mA cm⁻² on the basis of consumed Zn weight (Figure 5d), corresponding to an energy density of 1056 Wh kg_{Zn}⁻¹, which surpasses those of Pt/C||RuO₂ (768 mAh g_{Zn}⁻¹; 899 Wh kg_{Zn}⁻¹) and preciously reported state-of-art air cathodes (Table S5, Supporting Information). Moreover, the MnO/Co/PGC-based battery demonstrates superior cycle stability compared to that of Pt/C||RuO₂ catalyst (Figure 5e,f; Figure S16, Supporting Information). For Pt/C||RuO₂-based battery, the energy efficiency (discharge end voltage divided by charge end voltage) decreases from 63% at the first cycle to 47% at the seventy-fourth cycle (Figure 5e). Comparatively, the MnO/Co/PGC-based battery has a much better cycle life with a stable energy efficiency (59%) even after 350 cycles (Figure 5f). After the

charge/discharge cycles, the overall morphology and composition of the MnO/Co/PGC cathode material were well preserved (Figure S17, Supporting Information). These results verify the excellent activity and stability of MnO/Co/PGC as the air-cathode in aqueous rechargeable ZABs, which can be applied in practical applications.

In summary, we demonstrate that purposely interfacing MnO and Co in porous graphitic carbon (MnO/Co/PGC) can be obtained by one-step pyrolysis of bimetal-organic frameworks. Interface engineering of highly active MnO for ORR and Co for OER endows the sample with superior bifunctional electrocatalytic performance towards both OER and ORR, comparing with the state-of-the-art RuO₂ or Pt/C catalysts. The homogeneous dispersion of MnO/Co heterointerfaces within the porous graphitic carbon polyhedrons provides additional strong catalyst-support interaction to further enhance the catalytic activity and stability. Moreover, the MnO/Co/PGC-driven Zn-air batteries can be stably charged and discharged over 350 cycles with high energy efficiency, outperforming the more costly Pt/C||RuO₂-driven Zn-air batteries. This work provides a simple but effective approach for preparing durable, cost-effective and vastly active bifunctional electrocatalysts and demonstrates their practical application prospects in the field of electrochemical energy storage and conversion.

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Figures and captions

Figure 1. FESEM (a,c,e,g) and TEM (b,d,f,h) images of (a,b) Mn-MIL-100, (c,d) Co/Mn-MIL-100, (e,f) MnO/PAC, and (g,h) MnO/Co/PGC; (i,j) HRTEM images of MnO/Co/PGC; (k,l) The inverse fast Fourier transformation (IFFT) images, and (m,n) the corresponding line scan of the pink (k,m) and blue (l,n) dotted squares region in figure j; (o) Elemental mapping of MnO/Co/PGC.

Figure 2. (a) XRD patterns, (b) Raman spectra, and (c) EDX spectra of MnO/PAC, MnO/Co/PGC and Co/PGC; High-resolution XPS spectra of (d) Mn 2p for MnO/PAC and MnO/Co/PGC, (e) Co 2p for MnO/Co/PGC and Co/PGC, (f) O 1s for MnO/PAC, MnO/Co/PGC and Co/PGC.

Figure 3. Comparison of OER performance in 1.0 M KOH for RuO₂, MnO/PAC, Co/PGC and MnO/Co/PGC: (a) LSV curves, (b) Tafel slopes, (c) EIS spectra, (d) half of the capacitive current density difference at 0.92 V as a function of scan rate, and (e) chronopotentiometry curves at a constant current density of 10 mA cm⁻².

Figure 4. Comparison of ORR performance in O₂-saturated 0.1 M KOH for Pt/C, MnO/PAC, Co/PGC and MnO/Co/PGC: (a) LSV curves, (b) Tafel slopes, (c) Koutecky-Levich plots at 0.4 V, (d) the overall polarization curves within the ORR and OER potential window, inset shows the values of ΔE ($\Delta E = E_{j10} - E_{1/2}$), and (e) chronoamperometric responses at a constant potential of 0.68 V.

Figure 5. (a) A schematic configuration of the Zn-air battery; Comparison of performance for Zn-air batteries driven by Pt/C||RuO₂ and MnO/Co/PGC: (b) open-circuit plots (Inset is the photograph of a blue LED screen powered by two home-made Zn-air batteries in series with MnO/Co/PGC as the air-cathode), (c) discharge polarization and power density curves, (d) discharge curves of Zn-air batteries at 5 mA cm⁻², and long-term cycling performance at a current density of 10 mA cm⁻² with (e) Pt/C||RuO₂ and (f) MnO/Co/PGC as the air cathode.

for Table of Content Entry

Interface engineering of MnO and Co in porous graphitic carbon (MnO/Co/PGC) polyhedrons is realized by a one-step pyrolysis of bimetal-organic frameworks. Owing to the desired active heterointerfaces and robust graphitic carbon, the as-prepared MnO/Co/PGC exhibits extraordinary activity and stability towards both OER and ORR, making it a promising alternative to precious metal as the air cathode for highly efficient metal-air batteries.