Research paper

Cobalt-doped Mn_3O_4 nanocrystals embedded in graphene nanosheets as a high-performance bifunctional oxygen electrocatalyst for rechargeable Zn–Air batteries

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Abstract

A non-noble-metal bifunctional catalyst with efficient and durable activity towards both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) is crucial to the development of rechargeable Zn-air batteries. Herein, a facile one-step hydrothermal method is reported for the synthesis of a high-performance bifunctional oxygen electrocatalyst, cobalt-doped Mn_3O_4 nanocrystals supported on graphene nanosheets (Co– $\text{Mn}_3\text{O}_4/\text{G}$). Compare to pristine Mn_3O_4 , this Co– $\text{Mn}_3\text{O}_4/\text{G}$ exhibits greatly enhanced electrocatalytic activity, delivering a half-wave potential of 0.866 V for the ORR and a low overpotential of 275 mV at 10 mA cm^{-2} for the OER. The zinc-air battery built with Co– $\text{Mn}_3\text{O}_4/\text{G}$ shows a reduced charge–discharge voltage of 0.91 V at 10 mA cm^{-2} , an power density of 115.24 mW cm^{-2} and excellent stability without any degradation after 945 cycles (315 h), outperforming the state-of-the-art Pt/C–Ir/C catalyst-based device.

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Keywords: Mn_3O_4 ; Bifunctional electrocatalysts; Oxygen reduction reaction; Oxygen evolution reaction; Zinc air battery

1. Introduction

Rechargeable zinc-air batteries (ZABs), a promising post-lithium-ion battery technology, have received enormous attention in recent years due to their high energy densities, environmental protection and safety [1,2]. However, one of the obstacles affecting the application of ZABs is the sluggish kinetics of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) occurring at the air electrode, giving rise to low charge–discharge efficiency and poor stability [3–6]. The development of high-efficiency and well-tolerated catalysts as bifunctional ORR/OER air electrodes is

of great significance for improving the energy conversion efficiency of rechargeable ZABs [7–9]. Currently, noble metal (e.g., Pt, Ir and Ru)-based materials are recognized as highly active electrocatalysts for the ORR or OER. However, as scarce resources, their shortcomings include high costs and low anti-poisoning capabilities, which have limited their potentially large-scale application. Thus, intensive efforts have been devoted to the development of low-cost alternative bifunctional catalysts with high stability and comparable or even better catalytic properties than those of existing catalysts [10,11].

Mn_3O_4 , a typical spinel-type metal oxide, is considered one of the most promising bifunctional oxygen electrocatalysts due to its unique electronic structure, mixed valence $\text{Mn}^{2+/3+}$ centres with redox behaviours, abundance and environmental friendliness [12–15]. However, the intrinsic ORR and OER activities of Mn_3O_4 are still unsatisfactory because of its low

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electrical conductivity and unoptimized electronic structure [16,17]. To solve these issues, considerable efforts, including size modulation [18], the formation of mixed metal oxides [19–21], doping with other transition metals [22–26], and hybridization with conductive substrates [17,27,28], have been undertaken to enhance both the OER and ORR activities of pristine Mn_3O_4 . For instance, Chen and coworkers reported that a mixed-metal oxide, $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$, possessed an ORR performance similar to that of the counterpart Pt/C catalyst and proper OER activity, in which the Co/Mn composition and surface valence value were found to affect the extent of oxygen activation [22]. Additionally, Dong and coworkers developed Mn_3O_4 embedded in conductive carbon nanotubes to show enhanced OER and ORR performance, and the corresponding zinc-air battery exhibited a high power density of 86.6 mW cm^{-2} [27]. However, the overall bifunctional performance of Mn_3O_4 -based electrocatalysts is still not comparable with that of noble metal-based systems (e.g., Pt/C– IrO_2).

Here, we have proposed a facile hydrothermal method to synthesize cobalt-doped Mn_3O_4 nanocrystals embedded in graphene nanosheets (Co– $\text{Mn}_3\text{O}_4/\text{G}$) as high-performance bifunctional electrocatalysts for ZAB. It was demonstrated that the judicious doping of Co species and the combination with a highly conductive graphene substrate could dramatically boost the ORR and OER activities of pristine Mn_3O_4 . Our Co– $\text{Mn}_3\text{O}_4/\text{G}$ exhibited ORR and OER activities comparable with those of the benchmarks Pt/C and Ir/C, respectively. Furthermore, Zn-air battery fabrication with as-synthesized catalysts was conducted. The battery displayed a low charge–discharge voltage gap of 0.91 V, with a high energy density of $115.24 \text{ mW cm}^{-2}$, and exhibited stable activity for >315 h at 10 mA cm^{-2} , outperforming the Pt/C–Ir/C catalyst.

