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Enhanced utilization of active sites of Fe/N/C catalysts by pore-in-pore structures for ultrahigh mass activity

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Abstract

Carbon material doped with nitrogen and transition metal is a kind of promising candidate of the platinum for oxygen reduction reaction (ORR) process due to its low cost, efficiency and stability. Here we demonstrate an original type of Fe/N/C catalyst based on pore-in-pore structures (P–P Fe/N/C), showing one of the highest oxygen reduction reaction performances among all reported Fe/N/C-type catalysts (onset potential of 0.995 V, half-wave potential of 0.881 V vs. RHE with a relatively low mass loading of 0.32 mg cm⁻² and long-term durability (97% relative current in 60 000 s operation) in alkaline media. Such outstanding performances can be ascribed to the efficient active sites activated by the encapsulated atomic and subnanoscale iron, and great exposure of these active sites due to the unique pore-in-pore hierarchical construction. Once assembled in lithium–O₂ batteries, a specific capacity of 7250 mA h g⁻¹ at 70 mA g⁻¹ can be obtained by the P–P Fe/N/C catalyst. Moreover, upon cycling, the P–P Fe/N/C electrode can be cycled 150 times with no capacity loss, which is much longer than six cycles of pure Super P air electrode. These results evidently reveal the developed Fe/N/C catalyst holds great promise to serve as an alternative to the conventional Pt-based noble metal catalysts.

Supplementary material for this article is available online

Keywords: Fe/N/C, oxygen reduction activity, pore-in-pore, lithium-oxygen battery

(Some figures may appear in colour only in the online journal)

1. Introduction

For developing highly efficient metal-air batteries and fuel cells, the oxygen reduction reaction (ORR) is a critical electrochemical conversion process [1–3]. Pt and Pt-based alloys are the most efficient ORR catalysts and numerous studies have focused on catalysts with ultra-low Pt content to enhance ORR activity [4]. Nevertheless, practical applications of these Pt-based nanocatalysts were still impeded due to their prohibitive cost and shortage, low stability, and the

issue of methanol crossover [5, 6]. As a result, much effort has been made to develop effective, durable and low-cost nonprecious-metal catalysts (NPMCs) to substitute for the precious Pt-based ORR catalysts. Generally, the catalytic activity of NPMCs are dominated by two fundamental elements: (i) the essential nature of active sites, dependent on the chemical constitution and the interactions between different compositions; (ii) the kinetic performances of different oxygen reduction relevant species and access to active sites, which benefit from large specific surface area [7–9].

Many types of catalytic materials were explored, for example, transition-metal/nitrogen-doped carbon compounds (M/N/C, M = Co, Ni, Fe, etc) [10–12], metal-free

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Figure 1. (a) Schematic illustration of the synthesis process. (b) SEM image. (c) HAADF–STEM image. (d) HRTEM image with carbon nanopores. (e) HRTEM image with a nanoparticle–encapsulation structure. The inset was a SAED pattern. (f)–(h) Mapping images.

nitrogen-doped carbon materials [13-15], metal oxide [16-18] and chalcogenides [19]. However, the performance of these materials is still unsatisfactory for widespread commercial applications. Ternary M/N/C was generally considered as one of the most promising candidates because its effective active sites were deemed to involve doped nitrogen cooperated with metal elements in the carbon matrix [20, 21]. Iron and nitrogen co-doped carbon materials (Fe/N/C) have been experimentally and theoretically discovered to exhibit comparable ORR activities to the state-of-the-art Pt/C catalysts [22, 23]. However, there is still a need for higher kinetic activity in Fe/N/C catalysts for further reducing the overpotential. A new insight revealed the existence of porphyrinlike $FeN_4C_{12}O_2$ moieties in nitrogen- and iron-doped carbon could efficiently catalyze the four-electron dioxygen reduction to OH⁻. The formation of FeN4 pyridinic moieties and pyrrole-type C4N rings had been found more favorable when bridging in and at the edges of graphitic micropores [24].

