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Article

Low-temperature synthesis of ultrasmall spinel $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles for efficient oxygen reduction

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ABSTRACT

Spinel-type manganese-cobalt oxides have been regarded as important class of electrocatalysts for oxygen reduction reaction (ORR). However, they are usually synthesized through oxidation-precipitation under aqueous ammonia and then crystallization at high temperature (150–180 °C), which not only increases the energy consumption but also induces the growth of particles that is unfavorable for ORR. Herein, through a facile precipitation-dehydration method, ultrasmall spinel manganese-cobalt oxide nanoparticles (~5 nm) homogeneously dispersed on conductive carbon black ($\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{C}$) were fabricated at low temperature (60 °C). And the bimetallic composite oxide ($\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$) with cubic spinel structure and high Mn content exhibits remarkable enhancement of ORR activity and stability compared with single metal oxide (both $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Co}_3\text{O}_4/\text{C}$). The essential reason for the enhancement of activity can be attributed to the presence of the mixed Mn^{3+} and Mn^{4+} cations in $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$. Moreover, the ORR activity of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ is comparable to that of commercial 20 wt% Pt/C, and the relative current density only decreases 1.4% after 12 h test, exceeding that of Pt/C and most reported manganese-cobalt oxide electrocatalysts.

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1. Introduction

The exploitation of new generation of sustainable, clean and efficient energy conversion and storage devices, such as metal-air batteries and alkaline fuel cells, has attracted significant attention in recent years [1–4]. However, due to a complex multistep four-electron process, the kinetically sluggish oxygen reduction reaction (ORR) at the cathode is an obstacle for the effective using of such electrochemical energy devices [4–6]. To

date, the most efficient ORR electrocatalysts are Pt-based catalysts, but their high cost, scarce reserves, poor long-term stability and low methanol tolerance greatly limit their large-scale commercial application [4–9]. Accordingly, many researchers have devoted to searching for highly efficient and stable non-noble metal-based ORR electrocatalysts [4,9–14].

Mixed valence oxides of transition metals, especially spinel-type oxides M_3O_4 (M = transition metal) consisting of multivalent metal cations occupying tetrahedral (four-coordina-

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tion) and octahedral (six-coordination) sites, have emerged as an important and highly potential class of electrocatalytic material owing to their excellent activities, long-term stability and abundant reserves [15–20]. Nevertheless, the ORR performance of single metal spinel-type oxides still needs to be improved compared with that of Pt-based electrocatalysts. Researchers have found that constructing composite metal oxides consisting of two or more metallic elements is an effective way to improve the ORR activity [21–26]. Among the composited transition metal oxides, spinel manganese-cobalt oxides ($\text{Mn}_x\text{Co}_{3-x}\text{O}_4$), especially those combined with conductive materials, have shown large potential to replace Pt-based catalysts for ORR [24–25,27–31]. For instance, Liang *et al.* [28] synthesized manganese-cobalt spinel MnCo_2O_4 /graphene hybrid through a two-step solvothermal method, which exhibits boosted ORR performance compared with pure cobalt oxide hybrid in alkaline solutions. Ma *et al.* [30] prepared carbon nanotubes supported spinel cobalt-manganese oxide nanoparticles through an oxidation-precipitation and insertion-crystallization process. And the hybrid exhibits higher kinetic current and better stability than commercial Pt/C catalyst. Despite such considerable improvements, there is still a need for further enhancement of ORR performance of manganese-cobalt oxides for the purpose of practical application. On the other hand, in addition to the conventional high-temperature solid-state methods, $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ catalysts are usually synthesized through oxidation-precipitation under aqueous ammonia and then crystallization at high temperature (150–180 °C) [25,26,28–30], which not only increases the energy consumption but also can induce the growth of oxide nanoparticles [25]. However, the electrocatalytic performance of nanosized metal oxides is generally higher than that of larger-sized ones, since nanosized materials can reduce diffusion resistance and have larger surface areas, thus exposing more active sites. Hence, it is highly desirable to develop a facile and low-temperature synthesis method to fabricate homogeneously dispersed and ultrasmall nanocrystalline $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ hybrids.

