Dual-doped mesoporous carbon synthesized by a novel nanocasting method with superior catalytic activity for oxygen reduction

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Fe and N dual-doped mesoporous carbon catalyst demonstrated superior catalytic activity than Pt catalyst for both oxygen reduction and oxidation reactions in alkaline electrolyte. The catalyst was synthesized through a novel simple sublimation and capillary assisted nanocasting method. Using the method, multiple transition metal and nitrogen dual-doped mesoporous carbon electrocatalysts were also successfully made. It was believed that the excellent catalytic activity was resulted from the synergistic effects of highly active metal-nitrogen species, mesoporous structure, large interfacial surface and excellent conductivity. The present synthetic strategy offers a new insight into preparation of heteroatom-doped electrocatalysts with promising applications in metal-air batteries, fuel cells, and supercapacitors as well.

1. Introduction

Among many potential chemistries, the batteries with air cathode have attracted lots of attention because of their high theoretical energy density due to the abundance of O2, e.g. Li-air batteries [1–5]. Among various types of metal-air batteries under development, zinc-air battery is of great importance because of its low cost and safety apart from high energy density [6–9]. Zn-air coin cells have been on the hearing-aid market for many decades and are currently sold for more than 500 million dollars a year worldwide [10]. Two major obstacles toward large format and long lasting Zn-air cells are the electrolyte carbonization and poor durability of the O2 reduction catalyyst. Highly efficient and stable electrocatalysts towards oxygen reduction reaction (ORR) in an air electrode are essential to achieve optimal performance and lifetime for metal-air batteries due to the sluggish ORR kinetics [11–17]. Unlike PEM fuel cells where Pt catalyst is almost exclusively used, the alkaline environment in a Zn-air cell opens up avenues for non-noble metal catalysts. Among them, manganese dioxide (MnO2) is the catalyst used in commercial Zn-air cells [18]. However, Pt catalyst remains to the highest durability and catalytic activity against its non-noble metal counterparts. Therefore, there have been a continuous effort in quest of good performing catalysts for ORR in an alkaline electrode. Transition metal and nitrogen co-doped carbon materials have been actively pursued in recent years. For example, an iron/cobalt-nitrogen co-doped carbon exhibited an excellent power density of about 0.24 mW cm−2 [19]. Although the nature of the active sites and the catalytic mechanism are not yet clearly understood, it seems that the increase in surface density of accessible active sites plays an important role in enhancing the ORR activity of transition metal and nitrogen co-doped carbon catalysts [20–22].

Ordered mesoporous carbon possesses high porosity, large accessible surface area, excellent conductivity and superior stability, as well as extraordinarily broad chemical and structural diversity [23,24]. These unique features offer large interfacial area for reaction, fast pathway for charge transport, and shortened diffusion...
path for active species and oxygen gas. It therefore holds great promise as ORR electrocatalysts for metal-air batteries. The nanocasting technique with a porous metal oxide as hard templates was used regularly for the preparation of ordered mesoporous carbon materials. In this method, carbon precursors were infiltrated into the voids of the hard template with a specific structure to achieve a sufficiently high loading [25,26]. However, it is challenge to form a transition metal and nitrogen co-doped ordered porous carbon materials, owning to the poor solubility of metal-macrocyclic complexes in most solvents as well as the poor wettability of the solvent (or melted precursors) on the pore surface of the template. Taking the advantage of capillary condensation in narrow hydrophilic channels [27–31], an innovative method was developed based on the sublimation of the precursors and subsequent loading into the template through capillary condensation. The sublimation and capillary assisted nanocasting method (abbreviated as SCANC) was used for the synthesis of the material in this paper.

Benefiting from the merits of the highly active metal-nitrogen species, ordered porosity for facile reactant transportation, and large interfacial surface, sufficient active sites of the catalyst were exposed. The metal and nitrogen co-doped mesoporous carbon (M-N-MC) demonstrated outstanding catalytic activity toward ORR in alkaline environment. The new SCANC technique opens up a new avenue for the fabrication of heteroatom-doped electrode materials for energy storage and conversion devices.

