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Article

Phosphonate-derived nitrogen-doped cobalt phosphate/carbon nanotube hybrids as highly active oxygen reduction reaction electrocatalysts

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ARTICLE INFO

Article history:

Received 18 May 2019

Accepted 16 July 2019

Published 5 February 2020

Keywords:

Metal phosphonate

Metal phosphate

Carbon nanotubes

Oxygen reduction reaction

Electrocatalysis

ABSTRACT

The exploration of cost-effective non-noble-metal electrocatalysts is highly imperative to replace the state-of-the-art platinum-based catalysts for oxygen reduction reaction (ORR). Here, we prepared cobalt phosphonate-derived N-doped cobalt phosphate/carbon nanotube hybrids (CoPiC-N/CNTs) by hydrothermal treatment of N-containing cobalt phosphonate and oxidized carbon nanotubes (o-CNT) followed by high-temperature calcination under nitrogen atmosphere. The resultant CoPiC-N/CNT exhibits a superior electrocatalytic performance for the ORR in alkaline media, which is equal to the commercial Pt/C catalyst in the aspect of half-wave potential, onset potential and diffuse limiting current density. Furthermore, the excellent tolerance to methanol and strong durability outperform those of commercial Pt/C. It is found that cobalt phosphonate-derived N-doped cobalt phosphate and the *in-situ* formed graphitic carbons play key roles on the activity enhancement. Besides, introducing a suitable amount of CNTs enhances the electronic conductivity and further contributes to the improved ORR performance.

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1. Introduction

The excessive consumption of fossil fuels has led to increasing concerns about worldwide energy crisis and environmental pollution. The implement of high-efficiency and renewable energy storage and conversion techniques such as metal-air batteries and fuel cells offers an indispensable way for addressing these issues [1–3]. Oxygen reduction reaction (ORR) occurred at the cathode of fuel cells and the anode of metal-air batteries is the bottleneck of these techniques due to its sluggish kinetics [4–6]. Noble metal materials, such as Pt and its alloys, have been used as benchmark ORR catalysts to lower the activation energy and thus achieve considerable activity.

Nevertheless, their large-scale applications are limited because of their scarcity, high cost and easy deactivation by methanol and CO poisoning [7,8]. Hence, it is highly challenging but imperative to explore high-efficiency non-noble metal catalysts for ORR that could be readily used in metal-air batteries and fuel cells.

Composite materials integrating active species with N-doped carbon represent a system of alternative catalysts to Pt for ORR thanks to their high conductivity, good stability and considerable activity [9–11]. Co-based electrocatalysts and their composites have received much attention due to their low cost, earth abundance and superior ORR activity, such as Co-N_x/C, Co oxide/hydroxide, Co phosphide, Co-N/CNT and

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This work was supported by the National Natural Science Foundation of China (21421001, 21573115).

DOI: S1872-2067(19)63455-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 2, February 2020

Co₃O₄/GO [12–18]. Compared with other Co-based catalysts, Co phosphate has been extensively explored as a low-cost multifunctional material that can be applied in various fields such as supercapacitors and industrial catalysts [19,20]. Besides, its superior electrocatalytic performance for the OER in neutral solution has also been reported. The phosphate group was proven to not only act as the proton receptor to ensure the long-term stability of the catalyst system but also induce the distortion of the geometry structure of cobalt to facilitate the adsorption of water molecules and further promote the OER [21–24]. Subsequently, Co phosphate was also confirmed to show certain electrocatalytic performance for the ORR [25].

However, the inferior conductivity is not favorable for the charge transfer and transportation, thus leading to the low electrocatalytic activity. In this regards, integrating Co phosphate with conductive carbon is an effective solution. Besides, Co phosphate is unstable in the alkaline media, which greatly hinders its application for ORR. The further study is thus expected to develop a facile synthesis strategy for Co phosphate@carbon composite, wherein the carbons are evenly coated on Co phosphate to prevent the alkaline corrosion.

Metal phosphonates represent a system of hybrid materials consisting of metal cations bonded to organophosphonate ligands [26–29]. The simple calcination of metal phosphonates is an efficient way of preparing metal phosphates. Noticeably, the N-doped carbons can be *in-situ* produced and coated on Co phosphate during the pyrolysis process, further favoring the high conductivity and good catalytic performance [30]. Recently, Co₃(PO₄)₂, derived from cobalt phosphonate, was obtained for the preparation of an efficient ORR catalyst that comprised of N-doped cobalt phosphate supported on rGO [31]. However, the electrocatalytic activity is still not satisfactory compared to the noble metal catalysts.

