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Article

Co₃O₄ supported on N, P-doped carbon as a bifunctional electrocatalyst for oxygen reduction and evolution reactions

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ABSTRACT

Noble metals, such as platinum, ruthenium and iridium-group metals, are often used as oxygen reduction or evolution reaction (ORR/OER) electrocatalysts. To reduce the cost and provide an application of bifunctional catalysis, in this work, cobalt oxide supported on nitrogen and phosphorus co-doped carbon (Co₃O₄/NPC) was fabricated and examined as a bifunctional electrocatalyst for OER and ORR. To prepare Co₃O₄/NPC, NPC was pyrolyzed from melamine and phytic acid supported on carbon, followed by the solvothermal synthesis of Co₃O₄ on NPC. Linear sweep voltammetry was used to evaluate the activity for OER and ORR. For OER, Co₃O₄/NPC showed an onset potential of 0.54 V (versus the saturated calomel electrode) and a current density of 21.95 mA/cm² at 0.80 V, which was better than both Co₃O₄/C and NPC. The high activity of Co₃O₄/NPC was attributed to a synergistic effect of the N, P co-dopants and Co₃O₄. For ORR, Co₃O₄/NPC exhibited an activity close to commercial Pt/C in terms of the diffusion limited current density (−4.49 vs −4.76 mA/cm² at −0.80 V), and Co₃O₄ played the key role for the catalysis. Chronoamperometry (current versus time) was used to evaluate the stability, which showed that Co₃O₄/NPC maintained 46% current after the chronoamperometry test for OER and 95% current for ORR. Overall, Co₃O₄/NPC exhibited high activity and improved stability for both OER and ORR.

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1. Introduction

Metal-air batteries have attracted considerable interest because of their many advantages, such as environmental friendliness, high conversion efficiency, quick start-up and high energy density. However, improvements in the cathode catalysts are still the challenge for their application [1]. Bifunctional catalysts play key roles in metal-air batteries for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Platinum and its alloys are often used as mono-functional cata-

lysts for ORR [2–6]. Ruthenium or iridium-group metals remain the best known catalysts for OER but show poor performance for ORR [7,8]. Therefore, a cheap and bifunctional catalyst should be developed to meet the application.

Heteroatom-doped carbon has been much studied for ORR. The introduction of a heteroatom changes the local charge density as well as asymmetry spin density of the carbon lattice, which creates catalytic sites for ORR [9–20]. Doped carbon has been explored as a bifunctional oxygen catalyst. Zhang et al. [21], Li et al. [22] and Ma et al. [23], respectively, explored ni-

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trogen and phosphorus co-doped carbon as a bifunctional oxygen catalyst. With N, P co-doped carbon, OER is facilitated by N, P co-doped graphene, and the active site for ORR is the N dopant and it is enhanced by the P dopant [21,22].

Efforts to obtain bifunctional catalysts have resulted in cobalt-based catalysts supported on heteroatom-doped carbon. The cobalt-based catalysts have variable valence states for ORR and OER, but are hindered by a low electrical conductivity, which can be improved by its being hybridized with heteroatom-doped carbon. Liang et al. [24] designed Co_3O_4 hybridized with N-doped reduced graphene oxide (rGO) as a bifunctional oxygen catalyst, in which the N species enhanced ORR activity and Co_3O_4 catalyzed OER. Cobalt and N-doped carbon nanotubes showed high performance in a wide pH range for ORR and OER because of the combination of the embedded structure and doped nitrogen [25]. Co_3O_4 on N-doped carbon nanoweb has a large specific surface area and abundant active sites for catalyzing ORR and OER [26]. MnCo_2O_4 hybridized with N-rGO exhibited enhanced ORR reactivity [27,28]. Liang et al. [27] demonstrated that the substitution of Co^{3+} sites by Mn^{3+} increased the ORR reactivity compared with the pure Co_3O_4 , but decreased the OER activity, which was attributed to Co^{2+} as the active sites for ORR [29] and Co^{3+} for OER [27]. NiCo_2S_4 supported on N- and S-doped rGO has high ORR activity because of a synergistic effect. The doped rGO served as a synergist while NiCo_2S_4 was critical for OER reactivity [30]. CoFe_2O_4 supported on N- and S-doped rGO has enhanced activity for ORR and OER because of a similar synergistic effect [31]. Jin et al. [32] developed a one-pot method to prepare cobalt-cobalt oxide/N-doped carbon hybrids for OER, which showed excellent activity because of the variable valence states of cobalt, carbon-encapsulated structure and nitrogen dopant.

