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Article

ZnCl₂ salt facilitated preparation of FeNC: Enhancing the content of active species and their exposure for highly-efficient oxygen reduction reaction

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ABSTRACT

Introducing catalytically-active Fe and N into carbon materials results in promising FeNC catalysts for oxygen reduction reaction. However, the doped Fe and N species are frequently subject to heavy loss in a traditional carbonization process owing to Fe agglomeration and evaporation of N-contained small molecules. Besides, pyrolysis may make materials sintering which embeds a large number of active sites in the bulk phase and impedes direct exposure of reactive centers to the reactants. We here report that when calcinations, the addition of ZnCl₂, an ordinary salt with very wide melting temperature range well covering the carbonization process of the precursor iron porphyrin, can significantly enhance the doping level of the active species and simultaneously create highly porous structures for FeNC catalysts. The obtained FeNC demonstrates ultrahigh catalytic activities even significantly better than Pt/C in oxygen reduction reaction.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs), which convert the chemical energy of hydrogen into electrical power, while produce water as the only byproduct, are a type of potential power for future vehicles [1,2]. However, the Pt-based precious metals, as the most effective catalysts for oxygen reduction reaction (ORR) occurred at cathode, cannot be commercialized on a large scale because of high cost and scarce resource. To replace the Pt-type catalysts, Fe-, N-codoped carbon (FeNC) materials with relatively high ORR activities have been well explored [3–16].

However, the Fe and N species are frequently subject to

heavy loss when a typical carbonization-etching route was adopted to transfer the precursors into FeNC materials [6,17–19]. With temperature increase, the adjacent Fe atoms gradually aggregate and the resulted nanoparticles can be removed by acid etching (Scheme 1) [4,10,20–23]. Simultaneously, N-contained small molecules also easily evaporate and escape from the product. Thus how to remain a high doping degree for the active Fe and N species in the carbon product along the calcination treatment is especially important for acquiring a highly active FeNC catalyst.

On the other hand, the pyrolysis may also make materials sintering, which then embeds a large number of active sites in the bulk phase and impedes direct exposure of reactive centers

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Scheme 1. Preparation of Frame-FeNC (a) and Sphere-FeNC (b) catalysts; (c) The branch structures constructed by melt ZnCl₂ well separate the adjacent Fe to avoid their agglomeration; (d) The agglomeration and removal of Fe species along a traditional carbonization process.

to the reactants. To avoid the concealing of the active sites, constructing suitable interconnected porous structure for FeNC catalyst is also necessary.

In this work, we reported that adding ZnCl₂, a normal salt into the reactant system, is able to simultaneously improve the content of the reactive sites and material porosity. The detailed synthesis is illustrated in Scheme 1. By using SiO₂ photonic crystals and inverse crystals as macropore templates, two different FeNC structures, the frameworks (Frame-FeNC) and microspheres (Sphere-FeNC), can be finally prepared.

2. Experimental

2.1. Preparation of carbon samples

2.1.1. Preparation of SiO₂ photonic crystal

The monodisperse SiO₂ microspheres were prepared by using a slightly modified Stöber process [24–26]. In a typical preparation, 20 mL of deionized water and 120 mL of ethanol were firstly mixed, into which 10 mL of ammonia solution (37 wt% in water) was poured and the obtained solution was continuously stirred at 30 °C for 30 min. Subsequently, 20 mL of ethyl orthosilicate (TEOS) was further added and the mixture was stirred for another 12 h to obtain a milky white solution. After that, another 20 mL of TEOS was added at a rate of one drop per 3 s controlled by a constant pressure funnel, followed by further continuous stirring for 12 h. The obtained product was washed and re-dispersed in ethanol, which after natural sedimentation and ethanol evaporation would form SiO₂ (diameter = 500 nm) photonic crystal.