2. Experimental

2.1. Synthesis of ordered mesoporous silica SBA-15 template

SBA-15 template was synthesized with a soft template method [32]. Firstly, 4.0 g Pluronic® P123 triblockcopolymerpoly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (denoted by (PEO)20(PPO)70(PEO)20, M_{ave} = ~5800, Sigma-Aldrich) was added into 150 mL of a 1.6 M HCl solution in a round-bottom flask. The solution was stirred overnight at 35 °C. Tetraethyl orthosilicate (TEOS, Sinopharm) (8.5 g) was then quickly added to the solution under vigorous stirring. After stirring for 5 min, the mixture was rested at 35 °C for 20 h. The reaction mixture was then transferred to a PTFE-lined autoclave and heated at 130 °C for 24 h. The solid products were collected after filtration, washing (with water and ethanol), drying, and finally calcination at 550 °C for 6 h in air.

2.2. Synthesis of metal and nitrogen co-doped mesoporous carbon (M-N-MC)

Metallophthalocyanines (abbreviated as MPc, wherein M=Fe, Co, Ni or Cu) which have vapor pressures of about 100 Pa at 500–600 °C [33,34] were used as the sources of metal, nitrogen and carbon, while mesoporous silica were used as the hard template. The M-N-MCs were synthesized by a solid-state nanocasting method using SBA-15 as the scaffold template and MPc (including FePc, CoPc, NiPc and CuPc) as the carbon source. Briefly, 0.5 g of SBA-15 was mixed with 0.5 g of MPc, and the mixture was ground
for 10 min in a mortar. The mixture was sublimated at 550 °C for 1 h followed by calcination at 600–900 °C for 6 h with a ramping rate of 3 °C min⁻¹ in an argon atmosphere. Once sublimated, the metal-macrocyclic precursors entered the template structure and subsequently condensed inside the capillary structure of the template due to the difference in the saturated vapor pressures inside and outside the capillary. Sufficient high loading of precursors can thus be achieved, which made the structure of these carbon-based materials well controlled after carbonization. After calcination, the resultant carbon-silica composites were immersed in an aqueous solution of HF (10 wt%) for 24 h. The M-N-MCs were collected after filtration, washing (with water) and drying. Each obtained M-N-MC was denoted by M-N-MC-x, where x represented the calcination temperature.

2.3. Material characterizations

The microstructure of the samples was investigated by transmission electron microscopy (TEM, JEM2010-HR, 200 kV). The crystallographic structure and composition of the products were analyzed using a X-ray diffractometer (D/MAX-RB RU-200B, Japan) equipped with Cu Kα radiation (λ = 0.15406 nm), a micro-Raman system (Renishaw, INVIA, China) with an excitation energy of 2.41 eV (514 nm), and X-ray photoelectron spectroscopy (XPS) on a VG Multilab 2000X-spectrometer using an Al Kα X-ray source (1486 eV). The surface area was determined by liquid nitrogen cryosorption and the distribution of the micropore size was calculated by the Barrett-Joyner-Halenda (BJH) method.