Herein, cobalt phosphate/carbon nanotube composites (CoPiC-N/CNT) are fabricated via a facile hydrothermal treatment of cobalt phosphonate and carbon nanotube followed by high temperature calcination under inert atmosphere. When used as an ORR catalyst, CoPiC-N/CNT shows outstanding performance in terms of superb activity, favorable kinetics, and remarkable durability and resistance to methanol, even rivaling the precious Pt/C benchmark. It is found that the superior electrocatalytic performance stems from N-doped Co phosphate, the graphitic carbon layer and the carbon nanotube. The strategy developed in this work is believed to not only offer an efficient method to enrich the family of metal phosphate composites but also inspire the controllable design of more structures from metal phosphonates.

2. Experimental

2.1. preparation of cobalt phosphate/CNT composites

CNTs used in this work were prepared through a floating catalysis process by ethylene cracking on ceramic spheres. For the acid treatment of the CNTs, 1.0 g of CNTs were mixed with concentrated H₂SO₄ (98%, Sigma-Aldrich) and white fuming HNO₃ (Sigma-Aldrich) with a volume ratio of 3:1, and the solu-

tion was stirred at 100 °C for 6 h, followed by washing thoroughly with ethanol and deionized water. The resultant product was dried at 60 °C in air for use. For the preparation of cobalt phosphate/CNT composites, 1 mmol of ethylene diamine tetra(methylene phosphonic acid) sodium (EDTMPs) was dispersed into the mixture of 40 mL ethanol/water (volume ratio 1:1). After stirring for 1 h, a suitable amount of CNT was introduced into the above mixture, followed by the addition of cobalt (II) chloride hexahydrate (CoCl₂·6H₂O) (3 mmol) with stirring of 2 h. The solution was transferred into an autoclave and heated to 120 °C for 24 h. Then, the mixture was cooled down to room temperature, filtered and washed with deionized water and ethanol several times, and dried at 100 °C for 12 h. The resulting powder was carbonized in N₂ at 800 °C for 2 h with a heating rate of 5 °C min⁻¹. The obtained sample was denoted as CoPiC-N/CNT-*x*, wherein *x* represents the amount of CNT. For comparison, the sample without CNT adding was denoted as CoPiC-N. CoPiC was prepared with the same procedure as that of CoPiC-N except that EDTMPs was changed to 1-hydroxyethane-1,1-diphosphonic acid (HEDP). CoPi was prepared by using NaH₂PO₄·2H₂O to substitute EDTMPs in the absence of CNT.

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Focus diffractometer with operation voltage of 40 kV and current at 40 mA using Cu-K_α radiation ($\lambda = 0.15418$ nm). Scanning electron microscopy (SEM) was performed on a Jeol JSF-7500L microscope. Transmission electron microscopy (TEM) was carried out on a Jeol JEM-2100F microscope at 200 kV. X-ray photoelectron spectra (XPS) were obtained on a Kratos Axis Ultra DLD (delay line detector) spectrometer with Al-K_α as the X-ray source (1486.6 eV). Raman spectroscopy was performed on a Thermo-Fisher Scientific DXR spectrometer (514 nm radiation laser). N₂ adsorption-desorption isotherms were obtained on a Quantachrome NOVA 2000e automated surface area analyzer. Before the measurements, all the samples were outgassed at 200 °C overnight. Specific surface areas were calculated by the multipoint Brunauer-Emmett-Teller (BET) method using the data from adsorption branch.

2.3. Electrochemical measurements

Electrocatalytic ORR measurement was carried out in a three-electrode glass cell. The data were recorded using an electrochemical analysis station (Pine, USA). The reference electrode was Ag/AgCl, and Pt wire was used as the counter electrode. The working electrode was prepared as follows. 5 mg of the catalyst was dispersed ultrasonically in 1 mL of 1:1 (v/v) Milli-Q water/ethanol to obtain a homogenous dispersion. 10 μ L of the dispersion was drop casted onto a polished 5 mm-diameter glassy carbon electrode. After drying at room temperature overnight, 5 μ L of Nafion solutions (0.5 wt%) was dropped on the surface of electrode and allowed to dry. The resultant electrode served as a working electrode.

