Hierarchical Porous Double-Shelled Electrocatalyst with Tailored Lattice Alkalinity toward Bifunctional Oxygen Reactions for Metal–Air Batteries

Ya-Ping Deng,† Yi Jiang,† Dan Luo,† Jing Fu,† Ruilin Liang,† Shaobo Cheng,‡ Zhengyu Bai,*§ Yangshuai Liu,† Wen Lei,† Lin Yang,§ Jing Zhu,‡ and Zhongwei Chen*†

†Department of Chemical Engineering, Waterloo Institute for Nanotechnology, Waterloo Institute for Sustainable Energy, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
‡Beijing National Center for Electron Microscopy, School of Materials Science and Engineering, The State Key Laboratory of New Ceramics and Fine Processing, Laboratory of Advanced Materials (MOE), Tsinghua University, Beijing 100084, China
§School of Chemistry and Chemical Engineering, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, Collaborative Innovation Center of Henan Province for Fine Chemicals Green Manufacturing, Henan Normal University, Xinxiang 453007, China

*Supporting Information

ABSTRACT: Increasing both catalytic site accessibility and intrinsic activity of multishelled materials is critical to boost its efficiency for bifunctional oxygen electrocatalysis and initiate its application in metal–air batteries. Herein, a hierarchical porous double-shelled (Mg,Co)₃O₄ electrocatalyst with controllable Mg substitution is synthesized via a proposed in situ coordinating process. The hierarchical porosity optimizes the availability of active sites and broadens diffusion channels for oxygen species. Meanwhile, Mg substitution greatly increases electrical conductivity and realizes novel insight of tailoring lattice alkalinity. Specifically, Mg substitution positively influences oxygen electrocatalysis by inducing lattice buffer zones that promote hydroxyl detachment from nearby catalytic sites. As a result, the final hybrid of (Mg,Co)₃O₄ encapsulated in N-doped graphitized carbon affords superior bifunctional oxygen electrocatalytic activities, outperforming state-of-the-art noble-metal benchmarks. When serving as an air electrode in Zn–air batteries, a low charge–discharge gap and long-term cyclability for over 200 h are realized in ambient air.

Rechargeable metal–air batteries have received a considerable amount of research efforts recently as Li-ion batteries based on intercalation chemistry struggle to meet the increasing energy density demands of electric vehicles and other devices. Nevertheless, their practical applications are still hindered by sluggish oxygen electrocatalytic kinetics and poor rechargeability. Therefore, a highly efficient and durable bifunctional oxygen electrocatalyst is vital for advanced rechargeable metal–air batteries.

Oxygen-involved heterogeneous electrocatalysis, including oxygen reduction (ORR) and evolution (OER) reactions, is the core of rechargeable metal–air batteries, which require fast kinetics of both reactions to achieve high efficiency and cyclability. Although noble-metal catalysts, i.e., Pt, Ir, and Ru, have been considered as benchmarks for respective ORR and OER, their widespread application is prohibited by low reserves and high cost. More importantly, precious catalysts with a single element cannot provide ideal ORR and OER activities simultaneously. Lately, hybrid catalysts of spinel oxides composited with carbon-based materials have drawn intensive attention as alternative air electrodes for metal–air batteries. Among the hybrids, the spinel oxides, especially cobalt-based oxides, are explored to be decent OER electrocatalysts, despite their inefficient ORR activities. On the other hand, excellent ORR activities have been achieved on carbon materials via heteroatom doping, such as N, S, P, etc.

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components, hybrid catalysts with reasonable bifunctionality and durability have been demonstrated. 4,15,20