2.1.2. Preparation of SiO₂ inverse photonic crystal

We firstly prepared the polystyrene (PS) photonic crystal as the template for the SiO₂ inverse photonic crystal [27–29]. In a typical preparation, 150 mL of styrene was dispersed in 300 mL of deionized water, into which 40 mL of K₂S₂O₈ (0.7 wt%)

aqueous solution was slowly added under magnetic stirring. The mixture was then heated to 70 °C and held at the same temperature for 24 h under nitrogen protection to allow the polymerization of styrene. Finally, the obtained product was washed and re-dispersed in water, which after natural sedimentation and solvent evaporation would form PS (diameter = 300 nm) photonic crystal. Using this PS photonic crystal as the template, we further prepared the SiO₂ inverse photonic crystal. Particularly, 100 mL of ethanol, 4.5 mL of water and 0.5 mL of hydrochloric acid (12 mol L⁻¹) were mixed and stirred at 40 °C for 2 h, into which 10.4 g TEOS was slowly added and the obtained solution was continuously stirred for another 20 h at 40 °C. This solution was dropwisely infused into the PS photonic crystal template till the latter was fully filled. The achieved product was dried in a vacuum oven at 60 °C, and the infiltration was repeated three times. After a calcination was conducted at 550 °C for 6 h in a muffle furnace, the SiO₂ inverse photonic crystal templates can be finally prepared.

2.1.3. Preparation of FeNC samples

200 mg of iron porphyrin (FePc) and 1.0 g of ZnCl₂ were dissolved in 30 mL of acetone, into which 1.0 mL of concentrated hydrochloric acid was further added and the obtained solution was continuously sonicated for 1 h. This solution was dropwisely infused into the SiO₂ (inverse) photonic crystal template till the latter was fully filled. After dried in a vacuum oven at 60 °C, the SiO₂ photonic crystal was repeatedly infiltrated three times. The obtained composite samples were placed in a porcelain crucible, into which 10 g of ZnCl₂ was also added. To form a closed ZnCl₂ salt encapsulation on the sample, we placed the crucible on a heating plate and particularly, during heating process, we also added a small amount of water. After the salt formed uniform encapsulation on the samples, the mixture was firstly held at 60 °C for 12 h in a vacuum oven to remove the moisture and then calcined under nitrogen in a tube furnace at 900 °C for 2 h. The Frame-FeNC (Sphere-FeNC) products were achieved after etching the SiO₂ templates in 2.0 mol L⁻¹ NaOH solution and treating the products in 0.5 mol L⁻¹ H₂SO₄ for 12 h at 80 °C.

For comparison, we also prepared three control samples. The FeNC-in and FeNC-out were prepared following a route similar to that for getting Frame-FeNC, except adding the ZnCl₂ salt only in either step of the two. The FeNC-none was synthesized when no ZnCl₂ was used.

2.2. Characterization

X-ray diffraction (XRD) data were collected on a Shimadzu X-ray diffract meter, model 6000 at a scanning rate of 1° min⁻¹. Scanning electron microscopy (SEM) measurements were conducted on a JEOL JSM-7800F microscope operated at 20 kV. Transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectrum were achieved on a FEI Talos F200S TEM microscope operated at 200 kV. Nitrogen sorption isotherms were measured at -196 °C with a Micromeritics Gemini VII analyzer. Before measurements, the samples were degassed in vacuo at 180 °C for 8 h. X-ray photoelectron spectra (XPS)

were recorded on a Thermal ESCALAB250XI. Raman spectra were collected on a LabRAM HR Evolution, JobinYvon S.A.S, with He-Ne laser (532 nm) as the excitation source. Inductive coupled plasma (ICP) emission spectrum was measured with an iCAP 6300 Duo. Thermogravimetric analysis-differential thermal analysis (TGA-DTA) curves were collected on a TGA/DSC1/1600LF at a heating rate of 3 °C min⁻¹.

2.3. Electrochemical measurements

The electrochemical performance of the catalysts was characterized by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. All electrochemical experiments were detected on Princeton Parstat 4000 potentiostat. All potentials were given relative to the reversible hydrogen electrode (RHE). For the three electrode tests, a rotating disk electrode (RDE) with an exposed glassy carbon surface (0.19625 cm²) was used as the working electrode, with a graphite rod as counter electrode and an Ag/AgCl (0.1 M KOH, -0.972 V vs. RHE at 25 °C; 0.1 mol L⁻¹ HClO₄, -0.276 V vs. RHE at 25 °C) as a reference electrode. The catalyst ink was prepared by dispersing the catalyst powder (commercial Pt/C catalysts, 20 wt% Pt supported on Vulcan XC-72R, John-Matthey) into ethanol in an ultrasonic bath. In the three-electrode system test, the loading of FeNC catalyst on the working electrode was 0.5 mg cm⁻². For commercial Pt/C, the loading was 0.125 mg cm⁻², corresponding to the absolute Pt loading of 25 μg_{Pt} cm⁻².