2. Materials and methods

2.1. Synthesis of graphene supported cobalt doped Mn_3O_4 nanocrystals (Co– $\text{Mn}_3\text{O}_4/\text{G}$) and comparison samples

Graphene oxide (GO) was synthesized according to a modified Hummers' method [29]. For the synthesis of Co/ $\text{Mn}_3\text{O}_4/\text{G}$: 5 mg of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 1 mg of $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ and 10 mg of GO were ultrasonically dispersed in 5 mL of water for 20 min, and then 66.7 μL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added. This mixture was transferred into an autoclave and heated at 180°C for 12 h. After the reaction, the precipitates were collected and washed with ultrapure water and ethanol 3 times. The final Co– $\text{Mn}_3\text{O}_4/\text{G}$ was obtained by freeze-drying the precipitates. To illustrate the effect of cobalt doping on the electrocatalytic activity, graphene-supported pristine Mn_3O_4 nanocrystals ($\text{Mn}_3\text{O}_4/\text{G}$) and Co-doped Mn_3O_4 nanocrystals with different cobalt contents (Co– $\text{Mn}_3\text{O}_4/\text{G}$ -1, Co– $\text{Mn}_3\text{O}_4/\text{G}$ -2 and Co– $\text{Mn}_3\text{O}_4/\text{G}$ -3) were also prepared by procedures similar to those used for Co– $\text{Mn}_3\text{O}_4/\text{G}$, and the addition $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the precursor was 0 mg, 0.25 mg, 0.5 mg and 2.5 mg for $\text{Mn}_3\text{O}_4/\text{G}$,

G, Co– $\text{Mn}_3\text{O}_4/\text{G}$ -1, Co– $\text{Mn}_3\text{O}_4/\text{G}$ -2 and Co– $\text{Mn}_3\text{O}_4/\text{G}$ -3, respectively.

2.2. Materials and their characterization

Details are shown in the supporting information.

2.3. Electrochemical methods and Zn-air battery assembly

Details are shown in the supporting information.

3. Results and discussion

3.1. Synthesis and characterization of Co– $\text{Mn}_3\text{O}_4/\text{G}$

As illustrated in Fig. 1a, typical Co– $\text{Mn}_3\text{O}_4/\text{G}$ was synthesized by hydrothermal treatment of precursors containing MnCl_2 and CoCl_2 at a weight ratio of 5:1 and GO in an aqueous NH_4OH solution at 180°C for 12 h. The abundant functional groups of GO can preadsorb metal ions via redox interactions, which facilitate the nucleation of nanocrystals on the resultant graphene nanosheets during hydrothermal treatment [29]. Pristine Mn_3O_4 supported on graphene ($\text{Mn}_3\text{O}_4/\text{G}$) was also synthesized without the addition of CoCl_2 . The different weight ratios of the precursor ($\text{MnCl}_2:\text{CoCl}_2$) were 20:1, 10:1 and 2:1, resulting in products labelled Co– $\text{Mn}_3\text{O}_4/\text{G}$ -1, Co– $\text{Mn}_3\text{O}_4/\text{G}$ -2 and Co– $\text{Mn}_3\text{O}_4/\text{G}$ -3, respectively.