2.4. Rotating disk experiments

All electrochemical tests were carried out in a standard three-electrode cell with a nickel mesh as counter electrode and Ag/AgCl (or Hg/HgO) as reference electrode. Electrode potentials were converted to reversible hydrogen electrode (SHE) scale with \( E(\text{Hg/HgO}) = E(\text{SHE}) + 0.094 + 0.059 \text{ pH} \) or \( E(\text{Ag/AgCl}) = E(\text{SHE}) + 0.197 + 0.059 \text{ pH} \) [35]. An Autolab PGSTAT30 electrochemical test system (Metrohm) was used to conduct all electrochemical measurements. ORR tests were conducted in an oxygen saturated 0.1 M KOH electrolyte at a scan rate of 10 mV s⁻¹ on a rotating-disk electrode. The electrolyte was saturated with O₂ with bubbling high purity O₂ for 30 min before each experiment. The electrochemical measurements were performed under normal pressure. The working electrode was fabricated by casting the catalyst ink onto a glassy carbon electrode (diameter: 5 mm). To prepare the catalyst ink, each sample (4 mg) was ultrasonically dispersed for 30 min in 1 mL isopropanol containing a NaF solution (5 wt%, DuPont). An aliquot (20 μL) of the catalyst ink was coated onto the glassy carbon electrode. The electrode was then hand pressed on a soft glass plate to make the surface flat. Commercial platinum-loaded carbon catalyst (Pt/C, 20 wt% on Vulcan XC-72R, Johnson Matthey) was tested as comparison. The Pt/C catalyst loading is 0.41 mg cm⁻² on a gas diffusion electrode (GDE) prepared according to the procedures in refs [36,37]. The carbon and polytetrafluoroethylene (PTFE) loadings on the carbon paper (TGP-060, Toray Inc.) were about 2.4 mg cm⁻² and 1.1 mg cm⁻², respectively. The catalyst slurry was prepared by mixing 1 g of the catalysts (Fe-N-MC or 20 wt% Pt/C, Johnson Matthey) with 15 mL deionized water and 6.7 mL Nafion solution (DE 520, DuPont) under vigorous stirring, followed by ultrasonic treatment for 30 min and a high-speed homogenizer for 1 h. Then the catalyst slurry was screen-printed onto the gas diffusion layer. After drying at 60 °C for 10 min, the sample was heat-treated at 90 °C for 3 min under a nitrogen atmosphere. The catalyst loading of Fe-N-MC or Pt/C was 1.2 and 0.4 mg cm⁻², respectively.

Fig. 2. (a) TEM and (b) HRTEM images of the as-synthesized Fe-N-MC catalyst. Inset: Photos of the FePc/SBA-15 (left) and Fe-N-MC catalysts (right). (c) HAADF-STEM image of Fe-N-MC. EELS elemental mapping of (d) carbon, (e) Fe, and (f) N.
The GDEs were tested in a cell with a serpentine flow field. The air flow rates were 1000 sccm (standard cubic centimetre per minute). The electrolyte was a solution of 6 M KOH and 0.2 M zinc acetate. A small thin zinc plate was used as the anode. Hg/HgO was used as reference electrode.

3. Results and discussion

Metal and nitrogen dual-doped mesoporous carbon (M-N-MC) catalysts were prepared by a solid-state nanocasting method using SBA-15 as scaffold template and metallophthalocyanine as carbon source. Fig. 1 presents schematically the overall synthetic strategy for the M-N-MC catalysts, which involves evaporation-induced multicomponent self-assembly of metallophthalocyanine and SBA-15 to form a mesocomposite, followed by carbonization and then removal of the SBA-15 template. Taking the preparation of Fe-N-MC-700 (abbreviated as Fe-N-MC in the following) as an example, the FePc firstly diffused into the SBA-15 by heating the mixture of the FePc and SBA-15, and the mixture was heated at 550 °C for 1 h followed by carbonization at 700 °C for 6 h in an argon atmosphere. Finally, the Fe-N-MC catalysts were obtained after removing the SBA-15 template in an aqueous solution of HF. As can be seen from the low angle powder X-ray diffraction (XRD) patterns of the SBA-15 and Fe-N-MC samples (Fig. S1), the Fe-N-MC sample yields three well-resolved diffraction peaks which can be indexed to the (100), (110) and (200) reflections of the highly ordered two-dimensional (2D) hexagonal mesostructure of space group P6mm, indicating that the as-prepared Fe-N-MC possesses typical ordered structure of SBA-15. In comparison with the SBA-15, the position of the diffraction peaks for Fe-N-MC is shifted to higher angle region, suggesting that the Fe-N-MC has a smaller pore size. Additionally, there is no crystalline phase associated with iron oxides or iron nitrides in the powder XRD pattern of the Fe-N-MC sample (Fig. S2), revealing that the iron species are highly dispersed on the mesoporous framework. Transmission electron microscopic (TEM) analyses were conducted to investigate the porous structure of the Fe-N-MC sample. The TEM image shown in Fig. 2a is the Fe-N-MC viewed along the (001) direction. It is clearly demonstrated that the 2D-ordered hexagonal mesostructure can be well retained after removal of SBA-15. From the high resolution TEM (HRTEM) image shown in Fig. 2b, the average pore size and wall thickness were determined as 3.8 and 0.6 nm, respectively. Elemental mapping of C, Fe and N via electron energy loss spectroscopy (EELS) confirmed that Fe and N were homogeneously distributed throughout the porous carbon framework (Fig. 2d–f), which reveal the successful formation of Fe and N dual-doped mesoporous carbon framework.

