Macroscale cobalt-MOFs derived metallic Co nanoparticles embedded in N-doped porous carbon layers as efficient oxygen electrocatalysts

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Abstract

Metal-organic frameworks (MOFs) materials have aroused great research interest in different areas owing to their unique properties, such as high surface area, various composition, well-organized framework and controllable porous structure. Controllable fabrication of MOFs materials at macro-scale may be more promising for their large-scale practical applications. Here we report the synthesis of macro-scale Co-MOFs crystals using 1,3,5-benzenetricarboxylic acid (H₃BTC) linker

in the presence of Co^{2+} , triethylamine (TEA) and nonanoic acid by a facile solvothermal reaction. Further, the as-fabricated Co-MOFs as precursor was pyrolytically treated at different temperatures in N_2 atmosphere to obtain metallic Co nanoparticles embedded in N-doped porous carbon layers (denoted as Co@NPC). The results demonstrate that the Co-MOFs derived sample obtained at $900\text{ }^\circ\text{C}$ (Co@NPC-900) shows a porous structure (including micropore and mesopore) with a surface area of $110.8\text{ m}^2\text{ g}^{-1}$ and an N doping level of 1.62 at.% resulted from TEA in the pyrolysis process. As electrocatalyst, the Co@NPC-900 exhibits bifunctional electrocatalytic activities toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in alkaline media which are key reactions in some renewable energy technologies such as fuel cells and rechargeable metal-air batteries. The results indicate that the Co@NPC-900 can afford an onset potential of 1.50 V (vs. RHE) and an overpotential of 1.61 V (vs. RHE) at a current density of 10 mA cm^{-2} for OER and ORR with high applicable stability, respectively. The efficient catalytic activity of Co@NPC-900 as bifunctional oxygen electrocatalyst can be ascribed to N doping and embedded metallic Co nanoparticles in carbon structure providing catalytic active sites and porous structure favourable for electrocatalysis-related mass transport.

Keywords: Co-MOFs; Co@N-doped porous carbon; Bifunctional oxygen electrocatalyst; Oxygen reduction reaction; Oxygen evolution reaction

1. Introduction

Metal-organic frameworks (MOFs) made of metal nodes and organic building blocks

have been a class of ideal materials for different applications ranging from catalysis [1], gas storage [2], gas separation [3], optics [4] and so on [5-8] owing to their many unique properties, such as high surface area, diverse composition and controllable porous structure [9]. Thanks to the superiority of composition and structure, MOFs has been ideal precursor materials to fabricate non-precious metal incorporated porous carbon materials for electrocatalysis applications [10]. Additional advantage is that heteroatom (*e.g.*, N)-containing organic ligands in MOFs structure simultaneously act as heteroatom doping sources in the process of pyrolysis carbonization, improving the catalytic activity of pyrolytic sample [11]. Although MOFs materials have demonstrated great applicable potential in many fields, MOFs materials in most studies are almost exclusively synthesized at nanoscale to precisely tune the pore structure for gas adsorption and separation applications [2-4]. Such nanoscale MOFs materials may limit their large-scale practical applications in some fields (*e.g.*, catalysis [1], electrocatalysis [11]). Therefore, it is still highly desirable to synthesize macroscale MOFs materials with intact crystalline structure and precisely regulated pore structure as precursors for electrocatalysis applications.

Developing oxygen electrode catalysts with high activity at low cost for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is at the heart of key renewable-energy technologies, such as regenerative fuel cells, rechargeable metal-air batteries, electrocatalytic water splitting to generate hydrogen and oxygen, and other important clean energy devices [12]. Up to now, precious metals (*e.g.*, Pt) and metal oxides (such as RuO₂ and IrO₂) have been traditionally used to expedite the ORR and