Before the ORR measurement, the electrolyte (0.1 M KOH)

was ventilated with O₂ for 30 min to ensure O₂ saturation. Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were measured at a scanning rate of 20 and 10 mV s⁻¹ within a potential range from 1.2 to 0 V (vs RHE), respectively.

Rotating ring-disk electrode (RRDE) measurements were carried out to determine the electron transfer number (*n*) and peroxide percentage (%HO₂⁻). RRDE contains a glassy carbon disk with a Pt ring of outer diameter (7.92 mm) and internal diameter (6.25 mm). The calculation is as follows:

$$x(\text{H}_2\text{O}_2) = \frac{2i_R/N}{i_D + i_R/N} \times 100\%$$

$$n = \frac{4i_D}{i_D + i_R/N}$$

wherein *i_D*, *i_R* and *N* denote the disk current, ring current and current collection efficiency, respectively.

3. Results and discussion

As is known, metal phosphonate is formed by the incorporation of organic moieties into the inorganic framework. The organic functional groups are homogeneously distributed in the framework, allowing the regulation of their physicochemical properties [32]. More importantly, metal phosphonate can convert to metal phosphate@carbon composite via thermal treatment under inert atmosphere. The synthetic strategy of cobalt phosphate/CNT composites is illustrated in Scheme 1. First, the as-purchased MWCNTs were mildly oxidized by concentrated acid according to the literature method [33]. Afterward, the freshly oxidized MWCNTs were mixed with the Co²⁺ and organic EDTMPS solution to afford cobalt phosphonate/CNT precursor. Note that the acid oxidation of MWCNTs can introduce abundant oxygen-containing functional groups on their surface [34], which could facilitate the interaction between cobalt phosphonate and CNTs because of the hydroxyl interaction with phosphoric sites. Cobalt phosphate/CNT

composites were finally obtained after heating the prepared cobalt phosphonate/CNT precursor under nitrogen atmosphere. During the pyrolysis process, the organic and inorganic components in the cobalt phosphonate can be converted into cobalt phosphate and N-doped carbon via calcination under N₂ atmosphere, leading to the formation of a carbon layer coated on cobalt phosphate [30,35]. The as-obtained sample is denoted as CoPiC-N/CNT-*x*, where *x* is the amount of CNT used. For comparison, the carbon-free catalyst CoPi was prepared by using CoCl₂·6H₂O and NaH₂PO₄·2H₂O as the precursors in the absence of CNT. The nitrogen-free catalyst CoPiC was prepared by using CoCl₂·6H₂O and HEDP as the precursors in the absence of CNT. The nitrogen-containing catalyst CoPiC-N was prepared with CoCl₂·6H₂O and EDTMPS as the precursors in the absence of CNT.

XRD patterns of all the samples were recorded (Fig. 1), displaying several diffraction peaks at 2θ = 42.9°, 35.5° and 29.8°. These peaks are consistent with those of cobalt diphosphate (Co₂P₂O₇, JCPDS 34-1378). The Raman spectroscopy was performed to further verify the structural properties of the materials. As shown in Fig. 2(a), all the samples present a band at 1040 cm⁻¹, associated with the symmetric stretching vibration of P₂O₇⁴⁻, which is in accordance with the XRD results. It is worth noting that, besides the P₂O₇⁴⁻, CoPiC sample shows typical *D* and *G* bands at 1342 and 1588 cm⁻¹, respectively. The *G* band originates from the E_{2g} vibration of sp²-hybridized graphitic carbon and the *D* band is designated to the edges, defects and disordered carbon sites [36]. It indicates the existence of graphitic carbon materials in CoPiC due to the transformation of phosphonate groups during pyrolysis. Similarly, there also exhibit graphitic carbon and P₂O₇⁴⁻ in both CoPiC-N and CoPiC-N/CNT-*x* samples. In addition, the intensity ratio of *D* and *G* bands (*I_D*/*I_G*) was measured to assess the degree of defects in the carbon. By using N-containing phosphonate, the *G* band of CoPiC-N shifts toward a higher wavenumber of 1582 cm⁻¹ to-

Scheme 1. Illustration of the fabrication of cobalt phosphate/CNT composites.

Fig. 1. The XRD patterns of the synthesized samples.

gether with the increased I_D/I_G ratio (1.42) compared with that of CoPiC (1.22), thus signifying the generation of more defect carbon due to the introduction of nitrogen atoms. Furthermore, the I_D/I_G ratio of CoPiC-N is higher than that of CoPiC-N/CNT-3 (1.30), demonstrating the increase of degree of graphitization after integrating with CNTs.