Herein, through a facile precipitation-dehydration process at low temperature (60 °C), the hybrids of spinel manganese-cobalt oxide nanoparticles and conductive carbon black were successfully fabricated. Benefitting from the low temperature method, the particle size of metal oxides is ultrasmall (~5 nm) and the graphitic structure of carbon black is well maintained. The bimetallic composite oxide hybrid ($\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$) exhibits remarkable enhancement of ORR activity and stability compared to single metal oxides (both $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Co}_3\text{O}_4/\text{C}$). $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ is further integrated into a Zn-air battery as cathode catalyst and displays excellent discharge performance. And the essential reason for the enhancement of activity can be attributed to the presence of the mixed Mn^{3+} and Mn^{4+} cations.

2. Experimental

2.1. Materials

Manganese(II) acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and ethanol were obtained from Tianjin Guangfu Fine Chemical

Research Institute. Cobalt(II) acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) was purchased from Alfa Aesar. Potassium hydroxide was provided by Aladdin Industrial Corporation. Vulcan XC-72R was obtained from Carbot. 20 wt% Pt/C was supplied by Johnson Matthey. Nafion solution (5 wt%) was purchased from DuPont. Milli-Q ultrapure water ($> 18.25 \text{ M}\Omega \cdot \text{cm}^{-1}$) was used in all experiments. All the chemicals were reagent grade and used as received without further purification.

2.2. Synthesis of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{C}$ ($x = 0, 1.5, 3$)

The synthetic procedure was adapted from the literature [17]. In a typical reaction, 0.05 g of conductive carbon black (VXC-72R C) was ultrasonically dispersed in 50 mL anhydrous ethanol. Then 0.32 g $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 0.32 g $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were added to the carbon black suspension. After heating the mixture to 60 °C, 2.6 mL $\text{KOH}-\text{C}_2\text{H}_5\text{OH}$ solution (2 mol L^{-1}) was dropwise added under stirring and then maintained at 60 °C for 24 h. The product was separated and rinsed by repeated centrifugation with ethanol and deionized water, and dried overnight at 60 °C. The sample was then used after grinding into powder, without any further size selection. The obtained sample was denoted as $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$.

The synthesis of $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Co}_3\text{O}_4/\text{C}$ was similar to that of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$, except for the amount of metal salts added was 0.64 g manganese(II) acetate tetrahydrate or 0.64 g cobalt(II) acetate tetrahydrate, respectively.

2.3. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 focus (D8-S4) X-ray diffractometer equipped with a nickel-filtered $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at a scan rate of 5° min^{-1} . The Raman spectra were obtained by a Raman spectrometer (inVia reflex) using laser excitation at 532 nm. Transmission electron microscopy (TEM) and corresponding energy dispersive spectrum (EDS) characterization were performed with a JEM-2100F transmission electron microscope, working at 200 kV to analyze the morphology and composition of the prepared samples. X-ray photoelectron spectroscopy (XPS) analysis was performed on a PHI-1600 instrument equipped with $\text{Al } K_\alpha$ radiation and all the binding energies were calibrated by the C 1s peak at 284.8 eV.

2.4. Electrochemical measurements

All the electrochemical measurements were carried out on an IVIUMSTAT workstation (Ivium Technologies BV, Netherlands) equipped with a modulated speed rotator (MSR) (Pine Research Instrumentation, Inc.) in a standard three-electrode system (a modified glassy carbon electrode as the working electrode, a graphite rod as the counter electrode, and a Ag/AgCl (saturated KCl) electrode as the reference electrode by using 0.1 M KOH as the electrolyte. The working electrode modified with a thin catalyst film was prepared as follows: 5 mg catalyst was dispersed in 1 mL isopropanol-water mixture

with the volume ratio of 3:1 with 50 μL 5 wt% Nafion solution by ultrasonic dispersion to form a homogeneous ink. Then 10 μL the catalyst ink was dropped onto a glassy-carbon electrode (5 mm in diameter) which was newly polished and washed before use. The carbon electrode was dried under room temperature. For comparison, the ink of the commercial Pt/C catalyst (20 wt%) was prepared with the same procedure. Before each measurement, the electrolyte was purged with O_2 for at least 30 min. All data were reported without iR compensation.