The SEM (Fig. 1b) and TEM (Fig. 1c) images of Co– $\text{Mn}_3\text{O}_4/\text{G}$ revealed that Co-doped Mn_3O_4 nanocrystals with an average size of 50 nm grew well on the surface of the graphene nanosheets. A TEM image with higher resolution (Fig. 1d) indicated that the distance of the (101) crystal face in Co-doped Mn_3O_4 was 0.476 nm, which was slightly smaller than that of pristine Mn_3O_4 (0.489 nm), which is attributed to the substitution of smaller Co cations [30,31]. The EDS mapping in Fig. 1e further illustrated the homogeneous distribution of Co species in the Mn_3O_4 nanocrystals, indicating the successful incorporation in Co– $\text{Mn}_3\text{O}_4/\text{G}$. The atomic percentages of Co dopants were characterized by EDX technique, which were shown in Table S1. Additionally, the TEM and SEM images in Figs. S1–S4 demonstrated the formation of Mn_3O_4 nanocrystals and Co-doped Mn_3O_4 nanocrystals on graphene nanosheets in pristine $\text{Mn}_3\text{O}_4/\text{G}$, Co– $\text{Mn}_3\text{O}_4/\text{G}$ -1, Co– $\text{Mn}_3\text{O}_4/\text{G}$ -2 and Co– $\text{Mn}_3\text{O}_4/\text{G}$ -3. The Mn_3O_4 content in these hybrid materials was estimated to be approximately 39.2, 27.9, 36.7, 39.5, and 42.4% for Co– $\text{Mn}_3\text{O}_4/\text{G}$, $\text{Mn}_3\text{O}_4/\text{G}$, Co– $\text{Mn}_3\text{O}_4/\text{G}$ -1, Co– $\text{Mn}_3\text{O}_4/\text{G}$ -2 and Co– $\text{Mn}_3\text{O}_4/\text{G}$ -3, respectively (Fig. S5).

The XRD pattern of Co– $\text{Mn}_3\text{O}_4/\text{G}$ showed peaks identical to those of $\text{Mn}_3\text{O}_4/\text{G}$, consistent with the pattern of typical Mn_3O_4 (JCPDS 24–0734) and excluded the formation of CoMn_2O_4 (Fig. 2a, Fig. S6a) [22,32,33]. The Raman spectra of Co– $\text{Mn}_3\text{O}_4/\text{G}$ exhibited a dominant peak at 642 cm^{-1} and secondary peaks at 315 and 361 cm^{-1} that were attributed to Mn–O vibrations, which can be observed in all the Co– $\text{Mn}_3\text{O}_4/\text{G}$ composites. Two sharp peaks appeared at

Fig. 1. (a) Schematic illustration of the synthesis of Co-Mn₃O₄/G; (b) SEM, (c) TEM, and (d) HRTEM images and (e) EDS mapping of Co-Mn₃O₄/G.

Fig. 2. (a) XRD and (b) Raman spectra of Co-Mn₃O₄/G and Mn₃O₄/G.

approximately 1346 and 1593 cm^{-1} , attributed to the D and G bands of graphene, respectively. The small I_D/I_G intensity ratio (1.0) indicated that the graphitization degree of rGO is relatively high, which was favourable for improving the electrical conductivity of the nanocomposites (Fig. 2b and Fig. S6b) [34,35].

X-ray photoelectron spectroscopy (XPS) was conducted to study the surface chemical states of Co-Mn₃O₄/G. The XPS spectrum (Fig. 3a) of the full region of Co-Mn₃O₄/G definitively confirmed the presence of Mn, Co, C, N, and O. In comparison, Co was absent in Mn₃O₄/G. The high-resolution XPS spectrum of Co 2p region showed that the integral ratio of the peak area of Co²⁺/Co³⁺ was 1.97, indicating that the Co

was mainly in its +2 state (Fig. 3b) [36,37]. The high-resolution Mn 2p XPS spectrum (Fig. 3c) can be deconvoluted into two peaks, corresponding to Mn²⁺ and Mn³⁺ [38,39]. The percentage of Mn³⁺ increased on the surface of Co-Mn₃O₄/G compared to that on pristine Mn₃O₄/G. Due to the stronger electron loss ability of manganese than of cobalt, some of the mixed forms of Mn²⁺ and Mn³⁺ in the doped sample were oxidized and the content of Mn³⁺ increased [40]. Three kinds of oxygen bonds were observed in the deconvoluted O 1s spectra (Fig. 3d): Co-Mn-O bonds, adsorbed oxygen or H₂O bonds and oxygen vacancy bonds. The intensity of the oxygen vacancy bond peak increased (peak area ratios were 30.1% for Mn₃O₄/rGO and 69.7% for Co-Mn₃O₄/rGO),

Fig. 3. (a) XPS spectra of Co-Mn₃O₄/G; high-resolution XPS spectra of Co-Mn₃O₄/G and Mn₃O₄/G: (b) Co 2p, (c) Mn 2p and (d) O 1s.

which indicated a stronger adsorption capacity for O₂ after Co doping [41,42]. In summary, the above evidence demonstrates the successful growth of Co-doped Mn₃O₄ nanocrystals on graphene nanosheets. The incorporation of Co mainly causes a slightly reduced (101) lattice distance and increased surface Mn³⁺ and oxygen vacancies of Mn₃O₄ nanocrystals in Co-Mn₃O₄/G, which is thought to be the key reason for the enhanced electrocatalytic activity.