There are still few studies on cobalt-based catalyst supported on N, P co-doped carbon. Here, Co_3O_4 supported on N, P co-doped carbon ($\text{Co}_3\text{O}_4/\text{NPC}$) was fabricated as a bifunctional catalyst for ORR and OER. $\text{Co}_3\text{O}_4/\text{NPC}$ was prepared by two steps. First, NPC was pyrolyzed from melamine and phytic acid supported on carbon particles. Then $\text{Co}_3\text{O}_4/\text{NPC}$ was synthesized by the solvothermal method followed by oxidization in air. The activity of $\text{Co}_3\text{O}_4/\text{NPC}$ for OER was enhanced due to a synergistic effect between Co_3O_4 and NPC, and the stability was improved mainly by Co_3O_4 . For ORR, even though the activity was enhanced by the P dopant in NPC, the N, P co-dopants have little effect on the activity of $\text{Co}_3\text{O}_4/\text{NPC}$ and Co_3O_4 played the key role. Because of its overall oxygen electrode activity and stability, $\text{Co}_3\text{O}_4/\text{NPC}$ will be useful as a bifunctional electrocatalyst for OER and ORR.

2. Experimental

2.1. Catalyst preparation

To prepare NPC, 0.55 g melamine, 0.2 g Vulcan XC-72, 32 mL deionized water and 4 mL formaldehyde solution (37%) were heated and stirred at 70 °C for 5 min to form a homogeneous ink. Then phytic acid amine solution, which contained 2 mL phytic acid solution (50%), 8 mL deionized water and 2.5 mL

ammonia solution (25%) was added and the solution was stirred for another 10 min. The mixture was transferred into a 100 mL autoclave and heated at 160 °C for 4 h with a heating rate of 10 °C/min. After cooling, the powder was collected by filtration, washed, and dried. The dried powder was heated at 750 °C for 1.5 h under Ar. N-doped carbon (NC) was prepared without phytic acid amine solution and the other conditions were the same.

To prepare $\text{Co}_3\text{O}_4/\text{NPC}$, 0.09 mmol $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and 0.18 mmol urea were added into 10 mL ethylene glycol solution under continuous magnetic stirring. After the metal salt was dissolved, 0.075 g NPC was added and stirring continued for 30 min to form a homogeneous suspension. The mixture was transferred to a 25 mL autoclave and heated at 180 °C for 4 h. After cooling, the product was collected by centrifugation, washed with deionized water and dried overnight. The product was calcined in air at 350 °C for 2 h. $\text{Co}_3\text{O}_4/\text{C}$ was prepared using Vulcan XC-72 as the support instead of NPC.

Pt/C (20 wt% Pt on Vulcan XC72) was purchased from Sigma-Aldrich.

2.2. Sample characterization

The sample was pressed into a powder for X-ray diffraction (XRD) detection on a Rigaku UltimaIV X diffractometer using nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm). Transmission electron microscope (TEM) images were taken by a Tecnai G2 F20 microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250Xi with a monochromatic Al X-ray source.

2.3. Electrochemical measurements

All electrochemical tests were carried out on a Princeton Parstat 2273 electrochemical work station with a three-electrode cell. A platinum wire was employed for the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. A glassy carbon electrode (5 mm in diameter) coated with catalyst was used as the working electrode and as the rotating disk electrode. The working electrode was modified with the catalyst by dropping catalyst ink on the glassy carbon surface. The catalyst ink consisted of 1.31 mg of catalyst, 0.9 mL deionized water and 0.1 mL Nafion solution (5 wt%) mixed by sonication. The catalyst ink (0.015 mL) was added dropwise onto the glassy carbon surface. The catalyst loading was about 0.1 mg/cm².

Cyclic voltammetry (CV) experiments were done with a scan rate of 50 mV/s in N_2 or O_2 -saturated KOH solution (0.1 mol/L). Linear sweep voltammetry (LSV) experiments with a rotating disk electrode were carried out with a scan rate of 10 mV/s at various rotating rates in O_2 -saturated KOH (0.1 mol/L). The stability of the samples was evaluated by chronoamperometry (current versus time) in O_2 -saturated KOH (0.1 mol/L). Electrochemical impedance spectra (EIS) were recorded in the frequency range from 100 kHz to 10 mHz with an AC signal amplitude of 5 mV. To ensure O_2 saturation, the gas was bubbled into the electrolyte prior to the start of each experiment and

maintained over the electrolyte during each measurement.