The generation of graphitic carbon in organophosphate-derived materials (CoPiC, CoPiC-N and CoPiC-N/CNT- x) can be verified by the high-resolution TEM (HRTEM) images. As revealed in Fig. S1, the hollow sphere-like graphitic carbon shell is clearly observed in CoPiC, providing the evidence that the carbon shell can be in-situ formed around cobalt phosphate particles. It may be favorable for the enhancement of stability and electron conductivity of the materials. Fig. 3 demonstrates the FESEM and TEM images of the materials. The FESEM images

show that CoPi possesses a plate-like morphology (Fig. 3(a)), while the CoPiC is consisted of numerous small particles (Fig. 3(b)). Fig. 3(c)–(e) clearly shows that cobalt phosphate and carbon nanotube have been evenly and tightly integrated. Carbon nanotubes own high electric conductivity and superior stability, which have been extensively used as electrode materials in various energy conversion and storage systems. Integrating the active species and CNT can pronouncedly improve the conductivity of catalyst, thus favoring the electron transport during electrocatalytic process and further promoting the electrocatalytic activity [37,38]. The HRTEM image (Fig. 3(f)) shows the lattices of 0.221 and ~ 0.343 nm, corresponding to $\text{Co}_2\text{P}_2\text{O}_7$ and C, respectively. This result is consistent with the XRD and Raman analysis. The element-mapping images (Fig. 3(g)) demonstrate that Co, P, C, N elements are homogeneously distributed in the CoPiC-N/CNT-3.

The composition and electronic structure of the materials were further explored by XPS measurements. Fig. S2(a) and Fig. S2(b)–(e) show the XPS survey scans and high-resolution XPS spectra of CoPiC and CoPiC-N, respectively. CoPiC-N material possesses Co, P, C, N and O elements, while there exhibit Co, P, C and O elements in the surface of CoPiC material. It identifies the N-containing phosphonate (EDTMP) has been completely converted to N-doping carbon shell. As shown in Fig. 2(b)–(f), the survey XPS spectra of CoPiC-N/CNT-3 and the corresponding fine XPS spectra indicate the presence of Co, P, C, N and O elements and the successful N-doping. Co $2p$ XPS spectrum of CoPiC-N/CNT-3 displays the binding energy of Co $2p_{3/2}$ and $2p_{1/2}$ peaks at 782.1 and 798.0 eV with the corresponding satellite peaks at 786.6 and 820.8 eV, respectively, indicating the presence of Co(II) in the hybrid material. The high-resolution P $2p$ XPS spectra demonstrate the presence of two types of P

Fig. 2. (a) Raman spectra of the synthesized samples; XPS survey spectrum (b) and Co $2p$ (c), P $2p$ (d), N $1s$ (e) and C $1s$ (f) of CoPiC-N/CNT-3.

Fig. 3. FESEM images of CoPi (a), CoPiC (b) and CoPiC-N/CNT-3 (c, d). TEM images (e, f) and the STEM-EDX mappings (g) of Co, P, C and N of CoPiC-N/CNT-3.

species, i.e., P-C (134.3 eV) and P-O (135.5 eV). The fine N 1s spectra centered at 401.1 and 398.5 eV indicate the existence of graphitic N and pyridinic N, respectively [39–41]. Deconvolution of C 1s spectra reveals the presence of C-C (284.7 eV), C-O-P (285.6 eV), C-O (286.7 eV), and O-C=O (287.6 eV). These results suggest that N-doped cobalt phosphate/CNT hybrid materials have been successfully prepared.

Fig. S3 shows the N₂ sorption isotherms of the synthesized materials. The surface area of CoPiC-N is 73 m² g⁻¹, which is slightly higher than that of CoPi (63 m² g⁻¹) and CoPiC (70 m² g⁻¹). Besides, the surface area slightly decreases to 45, 42 and 24 m² g⁻¹ for CoPiC-N/CNT-1, CoPiC-N/CNT-3 and CoPiC-N/CNT-5 when introducing CNT.