Oxygen reduction reactions were conducted in a 0.1 mol L⁻¹ KOH and 0.1 mol L⁻¹ HClO₄ aqueous solution. The polarization curves were obtained by sweeping the potential from 1.1 to 0 V at a scan rate of 10 mV s⁻¹ and a rotation rate of 1600 rpm. The current density was normalized in reference to the ECSA of the catalyst. Based on the ORR polarization curves, the kinetic current density (*j_k*) was calculated using the Koutecky-Levich equation:

$$1/j = 1/j_d + 1/j_k = 1/(B\omega^{1/2}) + 1/j_k \quad (1)$$

where *j* is the measured current density, *j_k* and *j_d* are the kinetic and diffusion limiting current densities, respectively, *ω* is the electrode rotating rate, and *B* could be determined from the slope of the K-L plots based on the Levich equation as follows:

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6} \quad (2)$$

where *n* represents the electron transfer number, *F* is the Faraday constant (96485 C mol⁻¹), *D₀* is the diffusion coefficient of oxygen in 0.1 mol L⁻¹ KOH (1.9 × 10⁻⁵ cm² s⁻¹), *ν* is the kinematic viscosity of water (0.01 cm² s⁻¹), *C₀* is the bulk concentration of oxygen in oxygen-saturated 0.1 mol L⁻¹ KOH (1.2 × 10⁻⁶ mol cm⁻³), *ω* is the RDE rotation rate, and *n* is the electron transfer number for the ORR.

The electrochemical durability was examined using an accelerated durability test (ADT) by continuously cycling the potential between 0.6 and 1.1 V in O₂-saturated 0.1 mol L⁻¹ HClO₄ solution for 3000 times at a scan rate of 50 mV s⁻¹. The four-electron selectivity of catalysts was evaluated based on the H₂O₂ yield, calculated from the following equation:

$$\text{H}_2\text{O}_2 (\%) = 200 \times \frac{I_R/N}{(I_R/N) + I_D} \quad (3)$$

The electron transfer number can be calculated from the

following equation:

$$n = 4 \times \frac{I_D}{(I_R/N) + I_D} \quad (4)$$

Here, *I_D* and *I_R* are the disk and ring currents, respectively, and *N* = 0.37 is the ring collection efficiency.

2.4. Membrane electrode assembly (MEA) tests

The achieved Sphere-FeNC catalyst was made into cathode of the single cell to detect its performance. In details, Sphere-FeNC powder and Nafion ionomer (DuPont, 5 wt%) were dispersed into ethanol, and the obtained catalyst ink was then deposited onto a piece of gas diffusion layer with an effective area of 5.0 cm². The catalyst loading is 0.7 mg cm⁻² and the Nafion content is 25 wt% for the dried catalyst layer. The anode of the MEA was loaded with 40 wt% commercial Pt/C catalyst at a loading of 0.3 mg_{Pt} cm⁻². To get MEA, Nafion 112 membrane (DuPont, 50 μm) was pretreated in 3 vol% H₂O₂ solution at 80 °C for 40 min and in 0.5 mol L⁻¹ H₂SO₄ solution at 80 °C for 40 min sequentially to remove impurities, followed by washing with ultrapure water. After that, the Nafion membrane sandwiched between the cathode and the anode was subjected to a hot-pressing conducted at 130 °C, 3.0 MPa for 120 s. During MEA test, pure hydrogen at a flow rate of 160 mL min⁻¹ and pure oxygen at a flow rate of 160 mL min⁻¹ were supplied to the anode and cathode, respectively. The cell temperature was maintained at 80 °C and the back pressure was 200 kPa for both H₂ and O₂.