X-ray photoelectron spectroscopic (XPS) measurements were performed to further probe the elemental composition and bonding of the Fe-N-MC sample. The typical XPS survey spectrum (Fig. 3a) indicates the existence of Fe, N and C in the Fe-N-MC sample. As for the presence of oxygen, it probably originated from the atmospheric O₂, H₂O, or CO₂ adsorbed onto the surface of the
Fe-N-MC sample. The C1s core level XPS spectrum of the Fe-N-MC sample could be fitted to four different types of C functionalities that correspond to C—C (284.8 eV), C—O (285.6 eV), C—O (286.3 eV) and C—N (287.4 eV) bonds, respectively (Fig. 3b) [38,39]. Fig. 3c shows the N 1s core level XPS spectrum together with the deconvolution analysis result. The deconvoluted spectrum indicated the distribution of the N atoms in three different types of electronic environments in the Fe-N-MC sample. They were pyridinic N (398.4 eV, N1), pyrrolic N (400.1 eV, N2), and graphitic N (401.0 eV, N3). The results were consistent with that reported previously [38,39]. Noticeably, the peak at the binding energy of 398.4 eV should also include a contribution from N bound to Fe (denoted by Fe-N), because there is only a small difference between the two binding energies [40–42]. The Fe 2p spectrum displayed the peaks of Fe 2p1/2 and 2p3/2 of oxidized Fe species (Fig. S3) [43]. These results further demonstrated that N and Fe heteroatoms had been doped into the mesoporous carbon framework. The pore size distribution of the Fe-N-MC was determined through N2 adsorption/desorption isotherm using BJH model. The pore distribution is shown in Fig. 3d. A single narrow pore distribution with average pore size of 3.5 nm can be seen in Fig. 3d, which is in excellent agreement with that obtained from HTEM (3.8 nm, Fig. 2a). The BET specific surface area and total pore volume of the Fe-N-MC are calculated to be 988 m2 g−1 and 0.87 cm3 g−1, respectively.

The ORR catalytic activity of the Fe-N-MC was firstly demonstrated by the linear sweep voltammetry (LSV) in an Ar- or O2-saturated 0.1 M KOH solution. LSV for Fe-N-MC and Pt/C catalysts electrodes on a rotating disk electrode (RDE) was done at the rotation rate of 1600 rpm in an O2-saturated KOH solution (Fig. 4a). The Fe-N-MC exhibited a substantially positive ORR onset potential of 1.01 V vs. RHE and a half-wave potential at 0.94 V vs. RHE, which were at least compromised to those of commercial Pt/C catalysts. To the best of our knowledge (Table S1), the positive onset and half-wave potentials for the catalytic ORR were of the best reported for the non-noble metal catalysts, such as B- and N-doped graphene, [36] Fe3O4/N-GAs (3D N-doped graphene aerogels), [37] and Fe-N-C hybrid materials [21]. Furthermore, the diffusion-limiting current density of the Fe-N-MC electrode (5.8 mA cm−2) was even higher than those of the Pt/C electrode (5.3 mA cm−2). To determine the number of electrons transferred during the catalytic ORR, LSV of Fe-N-MC catalyzed ORR was conducted on the RDE at various rotation rates.