The electrocatalytic activity of the hybrid materials was first evaluated for cyclic voltammetry (CV) in 0.1 M KOH solution. As observed in Fig. 4(a) and (b), all the materials show obvious oxygen reduction peak in O₂-saturated solution. CoPiC possesses a more positive peak potential and larger peak area than those of CoPi, indicating the higher intrinsic activity of CoPiC for ORR due to the presence of graphitic carbons. The graphitic carbon shell can improve the stability and conductivity of the material and further contribute to the electrocatalytic activity. Similarly, the ORR activity of CoPiC-N is higher than that of CoPiC. This is because the N-doping can create more active sites. However, the performance is still inferior to that of CoPiC-N/CNT-3. The ORR cathodic peak of CoPiC-N/CNT-3 is 0.846 V, which is equal to that of Pt/C catalyst. This is an indication of synergistic interaction between the intrinsic ORR activity of cobalt phosphate and the superior electron transport proper-

ties of CNT. The observation is consistent with the LSV measurements (Fig. 4(c)). Specifically, the onset potential and half-wave potential of CoPiC is more positive than that of CoPi. In addition, CoPiC holds a large limiting current density in LSV, thus confirming the higher activity in comparison with CoPi. After being doped with nitrogen, CoPiC-N displays significant improvement with the onset potential of 0.84 V and half-wave potential of 0.66 V in comparison to CoPiC. CoPiC-N/CNT-3 shows the optimal performance with onset potential of 0.95 V and the half-wave potential of 0.85 V, which is the same as those of Pt/C catalyst. Moreover, the limiting current density is larger than that of Pt/C. The result shows that the introduction of CNT significantly improves the performance by favoring the formation of well-dispersed cobalt phosphate particles and higher electronic conductivity. The ORR activity of materials with different amount of CNTs has also been investigated. As shown in Fig. 4(c) and (d), the activity of CoPiC-N/CNT-3 outperforms CoPiC-N/CNT-1 and CoPiC-N/CNT-5 in the onset and half-wave potential and limiting current density, and is comparable to the previously reported ORR electrocatalysts (Table S1), revealing its remarkable ORR activity. It is crucial for introducing suitable amount of CNT into this catalyst system. However, the introduction of too much CNTs may induce the block of active sites, thus leading to the decrease in electrocatalytic activity.

Figs. 4(d) and S4 show the LSV curves of the catalysts with rotating rates ranging from 600 to 2500 rpm. It can be seen that the current density gradually increases with the increase of rotating speed, due to the enhanced diffusion rate at high

Fig. 4. CV curves (a, b) of the samples in O_2 -saturated 0.1 M KOH solution at a scan rate: 20 mV s^{-1} . (c) LSV curves of the samples and Pt/C in O_2 -saturated 0.1 M KOH solution (scan rate: 5 mV s^{-1} , rotating speed: 1600 rpm). (d) LSV curves of CoPiC-N/CNT-3 in O_2 -saturated 0.1 M KOH solution at various rotating speeds (scan rate: 5 mV s^{-1}). Transfer electron numbers (e) and H_2O_2 yields (f) of samples.

speeds. Notably, the LSV curves of both CoPi and CoPiC indicate an obvious $2e^-$ ORR pathway. As shown in Figs. 4(e) and (f), rotating ring-disk electrode (RRDE) measurements on the catalysts were performed to determine the ORR kinetics. CoPi show a highest H_2O_2 yield (above 25%) and the electron number is around 3.3, while these of CoPiC are above 20% and ~ 3.5 , respectively. It indicates that CoPiC has much higher selectivity compared with CoPi during the electrocatalytic process. The selectivity of CoPiC-N is better than CoPi and CoPiC, further proving the positive role of N-doping. The H_2O_2 yield of CoPiC-N/CNT-3 is below 7% over a large potential range of 0.2 to 0.8 V, offering an electron transfer number of ~ 4.0 . It suggests the predominance of a four-electron pathway for ORR on the catalyst. Besides, the introduction of lower CNT amount almost has no significant influence on the selectivity of catalyst, as evidenced by CoPiC-N/CNT-1 with H_2O_2 yield of $\sim 20\%$ and the electron number of ~ 3.6 . Nevertheless, the introduction of too much CNT also could not achieve optimal catalytic performance due to its blocking to the exposure of active sites. Compared with CoPiC-N/CNT-3, the CoPiC-N/CNT-5 shows poorer selectivity with H_2O_2 yield of $\sim 15\%$ and the electron number of ~ 3.7 .