3. Results and discussion

3.1. Synthesis and characterization

The preparation of Co_3O_4 supported on NPC is shown in Fig. 1. Initially, melamine (M) was reacted with formaldehyde (F) to form M-F, followed by adding phytic acid (PA) solution. Then the mixture was heated to 160 °C for 4 h for the cross-linking of M-F and the esterification of M-F and PA in the presence of the carbon nanoparticles (C) to form $(\text{M-F-PA})_n\text{-C}$, in which C was covered by $(\text{M-F-PA})_n$. To obtain NPC, $(\text{M-F-PA})_n\text{-C}$ was pyrolyzed at 750 °C for 1.5 h under Ar. Co_3O_4 was synthesized by the solvothermal method followed by oxidization in air at 350 °C.

XRD patterns shown in Fig. 2 revealed the crystalline structure of $\text{Co}_3\text{O}_4/\text{C}$, NPC and $\text{Co}_3\text{O}_4/\text{NPC}$. The diffraction peak at $2\theta = 24.6^\circ$ originated from the (002) plane of carbon. The peaks at $2\theta = 18.8^\circ, 31.1^\circ, 36.6^\circ, 44.6^\circ, 59.0^\circ$ and 65.0° corresponded to the (111), (220), (311), (400), (511) and (440) planes of crystalline Co_3O_4 in $\text{Co}_3\text{O}_4/\text{C}$, respectively. They are less well defined in $\text{Co}_3\text{O}_4/\text{NPC}$. The TEM images of these samples revealed that some nanoparticles and nanorods grew on the carbon powder (Fig. 3).

The composition of $\text{Co}_3\text{O}_4/\text{NPC}$ was investigated by XPS to reveal the valence state of the elements in the near surface region, as shown in Fig. 4(a). XPS revealed 84.8 at% C, 10.9 at% O, 2.1 at% Co, 1.2 at% N and 0.9 at% P in $\text{Co}_3\text{O}_4/\text{NPC}$. In the Co 2p spectra in Fig. 4(b), the Co $2p_{3/2}$ and Co $2p_{1/2}$ doublets were located at 781 and 797 eV, respectively. The peaks at 781.7 and 796.4 eV were assigned to Co^{3+} , and the peaks at 782.9 and 797.9 eV were assigned to Co^{2+} . The satellite peaks at 786 and 803 eV were two shake-up peaks of Co at the high binding energy side of the Co $2p_{3/2}$ and Co $2p_{1/2}$ edge, which indicated the presence of Co^{2+} or Co^{3+} in the sample [31,33]. The peak of N 1s (Fig. 4(c)) with a binding energy at 400 eV was deconvoluted into three peaks, revealing the presence of three types of nitrogen, pyridinic N (398.8 eV), pyrrolic N (399.9 eV) and graphitic N (400.6 eV). The high resolution P 2p spectrum (Fig. 4(d)) was also deconvoluted into three peaks, which were assigned to P–O (134.4 eV), P–N (133.7 eV) and P–C (133.1 eV) [19,23].

Fig. 2. XRD patterns of $\text{Co}_3\text{O}_4/\text{C}$, NPC and $\text{Co}_3\text{O}_4/\text{NPC}$.

Fig. 3. TEM images of $\text{Co}_3\text{O}_4/\text{C}$ (a) and $\text{Co}_3\text{O}_4/\text{NPC}$ (b).

3.2. Electrochemical measurements

To investigate the catalytic activity for OER, linear sweep voltammetry was carried out at a rotating rate of 1600 r/min in O_2 -saturated KOH solution (0.1 mol/L) for $\text{Co}_3\text{O}_4/\text{C}$, NPC and $\text{Co}_3\text{O}_4/\text{NPC}$ (Fig. 5(a)). The OER reactivity over the samples was evaluated by the onset potential and current density. Other samples, including single N-doped carbon (NC) and commercial 20 wt% Pt/C, were also examined for comparison. NC only showed a plateau in the tested potential range. By contrast, the onset potential of NPC occurred at 0.66 V (vs SCE) and the current density reached 8.17 mA/cm^2 at 0.80 V. These results demonstrated that the N-dopant has little activity and the N, P co-dopants were critical for OER, which was in agreement with other reported work [21,22]. $\text{Co}_3\text{O}_4/\text{C}$ was more active than NPC, which was evident from the lower onset potential (0.57 V)

Fig. 1. Schematic of the preparation of $\text{Co}_3\text{O}_4/\text{NPC}$.