The electron-transfer number (n) of the catalytic ORR was calculated with Koutecky-Levich (K-L) equation (Fig. 5a). The K-L plots are shown as the inset in Fig. 4C. As shown in Fig. S5, the calculated electron transfer number of Fe-N-MC catalyzed ORR was about 3.79–3.84 from 0.414 to 0.714 V, which is comparable to Pt/C catalysts (4.03–4.13), indicating that the ORR catalyzed by the Fe-N-MC is a quasi-four-electron process. The detail reaction mechanism is under investigation.

The durability of Fe-N-MC and Pt/C catalysts towards ORR was also evaluated by chronoamperometric measurements at 0.664 V vs. RHE for 10 h. Fig. 4d compares the stability of the Pt/C and Fe-
N-MC catalysts. The Pt/C catalyst showed a severe activity loss and retained only 61.1% of its initial activity after 10 h. In contrast, the Fe-N-MC catalyst exhibited remarkable improved stability with 85% retention of its initial activity during the same duration. Extra attention was paid to the electrode fabrication to ensure the integrity of the catalyst cast on the RDE. The loss of catalyst was proven not the cause of current decrease. It should be noted that the stability of the Fe-N-MC catalyst in alkaline electrolyte is at least comparable to or most of the time, higher than those non-noble metal catalysts reported in the literature, for example, Fe3O4/N-doped graphene aerogels (79.3% at 0.4 V vs. Ag/AgCl for 20,000 s),[37] P-doped graphene (87% at 0.7 V vs. RHE for 20,000 s)[44] and Fe-tpy-GO (5% at −0.3 V vs. SCE for 600 s)[24], to name a few. We further examined the methanol tolerance of the Fe-N-MC and Pt/C catalysts by adding 10% methanol to KOH. As shown in Fig. S6, the current density of Fe-N-MC catalyst displayed little degradation after adding methanol to the electrolyte, whereas the Pt/C catalyst showed a sharp loss of 18% in activity. All the results indicated that the Fe-N-MC catalyst possessed better ORR activity and durability than the commercial Pt/C catalyst, and thus held great potential as a cathode catalyst for alkaline fuel cells.

To gain insight into the impact of annealing temperature on the catalytic activity, the Fe-N-MC catalysts were prepared at a series of annealing temperatures. Fig. 4b compares the LSV curves of Fe-N-MC samples on the RDE at a rotation rate of 1600 rpm in an O2-saturated KOH solution. The Fe-N-MC-700 exhibited the highest catalytic activity. The comparison of the catalytic activities, BET surface area, N and Fe contents of Fe-N-MC at different temperature are tabulated in the Table S2 in the supplemental materials. In general, the pyridinic N, N-metal and graphitic N (Fig. S7) were believed to be the active sites participating the catalytic ORR [41,45,46]. On the other hands, the BET specific surface area for Fe-N-MC decreased with annealing temperature (Fig. S8). Raman spectroscopy revealed that the ratios of integrated intensities (I_D/I_G) were 1.12, 0.98, 0.96 and 0.94 for Fe-N-MC-600, Fe-N-MC-700, Fe-N-MC-800 and Fe-N-MC-900, respectively (Fig. S9). The decreasing ratio with increasing annealing temperature indicates the continuous graphitization during the heat treatment[23,47]. A more ordered structure with a graphitic structure domain would be beneficial for electrical conductivity of the derived carbon and transfer of electrons during the reaction. Therefore, the inferior catalytic activity of Fe-N-MC-600 may be mainly due to the poor conductivity and the lack of active nitrogen species.

For the Fe-N-MC-900 sample, although it had the highest degree of graphitization, it suffered from leaching of active nitrogen and iron species at high annealing temperature as illustrated in Table S2, derived from the analysis of XPS and Raman shown in Figs. S7 and S9, respectively. A poor ORR activity was observed for Fe-N-MC-900. The superior ORR catalytic activity of the Fe-N-MC-700 exhibited the importance of balancing between the degree of graphitization and the retention of active species at moderate annealing temperature.