3. Results and discussion

ZnCl₂ was involved in two separate steps of the preparation. Firstly, we removed the solvent from the mixed solution of ZnCl₂ and the precursor, iron porphyrin (FePc) to form ZnCl₂ micro-particles uniformly dispersed FePc matrix. Secondly, when the SiO₂/FePc/ZnCl₂-in composite precursors were ready, another layer of ZnCl₂ (ZnCl₂-out) was attached on the powder surface. The obtained precursor system was then transferred into the final FeNC product by calcination, during which ZnCl₂ functionalizes three critical roles: (1) as ZnCl₂ and FePc own similar but relatively low melting points (MP of ZnCl₂ = 283–293 °C; MP of FePc = ~300 °C), the two phases, once melt, would gradually mix together uniformly, and the multi-branches of melt ZnCl₂ well separate the adjacent Fe species, which greatly mitigates their further agglomeration and thus facilitates the formation of highly disperse Fe in the achieved materials (Scheme 1c); (2) the encapsulation of ZnCl₂ prevents the rapid escape of N-contained small molecules at high temperature, leading to remaining of a high content of N doping; (3) ZnCl₂ can be removed by evaporation at above 732 °C, which created additional micropores and small mesopores for exposing more active sites. As a result, the FeNC carbonized with the assistance of ZnCl₂ possesses a total N content of 4.37% and an absolute Fe-N_x ratio of 0.71%, being 3.2 and 13 times, respectively, the corresponding values for the catalyst prepared without ZnCl₂ used. Besides, the addition of ZnCl₂ enhances the specific surface area of the FeNC materials by 4.5

times. In the ORR test, the catalyst demonstrates superior activities with the beginning potentials of 1.080 and 1.075 V, and the half-wave potential of 0.906 and 0.896 V (vs RHE) in alkaline and acid medium, respectively. In principle, the present ZnCl_2 assisted method can be well used in preparation of various carbon materials to tune the effective doping species for improved activities.

The morphologies and microstructures of the FeNC materials were firstly investigated (Fig. 1). As shown in the electron microscopy images, Frame-FeNC displays the typical framework structures constructed by orderly arranged macropores, and Sphere-FeNC is composed of uniform microspheres with diameters of 300 nm (Fig. 1a–1b). In the TEM images (Figs. 1c and S1), no iron nanoparticle was observed in Frame-FeNC and Sphere-FeNC, and the elemental mapping verified the uniform dispersion of N, O, and Fe species in the carbon matrix, which reveals that iron species may exist at very tiny aggregates or even at atomic size level. Besides, N_2 adsorption-desorption tests were conducted to study the pore properties. As illustrated in Fig. 1d–1e, apart from FeNC-none, all other samples demonstrate type-IV N_2 adsorption-desorption isotherms with rapid increases in the very high P/P_0 (> 0.95) and very low P/P_0 (< 0.03) regions, implying the existence of abundant macropores and micropores. From the pore size distribution plots, all the materials have the micropores and small mesopores mainly less than 3.0 nm. Particularly, the prepared carbon catalysts show significantly different pore characteristics (Table 1). When no ZnCl_2 was added, the obtained FeNC-none displays

very low porosity, as the BET specific surface area ($234 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($0.21 \text{ cm}^3 \text{ g}^{-1}$) are quite small considering the carbon based materials. For FeNC-in and FeNC-out which adopted ZnCl_2 only in either step of the two, a distinctly higher surface area ($747\text{--}847 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.84\text{--}1.09 \text{ cm}^3 \text{ g}^{-1}$) can be achieved. When ZnCl_2 was applied in both steps, the prepared Frame-FeNC and Sphere-FeNC own the BET specific surface areas as high as above $1000 \text{ m}^2 \text{ g}^{-1}$ and the total pore volumes around $1.5 \text{ cm}^3 \text{ g}^{-1}$, which are almost four and seven times higher than corresponding values for FeNC-none, respectively. These observations indicate that ZnCl_2 assisted preparation functionalizes well in creating additional micropores and small mesopores for enhanced inner surfaces and porosity, and introducing ZnCl_2 in both steps is more efficient than using ZnCl_2 only in either step.