2.5. Zn-air battery test

Zinc-air batteries were fabricated with a zinc foil as the anode and catalysts loaded on carbon paper as the cathode (catalyst load 1.0 mg cm^{-2}) by using 6 M KOH as the electrolyte. The constant-current discharge test was carried out with a LANHE battery testing station and the polarization curve test was carried out with an IVIUM electrochemical workstation.

3. Results and discussion

3.1. Crystal structure of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{C}$ hybrids

The structures of the obtained materials were first characterized by XRD and Raman spectroscopy. As shown in Figure 1a, the XRD patterns of all the samples exhibit a broad peak at $2\theta \approx 25^\circ$, which is assigned to the (002) planes of graphitic carbon. The diffraction peaks of the sample prepared with only $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ or $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ as the metal source can be attributed to the characteristic peaks of tetragonal Mn_3O_4 (JCPDS No. 24-0734) or cubic Co_3O_4 (JCPDS No. 43-1003) respectively. The XRD pattern of bimetallic manganese-cobalt oxide can be assigned to the cubic spinel structure, which is consistent with the reported literature [29], and the peaks are slightly shifted to smaller angles compared with pure Co_3O_4 , implying the incorporation of larger sized Mn cations into cubic Co_3O_4 lattice [28,29]. Raman spectra of the prepared materials are shown in Fig. 1b. The peak at approximately 1350 cm^{-1} is attributed to D band representing the structural defects on the graphitic plane and the peak at approximately 1586 cm^{-1} is ascribed to G band reflecting the degree of graphitization of carbon. The peak intensity ratios of D to G band (I_D/I_G) of all the samples are approximately equal to 1 implying well

graphitic degree of all the samples. This result indicates that the low-temperature synthetic process does not destroy the structure of carbon, which is beneficial to the enhancement of electrical conductivity and promoting charge transfer in the loaded manganese-cobalt oxides [32].

As shown in the TEM images (Fig. 2), all the $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles are uniformly dispersed on conductive carbon black, and the particle sizes are all around 5 nm. It is worth noting that the particle sizes do not increase significantly with the change of composition. Recently, Zhao and her co-workers reported the synthesis of manganese-cobalt oxide/nitrogen-doped multiwalled carbon nanotube hybrids through a solvothermal method (150°C) and concluded that the particle size increased notably with increasing the Mn/Co ratio [25]. While the facile and low-temperature precipitation-dehydration method applied here not only the energy consumption but also prevents the increase of particle size with the change of Mn/Co ratio. The HR-TEM images (Figs. 2b, d, f and Fig. S1) and the selected area electron diffraction patterns (inset of Figs. 2b, d, f) indicate that these oxides particles are all well crystallized (partially highlighted by yellow circles). The corresponding elemental mapping images of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ (Figs. 2g–j) prove that Mn and Co are homogeneously dispersed on the carbon matrix. Mn/Co atomic ratio of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ measured by TEM-EDS (Fig. S2) and XPS (Fig. S3) is shown in Table S1, which is close to 1 and consistent with that of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ reported in the literature [29]. According to the reported literature [25,28], the crystal structure of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ is highly related to the Mn/Co ratio. Generally, low Mn content ($0 \leq x \leq 1.3$) tends to form the cubic phase, while high proportions of Mn favours the tetragonal phase. Hence, the most familiar and studied bimetallic manganese-cobalt oxide with cubic structure is MnCo_2O_4 [24,25,27,28,33]. Whereas, herein, the bimetallic manganese-cobalt oxide with cubic spinel structure and high Mn content ($x = 1.5$), which are both beneficial for ORR [25,29], is successfully synthesized by the facile precipitation-dehydration method at low temperature.