Fig. 4. (a) XPS spectrum of $\text{Co}_3\text{O}_4/\text{NPC}$; (b) High resolution Co 2p spectra; (c) High resolution N 1s spectra; (d) High resolution P 2p spectra.

Fig. 5. (a) Comparison of OER reactivity over the various samples by LSV in O_2 -saturated KOH (0.1 mol/L) with a sweep rate of 10 mV/s at 1600 r/min; (b) Tafel plots of $\text{Co}_3\text{O}_4/\text{C}$, NPC and $\text{Co}_3\text{O}_4/\text{NPC}$ for OER; (c) Electrochemical impedance spectra at the operating potential to deliver 2 mA/cm^2 current density for OER ($E_i = 2$); (d) Percentage of current retained versus operation time at $E = 0.55$ V in O_2 -saturated KOH (0.1 mol/L) at 1600 r/min.

and higher current density (11.04 mA/cm^2 at 0.80 V). $\text{Co}_3\text{O}_4/\text{NPC}$ showed the highest activity of all the samples with

an onset potential of 0.54 V and current density of 21.95 mA/cm^2 at 0.80 V. The improved OER reactivity of $\text{Co}_3\text{O}_4/\text{NPC}$

was further confirmed by the Tafel slope of 93 mV/dec at a low overpotential (Fig. 5(b)), while that of NPC was 104 mV/dec and $\text{Co}_3\text{O}_4/\text{C}$ was 132 mV/dec. Because Co_3O_4 supported on N-doped carbon has little improving effect on OER [24], the high activity of $\text{Co}_3\text{O}_4/\text{NPC}$ was attributed to the synergistic effect of Co_3O_4 and N, P co-dopants.

The charge transfer of the samples was compared by the electrochemical impedance spectra (EIS). As shown in Fig. 5(c), the smallest diameter of the semicircle in the Nyquist plot of $\text{Co}_3\text{O}_4/\text{NPC}$ suggested that $\text{Co}_3\text{O}_4/\text{NPC}$ had the lowest charge transfer resistance during OER. The stability of these three samples was compared by chronoamperometry (current versus time) at a rotating rate of 1600 r/min in O_2 -saturated KOH for OER. As shown in Fig. 5(d), the percentage of the remaining current dropped to 21% for NPC after 6 h, to 79% for $\text{Co}_3\text{O}_4/\text{C}$ and to 46% for $\text{Co}_3\text{O}_4/\text{NPC}$. Hence, the surface N, P co-dopants were unstable for OER but were improved by being hybridized with Co_3O_4 . In addition, the active site for OER may be related to Co_3O_4 in $\text{Co}_3\text{O}_4/\text{NPC}$, which was shown by the similar remaining current of $\text{Co}_3\text{O}_4/\text{NPC}$ (1.10 mA/cm²) and $\text{Co}_3\text{O}_4/\text{C}$ (1.04 mA/cm²) after this test.

To investigate the electrocatalytic properties for ORR, cyclic voltammetry (CV) was first carried out in N_2 and O_2 -saturated KOH solution (0.1 mol/L) (Fig. 6(a)). The CV showed well-defined ORR peaks at ~ 0.3 for all samples. The catalytic activity of the samples was further examined by LSV at a rotating rate of