The elemental identifications of the materials were analyzed by X-ray photoelectron spectroscopy (XPS) to investigate the effects of ZnCl_2 on the doping species and contents (Fig. S2). For all samples, the high-resolution N 1s spectrum can be fitted by five deconvoluted peaks located at 398.4, 399.5, 400.2, 401.3, and 403.5 eV, corresponding to pyridinic N, Fe-N_x , pyrrolic N, quaternary N, and oxide pyridinic N, respectively (Fig. 2a–2f) [30]. Particularly, as displayed in Table 2, the total N content is 3.90 at.% for Frame-FeNC and 4.37 at.% for Sphere-FeNC. When ZnCl_2 was used only in either step during preparation, the left N content is 3.21 at.% for FeNC-in and 1.81 at.% for FeNC-out. And the sample FeNC-none, using no ZnCl_2 in the synthesis, only contains a very low N doping level of 1.34 at.%. Besides, it is interesting to note that the contents of Fe-N_x in the total N species also follow a similar trend of Frame-FeNC/Sphere-FeNC $>$ FeNC-in $>$ FeNC-out $>$ FeNC-none, and the absolute Fe-N_x content of 0.54% in Sphere-FeNC and 0.71% in Frame-FeNC is indeed 10–13 times higher than that in FeNC-none. These observations indicate that: (1) the addition of ZnCl_2 is especially effective in improving both the N-doping and the Fe-N_x contents; (2) the supplies of ZnCl_2 in both steps display better N species manipulation ability than introducing ZnCl_2 only in either step.

The high-resolution Fe 2p spectra (Fig. S3) and EDX spectrum (Fig. S4) indicate the existence of Fe species in the prepared samples, and the ICP emission spectrometer measurement gives the Fe content of 0.81 wt% in Sphere-FeNC. The STEM mapping images clearly demonstrate the uniform distribution of Fe (Figs. 1c and S1) in the carbon matrix, showing that Fe species have been successfully doped into the FeNC

Fig. 1. FESEM images of (a) Frame-FeNC and (b) Sphere-FeNC; (c) TEM and mapping images of Sphere-FeNC; (d) Nitrogen adsorption-desorption isotherms; (e) Pore-size distribution plots of all samples.

Table 1

Pore parameters for the prepared carbon based materials.

Material	A_{BET}^a (m^2/g)	$V_{\text{meso/macro}}^b$ (cm^3/g)	V_{micro}^c (cm^3/g)	V_t^d (cm^3/g)
Frame-FeNC	1054	1.16	0.26	1.42
Sphere-FeNC	1021	1.24	0.31	1.56
FeNC-in	847	0.88	0.21	1.09
FeNC-out	747	0.65	0.19	0.84
FeNC-none	234	0.17	0.04	0.21

^a BET specific surface area. ^b $V_t - V_{\text{micro}}$. ^c t -plot micropore volume. ^d Single point adsorption total pore volume at $P/P_0 = 0.995$.

Fig. 2. N 1s high-resolution XPS spectra of Frame-FeNC (a), Sphere-FeNC (b), FeNC-in (c), FeNC-out (d), and FeNC-none (e); (f) Comparison of the absolute content of the different N species for the prepared materials.

product, and at a high degree of dispersion. Besides, all the XPS (Fig. S2), EDX (Fig. S4), and ICP measurements show no remaining of Zn in the Sphere-FeNC sample, indicating complete removal of Zn from the product.

The observed ZnCl₂-assisted formation of micro-/mesopores is discussed here. For ZnCl₂-none, the micropores are mainly derived from decomposition of FePc precursors during calcination, while the released volatile small molecules produce only a limited amount of micropores. For the ZnCl₂-involved system, both ZnCl₂ and FePc would melt when the calcination temperature exceeds their melting points, and the resulted flowing state made the two phases tend to mix together. Thus no matter ZnCl₂ was applied in either step or both, it would enter the FePc matrix and try to form uniform distribution. Particularly, we gave the optical image for the sample achieved at a calcination temperature of 300 °C (Fig. S5), in which it is found that white ZnCl₂ microparticles are evenly embedded in the FePc matrix. When the temperature

reaches the boiling point of ZnCl₂ (732 °C), ZnCl₂ gradually evaporates off and leaves copious micropores and small mesopores in the FeNC products.