OER; however, these precious-metal-based catalysts often suffer from high cost, low selectivity, and poor stability, thus limiting their large-scale production applications [13]. More importantly, it is found that Pt-based catalysts possess superior ORR activity, but poor OER activity, while RuO₂ and IrO₂ can afford excellent OER activity, but very low ORR activity [14]. Therefore, these commercially available catalysts cannot meet the requirements for practical applications in regenerative fuel cells and rechargeable metal-air batteries, in which electrocatalysts with bifunctional oxygen activities (ORR/OER) are necessary. Recent efforts to obtain replacements for precious metal-based catalysts for bifunctional ORR/OER have resulted in some new contenders, such as heteroatom (*e.g.*, N [15-19], S [20], P [21]) doped/co-doped carbon materials and non-precious metal based porous carbon materials [22]. In their studies, on the one hand, heteroatom doping/co-doping and non-precious metal species in carbon structures can provide rich catalytic active sites for ORR/OER [18]; on the other hand, carbon materials in their works possess high surface area, porous structure and high graphitization degree, favourable for the exposure of catalytic active sites, electrocatalysis-related mass transport and electron transfer, respectively [20]. Collectively, these advantages contribute their good bifunctional ORR/OER catalytic activities. Even so, most reported synthetic procedures of these bifunctional ORR/OER catalysts suffer from extremely complex process and time-consuming fabrication. Therefore, development of low-cost and highly-efficient non-precious metal catalysts with bifunctional ORR/OER catalytic activities is still highly needed for applications in related renewable energy technologies.

Herein, metallic Co nanoparticles embedded in N-doped porous carbon layers (Co@NPC) were successfully fabricated by pyrolytic treatment of macroscale Co-MOFs crystals obtained by using 1,3,5-benzenetricarboxylic acid (H₃BTC) as organic ligands in the presence of Co²⁺, triethylamine (TEA) and nonanoic acid by a facile solvothermal reaction. The Co-MOFs derived Co@NPC samples at different pyrolysis temperatures were investigated as electrocatalysts for ORR and OER. As a result, Co@NPC samples obtained at 900 °C and 1000 °C (Co@NPC-900 and Co@NPC-1000) as electrocatalysts exhibited bifunctional catalytic activities toward ORR and OER with high applicable stability. The corresponding catalysis mechanisms were discussed on the basis of experimental results.

2. Experimental section

2.1 Materials

All chemicals were commercially available and used without further purification: cobalt (II) nitrate hexahydrate (Co(NO₃)₃·6H₂O, Sigma-Aldrich, 99.99%), 1,3,5-benzenetricarboxylic acid (H₃BTC, Sigma-Aldrich, 99.99%), triethylamine (TEA, Sinopharm Chemical Reagent Co., Ltd, 99.99%), methanol (CH₃OH, Sinopharm Chemical Reagent Co., Ltd, >99%), nonanoic acid (C₉H₁₈O₂, Sinopharm Chemical Reagent Co., Ltd, >99%), ruthenium (IV) oxide powder (RuO₂, Sigma-Aldrich), Nafion® 117 ~ 5% in lower aliphatic alcohols and water (Sigma-Aldrich) and potassium hydroxide (KOH, J. T. Baker). Deionized water (18 MΩ) was supplied by a Millipore System (Millipore Q, USA).

2.2 Preparation of Co-MOFs and Co@NPC-T (T=800, 900, 1000)

A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.291 g), H_3BTC (0.5 mmol, 0.105 g), TEA (1.0 mL) was first dissolved in 4.0 mL of nonanoic acid, and then transferred into a 23 mL of Teflon-lined stainless-steel autoclave. The solvothermal reaction was performed at 160 °C for 5 days. Then, the autoclave was naturally cooled to room temperature and the product was collected and washed with methanol to obtain purple-black bar Co-MOFs crystals with a yield of 85%. The as-prepared Co-MOFs were used as precursors and pyrolytically treated at different temperatures ($T=800, 900, 1000$) in a tube furnace in N_2 atmosphere for 1 h with a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to obtain metallic Co nanoparticles embedded in N-doped porous carbon layers (Co@NPC).

