Atomic Cu dispersed ZIF-8 derived N-doped carbon for high-performance oxygen electrocatalysis in Zn-air battery

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Abstract

Single-atom catalysts have attracted widespread attention in recent years due to their high atom utilization and excellent catalytic performance, particularly, in oxygen electrocatalysis. Herein, we report to use ZIF-8 as precursor, which was annealed and subsequently mixed with melamine and transition metal salt to finally synthesize Cu-atoms modified N-doped carbon (NC) catalysts, which exhibited excellent oxygen reduction reaction activity and kinetic performance in alkaline solution. The constructed rechargeable Zn-air battery using Cu-NC and benchmark Pt/C catalyst supported on carbon fiber paper as the cathode and anode, respectively, exhibited superb super long-term stability with remaining voltaic efficiency of 56% at a charge/discharge current density of 5 mA cm⁻² after running 250 cycles (ca. 42 h). Moreover, the power density was as high as 104.5 mW cm⁻² at 0.65 V, and such three Zn-air batteries connected in series could light up 34 LED bulbs (2 V and 1.5 W for each) used for constructing a figure of ‘USTL’ for at least 12 h. This research provides a facile method on the synthesis of efficient and cost-effective ORR electrocatalysts in renewable energy storage and conversion systems.

1. Introduction

Metal-air batteries and hydrogen-oxygen fuel cells are indispensable in the next generation of renewable energy storage and conversion systems from sustainably environmental point of view [1]. However, the scarcity, high price, and low stability of the conventionally cathodic electrocatalyst, i.e. Pt and its alloys for oxygen reduction reaction (ORR) in those systems have severely hindered their large-scale application [2]. Moreover, the slow kinetic of ORR that occurs in the air electrode inevitably led to low discharge voltage, stability, and voltaic efficiency of the current metal-air batteries [3]. Although a lot of effort and time have been invested in the synthesis of high-performance non-noble metal catalysts, achieving stable and effective ORR electrocatalysts still remains a challenge [4].

Recently, due to the existence of metal, carbon and nitrogen species, metal-organic frameworks (MOFs) have been frequently reported as high-potential precursors to prepare high-performance ORR electrocatalysts [5, 6]. For example, the electrocatalysts derived from Co-based ZIFs exhibited excellent ORR activity, which was ascribed to the formation of porous structure with numerous active centers after pyrolysis. However, the active sites, e.g. highly dispersed Co–N–C groups were often located on the surface of micropores inside the ZIF-derived porous carbon. The long diffusion pathway of dissolved oxygen to the active sites in the limited pore channels would thus inevitably limit the efficient mass transfer and active site utilization [7]. In addition, due to the short spatial distance between adjacent Co atoms in Co-based
ZIFs [8], the aggregation of cobalt atoms into large nanoparticles were often taken place during high-temperature pyrolysis. As a result, the number of active sites would drastically decrease leading to the decline of ORR performance.

For various ORR catalysts, the number of active sites plays a decisive role in their electrocatalytic performance. Single atom catalysts (SACs) are considered as a new family of heterogeneous catalytic materials, which have demonstrated unique catalytic behavior in different reactions [9–12]. Specifically, the advantages of ultra-high intrinsic reactivity, maximized atomic efficiency, good electronic conductivity, and fast ion transport imparted by the carbon skeleton has positioned SACs among the best substitutional ORR catalysts. Therefore, SACs notably constitute the frontier of advanced electrocatalysis research.

