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Article

CoNiP/NC polyhedrons derived from cobalt-based zeolitic imidazolate frameworks as an active electrocatalyst for oxygen evolution

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ABSTRACT

The oxygen evolution reaction (OER) plays an important role in the development of energy conversion and storage technologies including water splitting and metal-air batteries, where the development of electrocatalysts is paramount. In this study, cobalt-nickel phosphide/N-doped porous carbon polyhedron electrocatalysts (CoNiP/NC) were prepared by a facile two-step carbonization method and subsequent phosphorization calcination in an Ar atmosphere using cobalt-based zeolitic imidazolate frameworks (ZIFs) as precursors. Among the electrocatalysts obtained by controlling the carbonization and phosphorization temperature, the CoNiP/NC700 catalyst, where 700 refers to the calcination temperature (°C), exhibited superior electrocatalytic activity for the OER with an onset overpotential of approximate 220 mV and an overpotential of approximate 300 mV in alkaline solution at a current density of 10 mA/cm². The CoNi/NC and Co/NC Samples were also tested for comparison and CoNiP/NC exhibited the better electrocatalytic activity at all the temperatures tested. The superior electrocatalytic activity of the phosphorization hybrid material can be attributed to the superior synergistic effect of Co, Ni, P and C due to their strong electron coupling interactions. The interconnected amorphous carbon anchored the active Co compounds to avoid aggregation and maintained conducting channels for electron transfer. The composite electrocatalyst prepared herein is a promising candidate for use in electrocatalytic OERs.

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1. Introduction

Recently, the depletion of fossil fuels and the associated exponential rise in global warming have stimulated considerable interest in alternative sources of renewable energy production and conversion [1,2]. The oxygen evolution reaction (OER), a half reaction involving electrochemical water splitting, has attracted considerable attention due to its critical role in water splitting and metal–air batteries and for hydrogen production

and metal regeneration [3,4]. High electrochemical overpotential typically results from the kinetically sluggish four-electron oxidation reaction at the anode [5]. Ruthenium and iridium oxides have been developed as the most efficient electrocatalysts for the OER to date due to their low overpotentials and high proton mobility efficiency. However, their high cost, scarce reserves, and poor durability considerably prohibit more extensive applications [6]. To reduce the reaction overpotentials and obtain good reaction rates with reduced input energy, the

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development of effective non-precious metal electrocatalysts with high activity and low cost is required [7]. To date, some efficient alternatives OER catalysts in alkaline electrolytes using noble metal-based non-precious electrocatalysts including layered double hydroxides [8,9], sulfides [10,11], transition-metal oxides [12], hydroxides [13], metal free catalysts [14] and phosphate [15] have been reported [16].

Among different electrocatalysts for OER, metal–organic frameworks (MOFs), and in particular zeolitic imidazolate frameworks (ZIFs), have gained attention as novel sacrificial templates to construct efficient porous carbon-based electrocatalysts [17]. These materials have been widely used in gas storage or separation [18], catalysis [19], CO₂ reduction [20], and water-splitting [21] because of their excellent chemical and physical properties including high specific surface area, large number of active sites (an active site means the point where catalysis reaction can happen) [22], and tunability of both metals and ligands in the MOFs [23]. MOFs have been used as precursors to synthesize OER catalysts because of their controllable porous structure and nearly infinite design possibilities. In addition, various MOF-derived carbon-based porous metal compounds can be obtained through direct carbonization without further processing or templating. Among cobalt-based MOF materials, ZIF-67 is one of the most investigated MOFs and offers a large number of active cobalt sites. For example, carbonization of ZIF-67 results in a porous Co@N-doped carbon composite (named N/Co-doped PCP//NRGO), which is very active toward the water splitting reaction [24]. In this study, we demonstrate a facile MOF-derived approach for the effective synthesis of OER electrocatalysts in 1.0 mol/L of KOH, producing CoNiP/NC derived from ZIF-67 and doped with nickel through a two-step carbonization and phosphorization calcination procedure in Ar atmosphere. Compared to a previous report of the phosphatization of sodium hypophosphite [25], the strategy described herein of simultaneous carbonization and phosphorization calcinations of Ni-doped ZIF-67 can more easily yield CoNiP/NC hybrid composites. These results suggest that the MOF-derived CoNiP/NC is a promising electrocatalysts for the OER for water splitting in alkaline electrolytes. The N-doped cobalt nickel phosphorus porous carbon electrocatalysts CoNiP/NC, and CoNiP/NC700, where 700 refers to the calcination temperature (°C), exhibited superior activity towards oxygen evolution with an onset overpotential of approximately 220 mV and an overpotential of approximately 300 mV in alkaline solution at a current density of 10 mA/cm². The better electrocatalytic activity of the hybrid material can be attributed to the superior synergistic effect of Co, Ni, P and C due to their strong electron coupling interactions. The interconnected amorphous carbon anchored the active Co compounds preventing aggregation and afforded conducting channels for electron transfer.