Methanol tolerance capacity is of significant importance in direct methanol fuel cell. Therefore, the possible methanol crossover effect was investigated on both CoPiC-N/CNT-3 and Pt/C by a chronoamperometric method. Specifically, 3M methanol was quickly injected into the alkaline electrolyte at around 450 s. As shown in Fig. 5(a), the current density of CoPiC-N/CNT-3 shows almost no negligible change after adding methanol, indicating the strong resistance to methanol crossover, while the commercial Pt/C catalyst loses 30% of the initial current (Fig. S5(a)). As shown in Fig. 5(b), the LSV curves of CoPiC-N/CNT-3 show a strong durability with almost no no-

ticeable change before and after adding methanol. In contrast, the Pt/C catalyst shows an extinctive peak, attributing to the oxidation of methanol on the catalyst surface (Fig. S5(b)). Furthermore, the durability is a key parameter in practical applications of catalysts. We have examined the CV curves under continuous potentiodynamic sweeps in the scan rate of 50 mV s^{-1} . After 1000 and 2000 cycles the CV curves show negligible change compared with the initial one (Fig. 5(c)). Besides, after long-term operation for 36,000 s at 0.7 V, CoPiC-N/CNT-3 keeps 93% of the initial voltammetric current while commercial Pt/C suffers from a 21% current loss as depicted in Fig. 5(d), indicating a good stability of CoPiC-N/CNT-3.

The prominent electrocatalytic activity and durability of CoPiC-N/CNT-3 can be ascribed to several factors: (1) the synergistic interaction between cobalt phosphate particles and the oxidized CNT can efficiently enhance the ORR catalytic activity. Importantly, assembling CNTs with cobalt phosphate was an advisable choice to overcome the poor conductivity of cobalt phosphate; (2) the good dispersion of cobalt phosphate in the composite allows full utilization of active sites of the catalyst; (3) the N-doping can modulate the surface polarities and electronic properties, thus improving the activity of catalyst; (4) the presence of the graphitic carbon layer in the catalyst may improve the electron conductivity and stability of the hybrids, thus facilitating the fast electron transfer and protecting cobalt phosphate particles against corrosion during the ORR process.

4. Conclusions

We have developed a high-performance non-noble metal catalyst derived from phosphonate-based metal-organic framework for ORR through pyrolysis of cobalt phosphonate and oxidized CNTs. In comparison with the catalyst synthesized

Fig. 5. (a) The chronoamperometric response curve of CoPiC-N/CNT-3 in O_2 -saturated 0.1 M KOH solution after the instant addition of 3 M methanol. (b) LSV curves of CoPiC-N/CNT-3 before and after adding methanol in O_2 -saturated 0.1 M KOH at a scan rate of 10 mV s^{-1} at 1600 rpm. (c) CV curves under continuous potentiodynamic sweeps in O_2 -saturated 0.1 M KOH solution (scan rate: 50 mV s^{-1}). (d) The chronoamperometric response curves of CoPiC-N/CNT-3 and Pt/C at 0.7 V (rotating speed: 1600 rpm).

using inorganic phosphate as precursor, the phosphonate-derived CoPiC exhibits a graphitic carbon layer around Co nanoparticles, which endows this material with good stability and conductivity. Moreover, using N-containing organophosphonate as precursor, N-doped cobalt phosphate/carbon hybrids (CoPiC-N) can be gained and the ORR electrocatalytic activity can be significantly ameliorated in comparison with cobalt phosphate without N-doping (CoPiC). Besides, the catalytic activity can be further promoted with the introduction of suitable amount of CNTs. The optimal catalyst CoPiC-N/CNT-3 show identical activity and superior durability as well as methanol tolerance for the ORR against the commercial Pt/C catalyst in 0.1 M KOH solution. It is revealed that the N-doped graphitic carbon, cobalt diphosphate and CNT in the composite synergistically boost the ORR activity of the resultant catalysts. This work offers a novel strategy to fabricate cobalt phosphate/carbon composites from organophosphonate-based metal-organic framework as the electrocatalysts with high-efficiency and superior stability, and will further promote the relevant research on the field of renewable and clean energy.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21421001, 21573115).

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Graphical Abstract

Chin. J. Catal., 2020, 41: 259–267 doi: S1872-2067(19)63455-8

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Phosphonate-derived nitrogen-doped cobalt phosphate/carbon nanotube hybrids were synthesized by a facile hydrothermal treatment followed by high temperature calcination under inert atmosphere, exhibiting superior catalytic activity towards ORR in alkaline media.