Despite the advantages of SACs, their manufacture is still a research challenge. A common method used to synthesize SACs materials is to pyrolyze metal-containing carbon matrix or MOFs enriched with carbon, nitrogen, and transition metals [13–15]. However, the elaborate synthesis process in terms of precise precursor preparation and stringent pyrolysis conditions are the limited factors to further develop SACs. Hence, efforts have been continuously made on identifying suitable precursors and optimizing fabrication processes to finally achieve high-performance SACs [16]. On the other hand, heteroatoms, such as N, doped in carbon matrix have been proved to be effective on improving the ORR performance by tuning the sp² spin density of adjacent carbon atoms, thereby adjusting their surface electronic structures and behaving as active centers with a strong oxygen adsorption capacity [17]. Their doping level could be further enlarged by binding with transition metal atoms, among which Cu and Zn ions have shown the strongest binding ability to form M–N–C (M = Cu or Zn) active sites [18]. In the famous ‘volcano plot’, Cu is located closely to Pt, which possesses excellent ORR activity [19].

In this work, we used ZIF-8 as precursor to fabricate porous carbon, followed by mixing it with melamine and copper acetate, which were used as additional N-dopants and Cu-atom precursors, respectively, to finally obtain Cu-atom modified N-doped porous carbon (PC) catalysts. During the pyrolysis process, fast diffusion of Cu ions could be confined by the microporous structure of ZIF-derived carbon resulting in the uniform distribution of Cu-atoms in carbon matrix [20]. Meanwhile, the existence of Cu would also favor the formation of Cu–N, thereby increase the content of N-dopants in carbon skeleton and enhance the ORR activity. The as-synthesized Cu-NC exhibited prominent charge/discharge activity, power density and stability in a constructed Zn-air battery. Importantly, it demonstrated an impressive practical application on lighting a LED-based figure.

2. Methodology

2.1. Preparation of samples

Zinc nitrate hexahydrate (2.94 g) was first mixed with 100 ml methanol to form the solution A.

2-methylimidazole (3.24 g) was separately mixed with 100 ml methanol to form the solution B. Then A and B were mixed and stirred for 24 h, followed by centrifuged, washed with methanol for three times, and dried under vacuum at 80 °C, to finally obtain ZIF-8.

ZIF-8 was then pyrolyzed in Ar at a heating rate of 10 °C min⁻¹ to 800 °C and kept at this temperature for 2 h. As a result, PC was obtained, which was subsequently used as carrier for transition metals.

Sixty milligram PC was then mixed with 6.7 mmol glucose, 0.3 mmol Cu(CH₃COO)₂, and sonicated for 30 min, washed with water, and dried under vacuum at 60 °C. The as-prepared sample was ground together with melamine with a mass ratio of 1:5 before being placed into a horizontal tube furnace, which was heated to 800 °C at a heating rate of 10 °C min⁻¹ in Ar and kept for 2 h before it was naturally cooled to room temperature. The black solid powder samples, denoted as Cu-NC, was obtained.

2.2. Characterization of samples

The morphology and structure of the prepared samples were investigated by scanning electron microscopy (SEM) using a TESCAN MIRA3 system and transmission electron microscopy (TEM) using a Tecnai F30 system. X-ray diffraction (XRD) measurements were performed with a Rigaku Smartlab diffractometer using a Cu Ka (k = 1.5418 Å) radiation. And x-ray photoelectron spectroscopy (XPS) measurements were carried out with a ESCALAB 250xi electron spectrometer.