3.2. ORR and OER electrocatalytic performance

The ORR activity of Co-Mn₃O₄/G and other samples was evaluated by cyclic voltammetry (CV) in a 0.1 M KOH solution saturated with O₂ or N₂. As shown in Fig. 4a, an ORR peak at approximately 0.83 V (vs. RHE) appeared in the O₂-saturated KOH solution for Co-Mn₃O₄/G. Similar ORR peaks at approximately 0.81 V, 0.82 V, 0.82 V, and 0.79 V were also present for Co-Mn₃O₄/G-1, Co-Mn₃O₄/G-2, Co-Mn₃O₄/G-3 and Mn₃O₄/G, which were all lower than that of Co-Mn₃O₄/G (Fig. S7). Impressively, Co-Mn₃O₄/G displayed the best ORR performance, with an onset potential of 0.931 V vs. RHE, which was only 30 mV more negative than that of the Pt/C benchmark, and the current density at 0.1 V (4.5 mA cm⁻²) was higher than the Pt/C result (4.0 mA cm⁻²). The comparison among the onset potentials of Co-Mn₃O₄/Gs

demonstrated the effect of the Co dopant on the ORR activity of the materials. Fig. 4b and Fig. S7 show the onset potentials of Co-Mn₃O₄/G (0.931 V), Co-Mn₃O₄/G-2 (0.912 V), Co-Mn₃O₄/G-3 (0.878 V), Co-Mn₃O₄/G-1 (0.854 V) and Mn₃O₄/G (0.824 V). The LSV curves of Co-Mn₃O₄/Gs and Mn₃O₄/G were used to investigate the ORR kinetics at different rotation speeds (Fig. 4c and Fig. S7), and the diffusion-limited current densities of Co-Mn₃O₄/Gs and Pt/C were positively correlated with different rotation speeds. Based on the ratio of I_d and I_r, the electron transfer numbers of Co-Mn₃O₄/Gs are 3.96, 3.54, 3.81, 3.42 and 4.02 for Co-Mn₃O₄/G, Co-Mn₃O₄/G-1, Co-Mn₃O₄/G-2, Co-Mn₃O₄/G-3 and Pt/C, respectively, at 0.4 V. The RRDE results proved the preference for the 4-electron pathway of the ORR process catalyzed by Co-Mn₃O₄/G [43]. As shown in Fig. 4d, the yield of H₂O₂ was less than 4% within the potential range of 0.2–0.8 V, were consistent with the results calculated by means of the K-L equation.

The electrocatalytic activity of Co-Mn₃O₄/Gs for the OER was further investigated. As shown in Fig. 4e, the activity of Mn₃O₄/G was enhanced as the overpotential decreased from 338 mV to 275 mV at a current density of 10 mA cm⁻² after Co doping, which indicated improvement of the reaction kinetics. With the increase in the doping ratio, the OER currents displayed a rising trend, which was ascribed to the Co cations serving as OER active sites in the catalyst materials. However,

Fig. 4. (a) CV curves of Co-Mn₃O₄/G on glassy carbon electrodes in O₂-saturated (red line) or N₂-saturated (black line) 0.1 M KOH; (b) LSV curves of Co-Mn₃O₄/G, Mn₃O₄/G, RGO, Mn₃O₄ nanoparticles and Pt/C in an O₂-saturated solution at a sweep rate of 10 mV/s at 1600 rpm for the ORR; (c) LSV curves of Co-Mn₃O₄/G in an O₂-saturated solution at different rotation speeds with a sweep rate of 10 mV s⁻¹ for the ORR. Inset: The corresponding K-L plots and electron transfer numbers; (d) RRDE result for Co-Mn₃O₄/G in an O₂-saturated solution at 1600 rpm. Inset: H₂O₂ yield. (e) LSV curves of Co-Mn₃O₄/G, Mn₃O₄/G, Ir/C and RGO in O₂-saturated solution at a sweep rate of 10 mV/s at 1600 rpm for the OER; (f) ORR half-wave potentials and OER over potentials of different ratios of Co-Mn₃O₄/Gs, Mn₃O₄/G and Pt/C-Ir/C.

little difference in the OER current between Co-Mn₃O₄/G and Co-Mn₃O₄/G-3 were observed (Fig. S8a), which could be explained by the active sites on the surface of the catalysts being saturated. Moreover, the ORR half-wave potentials and the OER over potentials @10 mA cm⁻² of Co-Mn₃O₄/Gs and the benchmarks (Pt/C and Ir/C) were calculated and are shown in Fig. 4f. The catalytic performance of Co-Mn₃O₄/G also surpassed that of other counterparts.