2. Experimental

2.1. Formation of CoNiP/NC

In total, 0.5 g of ZIF-67 particles were dispersed in 200 mL

of ethanol containing 1 g of nickel nitrate hexahydrate. After stirring for 30 min, the ZIF-67Ni yolk-shelled particles were formed, collected by centrifugation (at 9000 r/min for 10 min), and dried at 50 °C for 5 h. Subsequently, the CoNi/NC_x, which *x* refers to the calcination temperature (°C), were obtained by annealing the as-obtained yolk-shelled particles at temperatures of 600, 700, 800, 900, and 1000 °C for 3 h at a ramp rate of 5 °C/min under an Ar atmosphere. To obtain CoNiP/NC_x, 50 mg CoNi_x and 1.0 g sodium hypophosphite were placed at two separate positions in a combustion boat and subjected to phosphidation at 300 °C for 2 h at a ramp rate of 5 °C/min under an Ar atmosphere.

2.2. Characterization

The obtained samples were characterized using powder X-ray diffractometry (XRD, Bruker-AxsD8) with Cu K_α radiation ($\lambda = 0.15406$ nm) at $2\theta = 5^\circ\text{--}70^\circ$, operating at a voltage of 40 kV and current of 40 mA. The morphologies of the samples were characterized by field emission-scanning electron microscope (FE-SEM, Hitachi SU-70) operating at 10 kV. The samples used for SEM imaging were gold sputtered prior to analysis. X-ray photoelectron spectroscopy (XPS) data were acquired on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Scientific) using Al K_α radiation.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements were performed on an Autolab electrochemical workstation (NOVA 1.9). To prepare the electrodes for OER testing, 5 mg of active material was added to a mixture of 1.9 mL ethanol and 0.1 mL Nafion solution with sonication for 60 min. Subsequently, the catalyst (20 μ L) was pipetted out and dropped onto a glassy carbon electrode with a diameter of 5 mm and fully dried at room temperature for 12 h before measurements were taken (loading of ~ 0.255 mg/cm²). The electrochemical cell was assembled as a conventional three-electrode system with electrochemical workstation in KOH solution 1.0 mol/L. The counter and reference electrodes were composed of a Pt foil and an Ag/AgCl-saturated KCl electrode, respectively, and a glassy carbon electrode (GCE, 5 mm in diameter) was used as the working electrode. All measured potentials were normalized to the reversible hydrogen electrode (RHE) by adding a value of $(0.197 + 0.059 \text{ pH})$ V. A scan rate of 10 mV/s was used in the linear sweep voltammetry to

Fig. 1. Schematic diagram illustrating the OER catalytic principles on CoNiP/NC polyhedrons. Step I: transformation of ZIF-67 into CoNi/NC by a facile etching and deposition process and carbonization; Step II: formation of CoNiP/NC by phosphatizing CoNi/NC.

obtain the polarization curves, 1.0 V–1.8 V.