Herein, an original type of Fe/N/C NPMCs of pore-in-pore iron–nitrogen-doped carbon is demonstrated (hereafter called as P–P Fe/N/C), possessing the desired features for ORR: i) active sites activated by the encapsulated atomic and subnanoscale iron and a share of nitrogen doping of ~3.72 at% on the graphitic carbon; ii) access to active sites due to its high specific surface area of 893.73 m² g⁻¹ with pore-in-pore hierarchical construction. These beneficial characteristics led to outstanding ORR activity in the alkaline electrolyte (onset potential (E_{onset}) of 0.995 V versus the reversible hydrogen electrode (vs. RHE), half-wave potential $(E_{1/2})$ of 0.881 V vs. RHE with a relatively low mass loading of 0.32 mg cm⁻², 97% relative current retention in 60 000 s operation), illustrating one of the highest activities among all reported NPMCs. Once assembled in lithium-O2 batteries (LOBs), a specific capacity of 7250 mA h g⁻¹ at 70 mA g⁻¹ can be obtained by the P-P Fe/N/C catalyst. Moreover, upon cycling, the P-P Fe/N/C electrode can be cycled 150 times with no capacity loss, which was much longer than six cycles of pure Super P air electrode. These results evidently revealed the developed Fe/N/C catalyst was a promising alternative to Pt-based noble metal catalysts, which were mainly due to the favorable utilization of efficient ORR active sites benefitted from interactions between the encapsulated atomic and subnanoscale iron and nitrogen dopant species on unique pore-in-pore hierarchical graphitic carbon.

2. Results and discussion

The preparation of the P–P Fe/N/C involved three key steps, as shown in the schematic illustration of figure 1(a): (i)



Figure 2. (a) XRD profiles, (b) full XPS spectra, (c) high-resolution N 1s XPS spectra, and (d) N₂ sorption isotherms of P–P Fe/N/C. Inset: pore size distribution of P–P Fe/N/C. (e) Cyclic voltammograms of bare GCE and different samples modified GCE in a 10 mM K₃Fe(CN)₆ and 0.1 M KCl solution at a scan rate of 80 mV s⁻¹. (f) Peak currents as a function of scan rate for the determination of the effective working surface area.

the combination of hard-templating synthesis with PPy-Fe coordination complex as a precursor [25, 26]; (ii) pyrolysis of the prepared materials under flowing Ar atmosphere and removing the templates; and (iii) etching with 5% HF solution. The comparative electrocatalysts of CNs (carbon networks, with glucose as carbon source) and N-CNs (N-doped carbon networks, with dopamine as carbon and nitrogen sources) were produced with the same method (figure S1). The P-P Fe/N/C catalyst material was indicated to be uniform carbon networks consisted of spherical pores with an average diameter of about 150 nm in the SEM image of figure 1(b). The high-resolution TEM images is partly enlarged from the darkfield scanning transmission electron microscopy (HAADF-STEM, figures 1(c)-(e) evidently exhibited carbon nanopores and nanoparticle-encapsulated structure respectively in the networks, exactly reflecting the hierarchically pore-in-pore structures with uniform distribution of carbon, nitrogen, and iron as seen in the element mapping images (figures 1(f)-(h)). The clear lattice fringes observed in figures 1(d) and (e) revealed the good crystallinity of typical carbon mesopores and the Fe₃C nanoparticle. Well-defined crystalline lattice spacing of 0.21 nm was consistent with the (211) planes of Fe₃C and the lattice fringe with 0.34 nm was referred to the (002) planes of graphitic carbon. The selected area electron diffraction (SAED) pattern further implied the crystalline structure of graphite (the diffraction peak of 26.5° corresponding to the (002) plane of graphite) and confirmed the existence of Fe_3C phase, highly coordinating with the x-ray diffraction (XRD) results (JCPDS, no. 89-2867) (figures 2(a) and S2). However, the content of Fe₃C phase was extremely tiny, as the signals referred to Fe_3C shown in SAED and XRD profiles were so faint. The Fe content is approximately 2.81 wt% as determined by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. In the element mapping of figure 1(h), it was evident that Fe element homogeneously dispersed on the carbon networks, with a little in the form of Fe₃C nanoparticles but the majority in the other form, whose size was at the atomic or subnanoscale level as it could not be observed in the HRTEM images.

The chemical species and element bonding environment in the P-P Fe/N/C was elucidated by x-ray photoelectron spectroscopy (XPS) measurement, in which the peaks of C 1s, N 1s and O 1s are all clearly observed (figures 2(b) and S3). However, no Fe 2p signal was observed mainly because the Fe-based phase was greatly sealed in the N-doped carbon shell [27, 28]. The complex N 1s spectra 3.72 at% content within figure 2(c) can be deconvolved into pyridinic N or N-Fe, graphitic N, oxidized N, and pyrrolic N [29-31], in which some of them serve as the anchor points for iron. Significantly, Fe species at the atomic or subnanoscale level were highly uniformly distributed in a carbon/nitrogen matrix, and the existence of active Fe–N χ and C–N χ sites [32] were believed, which contributed largely to the high catalytic performance for oxygen reduction reaction. The great exposure of these active sites was first studied by the nitrogen sorption measurements. For P-P Fe/N/C, its Brunauer-Emmett-Teller (BET) surface area along with total pore volume were 893.73 m² g⁻¹ and 1.05 cm³ g⁻¹, respectively (figure 2(d), table S1), significantly larger than N-CN and CN (figure S4). Moreover, in order to evaluate the effective surface area, CV