Our present synthetic method can also be used to prepare other dual-doped mesoporous carbon (metal-N-MC) catalysts using various metal ions. Co-N-MC, Ni-N-MC and Cu-N-MC catalysts...
were synthesized simply by replacing FePc with corresponding metallophthalocyanine. Since the optimal carbonization temperature of 700 °C was identified for Fe-N-MC, the same carbonization temperature was also used for the synthesis of Co-N-MC, Ni-N-MC and Cu-N-MC. The structure of Co-N-MC was confirmed by TEM image shown in Fig. 5a. The well-ordered hexagonal arrays of mesopores with a P6mm symmetry reveal the 2D-ordered hexagonal mesostructure of the Co-N-MC. As shown in Fig. 5b–e, the Co and N are uniformly distributed throughout the Co-N-MC sample. Similarly, Cu and N co-doped mesoporous carbon (Cu-N-MC) and Ni and N co-doped mesoporous carbon (Ni-N-MC) were also successfully prepared via similar routes (Figs. 5f and S10). Moreover, all these as-prepared metal-N-MC catalysts exhibited good ORR activity close to that of the commercial Pt/C catalyst (Figs. 5g and S11). Evidently, Benefiting from the merits of highly active metal-nitrogen species, ordered porosity for facile reactant transportation, and large interfacial surface for the sufficient active site exposure, these M-N-MC samples exhibited outstanding catalytic activity toward ORR in alkaline environment.

To further test the M-N-MC catalyst in a system close to a real Zn-air battery, GDE containing Fe-N-MC-700 catalyst was made and tested in 6 M KOH electrolyte. Fig. 6A demonstrates the superior high kinetics for the ORR catalyzed by Fe-N-MC-700 in comparison with Pt/C. Normally, the state-of-art GDE in a Zn-air cell would be discharged at 100 mA cm⁻². As shown in Fig. 6A, the two catalysts were in parity when discharged below 100 mA cm⁻¹, but Fe-N-MC-700 exhibited significant superiority at higher rate. A typical flat discharge curve of Zn-air cell is shown in Fig. 6B with Fe-N-MC-700 as the catalyst in the GDE. The comparison of the anodic LSV for Fe-N-MC-700 and Pt on a RDE was shown in Fig. 6C. Interestingly, Fe-N-MC-700 unveiled much better electrocatalytic activity for the oxygen evolution reaction (OER) than Pt. Indeed, the ultimate goal for a GDE catalyst is to make it bi-functional. So the catalyst can catalyze both ORR and OER. The bi-functional catalyst is the major challenge to Zn-air cell electrochemically rechargeable. Fig. 6C shows clear superiority of Fe-N-MC-700 in the catalytic oxidation reaction than Pt/C.

4. Conclusions

The transition metal and nitrogen dual-doped mesoporous carbon electrocatalysts were successfully fabricated from a novel and simple sublimation and capillary assisted nanocasting method (SCANC). The catalysts synthesized using corresponding metallophthalocyanines and mesoporous silica as precursors demonstrated superior or equal catalytic activity for ORR than Pt/C catalyst in alkaline electrolytes. The synergistic effects of highly active metal-nitrogen species, mesoporous structure, large interfacial area and excellent conductivity endowed these M-N-MC catalysts with outstanding ORR activity, Fe-N-MC annealed at 700 °C exhibited substantially better ORR catalytic activity than the commercial Pt/C catalyst which is the first time the ORR catalytic activity of a non-noble metal was better than a Pt catalyst. Moreover, the Fe-N-MC catalyst exhibited excellent methanol tolerance. The great potential of these catalysts in rechargeable zinc-air battery applications has been demonstrated. Our research results not only constitute a new insight into designing the highly active and low cost ORR catalysts, but also open up a route for constructing more multifunctional and mesoporous architectures for various applications, including catalysis, supercapacitors and sensors.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2016.05.015.