Morphological tuning on electrocatalysts to expand porosity and active site availability is the most effective strategy to optimize oxygen electrocatalysis. In recent decades, multishelled microstructured metal oxides with a unique hollow architecture and large surface area have been developed for different applications. 21–25 Theoretically, those hollow materials can enhance the accessibility of electrolytes and reactants. However, they are never applied as bifunctional oxygen electrocatalysts for metal–air batteries because their limited porosity hinders efficient ORR and OER. In other words, if hierarchical porosity is achieved on multishelled materials, their electrocatalytic site abundance could be improved drastically. Such an open system is also beneficial for mass transfer of oxygen species, i.e., \( \text{OH}^- \), \( \text{O}_2 \), and \( \text{H}_2\text{O} \). 26 The hard-template method is the most commonly adopted to synthesize multishelled metal oxides. It usually contains tedious steps, including carbonaceous template preparation, repeated cation adsorption, and template removal. During the repeated cation adsorption process, the interconnection between the metal cations and the negative charged template surface is mainly driven by electrostatic attraction, while the empty d orbitals of transition-metal ions can also be occupied by p electrons of oxygen-involved functional groups on the hydrophilic surface of carbonaceous microspheres. 21 Therefore, the metal cations densely gather on the hydrophilic surface and rarely penetrate into the carbonized core of the template (Figure S1a,b). 27 Upon gradual removal of the carbonaceous template, metal oxides will form into shells with very limited porosity. In contrast, if the metal ions are uniformly distributed within a carbonaceous template, pore-rich multishelled metal oxides could be produced. Therefore, a general and feasible blueprint to synthesize multishelled materials with hierarchical porosity is highly desirable for the development of exceptionally efficient electrocatalysts for metal–air batteries.

Another strategy of improving performance focuses on modifying the intrinsic electrocatalytic activity of spinel cobalt-based components in hybrids. The incorporation of transition-metal ions, e.g., Zn, Mn, and Ni, with a tunable chemical state is commonly adopted. 3,14,28 Alternatively, with the aim to expedite their poor intrinsic ORR activity, the controlled substitution of metal ions with low hydroxyl coordination capability, such as Mg2+, should also be an effective approach. Because Mg substitution would create buffer zones with weakened lattice alkalinity, it would hence facilitate the extraction of ORR resultants (\( \text{OH}^- \)) away from lattice. However, previous attempts in increasing oxygen electrocatalysis of \( \text{Co}_3\text{O}_4 \) via Mg substitution have not been successful despite the boosted electrical conductivity. 13,29 The root cause of the failures is the excessive occupation of bivalence Mg that is inactive for oxygen electrocatalysis. 3 Hence, controllable occupation of Mg2+ at relatively low amount is the key factor to realize the insight of tailoring lattice alkalinity.

With the aim to realize the above hypotheses, a novel in situ coordinating process is proposed to synthesize double-shelled spinel \( \text{(Mg,Co)}_3\text{O}_4 \) with hierarchical pores (HP-DS) and controlled Mg2+ doping. The positive effects of Mg modulation on the spinel structure and electrocatalytic performance are studied systemically. With the addition of a uniform layer of N-doped graphitized carbon (NGC) onto \( \text{(Mg,Co)}_3\text{O}_4 \), the final hybrid catalyst, signified as \( \text{(Mg,Co)}_3\text{O}_4@\text{NGC} \), demonstrates superior bifunctional oxygen electrocatalytic activities. As a practical demonstration, Zn–air batteries fabricated using \( \text{(Mg,Co)}_3\text{O}_4@\text{NGC} \) as an air electrode exhibit narrow charge–discharge voltage gaps and long-term rechargability in ambient air.

A one-step hydrothermal synthesis is presented here, as illustrated in Figure 1. First, a homogeneous solution of metal nitrates and glucose is sealed and heated in a Teflon reactor. During the gradual condensation of glucose under hydrothermal condition, the metal cations (\( \text{Co}^{2+} \) and \( \text{Mg}^{2+} \)) are adsorbed via an in situ coordinating process that includes intermolecular condensation of glucose and simultaneous coordination with metal ions. These metal ions can then act as “bridges” to interconnect glucose, leading to the incorporation of metal cations within the carbonaceous microspherical frameworks (Figure S1c,d). Moreover, there is a competition for free sites between \( \text{Co}^{2+} \) and \( \text{Mg}^{2+} \) throughout the in situ coordinating process. Due to the filled 2p orbitals of Mg2+, its interaction with the functional group is much weaker than that of Co2+ with empty d orbitals, and hence, the Mg2+ amount is...
controlled at a low level. Afterwards, the carbonaceous frameworks are removed to obtain HP-DS (Mg,Co)₃O₄. Finally, self-polymerization of dopamine and subsequent cobalt-catalyzed graphitization in pyrolysis are conducted for encapsulation of metal oxides within a uniform layer of NGC to attain a targeted hybrid.³⁰