1600 r/min in O_2 -saturated KOH solution (0.1 mol/L) (Fig. 6(b)). NC showed a plateau of limited diffusion current density when E was more negative than -0.45 V. For NPC, the current density began to increase at -0.48 V and reached -4.43 mA/cm² at -0.80 V. Hence, doped N was critical for ORR and the catalytic activity was enhanced by doped P at negative potential. To further improve the activity, Co_3O_4 was synthesized directly on NPC. For comparison, $\text{Co}_3\text{O}_4/\text{NPC}$ showed a close ORR catalytic activity (onset potential of -0.18 V, current density of -4.49 mA/cm² at -0.80 V) to commercial 20 wt% Pt/C (-0.10 V, -4.76 mA/cm²) for ORR. As for $\text{Co}_3\text{O}_4/\text{NPC}$, unexpectedly, there was a negative shift for the current plateau in contrast with $\text{Co}_3\text{O}_4/\text{C}$, which suggested the N, P co-dopants gave a small disadvantage for ORR. The catalytic stability was tested by chronoamperometry (current vs time). As shown in Fig. 6(c), the current of $\text{Co}_3\text{O}_4/\text{NPC}$ remained at 95% after 6 h, which was higher than NPC (75%) and similar to $\text{Co}_3\text{O}_4/\text{C}$ (92%). Methanol was added into the electrolyte at the beginning of the chronoamperometry to compare the resistance. As shown in Fig. 6(g), after adding methanol, the remaining current of Pt/C dropped to 20 % immediately, but with $\text{Co}_3\text{O}_4/\text{NPC}$, it remained at 100%. These results suggested that $\text{Co}_3\text{O}_4/\text{NPC}$ outperformed Pt/C in term of resistance to methanol. In summary, it was found that even though ORR was catalyzed by the N, P co-dopants in NPC, the N, P co-dopants gave little advantageous effect for the activity and Co_3O_4 played the

Fig. 6. (a) CV curves of $\text{Co}_3\text{O}_4/\text{C}$, NPC and $\text{Co}_3\text{O}_4/\text{NPC}$ in O_2 -saturated (solid line) and N_2 -saturated (dash line) in KOH solution (0.1 mol/L); (b) LSV curves of samples on the working electrode in O_2 -saturated KOH (0.1 mol/L) with a sweep rate of 10 mV/s at 1600 r/min; (c) LSV curves of $\text{Co}_3\text{O}_4/\text{NPC}$ at different rotation rates in O_2 -saturated KOH (0.1 mol/L); (d) Chronoamperometry (current vs time) at a rotating rate of 1600 r/min in O_2 -saturated KOH for OER. As shown in Fig. 5(d), the percentage of the remaining current dropped to 21% for NPC after 6 h, to 79% for $\text{Co}_3\text{O}_4/\text{C}$ and to 46% for $\text{Co}_3\text{O}_4/\text{NPC}$. Hence, the surface N, P co-dopants were unstable for OER but were improved by being hybridized with Co_3O_4 . In addition, the active site for OER may be related to Co_3O_4 in $\text{Co}_3\text{O}_4/\text{NPC}$, which was shown by the similar remaining current of $\text{Co}_3\text{O}_4/\text{NPC}$ (1.10 mA/cm²) and $\text{Co}_3\text{O}_4/\text{C}$ (1.04 mA/cm²) after this test. To investigate the electrocatalytic properties for ORR, cyclic voltammetry (CV) was first carried out in N_2 and O_2 -saturated KOH solution (0.1 mol/L) (Fig. 6(a)). The CV showed well-defined ORR peaks at ~ 0.3 for all samples. The catalytic activity of the samples was further examined by LSV at a rotating rate of 1600 r/min in O_2 -saturated KOH solution (0.1 mol/L) (Fig. 6(b)). NC showed a plateau of limited diffusion current density when E was more negative than -0.45 V. For NPC, the current density began to increase at -0.48 V and reached -4.43 mA/cm² at -0.80 V. Hence, doped N was critical for ORR and the catalytic activity was enhanced by doped P at negative potential. To further improve the activity, Co_3O_4 was synthesized directly on NPC. For comparison, $\text{Co}_3\text{O}_4/\text{NPC}$ showed a close ORR catalytic activity (onset potential of -0.18 V, current density of -4.49 mA/cm² at -0.80 V) to commercial 20 wt% Pt/C (-0.10 V, -4.76 mA/cm²) for ORR. As for $\text{Co}_3\text{O}_4/\text{NPC}$, unexpectedly, there was a negative shift for the current plateau in contrast with $\text{Co}_3\text{O}_4/\text{C}$, which suggested the N, P co-dopants gave a small disadvantage for ORR. The catalytic stability was tested by chronoamperometry (current vs time). As shown in Fig. 6(c), the current of $\text{Co}_3\text{O}_4/\text{NPC}$ remained at 95% after 6 h, which was higher than NPC (75%) and similar to $\text{Co}_3\text{O}_4/\text{C}$ (92%). Methanol was added into the electrolyte at the beginning of the chronoamperometry to compare the resistance. As shown in Fig. 6(g), after adding methanol, the remaining current of Pt/C dropped to 20 % immediately, but with $\text{Co}_3\text{O}_4/\text{NPC}$, it remained at 100%. These results suggested that $\text{Co}_3\text{O}_4/\text{NPC}$ outperformed Pt/C in term of resistance to methanol. In summary, it was found that even though ORR was catalyzed by the N, P co-dopants in NPC, the N, P co-dopants gave little advantageous effect for the activity and Co_3O_4 played the

key role for ORR in Co₃O₄/NPC.