3.2. ORR performance of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{C}$ materials

The ORR catalytic activities of as-prepared $\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{C}$ were first evaluated by linear sweep voltammetry (LSV) on a rotating disk electrode (RDE) in O_2 -saturated 0.1 M KOH with a

Fig. 1. (a) XRD patterns and (b) Raman spectra of synthesized $\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{C}$ ($x = 0, 1.5, 3$).

Fig. 2. TEM and HR-TEM images of (a, b) $\text{Mn}_3\text{O}_4/\text{C}$, (c, d) $\text{Co}_3\text{O}_4/\text{C}$, (e, f) $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ and (g–j) EDS element mapping of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$.

scan rate of 10 mV s^{-1} , which is commonly used in the literature [25,27,34]. As shown in Figure 3a and Table S2, $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ has much better ORR activity than $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Co}_3\text{O}_4/\text{C}$. The half-wave potential ($E_{1/2}$) and diffusion limiting current density (j_L) of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ are 0.820 V vs RHE and 5.6 mA cm^{-2} , respectively, which are comparable to those of commercial 20 wt% Pt/C (0.814 V vs RHE , 5.6 mA cm^{-2}) used here and in the literature [25,34,35]. It is worth noting that the polarization curve of $\text{Mn}_3\text{O}_4/\text{C}$ is steeper than that of $\text{Co}_3\text{O}_4/\text{C}$ in the kinetic control zone ($1.0\text{--}0.85 \text{ V vs RHE}$). The initial activity of $\text{Mn}_3\text{O}_4/\text{C}$ is better, that is, the current response increases faster with the change of voltage, suggesting that the intrinsic ORR activity of manganese is superior to that of cobalt. While, the ORR activity of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ in the kinetic region is better than that of $\text{Co}_3\text{O}_4/\text{C}$ and even $\text{Mn}_3\text{O}_4/\text{C}$. As shown in Table S2, kinetic current density (j_k) (at 0.90 V vs RHE in 0.1 M KOH) of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ (1.34 mA cm^{-2}) is much higher than that of $\text{Mn}_3\text{O}_4/\text{C}$ (0.65 mA cm^{-2}) and $\text{Co}_3\text{O}_4/\text{C}$ (0.15 mA cm^{-2}), indicating that constructing bimetal oxides can enhance ORR performance, which is consistent with reported literature [21,25,28]. The kinetic performance was further quantitatively evaluated by mass transfer corrective Tafel plots. As shown in Fig. 3b, Tafel slopes are in the order of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ (98 mV dec^{-1}) < $\text{Mn}_3\text{O}_4/\text{C}$ (107 mV dec^{-1}) < $\text{Co}_3\text{O}_4/\text{C}$ (163 mV dec^{-1}), which is consistent with the result of ORR polarization curves.

Then, the ORR catalytic performance of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{C}$ was investigated by cyclic voltammetry (CV), $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ exhibits a bigger closed-cycle than the others in the CV curves (Fig. 3c). A larger closed-loop indicates a larger current density response at a certain overpotential, implying a higher ORR activity. The result of CV curves that $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ has higher ORR activity is well consistent with that of ORR polarization curves.

ORR efficiency of prepared catalysts was further evaluated by measuring the electron transfer number (n) and yield of peroxide species. The electron transfer number can be obtained from polarization curves at different rotating speeds on rotating disk electrode (RDE) (Figs. 4a–d and Fig. S4) and the ring and disk current recorded on rotating ring-disk electrode (RRDE) (Figs. 4e, f). Although the Koutecky-Levich (K-L) method is not suitable for calculating the exact n value of ORR [36,37], it can be evidently seen from K-L plots (Fig. 4d) that the n values of the hybrids of spinel oxides and carbon black remarkably increase compared with carbon black. As shown in Fig. 4e, the disk current represents the oxygen reduction current and the ring current represents the oxidation current of peroxide species. The ring current of $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ is lower than that of $\text{Co}_3\text{O}_4/\text{C}$ and close to 0, implying that the production of peroxides is very little. As shown in Figure 4f, the n values of $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ are calculated to be above 3.95 in the range of $0.4\text{--}0.8 \text{ V vs}$

Fig. 3. ORR performance of $\text{Mn}_3\text{O}_4/\text{C}$, $\text{Co}_3\text{O}_4/\text{C}$, $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ and Pt/C in O_2 -saturated 0.1 M KOH . (a) ORR polarization curves with a scan rate of 10 mV s^{-1} at 1600 rpm , (b) Tafel plots derived polarization curves by mass-transport correction and (c) CV plots with a scan rate of 100 mV s^{-1} .