It is worth mentioning that, based on the proposed in situ coordinating mechanism, the morphology of spinel oxides can be rationally tuned by using metal salts with various anions. As an example, when metal acetates are adopted as raw materials with the same stoichiometric amount, quadruple-shelled hollow microspheres with limited porosity (LP-QS) are synthesized. The different acidity of anions is considered to be the main reason responsible for the morphology transformation. Through the in situ coordinating process, nanoparticle-aggregated microspheres with diameters of ca. 1.5 μm, uniform morphology, and high purity are obtained (Figure 2a). The mesh-like interconnected porous shells of HP-DS (Mg,Co)₃O₄ are clearly revealed by scanning electron microscopy (SEM, Figure 2b). In the SEM image of a broken microsphere (Figure 2c), the hollow interior and the porous inner shell can be easily witnessed. Furthermore, the NGC coating appears to be uniform and well-defined in (Mg,Co)₃O₄@NGC, and the coating process did not alternate the original morphology (Figure 2d–f). The architectural visualization of HP-DS is enhanced by three-dimensional (3D) tomography in Figure S2a,b, and the corresponding reconstructed 3D animation is provided in Video S1. The porous structures on both shells can be clearly observed at different rotational degrees and representative slices through the 3D volume of a single microsphere at different depths. The limited porosity and quadruple-shelled structure of acetate-based LP-QS (Mg,Co)₃O₄ is also unveiled in Figure S3.

Transmission electron microscopy (TEM) images and associated elemental mapping of HP-DS (Mg,Co)₃O₄ and (Mg,Co)₃O₄@NGC are provided in Figure 3. The primary particles of HP-DS (Mg,Co)₃O₄ are identified with an average particle size of 20.1 nm (Figure S4). The energy-dispersive spectroscopy (EDS) results verify the uniform distribution of Co, Mg, and O. The homogeneous dispersion of C and N illustrates the successful coating of NGC (Figures 3e and S5). High-resolution TEM (HRTEM) images in Figure 3c,f suggest high crystallinity of the primary particles for both (Mg,Co)₃O₄ and (Mg,Co)₃O₄@NGC, in which the typical cubic spinel patterns are defined by the lattice fringes and fast Fourier transform (FFT). Also, intimate contact between the
(Mg,Co)₃O₄ particle and the graphitized carbon layer is revealed with characteristic d spacings (Figure 3f). These results coincide with the polycrystalline selected area electron diffraction (SAED) patterns and Raman spectrum (Figures S6 and S7). The highly graphitized degree of NGC is confirmed by the low-intensity ratio of disorder (D) and graphic (G) peaks (I_D/I_G is 0.96) in Raman spectra.19

The surface area and pore size distribution of the catalysts are examined by N₂ adsorption/desorption analysis. Although LP-QS consists of two additional inner shells, its estimated surface area of 32 m² g⁻¹ is much lower than 84 m² g⁻¹ of HP-DS that exhibits an obvious hierarchical pore distribution (Figure S8, Table S1). Additionally, the surface area and porosity are greatly increased by the NGC coating on (Mg,Co)₃O₄. A typical type-IV isotherm is observed for (Mg,Co)₃O₄@NGC with surface area as high as 194 m² g⁻¹ (Figure 4a, Table S1), demonstrating its apparent hierarchical porosity. 4 The pore distribution indicates the well-defined coexistence of micropores with a diameter less than 2 nm, mesopores distributed around 16 nm, and macropores with an average size of 75 nm.

X-ray photoelectron spectroscopy (XPS) is performed to analyze the effects of polydopamine coating on (Mg,Co)₃O₄ (Figures 4b and S9). The result signifies that the chemical valencies of Co and Mg are maintained, and a newly observed peak attributed to N 1s is marked in (Mg,Co)₃O₄@NGC. The high-resolution N 1s spectrum demonstrates four types of N species at 398.3, 399.6, 400.9, and 403.4 eV, representing pyridinic, quaternary, pyrrolic, and oxidized N, respectively.18 Among these species, the quaternary N is responsible for the ORR activity because it induces O₂ adsorption on the adjacent carbons; the OER activity is provided by the pyridinic N that expedites adsorption of the oxidation intermediates, such as OH⁻ and OOH⁻.31