2.3 Characterizations

The crystalline structures of samples were identified by X-ray diffraction analysis (XRD, Philips X'pert PRO) using Ni filtered monochromatic Cu K_α radiation ($K_\alpha=1.5418\text{ \AA}$) at 40 kV and 40 mA. The crystalline shape of Co-MOFs were observed by Optical microscope (BTL-358). The morphology and structure of samples were characterized by field emission scanning electron microscopy (FESEM, Quanta 200FEG) and transmission electron microscopy (TEM, JEOL 2010) with an energy dispersive X-ray spectrometer (EDS Oxford, Link ISIS). X-ray photoelectron spectroscopy (XPS) analysis of the samples was performed on ESCALAB 250 X-ray photoelectron spectrometer (Thermo, America) equipped with Al K_α monochromatized radiation at 1486.6 eV X-ray source. The surface area and porosity of samples were measured by a Surface Area and Porosity Analyzer (Tristar3020M).

2.4 Electrochemical measurements

Electrochemical measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments, Shanghai, China) coupled with a PINE rotating disk electrode (RDE) system (Pine Instruments Co. Ltd. USA). A standard three-electrode electrochemical cell equipped with gas flow system was employed during measurements. Prior to measurements, rotating disk electrode (RDE, 5.0mm in diameter) was first polished with 5.0, 3.0 and 0.05 μ m alumina slurry sequentially and then washed ultrasonically in water and ethanol for 30 s, respectively. The cleaned electrode was dried with a high-purity nitrogen stream. The Co@NPC-T (T=800, 900, 1000) catalyst inks were prepared by dispersing catalyst powder (2.0 mg) into a mixture including 40 μ L of Nafion solution (0.5 wt.%) and 460 μ L of ethanol, followed by ultrasonic treatment for 2 min. After that, 20 μ L of catalyst ink was cast onto glassy carbon (GC) electrode surface, leading to a catalyst loading amount of 407 μ g cm⁻². For comparison, commercial Pt/C and RuO₂ catalyst inks were also made as the same procedure as Co@NPC-T (T=800, 900, 1000) catalyst ink. The ORR performance of catalysts was investigated by cyclic voltammogram (CV) and linear sweep voltammogram (LSV) measurements in O₂ (or N₂)-saturated 0.1 M KOH solution. CV curves were measured at a scan rate of 50 mV s⁻¹. LSV curves were measured at a scan rate of 5.0 mV s⁻¹ under different disk rotation rates of 225, 400, 625, 900, 1225, 1600 and 2025 rpm. All the potentials in this work were recorded with respect to the Ag/AgCl reference electrode. The electron transfer number (*n*) per oxygen molecule in the ORR process was calculated by the Koutecky-Levich (K-L)

equation [23]:

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

$$B = 0.62nFA(D_0)^{2/3}\nu^{-1/6}C_0 \quad (2)$$

$$j_K = nFKC_0 \quad (3)$$

where j , j_K and j_D corresponds to the measured, kinetic and diffusion limiting current, respectively, B is the slope of K-L plots, ω is the electrode rotating angular velocity ($\omega=2\pi N$, N is the linear rotation speed), n is the electron number transferred, F is the Faraday constant ($F=96485 \text{ C mol}^{-1}$), A is the geometric electrode area ($A=0.196 \text{ cm}^2$), D_0 is the diffusion coefficient of oxygen ($D_0=1.9\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinetic viscosity of electrolyte ($\nu=0.01 \text{ cm}^2 \text{ s}^{-1}$), and C_0 is the saturated oxygen concentration in 0.1 M KOH solution ($C_0=1.2\times 10^{-3} \text{ mol L}^{-1}$).

The OER activities of all catalysts were investigated by the LSV method at a scan rate of 5.0 mV s^{-1} in 0.1 mol L^{-1} KOH solution. The durability test for OER was performed by cycling the electrode potential between 0.96 and 1.76 V at 200 mV s^{-1} for 1000 cycles. All the potentials reported in this study were all quoted against the Reversible Hydrogen Electrode (RHE) using eqn (4) [24].