Figure 3. (a) CV curves of P–P Fe/N/C and Pt/C in O_2 – and N_2 -saturated 0.1 M KOH electrolyte. (b) LSV curves of different samples at a rotation rate of 2025 rpm in the O_2 -saturated 0.1 M KOH electrolyte. (c) Tafel plots constructed from the voltammetry data. (d) LSVs curves with various rotation rates and (e) corresponding K–L plots at different potentials of P–P Fe/N/C. (f) Durability comparison of the P–P Fe/N/C and Pt/C catalyst.

measurements in a three-electrode cell were carried out in a solution mixing 10 mM $K_3Fe(CN)_6$ and 1 M KCl. The surface area of the bare glassy carbon electrode was calculated to be approximately 0.068 cm², corresponding to the geometric area of 0.071 cm² [33, 34]. The CN, N–CN and P–P Fe/N/C modified electrodes were calculated to exhibit effective surface areas of 0.076, 0.084 and 0.166 cm², respectively (figures 2(e) and (f)). The latter was 2 times larger than the former two samples, illustrating that the effective access to active sites of P–P Fe/N/C was greatly enhanced, which are in favor of the accessibility of active sites and fast transport of oxygen intermediates.

The excellent ORR activity of the P-P Fe/N/C catalyst was first confirmed by the cyclic voltammetry (CV) measurements in 0.1 M KOH (figure 3(a)), with a commercial Pt/C catalyst, CN and N-CN for comparison (figure S5). In the O₂-saturated electrolyte, P-P Fe/N/C exhibited a peak potential at 0.791 V vs. RHE, much higher than that of the reference samples. The linear sweep voltammetry (LSV) measurements were subsequently performed (figure 3(b)). The hierarchical P-P Fe/N/C catalyst exhibited substantial improvement in ORR performance with the Eonset of 0.995 V vs. RHE, $E_{1/2}$ of 0.881 V vs. RHE and limiting current of 6.61 mA cm⁻² (table S2), much better than the noble metal and other reported values of Fe/N/C-type catalysts [35, 36]. For comparison, the LSV measurements for CN and N-CN were conducted with the same mass loading (figure S6). The CN exhibited poorer catalytic property with a larger overpotential due to its nature of chemistry. The introduction of nitrogen into carbon materials was regarded as one of the most efficient methods to generate active sites [37], thus the N–CN derived from dopamine showed relatively enhanced ORR performance (E_{onset} of 0.884 V vs. RHE and $E_{1/2}$ of 0.763 V vs. RHE, table S2). The Tafel slope of P–P Fe/N/C was the lowest and the exchange current density was the largest among all samples, further confirming its remarkable ORR performance (figure 3(c) and table S3) [38, 39].

The electron transfer number (n) can be obtained based on the link between the rotating speed and the limiting diffusion current density via the Koutechy-Levich (K-L) equation (figures 3(d) and (e)). Evidently, the n for P–P Fe/N/C can be comparable to the theoretical value of 4.00, indicating an efficient four-electron dominant process. The superb ORR kinetics of P-P Fe/N/C can further be identified by its desirable conductivity as confirmed by the electrochemical impedance spectroscopy (EIS) measurements (figure S7). The long-term durability of P-P Fe/N/C was evaluated by the chronoamperometric method at a fixed voltage of 0.56 V vs. RHE with 20% Pt/C catalyst as a comparison. Pt/C catalyst exhibited a rapid current decay of 19% (figure 3(f)) due to its poor durability [40, 41]. Impressively, the P-P Fe/N/C exhibited a high current retention of 97% during 60 000 s operation, demonstrating its outstanding stability toward ORR. Chronoamperometric responses to methanol were also measured and compared (figure S8). No noticeable change was observed in the ORR current on the P-P Fe/N/C catalyst after the addition of 1 M methanol, suggesting a great methanol-tolerant ability.