The X-ray diffraction (XRD) patterns in Figure 4c exhibit a typical Fd3’m spinel structure for (Mg,Co)₃O₄ and (Mg,Co)₃O₄@NGC. Additionally, a broad peak at about 25° attributed to a (002) graphitic facet is observed in (Mg,Co)₃O₄@NGC.32 When compared to the XRD pattern of Co₃O₄ with the same morphology (Figures S10 and S11), a significant negative shift of (Mg,Co)₃O₄ suggests a larger lattice volume that is beneficial for the transportation of oxygen species within the lattice.28,33 Meanwhile, a sharp increase in electrical conductivity is also realized via Mg substitution in (Mg,Co)₃O₄ (Figure S11c,d), which coincides with previous reports regarding Mg²⁺ doping.29 As a result, an enhanced mass- and charge-transfer proficiency is expected. It is critical to confirm the amount of bivalent Mg²⁺ because it is inactive for oxygen electrocatalysis. According to inductively coupled plasma atomic emission spectroscopy (ICP-AES) results in Table S2, the atomic ratio of Co/Mg in (Mg,Co)₃O₄ is controlled at 18.2. Hence, the Mg²⁺ occupation in the lattice is illustrated in Figure 4d. The low Mg substitution is attributed to competition for free sites between Co²⁺ and Mg²⁺ during an in situ coordination process.

Bifunctional ORR and OER activities are measured by linear sweep voltammetry (LSV) with 0.1 M KOH electrolyte, as shown in Figure 5a,b. The influence of hierarchical porosity on oxygen electrocatalysis is investigated. HP-DS (Mg,Co)₃O₄ exhibits superior performance, i.e., better bifunctional activity of 0.889 V (vs the reversible hydrogen electrode, RHE) defined on the gap (ΔE) between the OER potential at 10 mA cm⁻² (E₁₀) and the ORR half-wave potential (E_{half-wave}), compared to that of LP-QS of 1.046 V. Its lower Tafel slopes than LP-QS also unveil its improved bifunctional electrocatalytic kinetics (Figure S12c,d). The high surface area, nanosized primary particles, and hierarchical porosity of HP-DS are decisive factors for its excellent bifunctional activities. The hierarchical porosity is of great significance as the micropores provide abundant exposed active sites for oxygen electrocatalysis, while
the meso/macropores encourage efficient transportation of oxygen species toward and away from electroactive sites.

The effects of Mg modulation on the intrinsic electrocatalytic activity of (Mg,Co)₃O₄ are discussed in detail. HP-DS Co₃O₄ with the same morphology is also tested to eliminate any geometric influences. In the ORR segment (Figure 5a,b), HP-DS Co₃O₄ offers an $E_{1/2}$ of 0.713 V and a limiting current density ($j_l$) of 4.35 mA cm⁻², which are noticeably inferior to those of HP-DS (Mg,Co)₃O₄ with an $E_{1/2}$ of 0.747 V and $j_l$ of 4.45 mA cm⁻². To explain the improved ORR kinetics of (Mg,Co)₃O₄, a Mg-assisted mechanism based on coordination chemistry is described here for the first time. As illustrated in Figure 5c, the ORR process at octahedral Co sites involves a four-step proton/electron-coupled mechanism, in which the steps 1 and 4 are the rate-limiting steps due to the unstable Co₉₋₅−OO₂⁻⁻ bond (step 1) and the strong Co₉₋₅−O²⁻⁻ bond (step 4). An effective strategy to accelerate ORR kinetics is to expedite the removal of resultants (OH⁻) from the lattice. Because Mg²⁺ ions form far weaker coordination bonds with OH⁻ than Co²⁺ with empty 3d orbitals, they are expected to greatly lower the OH⁻ concentration in nearby space. This can create buffer zones that provide a thermodynamically favorable environment for the detachment of OH⁻ and thus accelerate the intermediate steps. Meanwhile, enhanced OER kinetics is also achieved by (Mg,Co)₃O₄, including a lower onset potential and overpotential of 0.406 V at 10 mA cm⁻² when compared to that of Co₃O₄ (0.424 V). The optimized bifunctional electrocatalytic kinetics is contributed to by the boosted mass- and electron-transfer properties through Mg modulation, which is supported by the lower ORR/OER Tafel slopes of (Mg,Co)₃O₄ in comparison to Co₃O₄ (Figure S12c,d).