To further understand the ORR kinetics on Co₃O₄/NPC, LSV was carried out at a different rotating rate in O₂-saturated KOH solution (0.1 mol/L) (Fig. 6(d)). Koutecky-Levich plots (Fig. 6(e)) were generated from Fig. 6(d), which were used to investigate the ORR mechanism on Co₃O₄/NPC. The least squares-fitted slopes were used to calculate the number of electrons transferred (n) on the basis of the Koutecky Levich equation [34]:

$$j^{-1} = j_L^{-1} + j_K^{-1} = (B\omega^{1/2})^{-1} + j_K^{-1} \quad (1)$$

$$B = 0.2nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

$$j_K = nFkC_0 \quad (3)$$

where j is the measured current density, j_L and j_K are the diffusion and kinetic-limiting current density, ω is the angular velocity (r/min), n is the transfer electron number, C_0 is the bulk concentration of O₂ (1.2×10^{-6} mol/cm³), D_0 is the diffusion coefficient of O₂ (1.9×10^{-5} cm²/s), ν is the kinematic viscosity of the electrolyte (0.0113 cm²/s), F is the Faraday constant (96485000 mA s/mol), and k is the electron-transfer rate constant. The n of Co₃O₄/NPC was calculated to be from 3.66 to 3.76 at the indicated potentials (Fig. 6(e)). The n of Co₃O₄/C and NPC was obtained by the same method and the results are shown in Fig. 6(f). All samples favored a four-electron oxygen reduction pathway.

The overall oxygen electrode activity is usually evaluated by the difference of the OER and ORR metrics, ΔE ($\Delta E = E_{\text{OER}} - E_{\text{ORR}}$) [35]. E_{OER} is the operating potential to deliver 10 mA/cm² current density for OER, which is a critical metric for solar fuel synthesis [36]. E_{ORR} is the operating potential to deliver -1 mA/cm² current density for ORR. A smaller ΔE indicates a catalyst closer to an ideal reversible oxygen electrode. But ΔE is affected by the catalyst loading. Our experience is that $E_{j=10}$ can be shifted negatively and $E_{j=-1}$ can be shifted positively by increasing the catalyst loading on the working electrode. The overall activity for the samples was shown in Fig. 7. ΔE of Co₃O₄/C, NPC and Co₃O₄/NPC was 1.01, 1.12 and 0.89 V, respectively, with a catalyst loading of 0.1 mg/cm². Co₃O₄/NPC outperformed some noble-metals, such as RuO₂, IrO₂ and Pt/C (1.10, 1.32 and 0.94 V, respectively, with 0.21 mg/cm²) and was close to (or even outperformed) similar materials such as Co_xO_y/NC and Mn_xO_y/NC (0.86 and 0.87 V, respectively, with 0.21 mg/cm²) [35]. This overall activity of Co₃O₄/NPC suggested that Co₃O₄/NPC will be useful as a bifunctional electrocata-

Fig. 7. Overall LSV curves of Co₃O₄/C, NPC and Co₃O₄/NPC in O₂-saturated KOH (0.1 mol/L) with a sweep rate of 10 mV/s at 1600 r/min.

lyst for OER and ORR.

4. Conclusions

Co₃O₄ supported on N, P co-doped carbon (Co₃O₄/NPC) was prepared and examined as a bifunctional electrocatalyst for OER and ORR. For OER, N-doped carbon has little activity and the N, P co-dopants were critical for the catalysis by NPC. Co₃O₄/NPC showed higher activity than NPC or Co₃O₄/C for OER, which was due to a synergistic effect of the N, P co-dopants and Co₃O₄. The surface N, P co-dopants were unstable for OER but were improved by being hybridized with Co₃O₄, which is the active site for OER. For ORR, even though the N, P co-dopants exhibited catalytic activity, there was little improvement of Co₃O₄/NPC compared to Co₃O₄/C and Co₃O₄ played the key role for ORR. Co₃O₄/NPC exhibited an activity close to commercial Pt/C for ORR. Combining the advantages of Co₃O₄ and NPC, Co₃O₄/NPC showed improved stability and high overall oxygen electrode activity, and is anticipated would be a good bifunctional oxygen electrode for metal-air batteries.