The enhanced Fe and N doping made by ZnCl₂-facilitated calcination is further explained here. It is believed that encapsulation of the melt ZnCl₂ on the precursor FePc, like a cover, well prevents the N-contained small molecules from direct escape and reduces the mass loss of FePc during pyrolysis, thus leading to a high doping content for the material. The TGA investigations well confirm this. In Fig. S6, FePc begins the decomposition at around 300 °C, but the mixture of ZnCl₂ and FePc starts a weight loss till above 400 °C, confirming the encapsulation of ZnCl₂ significantly retards the release of volatile molecules to a higher temperature. Besides, ZnCl₂ made branch structures also prevent the adjacent Fe species from direct contact and agglomeration, thus facilitating the remaining of highly disperse Fe-N_x coordination in the achieved materials, as displayed in Scheme 1. Particularly, it should be noted that although ZnCl₂ begins to evaporate at 732 °C, the products acquired after carbonization treatment at 900 °C still include a certain amount of ZnCl₂, which need to be removed by additional water washing. It means that ZnCl₂ supplied in the precursor system is significantly excessive and cannot be fully removed by evaporation. Thus although in principle the melting state of ZnCl₂ lasts the temperature range from ~290 °C to 732 °C, the ZnCl₂ indeed provides a nice protection to the doping species in almost the whole carbonization process of FePc till 900 °C, which acts well in manipulating the elemental doping for the carbon materials.

The crystal structures of the FeNC materials were explored by XRD. As shown in Fig. S7b, all five materials show quite similar XRD patterns, in which the two diffraction peaks located at $2\theta = 25^\circ$ and 43° correspond exactly to the (002) and (100) planes of graphite, respectively, indicating the carbon materials and their high degrees of graphitization [22]. Besides, all the Raman spectra curves (Fig. S7a) show the G (1590 cm⁻¹) and D (1348 cm⁻¹) bands of the typical carbon materials, representing the relative movement of the *sp*² hybridized carbon atoms, and the breathing mode of *sp*² carbon atoms in the ring, respectively [31]. In this work, the *I*_D/*I*_G is 1.047 for Frame-FeNC and 1.042 for Sphere-FeNC, both of which are lower than those for the three control samples (1.051, 1.070, and 1.155 for FeNC-in, FeNC-out and FeNC-none, respectively), indicating that ZnCl₂-assisted carbonization can enhance the graphitization degree of the carbon materials to a certain extent.

The ORR activities of the as-prepared FeNC catalysts were

Table 2

The N contents derived from XPS investigations.

Sample	N content (%)	Ratio (%)				
		Pyridinic N	Fe-N	Pyrrolic N	Quaternary N	Oxide pyridinic N
Frame-FeNC	3.9	28.83	14.05	18.61	30.75	7.76
Sphere-FeNC	4.37	27.84	16.3	35.15	14.67	6.04
FeNC-in	3.21	33.44	8.32	35.21	19.29	3.74
FeNC-out	1.81	29.12	4.18	39.6	17.12	9.98
FeNC-none	1.34	35.96	4.07	34.34	13.51	12.12

Fig. 3. (a) Cyclic voltammetry (CV) curves measured in N_2 -/ O_2 -saturated 0.1 mol L^{-1} KOH at the scan rate of 50 mV s^{-1} ; (b) LSV curves tested in O_2 -saturated 0.1 mol L^{-1} KOH at 1600 rpm ; (c) LSV curves of Frame-FeNC and Sphere-FeNC, acquired in O_2 -saturated 0.1 mol L^{-1} $HClO_4$ at 1600 rpm ; (d) The Koutecky-Levich plots of Frame-FeNC and Sphere-FeNC at 0.65 V derived from the LSV curves shown in Fig. S8; (e) Hydrogen peroxide yields and electron-transfer numbers (n) of Sphere-FeNC tested in 0.1 mol L^{-1} KOH; (f) Chronoamperometric responses of Sphere-FeNC and Pt/C upon the addition of 10% (v/v) methanol into 0.1 mol L^{-1} KOH after about 200 s ; (g) LSV polarization plots and CV curves (inset) of Sphere-FeNC for ORR in O_2 -saturated 0.1 mol L^{-1} $HClO_4$ before and after 3000 cycles; (h) The cell voltage and power density of the single cell. Cathode: 0.7 mg cm^{-2} Sphere-FeNC; anode: 0.3 mgPt cm^{-2} commercial Pt/C; temperature: 80°C ; back pressure: 200 kPa for both H_2 and O_2 .