The above results indicated that the Co doping enhanced the oxygen electrocatalytic activity of Mn₃O₄. Based on these results, we believe that there are two main factors attributed to the remarkable electrocatalytic activity: 1) The cobalt doping process alters the surface atomic arrangement and electronic property, resulting in optimal adsorption behaviour of oxygen molecules, which explains the promotion of the ORR and OER activities of the Co-Mn₃O₄/G materials [44,45]. 2) The hybridization of the spinel nanocrystals with the two-dimensional graphene nanosheets improves the electron conductivity and the dispersion of the spinel nanocrystals, thus preventing the aggregation and promoting the mass transfer of the oxygen molecules.

3.3. Zinc-air battery performance

A rechargeable zinc-air battery was constructed by employing Co-Mn₃O₄/G as the active material of the air electrode. An open-circuit voltage (OCV) of 1.415 V was achieved (Fig. 5a), which is higher than that of the battery using Pt/C-Ir/C as the active material (1.39 V). The polarization and corresponding power density curves are presented in Fig. 5b, and the peak power density (115.24 mW cm⁻²) was also superior to that of Pt/C-Ir/C (91 mW cm⁻²). As shown in Fig. 5c, at different current densities, a-Co-Mn₃O₄/G ZAB exhibited stable discharge, maintaining a value of 0.91 V even at a high current density of 50 mA cm⁻². When the current density increased to 50 mA cm⁻² and then returned to 1 mA cm⁻², the discharge voltage reached 97% of that previously tested at 1 mA cm⁻². Moreover, the battery was still able to operate for more than 250 min with a negligible potential drop at a current density of 20 mA cm⁻² (Fig. 5d). The rechargeable performance of the Co-Mn₃O₄/G battery at various current densities was explored. Fig. 5e shows that the Co-Mn₃O₄/G sample underwent a charge-discharge process with a constant voltage gap for a long time, indicating an

Fig. 5. Electrochemical evaluation of the Co-Mn₃O₄/G cathode in a rechargeable Zn-air battery. (a) Open-circuit potential of the Zn-air battery with Co-Mn₃O₄/G as the bifunctional electrocatalyst; (b) polarization and power density of Zn-air batteries with Co-Mn₃O₄/G and Pt/C-Ir/C as electrocatalysts; (c) discharge profiles at various current densities; (d) discharge curves of Zn-air batteries using Co-Mn₃O₄/G and Pt/C-Ir/C at a current density of 20 mA cm⁻²; (e) cycle performances of Zn-air batteries with Co-Mn₃O₄/G and Pt/C-Ir/C as electrocatalysts at a current density of 10 mA cm⁻².

efficient rechargeability. The charge/discharge voltage gap was kept at 0.89 V for more than 450 cycles (inset in Fig. 5e), maintaining a value of 0.91 V at the 945-th discharge-charge cycle (after 315 h), while cycling at a constant current density of 10 mA cm⁻², further suggesting excellent cycling stability (Fig. 5e). SEM images of Co-Mn₃O₄/G after the 945-th discharge-charge cycle were shown in Fig. S9, the morphology displayed similar structures as in Fig. 1b.

4. Conclusion

In summary, we have demonstrated an efficient strategy to validate a series of cobalt-doped Mn₃O₄ nanocrystal hybrids with graphene nanosheets and evaluated their electrocatalytic activities. Notably, the Co-Mn₃O₄/G hybrid showed ORR and OER performances comparable to those of the benchmark Pt/C and Ir/C catalysts, respectively. As expected, the Zn-air

battery assembled with Co–Mn₃O₄/G exhibited a high peak power density of 115.24 mW cm^{−2} and superior cycling durability. The present work offers an efficient strategy to synthesize spinel-type complex oxide materials in high-performance bifunctional oxygen electrocatalyst areas.

Declaration of Competing Interest

There are no conflicts of interest to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gee.2020.06.022>.

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