3. Results and discussion

Fig. S1 (Supporting Information) shows the XRD patterns of ZIF-67-Simulated, ZIF-67, ZIF-67Ni, Co/NC700, CoNi/NC700, and CoNiP/NC700 samples. Compared to the simulated data of ZIF-67, the ZIF-67 precursor has similar diffraction peaks, indicating the successful synthesis of ZIF-67 [26]. The XRD patterns of ZIF-67Ni is similar to that of ZIF-67 [27]. The standard spectral data of Co (PDF #01-1255) and Ni (PDF #71-2336) exhibit the same diffraction peaks as these of Co/NC700 and CoNi/NC700. According to the CoNiP standard (PDF #71-2336) spectrum shown in Fig. 2(f), the CoNiP/NC700 was successfully synthesized. However, it is difficult to ascertain the exact stoichiometry of CoNiP/NC because the polymorphs of cobalt nickel phosphides contains several types; $\text{Co}_{1.49}\text{Ni}_{0.51}\text{P}$ (ICDD No. 04-019-5182), $\text{Co}_{1.4}\text{Ni}_{0.6}\text{P}$ (ICDD No. 04-005-5616), and CoNiP (ICDD No. 04-001-4562). Furthermore, the various XRD patterns obtained under different conditions are shown in Fig. S1.

The SEM image in Fig. 2(a) indicates that ZIF-67 is a regular polyhedron with an obvious edge and diameter of approximately 700 nm. Fig. 2(c) shows that ZIF-67Ni conserves polyhedron shape, but with a rougher surface due to the reaction with $\text{Ni}(\text{NO}_3)_2$ in ethanol solution for 30 min. The CoNi/NC700 obtained by the calcination of ZIF-67Ni in Ar for 3 h at 700 °C was shown Fig. 2(d). The size and shape of the final product, CoNiP/NC700, was largely unchanged after subsequent phosphidation step for 300 °C (Fig. 2(e)). With higher calcination temperatures, more serious ZIF-67 deformation occurs. Furthermore, the various SEM images obtained under different

Fig. 2. SEM images of ZIF-67 (a), ZIF-67Ni (b), Co/NC700 (c), CoNi/NC700 (d), CoNiP/NC700 (e) and their corresponding XRD patterns (f).

conditions are shown in Fig. S2.

To determine the detailed elemental composition, valence state, and OER activity of CoNi/NC and CoNiP/NC materials, XPS tests were performed (Fig. S4 and Fig. 3). Fig. 4(a) indi-

Fig. 3. XPS survey spectra of CoNiP/NC700 (a–d).

Fig. 4. (a) Polarization curves in KOH solution (1.0 mol/L; scan rate: 10 mV/s); (b) Tafel plots derived from (a); (c) Polarization curves in KOH solution (1.0 mol/L; scan rate: 10 mV/s); (d) Polarization curves in KOH solution (1.0 mol/L; scan rate: 10 mV/s).

icates the presence of Co, Ni, P, C, N and O in CoNiP/NC700. In addition, a small amount of N was detected in the CoNiP/NC700 samples, likely originating from the organic ligands, 2MI, in the MOFs. In the high-resolution Co 2p XPS spectra (Fig. S4 and Fig. 3(c)), the CoNiP/NC700 samples show two main peaks at 781.6 and 793.7 eV [5,17]. The Ni 2p spectrum of CoNi/NC800 exhibits two major peaks at 853.8 and 869.9 eV (Fig. S4), which can be attributed to Ni^{δ+} in the Ni–P compound [4,28]. The Ni 2p spectrum of CoNiP/NC700 exhibits two major peaks at 856.2 and 874.3 eV. For Ni 2p_{1/2}, the corresponding peak attributed to Ni^{δ+} in the Ni–P compound was observed at 869.7 eV and peaks assigned to Ni²⁺ are located at 874.3 eV. A high-resolution spectrum of the P 2p region shows a peak at 133.4 eV, reflecting the binding energy of P 2p_{3/2} [5]. The XPS data demonstrate the successful chemical conversion of CoNi/NC to CoNiP/NC via the low-temperature gas phosphidation process.