investigated. The cyclic voltammetry (CV) curves in Fig. 3a were collected at a scanning speed of 50 mV s^{-1} , in which the curves are featureless when N_2 -saturated 0.1 mol L^{-1} KOH solution was applied as the electrolyte. When O_2 was supplied, all curves show the distinct electrochemical reduction peaks. The dot line shows that Sphere-FeNC owns the highest half-wave potential in all the prepared samples. The linear sweep voltammetry (LSV) curves were measured using a rotating disk electrode at 1600 rpm with a scanning speed of 10 mV s^{-1} in a O_2 -saturated 0.1 mol L^{-1} KOH solution (Fig. 3b). The Sphere-FeNC and Frame-FeNC demonstrate the onset potentials of 1.080 and 1.075 V , and the half-wave potentials of 0.906 and 0.896 V , respectively, which are significantly higher than the values for the three control samples and even superior to the $40 \text{ wt}\%$ commercial Pt/C (onset potential = 1.031 V , if-wave potential = 0.854 V). The diffusion limited current density for the two typical products reaches as high as 5.9 mA cm^{-2} at 0.35 V (vs. RHE), also being much better than commercial Pt/C (5.3 mA cm^{-2}) and all control samples. Besides, the ORR catalytic activity was also explored in an acidic medium (Fig. 3c), for which the LSV curves were measured in O_2 -saturated 0.1 mol L^{-1} $HClO_4$ solution at 1600 rpm with a scanning speed of 10 mV s^{-1} . The half-wave potentials of Sphere-FeNC and Frame-FeNC reach 0.799 and 0.762 V , respectively, which is

indeed comparable to the best activities of the state-of-art non-precious metal catalysts, as listed in Table S1.

Figure S8 shows the LSV curves collected at different rotation speeds in O_2 -saturated KOH solution, and the calculated Koutecky-Levich (K-L) plots display nice linearity at 0.65 V (Fig. 3d). The estimated electron transfer number is 3.99 for Sphere-FeNC and 3.93 for Frame-FeNC, implying almost $4e^-$ ORR processes. Rotating ring-disk electrodes (RRDE) testing results (Fig. 3e) indicate that for Sphere-FeNC, the peroxide intermediate produced by $2e^-$ process is no more than 5% through the whole oxygen reduction reaction, and the calculated electron transfer number is 3.85 – 3.99 in the potential range from 0.1 to 0.7 V (vs. RHE), corresponding well to the four-electron process suggested by K-L plots.

The methanol cross-tolerance ability and the cycling stability of Sphere-FeNC catalyst were also measured. In Fig. 3f, adding methanol induced an immediate reverse of current output for the commercial Pt/C-catalyzed system, which is due to instant methanol oxidation on the Pt surface. In contrast, it gives negligible change to the Sphere-FeNC, demonstrating the excellent methanol tolerance capability of the latter. Besides, we studied the stability of Sphere-FeNC by continuously scanning CV within the potential range from 0.6 to 1.2 V in an O_2 -saturated 0.1 mol L^{-1} $HClO_4$, particularly for 3000

continuous cycles, which resulted in only 6 mV negative shift of the half-wave potential, revealing the good stability of the catalyst (Fig. 3g).

Finally, the sample Sphere-FeNC was also tested in a single cell as the cathode catalyst. In Fig. 3h, the open circuit potential and the maximal output power reaches 0.905 V and 0.72 W mg^{-1} , respectively, at the operating temperature of 80 °C, corresponding to a very good fuel cell performance.