Furthermore, we studied the impact of catalyst loading on catalytic performance (figures 4(a) and S9). The best performance was yielded with a catalyst loading of



Figure 4. (a) ORR LSV curves of different mass loadings of P–P Fe/N/C at rotation rate of 2025 rpm to investigate influence of mass loading on ORR activity in 0.1 M KOH solution. (b) Tafel plots constructed from the voltammetry data. (c) Required potentials for $j = 3 \text{ mA cm}^{-2}$, and current densities at 0.82 V.



Figure 5. LOBs performance of the catalysts. (a) Schematic illustration of P-P Fe/N/C effect during discharge. (b) The discharge curves of P-P Fe/N/C and Super P electrode at different current densities. (c) Discharge capacity and the discharge terminal voltage vs. the cycle number.

 0.32 mg cm^{-2} and an electron transferred (n) of 4.1 was achieved, indicating a four-electron transfer process in an alkaline aqueous medium. With 0.15 mg cm⁻² loading, the P-P Fe/N/C exhibited almost the same Tafel slope and n with those of 0.32 mg cm⁻² (figure 4(b)), and obviously superior ORR activity to that of Pt/C. In addition, higher electrocatalytic activity than Pt/C materials was delivered by P-P Fe/N/C catalyst even with lower loading of 0.08 mg cm $^{-2}$. The ORR performance comparison of different samples can be also observed from the required potentials to reach a given current (j) of 3 mA cm⁻² or the j values at a given potential of 0.82 V (figure 4(c)). It was obvious that P-P Fe/N/C exhibited superior ORR activity to Pt/C catalyst even with less mass loading. The exact values were shown in figure 4(c) and the calculated mass activities were listed in the table S4. Significantly, a distinctive characteristic of the P-P Fe/N/C catalyst was obtained, promising to replace Pt-based noble metal catalysts.

The electrochemical performance of P-P Fe/N/C as air cathodes was tested to explore its application in LOBs (figure 5(a)). The discharge specific capacity of the P–P Fe/N/C cathode was evaluated by the galvanostatic discharge-charge test. As shown in figure 5(b), when tested at 70 mA g^{-1} , the LOB with catalyst P-P Fe/N/C exhibited a specific capacity of 7250 mA h g^{-1} , much higher than the pure Super P electrodes with 2725 mA h g^{-1} [42]. It was found that its discharging platform for the first cycle was about 2.70 V, revealing its superior ORR activity. Besides, the overpotential between the charging and discharging platforms of the P-P Fe/N/C catalyzed electrode was 1.4 V, less than 1.8 V for Super P cathode, indicating that P-P Fe/N/C can effectively reduce the overpotential of the discharge-charge process, consequently yielding an enhanced round-trip efficiency [43, 44]. Meanwhile, the P-P Fe/N/C electrode delivered specific capacities of 5114, 2814 mA h g⁻¹ at current densities of 200 and 500 mA g⁻¹ respectively, exhibiting good rate performance of P-P Fe/N/C catalysts. Cycling performance of the batteries was another big concern for practical applications. LOB was cycled with a lower restricting capacity of 1000 mA h g⁻¹ at 200 mA g⁻¹ as shown in figure 5(c). Apparently, the P-P Fe/N/C electrode can be cycled 150 times with no capacity loss, which was much longer than six cycles of pure Super P air electrode [44]. These results confirmed that the P-P Fe/N/C was beneficial for enhancing the LOB properties as the cathode catalyst.

3. Conclusion

In conclusion, the non-precious Fe/N/C catalysts with enhanced utilization of active sites by pore-in-pore structures for ultrahigh mass activity was reported as an alternative to the noble metal catalysts, which possessed desired features for ORR: (i) active sites activated by the encapsulated atomic and subnanoscale iron and a share of nitrogen doping of ~3.72 at% on the graphitic carbon; (ii) access to active sites due to its high specific surface area of 893.73 m² g⁻¹ with pore-in-pore hierarchical construction. The catalyst exhibited excellent ORR electrocatalytic activity with E_{onset} of 0.995 V vs. RHE, $E_{1/2}$ of 0.881 V vs. RHE with a relatively low mass loading of 0.32 mg cm⁻², and 97% relative current retention in 60 000 s operation in alkaline. Once assembled in LOBs, a specific capacity of 7250 mA h g⁻¹ at 70 mA g⁻¹ can be obtained by the P–P Fe/N/C catalyst. Moreover, upon cycling, the P–P Fe/N/C electrode can be cycled 150 times with no capacity loss, which was longer than six cycles of the pure Super P air electrode. This type of carbon material based on non-precious transition metal and nitrogen doping was a promising candidate for Pt-based catalysts for the ORR process.

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Data availability

The data that supports the findings of this study are available from the corresponding author upon reasonable request.

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