By combining the merits of HP-DS (Mg,Co)₃O₄ and highly conductive NGC, (Mg,Co)₃O₄@NGC offers remarkable bifunctional performance. As a comparison, start-of-the-art Pt/C and Ir/C are measured as ORR or OER benchmarks, respectively. In the ORR branch, (Mg,Co)₃O₄@NGC provides an onset potential ($E_{onset}$) of 0.925 V and an $E_{1/2}$ of 0.842 V, which are superior to those of Pt/C ($E_{onset}$ = 0.920 V, $E_{1/2}$ = 0.842 V).
A first-order four-electron-transfer ORR pathway for (Mg,Co)₃O₄@NGC is identified by the Koutecky–Levich (K–L) equation based on ORR curves at various rotation rates (Figure S12a,b). As for the OER branch, despite a slightly higher onset potential, (Mg,Co)₃O₄@NGC affords a steeper polarization curve and reaches a current density of 10 mA cm⁻² with a lower overpotential of 0.346 V in comparison to that of Ir/C (0.373 V). The bifunctional activity (ΔE) of 0.734 V demonstrated by (Mg,Co)₃O₄@NGC establishes it to be one of the top-tier bifunctional oxygen electrocatalysts (Table S3). The excellent bifunctional catalytic kinetics of (Mg,Co)₃O₄@NGC are further confirmed by its low Tafel slopes (Figure S12c,d). The synergistic effects of the two components and the optimized hierarchical porosity are the keys for such promising bifunctional performance.

Rechargeable Zn–air batteries are fabricated using (Mg,Co)₃O₄@NGC as an air electrode to explore its potential for practical application in ambient air. Pt/C and Ir/C (1:1 weight ratio) mixedtures of the same mass loading are also used to fabricate the reference Zn-air batteries. The galvanodynamic charge and discharge curves are presented in Figure 5d. Both Zn-air batteries deliver a similar open-circuit voltage at ca. 1.45 V and comparable charge performance. However, the Zn-air battery using (Mg,Co)₃O₄@NGC as the air electrode outperforms the reference in the discharge segment, especially at relatively high current density; its power density (125 mW cm⁻²) is much higher than the noble-metal reference (90 mW cm⁻²; Figure S13).

Notably, excellent durability is achieved by (Mg,Co)₃O₄@NGC, as indicated in Figures 5e and S14. When cycling at a constant current density of 10 mA cm⁻² with a charge-discharge period of 2 h, the (Mg,Co)₃O₄@NGC assembled Zn-air battery demonstrates a charge-discharge voltage gap as low as 0.80 V and long-term cycling stability without discernible voltage degradation for over 200 h, surpassing significantly the noble-metal cathode. Even at a high current density of 20 mA cm⁻², a narrow charge-discharge voltage gap of 0.90 V and durable cyclability over 100 h are also delivered by (Mg,Co)₃O₄@NGC, while the noble-metal catalyst offers very limited durability of less than 40 h.

In summary, benefiting from the proposed in situ coordinating strategy, double-shelled (Mg,Co)₃O₄@NGC microspheres with hierarchical porosity are designed as promising bifunctional oxygen electrocatalysts with the following merits. First, the double-shelled architecture with hierarchical porosity greatly enhances ORR/OER kinetics. Second, the Mg modulation positively influences electrocatalytic activity by facilitating reactant transportation and improving electrical conductivity. Finally, a novel Mg-assisted mechanism based on coordination chemistry for tailoring lattice alkalinity is proposed to modify oxygen electrocatalysis. It is believed that tailoring of lattice alkalinity via controllable occupation of specific metal ions is a feasible and general strategy to alter oxygen electrocatalysts. These results open inspiring insight into rational design of efficient oxygen electrocatalysts for practical energy conversion systems.

**ASSOCIATED CONTENT**

Supporting Information

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**AUTHOR INFORMATION**

**Corresponding Authors**
*E-mail: zhwench@uwaterloo.ca (Z.C.).
E-mail: baizhengyu2000@163.com (Z.B.).

**ORCID**
Yi Jiang: 0000-0002-5612-1499
Jing Zhu: 0000-0002-2175-9476
Zhongwei Chen: 0000-0003-3463-5509

**Notes**
The authors declare no competing financial interest.

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