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有机膦酸盐衍生的氮掺杂的磷酸钴/碳纳米管杂化材料作为高效氧还原电催化剂

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摘要: 随着环境污染和能源危机的日益严重, 探索高效的非贵金属氧还原电催化剂来替代商业Pt/C迫在眉睫。其中, 报道比较多的是具有钴基活性物种和氮掺杂碳的复合材料例如Co-N_x-C, Co₃O₄/GO, Co-N/CNT等, 该复合材料具有高导电性、良好的稳定性和优异的催化活性。与其他钴基催化剂相比, 磷酸钴由于其成本低廉, 对环境友好, 多功能的优良特性, 已被广泛应用于催化、吸附、分离及储能等领域, 在电催化方面也有极大的应用潜力。研究表明, 磷酸基团不仅可以充当质子受体, 也会诱导局部钴原子的几何结构发生扭曲, 从而有利于水分子的吸附并促进析氧反应的发生。此外, 磷酸钴也被证

实具有一定的氧还原活性。尽管磷酸钴电催化剂的研究已经取得了一定进展,磷酸根有利于质子传输,但是其导电性很差,不利于电荷的转移和传输,使得其电催化活性不高。将磷酸钴和导电碳材料复合是解决问题的有效方法。而且,磷酸钴在碱性溶液中并不稳定,极大限制了其在电催化氧还原中的应用。金属有机膦酸盐是一类包含金属离子和有机膦酸配体的杂化材料,通过简单的焙烧便可以很容易地得到金属无机膦酸盐,并且在焙烧过程中氮掺杂的碳也会原位产生,并包覆在磷酸钴的表面,使得其导电性和催化活性大大提高。为此,本研究组制备了有机膦酸钴衍生的磷酸钴和氮掺杂的石墨烯的复合材料并用于电催化氧还原和析氧反应,所得到的材料导电性和稳定性良好,然而,该催化剂的表观活性与商业Pt/C相比仍有较大差距,且使用有机膦酸钴作为前驱体对活性的影响也不甚清楚。因此,本文采用含氮的有机膦酸配体乙二胺四亚甲基膦酸钠(EDTMPs)为磷源制备了氮掺杂的磷酸钴/碳纳米管杂化材料(CoPiC-N/CNT-3),其催化活性和稳定性良好,并进一步探讨了各种不同因素对电催化活性的影响。

XRD和TEM结果表明,用这种方法得到的磷酸钴(CoPiC)为 $\text{Co}_2\text{P}_2\text{O}_7$ 物相,与磷酸二氢钠为磷源制备得到的CoPi相比,CoPiC的表面有石墨化碳层的存在,EDS图谱表明,Co, P, C, N均匀地掺杂到复合材料的骨架结构中。Raman光谱结果表明,石墨化碳层的存在和适量的碳纳米管的引入均可以增强复合材料的石墨化程度并提高了导电性,而氮掺杂导致其缺陷位点增多。XPS结果进一步表明,有机膦酸钴可以作为前驱体可制得氮掺杂的磷酸钴/碳纳米管杂化材料。电催化反应测试表明,CoPiC-N/CNT-3的氧还原活性与商业Pt/C相当,其遵循的是4电子的反应路径,而且抗甲醇氧化能力和稳定性均优于Pt/C。原因主要归结于以下几点:(1)磷酸钴颗粒与氧化碳纳米管的协同作用可以显著增强氧还原催化活性,引入的碳纳米管可以克服磷酸钴导电性差的缺陷;(2)磷酸钴在复合材料中分散均匀,使得可以充分利用催化剂的活性位点;(3)氮掺杂可以调变材料的电子结构,从而改善催化活性;(4)石墨化碳层的存在可以改善材料的电子导电性和稳定性,有利于电子转移并可以保护磷酸钴颗粒在催化氧还原反应过程中不被电解液腐蚀。可见,所制有机膦酸衍生的氮掺杂的磷酸钴/碳纳米管杂化材料有望替代Pt/C催化剂,并推动清洁可再生能源领域的相关研究。

关键词: 金属膦酸盐; 金属磷酸盐; 碳纳米管; 氧还原反应; 电催化剂

收稿日期: 2019-05-18. 接受日期: 2019-07-16. 出版日期: 2020-02-05.

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基金来源: 国家自然科学基金(21421001, 21573115).

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