2.3. Electrochemical measurements

Electrochemical measurement of the as-synthesized electrocatalysts was carried out in a three-electrode system with the combination of CHI 760 E electrochemical workstation (CHI Instruments, China) and RRDE-3A research instrumentation (ALS, Japan). A rotated ring disk electrode (RRDE) was used as working electrode (glassy carbon with an area of 0.1256 cm² and Pt with an area of 0.157 cm² were used as disk and ring, respectively). An Ag/AgCl/3 M KCl electrode and a Pt-mesh (1 × 1 cm²) were used as the reference and
counter electrodes, respectively. Five milligram of catalyst powder was dispersed in a mixture of 0.49 ml water, 0.49 ml ethanol and 0.02 ml Nafion (5 wt.%), and ultrasonicated for about 30 min to obtain an uniform catalyst suspension. The catalyst loading of 0.21 mg cm\(^{-2}\) was obtained by coating 5.5 \(\mu\)l catalyst ink on the glassy carbon of RRDE followed by drying at room temperature for 30 min. Oxygen was purged into 0.1 M KOH electrolyte before measurements to research the saturation. Linear sweep voltammetry (LSV) was applied in the voltage range of 0.2 \(-\) 1.0 V to evaluate the catalyst with rotating the electrode at different rotation speeds (100, 400, 900 and 1600 rpm). Pt-ring was constantly polarized at a potential of 0.4 V to detect the production of hydrogen peroxide during ORR over the prepared catalyst supported on glassy carbon. The electron transfer number was calculated according to Koutecky–Levich equations [21]. The electron transfer number \((n)\) and hydrogen peroxide yield (H\(_2\)O\(_2\) %) were also determined based on the RRDE measurements according to the equations described [21]. Calculation details are presented in supplementary document (available online at stacks.iop.org/JPMATER/4/024006/mmedia). The kinetic performance of the catalyst was verified by using multi-step chronamperometry (\(-0.1 \sim -3.5\) mA cm\(^{-2}\), interval of 0.5 mA cm\(^{-2}\)) in O\(_2\)-saturated 0.1 M KOH. Stability test was carried out for 65 h in 0.1 M KOH with continuously supplying oxygen at a constant current density of \(-1\) mA cm\(^{-2}\). In this case, graphite electrode was used as catalyst support in order to achieve better catalyst adhesion for long-term measurement. In this work, the potentials were reported against reversible hydrogen electrode (RHE) [21].

2.4. Assembly of rechargeable Zn-air battery

The Zn-air battery was assembled by using the catalyst supported on carbon fiber paper as the cathode, and a Zn-plate as the anode. ZnCl\(_2\) (0.2 M)/KOH (6.0 M) was the electrolyte. Two times of 0.02 ml catalyst ink of Cu-NC (5 mg ml\(^{-1}\)) was casted on carbon fiber paper (\(A = 0.2\) cm\(^2\)) in order to achieve a final loading of 1 mg cm\(^{-2}\). LAND-CT3001A (LAND Electronics Co. Ltd, China) testing device was applied to evaluate the charge/discharge performance and cycling reversibility of the constructed battery. During the measurements, oxygen was continuously fed into the cathode. The charge/discharge current density was 5 mA cm\(^{-2}\) and lasted for 250 cycles with each cycle of 600 s.

3. Results and discussion

The morphologies and components of the as-prepared PC and Cu-NC sample were studied by SEM and energy dispersive x-ray spectroscopy (EDS) (figures 1(a) and (b)). The original ZIF-8 that was known with polyhedral shape [22] was distorted after pyrolysis as shown in figure 1(a). Despite of the detectable elemental Pt and Al originated from the conductive coating prior to the SEM measurement and the SEM-holder, respectively, the EDS spectrum confirms the existence of the dominated elemental components, such as C, N, O and Zn. However, with the introduction of melamine and copper acetate as the N-dopants and single Cu-atom sources, the formation of clear cross-linked structure was observed (figure 1(b)). This was most likely due to the presence of melamine enveloping ZIF-8 structures. The presence of Cu elements in its corresponding EDS spectrum indicated that Cu has been successfully loaded onto the PC. TEM images further confirm the microstructure of the prepared samples (figures 1(c)\(-\)1(f)). Bulky objects with diameters of ca. 30 \sim 100 nm were presented in the PC sample (figure 1(c)) and typically with micropores (figure 1(d)). However, the bulky objects were merged together for the Cu-NC sample (figure 1(e)), in agreement with SEM results. It is particularly important to note that there were no metal/metal oxide crystals observed in the high-resolution TEM image of the formed Cu-NC. On the contrary, much densed bright spots marked partially with red circles was clearly visible, which were believed to be isolated Cu-atoms (figure 1(f)). Multiple heteroatoms such as transition metals (Cu and Zn) and N in carbon composites would conjointly play active roles as active centers to enhance the oxygen electrocatalysis [21, 23].