4. Conclusions

In summary, we reported that ZnCl_2 , an ordinary salt with very wide melting temperature range well covering the carbonization process of FePc, can be well utilized to manipulate the elemental doping and porous structures for the FeNC catalyst product. Firstly, under melting state, the excessive ZnCl_2 forms branch structures to prevent the adjacent Fe species from direct contact and agglomeration; secondly, encapsulation of ZnCl_2 , like a cover, avoids rapid escape of volatile N-contained small molecules, thus facilitating the retention of a significant ratio of active species in the achieved materials; thirdly, removing ZnCl_2 produces copious micro-/mesopores for exposing more active sites. In principle, the ZnCl_2 -assisted method can be used in various carbonization processes to construct carbon materials with desired doping species and copious micropore distribution.

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Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

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ZnCl_2 salt facilitated preparation of FeNC: Enhancing the content of active species and their exposure for highly-efficient oxygen reduction reaction

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ZnCl_2 facilitated calcination functionalizes well in boosting the doping content of highly active species and constructing porous microstructures for FeNC catalysts.

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ZnCl₂辅助制备FeNC催化剂：增加活性位点密度以提高氧还原活性

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摘要: Fe、N掺杂的碳材料(FeNC)是最有希望取代贵金属用作氧还原反应的催化剂之一。然而, 传统FeNC材料制备过程中所采用的高温碳化-蚀刻步骤会造成相邻Fe原子随温度升高而逐渐团聚, 形成较大尺寸金属铁单质、铁氧化物或碳化物的聚集颗粒, 并在后续酸刻蚀处理中被移出, 铁元素损失严重, 无法形成有效活性位点。同时高温下含N小分子物质也容易分解并从产物中逸出, 导致N元素掺杂量较低。直接焙烧还加重了碳的团聚, 造成材料内部孔道有限, 比表面积低, 活性位难以暴露于三相界面。因此, 焙烧处理过程中如何形成Fe、N元素的高含量、均匀分散掺杂, 同时构建大量内部联通孔道, 是形成高活性FeNC催化剂的关键。本文采用ZnCl₂辅助焙烧方法制备出具有高活性位点密度和大材料孔隙率的FeNC催化剂; 通过TEM、N₂吸附和XPS等一系列物理手段对所制备样品进行了形貌、结构及组成表征, 提出了ZnCl₂辅助催化剂合成机理; 结合CV和LSV等电化学测试结果详细探讨了ZnCl₂辅助方法对催化剂结构和催化性能的影响。

普通共价盐ZnCl₂在283–732 °C的较宽温度范围内呈现熔融态, 同卟啉铁(FePc)碳化温度区间恰好匹配, 可以辅助FeNC催化剂进行元素掺杂和多级孔结构的构建。首先, 在熔融状态下, 过量的ZnCl₂形成分支结构, 阻止相邻Fe物种直接接触和聚集, 有利于形成高度分散的FeN_x活性位点。其次, 熔融的ZnCl₂像盖子一样包封住催化剂前驱体, 避免了挥发性含N小分子的快速逸出, 使得N原子在高温下有可能重新在碳骨架中形成掺杂, 有助于在材料中保留更高比例的活性N物质。在ZnCl₂的辅助下碳化FePc得到的Sphere-FeNC样品具有高达4.37%的总N含量, 并且Fe-N_x含量也高达0.71%, 分别是不使用ZnCl₂制备的对比催化剂FeNC-none的3.2和13倍。同时, ZnCl₂辅助合成方法将FeNC材料的比表面积增加4.5倍, 总孔体积增加7倍。三电极氧还原反应性能测试表明, Sphere-FeNC在碱性和酸性介质的初始电位分别为1.080和1.015 V (vs RHE), 半波电位分别为0.906和0.799 V (vs RHE), 活性优异。以Sphere-FeNC为阴极催化剂组装的单电池功率达到0.72 W mg⁻¹, 高于已报道的FeNC和Pt/C催化剂。因此, ZnCl₂辅助焙烧碳化的方法可以作为一种普适手段用于构建具有高密度活性元素掺杂和大量微孔介孔分布的碳基催化材料, 并应用于各类催化反应。

关键词: FeNC催化剂; 氯化锌; 多孔碳; 氧还原反应; 燃料电池

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