The OER activity of the samples with the same mass loading of 0.255 mg/cm² was evaluated in KOH solution 1.0 mol/L at room temperature. Fig. 4(a) shows the polarization curves obtained by LSV measurements. For comparison, a bare GCE, ZIF-67, and ZIF-67Ni, were also studied (Fig. S5.1). The bare GCE, ZIF-67, and ZIF-67Ni had onset overpotentials of approximately 370, 310, and 330 mV vs RHE, respectively, and an overpotentials of approximate 550, 450, and 440 mV, respectively, at a current density of 10 mA/cm², indicating negligible electrocatalytic activity and a low OER response. Fig. 4(a) shows that the polarization curve of CoNiP/NC700 exhibits the superior activity toward the OER compared to these of Co-

Ni/NC700 and Co/NC700, and shows an onset overpotential of approximate 220 mV vs RHE and an overpotential of approximate 300 mV at a current density of 10 mA/cm².

Meanwhile, the polarization curve of CoNiP/NC also exhibits the superior electrocatalytic activity toward the OER compared to these of CoNi/NC and Co/NC (Fig. S6), suggesting that the overpotential of CoNiP/NC is relatively lower than these of CoNi/NC and Co/NC. The better electrocatalytic activity of the hybrid material can be attributed to the superior synergistic effect between Co, Ni, P and C due to their strong electron coupling interactions. The interconnected amorphous carbon anchored the active Co compounds preventing aggregation and afforded conducting channels for electron transfer. It should be noted that the overpotential for the OER activity of CoNiP/NC700 is much lower than that of most reported metal-free and transition metal oxides OER catalysts (Table S1, Supporting Information). Among reported electrocatalytic materials, the CoNiP/NC700 showed the highest electrocatalytic activity (Fig. 4(d)), due to its MOF-derived porous carbon structure and N/Co/Ni-doping effect [27,29]. The Tafel plots of Co/NC700, CoNi/NC700 in Fig. 4(b) were derived from the polarization curves in Fig. 4(a). A lower Tafel slope value indicates more rapid OER kinetics and significant chemical and electronic coupling [30]. In comparison to Co/NC700 and CoNi/NC700, the CoNiP/NC700 electrocatalyst exhibits a lower onset potential and higher current density for the OER. It is clear that CoNiP/NC700 shows the lowest Tafel slope (Fig. 4(b)) among the materials tested. The superior electrocatalytic activity of the hybrid material can be attributed to the synergis-

Fig. 5. Polarization curves before (black) and after (red) 10 h of electrocatalytic OER operation.

tic effect between Co, Ni, P and C due to their strong electron coupling interactions. The interconnected amorphous carbon anchored the active Co compounds preventing aggregation and afforded conducting channels for electron transfer. Furthermore, Figs. S6.1–S6.4 show the various polarization curves and Tafel plots obtained under different conditions. The excellent stability of the electrode was confirmed by the polarization curve stability after continuous potential sweeps (Fig. 5).

A negligible difference was observed in the polarization curves after 10 h of continuous testing in 1.0 mol/L KOH. These results indicate that CoNiP/NC700 exhibits the excellent stability in alkaline solution. The stability of CoNiP/NC700 catalysts for the OER was measured by the *i*-*t* tests at a constant potential of 1.53 V vs. RHE. It is clear that the CoNiP/NC700 catalysts annealed at 700 °C exhibit superior durability, with negligible decay (4.0 %) in OER activity during 10 h of continuous operation (Fig. 5).