Fig. 4. (a–c) ORR polarization curves of $\text{Mn}_3\text{O}_4/\text{C}$, $\text{Co}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ at different rotating speeds from 400 to 2400 rpm in O_2 -saturated 0.1 M KOH, (d) the corresponding K-L plots at 0.4 V vs RHE, (e) rotating ring-disk electrode (RRDE) voltammograms in O_2 -saturated 0.1 M KOH at 1600 rpm (the ring potential was set as 1.3 V vs RHE), (f) Electron transfer number (solid curves) and peroxide yield (dashed lines) at various potentials.

RHE) and the percentages of generated peroxide species are below 5%. In comparison, $\text{Co}_3\text{O}_4/\text{C}$ has a lower electron transfer number and obvious peroxide species are produced during oxygen reduction.

For practical application, long-term durability is an important parameter of catalytic activity. The stability of prepared catalysts was evaluated by chronoamperometric measurement at 1600 rpm in O_2 -saturated 0.1 M KOH. As shown in Fig. 5a, the relative current density of $\text{Co}_3\text{O}_4/\text{C}$ decreases to 81.2% after 12 h test, while that of $\text{Mn}_3\text{O}_4/\text{C}$ decreases even more and only remains 62.4%. Whereas, the relative current density of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ only decreases 1.4% after 12 h test, showing much better stability than $\text{Co}_3\text{O}_4/\text{C}$, $\text{Mn}_3\text{O}_4/\text{C}$ and commercial Pt/C (decreasing 12% only after 20000 s test) (Fig. S5). Constructing of bimetallic oxide greatly improves the long-term durability, which may be directly attributed to the ascending of

valence state of Mn and the formation of new metal-ion redox couples [25].

To further investigate the performance of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ catalyst in practical application, the primary Zn-air batteries were constructed using a polished zinc plate as the anode and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ or Pt/C catalyst as the air cathode. As shown in Figure 5b, although the voltage drop of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ catalyst is larger than that of Pt/C, the initial galvanostatic discharge voltage with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ catalyst is ~ 1.3 V, which is a little higher than that with the benchmark Pt/C (~ 1.2 V). As displayed in the polarization and corresponding power density curves (Fig. 5c), the peak discharge power density with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ catalyst is 173 mW cm^{-2} at 276.7 mA cm^{-2} , superior to those with Pt/C catalyst (142 mW cm^{-2} at 198.3 mA cm^{-2}), indicating an excellent performance as a cathode catalyst in Zn-air battery and a potential for future application.

Fig. 5. (a) Chronoamperometric responses of $\text{Mn}_3\text{O}_4/\text{C}$, $\text{Co}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ under 1600 rpm at 0.46 V vs RHE in O_2 -saturated 0.1 M KOH. (b) Galvanostatic discharge curves (inset: photograph of assembled Zn-air battery) and (c) polarization and corresponding power density curves of primary Zn-air batteries using $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ and Pt/C as the cathode catalyst.

All the above results indicate that $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ catalyst exhibits remarkable enhancement of ORR activity and stability, and is one of the most effective and stable manganese-cobalt oxide electrocatalysts for ORR compared with the reported ones listed in Table S3.

3.3. Essential reasons for enhancement of activity

In order to explore the essential reasons for the enhancement of activity of spinel manganese-cobalt oxides, XPS measurement was performed to analyze the differences in surface electronic structures of prepared catalysts. As Mn in manganese-cobalt oxides has been identified as an active site for ORR [38] and the initial activity of $\text{Mn}_3\text{O}_4/\text{C}$ is better than that of $\text{Co}_3\text{O}_4/\text{C}$ in the kinetic region as shown in Fig. 3a, only the differences in Mn electronic states of $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ were investigated.