$$E(RHE) = E(Ag / AgCl) + 0.059 \times pH + 0.197 \quad (4)$$

3. Result and discussion

The crystalline X-ray diffraction (XRD) patterns of as-prepared Co-MOFs and Co@NPC-T (T=800, 900, 1000) are obtained by XRD characterization technique. The XRD patterns of as-prepared Co-MOFs are found to be in perfect agreement with

the simulated Co-MOFs crystal structure (Figure 1a) [5]. Figure 1b shows the XRD patterns of Co-MOFs derived Co@NPC samples obtained at different pyrolysis temperatures. As shown, the diffraction peak at 26.6° corresponds to the (002) plane of graphitic carbon (JCPDS 13-0148) [25], while the other diffraction peaks at $2\theta=44.2^\circ$, 51.5° and 75.8° can be indexed to the (111), (200), and (220) crystal planes of metallic cobalt phase (JCPDS 15-0806), respectively [26]. The above results demonstrate that Co-MOFs derived Co@NPC samples are mainly composed of graphitic carbon and metallic Co under given experimental conditions, possibly favourable for electrocatalysis applications. Figure 1c shows the optical photo of as-prepared Co-MOFs crystals. Apparently, purple-black bar Co-MOFs crystals at macro-scale with a yield of 85% can be observed, indicating the superiority of the synthetic method for preparation of large-sized Co-MOFs crystals. In this work, triethylamine (TEA) can effectively deprotonate 1,3,5-benzenetricarboxylic acid (H_3BTC), thus dramatically promoting the linkage of Co^{2+} and deprotonated H_3BTC to form Co-MOFs growth units and macro-scale Co-MOFs crystals with reaction time. To obtain a balance of the charge, TEA readily adsorbs on the channel structures of Co-MOFs crystals, resulting in the grown Co-MOFs crystals with TEA, thus possible N doping in Co-MOFs pyrolytically converted carbon materials [19]. This may be very beneficial for improving the electrocatalytic activity of Co-MOFs derived electrocatalyst. After pyrolysis treatment, porous carbon structure with rough surface can be clearly observed, as shown in Figure 1d (taking Co@NPC-900 as an example).

Figure 1. XRD patterns of (a) Co-MOFs and (b) thermolyzed Co@NPC-T (T=800, 900, 1000) samples. (c) The photograph of Co-MOFs distributed in weighing paper under optical microscope, (d) the characterization of Co@NPC-900 SEM image.

The detailed structure information of Co-MOFs derived Co@NPC sample (taking Co@NPC-900 as an example) was obtained by TEM analysis. After pyrolysis treatment, TEM image of Co@NPC-900 displays carbon layered structures with relatively uniformly distributed Co nanoparticles with particle sizes of 5.0~30 nm (Figure 2a). Further high resolution TEM (HRTEM) analysis confirms metallic Co nanoparticle embedded in graphitic carbon layers, moreover, the lattice spacing of 0.20nm, 0.18nm can be due to the (111), (200) crystal plane of metallic Co (Figure 2b) [26]. The above characterization results indicate the formation of metallic Co nanoparticles embedded in graphitic carbon layers after pyrolysis treatment of

Co-MOFs. This graphitic carbon layered structures with embedded metallic Co nanoparticles are very important for improving the applicable stability of catalyst during electrocatalysis [23]. The elemental mapping analysis of Co@NPC-900 confirms the presence of Co, C, N and O elements (Figure 2d). Moreover, Co element is existent in the form of Co nanoparticles and N element is uniformly distributed over the entire carbon layer, indicating a successful N doping in graphitic carbon structure owing to the presence of TEA in Co-MOFs precursor. N doping in graphitic carbon is very helpful to improve the electrocatalytic activity for ~~of an~~ electrocatalyst [27].

Figure 2. (a) TEM image and (b) high resolution TEM images of Co@NPC-900, (c) a selected area electron diffraction pattern of Co@NPC-900, (d) images of elemental mapping of Co@NPC-900 for Co, C, N and O.

Figure 3. (a) Nitrogen adsorption-desorption isotherm and (b) the corresponding pore diameter distribution of Co-MOFs (the insert picture is the crystal structure of Co-MOFs), (c) Nitrogen adsorption-desorption isotherm and (d) the corresponding pore diameter distribution of Co-NPC-900.