The XRD patterns of PC and Cu-NC present two broad diffraction peaks at around 26.0\(^\circ\) and 44.2\(^\circ\) (figure 2(a)), which are well indexed to the (002) and (100) reflections of graphitic carbon, respectively [20]. Although it was not observable in TEM images, the peaks observed at 43.3\(^\circ\), 50.4\(^\circ\) and 74.1\(^\circ\) for Cu-NC corresponding to the (111), (200) and (220) reflections of metallic Cu hint the possible existence of crystallized Cu (PDF\#04-0836). Raman spectra of PC and Cu-NC are shown in figure 2(b). The D-band at 1351 cm\(^{-1}\) and the G-band at 1594 cm\(^{-1}\) correspond to structural defects and graphitic structures, respectively [24]. The increased intensity ratio of D-band to G-band (\(I_D/I_G\)) in Cu-NC (1.43) in comparison with PC (1.26) reflected the increased defective level of carbon, which was ascribed to the heteroatom-doped configurations in carbonaceous matrix. On the one hand, the incorporated N possibly occupies the lattice positions of carbon, thereby increasing the disordered level in the carbon structure. Such defects are realized to alter the specific surface area and surface hydrophobicity of the carbon material, the contact with the electrolyte. On the other hand, it is believed that the adsorption/desorption of the oxygen and the intermediates during ORR would be improved by the introduction of heteroatoms in the carbon matrix due
Figure 1. EDS spectra and the corresponding SEM images (insets) of (a) PC and (b) Cu-NC, TEM images of (c) PC and (d) Cu-NC, and high-resolution TEM images of (e) PC and (f) Cu-NC.

Figure 2. (a) XRD patterns, and (b) Raman spectra of PC and Cu-NC.
to their function on the modulation of the local spin or charge density of the adjacent carbon atoms [25–27].

The intensity ratios of 2D-band at 2710 cm\(^{-1}\) and (D + G)-band at 2945 cm\(^{-1}\) (I\(_{2D}/I_{D+G}\)) were 1.06 and 1.20 for PC and Cu-NC, respectively. Obviously, there was a stronger distortion of aromatic carbon rings in Cu-NC due to the introduction of Cu. It has been reported that the increased defective active sites and structural distortion would promote the oxygen reactions [21].

XPS was used to reveal the chemical composition of the sample surfaces since its maximum detection depth was ca. 10 nm (figure 3(a)) [28]. The characteristic peaks of Cu 2p\(_{3/2}\) and Cu 2p\(_{1/2}\) were clearly detected indicating that Cu was well dispersed on the surface of Cu-NC catalyst (inset of figure 3(a)). The characteristic peaks of the XP Cu 2p spectrum at 932.5 eV was attributed to Cu(0)/Cu(I) species [22, 29]. The detection of Cu(0) species agrees well with the XRD result, whereas the satellite peak ranged from 940 to 946 eV confirmed the existence of Cu(II) species possibly due to the partial oxidation of Cu in natural oxidative environment [29, 30]. The XPS N 1s spectrum of PC were deconvoluted into three peaks at 398.5,
The excellent electrocatalytic ORR activity, selectivity and durability of Cu-NC prompted us to study its feasibility in practical applications. Therefore, we constructed a homemade Zn-air battery, in which Zn-plate was the anode, Cu-NC catalyst loaded on carbon fiber paper was the air cathode, and the mixed 6 M KOH solution was the electrolyte. Three fabricated Zn-air batteries connected in series could successfully light up 34 red light-emitting diodes (LEDs, 2 V and 1.5 W for each) with forming a ‘USTL’
Figure 4. ORR performance of PC and Cu-NC. (a) LSV curves recorded at the glassy carbon (disk) and Pt (ring) electrode of RRDE at a scan rate of 5 mV s\(^{-1}\) showing the ORR and \(\text{H}_2\text{O}_2\) generation. (b) Electron transfer number \((n)\) and average percentage of \(\text{H}_2\text{O}_2\) production in the potential range of 0.2 \sim 0.8 V. (c) Corresponding Tafel plots derived from (a). (d) LSV curves of Cu-NC recorded at different rotation speeds, and Koutecky–Levich plots at diverse potentials (0.2 \sim 0.8 V) (inset). (e) Time dependence of potentials of Cu-NC recorded at different current densities. (f) Chronoamperometric responses at a constant current density of \(-1\) mA cm\(^{-2}\) showing the long-term durability of Cu-NC.