XPS spectra of $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ are shown in Fig. 6, which all have been calibrated by using the carbon peak at 284.8 eV (Fig. S6). As shown in Mn 2p spectra (Fig. 6a), there are two peaks at 642.1 eV and 653.7 eV and the space between two peaks is about 11.6 eV corresponded to Mn 2p spin-orbital splits $2p_{3/2}$ and $2p_{1/2}$, which are the characteristic peaks of Mn_3O_4 [39,40]. Compared with $\text{Mn}_3\text{O}_4/\text{C}$, the two peaks of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ shift toward higher binding energy, indicating the presence of more Mn cations with the high valence state in bimetallic oxides. The deconvoluted Mn 2p spectra can be fitted with three pairs of spin-orbit triplet peaks, representing the oxidation states of Mn^{2+} , Mn^{3+} and Mn^{4+} , respectively [30,41]. However, the differences among the oxidation states of Mn^{2+} , Mn^{3+} and Mn^{4+} are very little and difficult to distinguish, hence the further differentiation-imitating analysis will engender fairly great errors. Fortunately, Mn 3s orbital can split into two peaks due to the coupling between the nonionizing electron and valence electron. And the space between the two peaks (ΔE) in Mn 3s spectra is sensitive to the variation of the oxidation state of Mn, which can be utilized to identify the exact valence state of Mn in the oxides [40,42,43]. As shown in Figure 6b, the energy separation of Mn 3s for $\text{Mn}_3\text{O}_4/\text{C}$ is 5.55 eV, indicating that the Mn oxidation state is 2–3, and Mn exists as a mixture of Mn^{2+} and Mn^{3+} . Whereas, the energy separation for $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ is 4.95 eV, which significantly decreases com-

pared with $\text{Mn}_3\text{O}_4/\text{C}$, implying the ascending of valence state of Mn and the presence of Mn^{3+} and Mn^{4+} in the bimetallic oxide. Mn^{4+} cations derive from partial electron transfer between Mn^{3+} and Co^{3+} in the octahedral sites, namely, $\text{Mn}^{3+} + \text{Co}^{3+} \rightarrow \text{Mn}^{4+} + \text{Co}^{2+}$ [44,45]. As shown in Fig. S7, Co $2p_{1/2}$ of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ shifts toward lower binding energy compared with that of Co_3O_4 , indicating the decrease in valence of Co, which is consistent with the results of Mn 2p and 3s spectra. Mn cations with high valence states, especially the mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence states, are more beneficial for ORR, hence $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ exhibits enhancement of ORR activity compared with $\text{Mn}_3\text{O}_4/\text{C}$. And the high stability of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ could also be ascribed to the intrinsic Mn cations with high valence state, as well as Mn^{4+} generated during the process of testing.

4. Conclusions

In summary, we provide a facile and low-temperature precipitation-dehydration method to fabricate homogeneously dispersed and ultrasmall nanocrystalline $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ hybrids. And the bimetallic composite oxide ($\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$) hybrid, which possesses ultrasmall particle size (~ 5 nm), cubic spinel structure and high Mn content, exhibits remarkable enhancement of activity and stability for ORR compared with single metal oxide (both $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Co}_3\text{O}_4/\text{C}$). In addition, $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ displays an excellent discharge performance in the Zn-air battery as a cathode catalyst. We also explore the differences in Mn electronic states of $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ and conclude that the enhancement of ORR activity of manganese-cobalt bimetallic oxides can be ascribed to the presence of the mixed Mn^{3+} and Mn^{4+} cations.

Supporting Information

The energy-dispersive spectroscopy (EDS) and XPS survey spectrum of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$; ORR polarization curves of VXC-72R C at different rotating speeds; chronoamperometric response of Pt/C; C 1s XPS spectra of $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$; Mn/Co atomic ratio of $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ characterized by TEM and XPS; ORR activities of $\text{Mn}_x\text{Co}_{3-x}\text{O}_4/\text{C}$ ($x = 0, 1.5, 3$) and Pt/C catalysts; comparison of ORR activities with the reported $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ catalysts in alkaline media.