The N₂ adsorption-desorption isotherm and the corresponding pore-size distribution curve of compounds (Co-MOFs, Co@NPC-900) are shown in Figure 3. As shown in Figure 3a, the sample exhibited type I isotherms in N₂ adsorption isotherms at 77K with no hysteresis, and the BET surface area of Co-MOFs was 11.8 m² g⁻¹ with a corresponding cumulative pore volume of 0.05 cm³ g⁻¹, respectively. The reason for the smaller BET surface area of Co-MOFs is that triethylamine is filled with holes in the crystal structure of Co-MOFs. The pore size is concentrated at 1.9 nm distribution curve is calculated by using the BJH method (Figure 3b), indicative of

permanent microporosity and found to be agreement with the Co-MOFs crystal structure, respectively. The N₂ adsorption-desorption isotherm exhibits the type IV with a H₃-type hysteresis loop ($P/P_0 > 0.4$) [28], demonstrating the mesoporous characteristic of Co@NPC-900 (Figure 3c). The pore size distribution curve is also calculated by using the BJH method, as shown in Figure 3d. As a result, the pore sizes are mainly concentrated at 1.9 nm and 20 nm, the BET surface area and corresponding cumulative pore volume of Co@NPC-900 are 110.8 m² g⁻¹ and 0.193 cm³ g⁻¹, respectively. Through comparison, we found that the surface area and pore volume of the pyrolysis (Co@NPC-900) is higher than that before pyrolysis Co-MOFs. The above results indicate that the Co@NPC-900 possesses high surface area and porous structure (including micropore and mesopore), which are favourable for the exposure of catalytic active sites and electrocatalysis-related mass transport when used as electrocatalyst.

The elemental composition information of Co@NPC-900 was investigated in detail by X-ray photoelectron spectrometry (XPS) technique. Figure 4a shows the surface survey XPS spectrum of Co@NPC-900, indicating the presence of C (87.6 at.%), N (1.62 at.%), O (9.33 at.%) and Co (1.45 at.%), further confirming the N doping in Co@NPC-900. The high resolution C 1s XPS spectrum (Figure 4b) shows a slightly asymmetric tail at higher binding energy, which is a common characteristic of N-doped carbon materials [29]. The two main peaks at 284.5 and 285.6 eV are assigned to sp²-hybridized graphite-like carbon (C-C sp²) and sp³-hybridized diamond-like carbon (C-C sp³), respectively [30]. The XPS peaks centered at 286.6, 287.6 and

289.1 eV are attributed to surface oxygen and nitrogen functional groups of C-O/C-N, C=O/C=N and O=C-O, respectively [31]. The appearance of p-p* shake up satellites of sp² graphite-like carbon at 291.0 eV indicates the further carbonization and aromatization with the prolonged pyrolysis time. The high resolution N 1s XPS spectrum (Figure 4c) can be deconvoluted to four sub-peaks due to the spin-orbit coupling, including pyridinic-N (398.5 eV), pyrrolic-N (399.7 eV), graphitic-N (400.7 eV) and pyridine-N-oxide groups (401.7 eV) [32]. It has been generally accepted that pyridinic-N and graphitic-N are mainly responsible for electrocatalytic activity of oxygen reduction reaction [33-34]. Figure 4d shows the Co2P spectrum, which can be deconvoluted into six peaks. Among them, two pairs of spin-orbit doublets at 778.2 and 798.2 eV indicates the coexistence of Co²⁺ and Co³⁺ in Co@NPC-900, the binding energy at 781.4 and 786.5 eV is characteristic of Co²⁺ 2P_{3/2} and Co³⁺ 2P_{3/2} satellite peaks and the other binding energy at 796.8 and 804.1 eV is characteristic of Co²⁺ 2P_{1/2} and Co³⁺ 2P_{1/2} satellite peaks, respectively [35]. The Co active species with different valence states on metallic Co nanoparticles should be also the origins of electrocatalytic activity when Co@NPC-900 is used as electrocatalyst.

Figure 4. Typical (a) survey scan XPS spectrum, (b) deconvoluted C1s spectrum and, (c) deconvoluted N1s spectrum, (d) deconvoluted Co 2p spectrum of Co@NPC-900.