figure for at least 12 h demonstrating a high capacity (figures 5(a) and (b)). The open circuit voltage of the Zn-air battery based on Cu-NC was as high as 1.4 V (figure 5(c)), close to the battery assembled with the most advanced benchmark Pt/C + Ir/C catalysts (1.42 V) [43]. The discharge rate capability was examined as a function of current density (5 \sim 50 mA cm\(^{-2}\)) (figure 5(d)). The battery discharge overpotential was increased with increasing current density as expected [44]. The small voltage gap between the charge and discharge polarization curves indicated the prominent charge/discharge ability of the constructed Zn-air battery (figure 5(e)) [45]. The peak power density of the constructed Zn-air battery assembled with Cu-NC at 0.65 V was as high as 104.5 mW cm\(^{-2}\), notably better than the battery constructed with commercialized Pt/C + RuO\(_2\) catalyst as the cathode (figure 5(f)). The long-term galvanostatic charge/discharge cycling life of the constructed battery was further tested at an alternative current density of 5 mA cm\(^{-2}\) for 250 cycles with each cycle lasting for 10 min (figure 5(g)). The voltaic efficiency increased from 54.6% to 56% after running 250 cycles (ca. 42 h) revealing superior rechargeability and stability of the constructed Zn-air battery.

In short, the impressive performance of the prepared Cu-NC sample can be ascribed to the following reasons: (a) the atomic interface chemistry between the metal-atom-isolated active species and the carbon carrier could realize the adjustment of the local coordination environment and electronic state. (b) The heteroatom N in the carbon matrix could behave as the anchoring centers to fix the monodispersed active Cu atoms forming Cu–N–C groups, which are important active sites for ORR. (c) The introduction of Cu would increase the total nitrogen content in the catalyst through the combination of Cu with N, resulting in the effective improvement of ORR activity. (d) The high surface area donated by the three-dimensional porous structure would favor the homogeneous dispersion of atomic Cu and the Cu–N–C groups, thereby accelerating the ORR process. (e) The porous structure with large specific surface area allows the fast mass
Figure 5. The performance of constructed Zn-air battery. (a), (b) Thirty-four LEDs lighted up for at least 12 h by three Zn-air batteries connected in series. (c) Open circuit potential. (d) Discharge curves at different current densities. (e) Charge and discharge polarization curves. (f) Discharge and power density curves. (g) Charge/discharge profiles of rechargeable Zn-air battery containing Cu-NC as the cathode catalyst and Zn-plate as the anode with duration of 10 min per cycle at an alternative current density of 5 mA cm$^{-2}$, and the enlarged curve for the last ten discharge/charge cycles (inset).

4. Conclusion

We have reported a high-performance ORR electrocatalyst, which was synthesized using ZIF-8 as the precursor. The presence of heteroatoms such as Cu and N-dopants concomitantly promoted the electrochemical performance of the as-synthesized Cu-NC catalyst in a constructed rechargeable Zn-air battery. The voltaic efficiency remained 56% after 250 durability cycles (ca. 42 h) at an alternative charge/discharge current density of 5 mA cm$^{-2}$. Importantly, it demonstrated its practical application in and electron transfer. (f) The coexistence of bimetallic Cu and Zn would possibly synergistically improve the ORR performance.
lighting a LED-based figure for at least 12 h. Consequently, our prepared electrocatalyst possesses a broad commercialized prospect in renewable energy conversion systems, in which ORR is involved.

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

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