Fig. 6. XPS spectra of $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$: (a) Mn 2p and (b) Mn 3s.

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Graphical Abstract

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Low-temperature synthesis of ultrasmall spinel $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ nanoparticles for efficient oxygen reduction

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Supported ultrasmall spinel manganese-cobalt oxide nanoparticles prepared at low temperature (60 °C) exhibit excellent ORR activity and stability compared with single metal oxide (both $\text{Mn}_3\text{O}_4/\text{C}$ and $\text{Co}_3\text{O}_4/\text{C}$).

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超细尖晶石 $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ 颗粒低温合成及氧还原催化性能

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摘要: 尖晶石型锰钴氧化物($\text{Mn}_x\text{Co}_{3-x}\text{O}_4$)被认为是一类重要的氧还原反应(ORR)电催化剂。除了传统的高温固态合成方法, $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ 通常是通过前驱体在氨水中氧化-沉淀, 再在高温(150–180 °C)下晶化而合成的。高温合成方法不仅增加了能源消耗, 还会导致氧化物纳米颗粒的生长。与较大颗粒的金属氧化物相比, 金属氧化物超细纳米颗粒不仅可以降低扩散阻力, 而且具有更大的比表面积, 从而暴露出更多的活性位点, 更有利于ORR的进行。因此, 开发一种用于制备尖晶石型锰钴氧化物超细纳米颗粒的简便、低温合成方法是非常必要的。

本文通过一种简单的低温沉淀-脱水方法, 成功地合成了导电炭黑负载的尖晶石锰钴氧化物超细纳米颗粒($\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$)。采用X射线衍射(XRD)、拉曼光谱(Raman)、透射电子显微镜(TEM)、X射线光电子能谱(XPS)等表征手段研究了所制备尖晶石氧化物的结构和形貌, 通过电催化反应及表征测试了氧化物的ORR催化性能, 并探究了双金属催化剂 $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ 活性提升的本质原因。

TEM图显示 $\text{Mn}_x\text{Co}_{3-x}\text{O}_4$ 氧化物纳米颗粒均匀分布在导电炭黑载体上, 并且颗粒尺寸(~5 nm)较小。高分辨透射电子显微镜(HRTEM)图中有明显的晶格条纹和多晶衍射环, 表明氧化物纳米颗粒具有较好的结晶性。XRD表征结果表明, 双金属氧化物 $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ 具有立方尖晶石结构; 并且与纯 Co_3O_4 相比, $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ 的衍射峰略向小角度偏移, 表明较大尺寸的Mn阳离子掺入立方 Co_3O_4 晶格中。分别采用TEM-EDS(能谱)和XPS测得的Mn/Co原子比都接近1, 与投料比及文献中 $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ 金属原子比一致。以上结果说明通过这种简便的一步法可以成功制得组分可控的尖晶石锰钴氧化物。

电催化测试表明, 相比于单金属 $\text{Mn}_3\text{O}_4/\text{C}$ 和 $\text{Co}_3\text{O}_4/\text{C}$, 复合双金属催化剂 $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ 的ORR活性和稳定性均显著增强。此外, $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ 的ORR活性与商业化的20 wt% Pt/C相当, 并且12 h后其相对电流密度仅降低1.4%, 稳定性超过了Pt/C和大多数已报道的锰钴氧化物电催化剂。此外, $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ 作为阴极催化剂在锌空气电池中表现出优异的放电性能。我们还通过XPS研究了 $\text{Mn}_3\text{O}_4/\text{C}$ 和 $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4/\text{C}$ 中Mn电子态的差异, 并推断锰钴双金属氧化物ORR活性和稳定性的增强可归因于高价态的Mn阳离子, 特别是 Mn^{3+} 和 Mn^{4+} 混合态阳离子的存在。

关键词: 氧还原反应; 尖晶石 $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$; 低温; 沉淀-脱水方法; 超细纳米颗粒

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