Owing to the important roles of oxygen reduction reaction (ORR) and oxygen revolution reaction (OER) in some renewable technologies, Co-MOFs derived Co@NPC samples as electrocatalysts were investigated for ORR and OER in this work. To evaluate the ORR activities of Co@NPC samples, cyclic voltammetry (CV) measurement was initially performed in 0.1 M KOH solution. For comparison, a commercial Pt/C (20 wt.% Pt on Vulcan carbon black) was also tested under identical experimental conditions. Figure 5a shows typical CV curves of Co@NPC-900 in N₂- and O₂-saturated 0.1 M KOH solution at a scan rate of 50 mV s⁻¹. Obviously, a negligible redox peak can be observed for Co@NPC-900 in N₂-saturated 0.1 M KOH solution, while a strong reduction peak at 0.73 V can be achieved for Co@NPC-900

in O₂-saturated 0.1 M KOH solution, indicating an intrinsic ORR activity of Co@NPC-900. Figure 5b shows the line sweep voltammetry (LSV) curves of Co@NPC-800, Co@NPC-900, Co@NPC-1000 and commercial Pt/C catalysts. The Co@NPC catalysts obtained at different pyrolysis temperatures exhibit similar onset potential value at 0.88 V, very close to that (0.92 V) of commercial Pt/C. Moreover, all Co@NPC catalysts show very close limitation current densities within the given potential range, indicating their similar catalytic kinetic properties. Figure 5c shows the LSV curves of Co@NPC-900 in O₂-saturated 0.1 M KOH solution at a scan rate of 5.0 mV s⁻¹ under different rotation rates, indicating a mass transfer controlled process [20]. Based on the *K-L* plots (Figure 5d) derived from Figure 5c, the average value of transferred electron number ($\bar{n}$) was calculated to be 3.7 at 0.5 V~0.75 V (vs. Ag/AgCl) (Figure 5e), suggesting that the Co@NPC-900 possesses an approximate four electron ORR process in 0.1 M KOH solution. Figure 5f shows the stability test of Co@NPC-900 and commercial Pt/C catalysts. As shown, a respectable current retention of 90% can be maintained for Co@NPC-900 after 8 h, while only 70% of activity of commercial Pt/C catalyst can be achieved, indicating high applicable stability of Co@NPC-900. N doping in graphitic carbon structures has been theoretically and experimentally proven to be responsible for ORR activity of an electrocatalyst [20]. Recently, some studies have demonstrated that transition metal (*e.g.*, Fe, Co, Ni) active species embedded in graphitic carbon structures can effectively influence the charge distribution of outer carbon layers, thus improving the ORR activity [15, 35, 36]. In this work, the good ORR activity of Co@NPC catalysts

derived from Co-MOFs may be ascribed to a synergistic effect between ORR active species of N doping and metallic Co nanoparticles in graphitic carbon layers and advantageous structure factors of high surface area favourable for the catalytic active sites exposure, porous structure beneficial for ORR-related mass transport, and graphitic carbon structure to improve electron transfer.

Figure 5. (a) Comparative cyclic voltammograms of Co@NPC-900, (b) linear-sweep voltammograms of Co@NPC-T (T=800, 900, 1000) and Pt/C in O_2 -saturated 0.1 M

KOH with a sweep rate of 5 mV s^{-1} and electrode rotation speed of 1600 rpm, (c) linear-sweep voltammograms of Co@NPC-900 at different rotation speeds, (d) the Koutecky-Levich (K-L) plots at different potentials, (e) the electron transfer number as a function of potential for Co@NPC-900, (f) Current-time (i-t) chronoamperometric responses of Co@NPC-900 and Pt/C electrodes (1600 rpm) at -0.35 V in O_2 -saturated 0.1 M KOH solution.