4. Conclusions

CoNiP/NC materials were successfully developed as efficient electrocatalysts for the OER by carbonization and phosphorization calcinations of preformed Co-based MOFs. The CoNiP/NC700 electrocatalyst exhibited excellent catalytic performance with a low overpotential of 300 mV at a current den-

sity of 10 mA/cm² and Tafel slopes of 66 mV/dec in alkaline electrolytes, due to its MOF-derived porous carbon structure and the N/Co/Ni-doping effect. The CoNiP/NC electrocatalyst obtained at different temperatures exhibited better electrocatalytic activity than these of the Co/NC and CoNi/NC materials. In addition, the facile synthesis method based on MOF templates for the preparation of CoNiP/NC is low cost and uses abundant resources, providing a synthetic method for practical applications. The catalysts developed herein are expected to find use in clean energy devices, and the synthesis methods could be extended to other materials with different structures and properties, especially for bimetallic or trimetallic hybrid composites.

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Graphical Abstract

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Schematic diagram to illustrate the OER catalytic principles on CoNiP/NC polyhedrons. Step I: transformation of ZIF-67 into CoNi/NC by a facile etching and deposition process and carbonization; Step II: formation of CoNiP/NC by phosphatizing CoNi/NC.

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钴基类沸石咪唑酯框架材料衍生的析氧反应活性催化剂

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摘要: 析氧反应 (OER) 在能量转换和储存技术中扮演着重要角色, 例如在水分解和金属空气电池中, 电催化剂的发展是主要任务. 本文采用钴基的类沸石咪唑酯骨架结构材料 (ZIFs) 作为前驱体, 在氩气保护气氛下, 成功制备了氮掺杂钴镍磷多孔碳多面体电催化剂 (CoNiP/NC). 首先, 采用 ZIF-67 作为前驱体, 将 ZIF-67 和六水合硝酸镍按照一定比例在乙醇溶液中搅拌 30 min, 达到掺杂镍的目的, 然后将其在不同温度下煅烧, 得到的样品在 300 °C 氩气保护气氛下磷化, 得到最终产物. 所有电催化剂均通过控制碳化和磷化作用温度获得. 通过对样品 ZIF-67Ni 进行 EDS 分析, 证明镍成功负载到 ZIF-67 上, XPS 结果也证明了这一点. 由扫描电镜图可以看出, 前驱体 ZIF-67 在负载 Ni 之后, 样品表面形貌发生明显变化, 表面变得粗糙, 有明显的条纹. 磷化后样品的 XRD 结果说明磷化方法是成功的, 同时 XPS 结果表明样品中有 P 元素存在. 从扫描电镜图片可以明显看出, 样品在煅烧之后表面形貌发生明显变化, 由棱角明显变为表面粗糙, 但是并未发生明显的团聚现象. XPS 显示, 样品 CoNiP/NC700 (700 指煅烧温度 (°C)) 中存在钴、镍、磷、碳、氮、氧这六种元素, 另外还分析了其高分辨图. 结果显示, 电催化剂 CoNiP/NC700 表现出优越的电催化效率, 在碱性溶液的电流密度 10 mA/cm² 条件下, 其开路电压约为 220 mV, 过电位约为 300 mV. 掺杂镍之后的样品性能比煅烧 ZIF-67 的样品好, 说明镍对于提高析氧反应效率有益; 同样, 磷化之后样品的 OER 性能也有所提高. 相比较而言, 对于磷化之后的样品, 煅烧温度是 700 °C 时, OER 催化效率最好. 磷化杂化材料优越的电催化活性是由于其强的电子耦合相互作用而产生的协同效应, 在镍、磷、碳等方面具有较强的协同效应. 相互联系的非定形碳不仅固定了活性碳化合物以避免聚集, 而且还为电子转移提供了传导通道. 对样品 CoNiP/NC700 进行了稳定性测试, 结果表明其稳定性较好, 在循环 10 h 之后, 活性仅下降了 4%. 这一研究表明, 该复合电催化剂可能是电催化氧化反应的一个很有前景的候选催化剂.

关键词: ZIF-67; 碳化; 磷化; 电催化; 析氧反应

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