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Graphical Abstract

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Co₃O₄ supported on N, P-doped carbon as a bifunctional electrocatalyst for oxygen reduction and evolution reactions

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Cobalt oxide supported on nitrogen and phosphorus co-doped carbon (Co₃O₄/NPC) was fabricated as a bifunctional electrocatalyst for the oxygen reduction and evolution reactions (ORR, OER), and gave improved OER performance.

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氧还原和析氧反应的双功能电催化剂——氮磷共掺碳负载四氧化三钴

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摘要: 金属-空气电池具备诸多优势, 譬如绿色环保、能量转化率高、启动快速、能量密度高、使用寿命和干态存储时间长等. 与燃料电池相比, 金属-空气电池结构简单, 放电电压平稳, 成本低, 但依然存在一些制约发展的问题, 如阴极催化剂. 阴极催化剂在金属-空气电池中发挥催化氧还原反应 (oxygen reduction reaction, ORR) 和析氧反应 (oxygen evolution reaction, OER) 的关键作用. 铂及其合金常用作 ORR 的单功能催化剂, 而钨和铱等是目前 OER 催化效率最高的, 但 ORR 活性很低, 因此需要开发出一种廉价而又具备双功能催化作用的催化剂.

单异原子掺杂的碳基催化剂的研究集中在 ORR 催化性能上, 而多异原子共掺碳最近有研究表明具有双催化氧的性质, 如氮磷共掺碳. 在这些氮磷共掺的碳架中, 氮磷共掺物起着 OER 催化作用, 掺氮物为 ORR 催化的活性位点, 而掺磷物起着强化作用. 异原子掺杂负载的钴基催化剂 (如掺氮还原氧化石墨烯载 Co_3O_4) 是近年来双功能催化剂研究的另一个热点. 钴基催化剂有着催化 ORR 和 OER 的多价价态, 然而其本身导电性能差, 这一缺陷可通过杂化石墨化碳来弥补, 石墨化碳有着优良的导电性能. 据我们所知, 目前仍没有关于氮磷共掺碳负载的 Co_3O_4 双催化氧的研究. 我们合成了氮磷共掺碳 (NPC) 负载的 Co_3O_4 ($\text{Co}_3\text{O}_4/\text{NPC}$), 并首次探索了其氧还原和析氧性能. $\text{Co}_3\text{O}_4/\text{NPC}$ 合成成分两步进行. 首先通过三聚氰胺与植酸之间的酯化或缩聚覆盖在导电炭黑颗粒表面, 在保护气氛下焙烧得到 NPC, 然后经溶剂热反应以及空气中氧化合成 $\text{Co}_3\text{O}_4/\text{NPC}$.

催化剂的性能综合考虑了催化活性和稳定性两方面. 采用线性扫描伏安法评估了 OER 和 ORR 的催化活性. 对于 OER, $\text{Co}_3\text{O}_4/\text{NPC}$ 的起始电势是 0.54 V (以饱和甘汞电极为参比电极), 在 0.80 V 时电流密度达到 21.95 mA/cm^2 , 均优于 $\text{Co}_3\text{O}_4/\text{C}$ 和 NPC. $\text{Co}_3\text{O}_4/\text{NPC}$ 的高效 OER 催化可归因于氮磷共掺物与 Co_3O_4 之间的协同作用. 对于 ORR, $\text{Co}_3\text{O}_4/\text{NPC}$ 的

催化效率与商用 Pt/C 相近, 它们的扩散极限电流密度分别为 -4.49 和 -4.76 mA/cm^2 ($E = -0.80 \text{ V}$). 在 ORR 过程中, Co_3O_4 起到主要的催化作用. 采用计时电流 (电流-时间) 法评估了催化剂的稳定性. 经 6 h 测定, 对于 OER, $\text{Co}_3\text{O}_4/\text{NPC}$ 剩 46% 电流; 而对于 ORR, 剩 95% 电流. 整体而言, $\text{Co}_3\text{O}_4/\text{NPC}$ 在 OER 和 ORR 中都表现出高的催化效率以及良好的稳定性.

关键词: 阴极催化剂; 氧还原反应; 析氧反应; 掺杂碳; 钴

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