A certain range of potential from 0.96 V to 1.76 V (vs. RHE) was applied in O_2 -saturated 0.1 M KOH solution with a three-electrode system at a scan rate of 5.0 mV s^{-1} to investigate the OER catalytic performance of the prepared samples. For comparison, commercial RuO_2 was selected as catalyst for OER measurement. As reported, the potential required for water oxidation is usually applied to evaluate the OER performance at the current density of 10 mA cm^{-2} [38, 39]. As shown in Figure 6a, the current density of Co@NPC-900 and Co@NPC-1000 reaches 10 mA cm^{-2} at the potential values of 1.61 V and 1.60 V , respectively, which are close to that (1.50 V) of commercial RuO_2 catalyst and obviously better than that (1.68 V) of Co@NPC-800 at a current density of 10 mA cm^{-2} , indicating good OER activity of Co@NPC catalysts obtained at higher pyrolysis temperature. A stability test (Figure 6b) indicates that Co@NPC-1000 can afford a similar i - V curve as before, with negligible current loss after 1000 cycles, suggesting the superior durability of Co@NPC-1000. The above results demonstrate Co-MOFs derived Co@NPC catalysts obtained at higher pyrolysis temperatures possess simultaneously bifunctional catalytic activities toward ORR and OER, indicating great potential as bifunctional oxygen catalysts for applications in regenerative fuel cells and rechargeable metal-air batteries.

Figure 6. (a) LSV curves of Co@NPC-T (T=800, 900, 1000) and Pt/C in O₂-saturated 0.1 M KOH with a sweep rate of 5 mV s⁻¹, (b) LSV curve of Co@NPC-1000 before and after 1000 cycles.

To best our knowledge, the bi-functional catalytic activity was calculated by taking the difference in potential between the ORR current density at -3 mA cm⁻² and OER current density at 10 mA cm⁻², current density is of practical importance for electrochemical applications [40]. The smaller the difference, the better is the potential of the material to be used for practical applications [41]. The oxygen electrode activities are shown in Table 1. When compared with similar non-precious metal catalysts prepared by other routes, our catalysts afford an oxygen electrode potential with more improved catalytic activity than or similar to recently reported N-MCN/CNT (nitrogen-doped mesoporous carbon nanosheet/carbon nanotube) [42] and NGM (nitrogen-doped graphene mesh denoted as NGM) [43] and Co₉S₈@CNS900 (Co₉S₈@N and S dual-doped porous carbons) [44] and Co-MOF@CNTs (5%) [45]. More importantly, the substantial improvements in regard to both ORR and OER catalysis illustrate the effectiveness of the simple preparation technique adapted in this work to prepare bi-functional catalysts for

rechargeable metal-air batteries.

Table 1. Comparison of bifunctional oxygen electrode activities of Co@NPC with other reported non-precious metal based catalysts.

Components	E _{ORR} (V) at onset potential	E _{ORR} (V) at J=-3 mA cm ⁻²	E _{OER} (V) at J=10 mA cm ⁻²	Oxygen electrode ΔE (V)	ref
Co@NPC-800	0.89	0.70	1.68	0.98	this work
Co@NPC-900	0.88	0.76	1.61	0.85	this work
Co@NPC-1000	0.88	0.75	1.60	0.85	this work
N-MCN/CNT	0.95	0.82	1.55	0.73	42
NGM	0.89	0.77	1.67	0.90	43
Co ₉ S ₈ @CNS900	0.92	0.80	—	—	44
Co-MOF@CN Ts (5%)	0.91	0.82	1.57	0.75	45

4. Conclusions

In summary, we have synthesized metallic Co nanoparticles embedded in N-doped porous graphitic carbon layers as efficient bifunctional electrocatalysts for both ORR and OER by pyrolysis treatment of macroscale Co-MOFs crystals. The introduction of triethylamine (TEA) in reaction system has dual roles: (1) as protonation reagent to deprotonate 1,3,5-benzenetricarboxylic acid (H₃BTC) to promote the linkage of Co²⁺ and H₃BTC and the growth of Co-MOFs crystals; (2) as N source to realize N doping in graphitic carbon structure during Co-MOFs pyrolysis. Moreover, metallic Co nanoparticles in situ embed in the porous graphitic carbon layers during Co-MOFs pyrolysis, improving the applicable stability of Co-MOFs derived electrocatalysts.

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