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Ultrahigh pressure (UHP) method was employed to rapidly synthesize (5 min) a high-efficiency ORR FeNx/C catalyst for the first time.



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Ultrahigh Pressure Synthesis of Highly Efficient FeN_x/C **Electrocatalysts for Oxygen Reduction Reaction**

Xin Guo,^{a,b} Xiaopeng Jia,^c Ping Song,^a Jing Liu,^{a,d} Erling Li,^{a,d} Mingbo Ruan^a and Weilin Xu^{a,*}

Ultrahigh pressure (UHP) was employed for the first time as a green method for the synthesis of highly efficient Fe, N codoped carbon-based (FeN_x/C) electrocatalysts for oxygen reduction reaction (ORR). Compared with traditional pyrolysis under atmospheric condition, the synthesis of FeN_x/C catalysts under UHP could be done efficiently with much less consumption of time, energy and chemicals. The observed highly efficient synthesis and high ORR activity of such catalysts could be due to the fast heating system (12°C/second) under UHP, which leads to highly efficient doping of heteroatoms on carbon with much less consumption of chemicals and energy; the UHP-induced high graphitization degree of carbon support and the selective formation of highly active sites of pyridinic N and Fe-Nx for ORR also contribute in part to the high ORR catalytic activity of the catalyst. The work presented here paves a new way for the green, environmentally friendly synthesis of heteroatoms-doped highly efficient catalysts for energy or chemical process.

1. Introduction

With increasingly severe energy crisis and environmental pollution, fuel cells have attracted extensive interest due to their advantages in sustainable energy conversion, wherein the oxygen reduction reaction (ORR) is a critical process at the cathode of polymer electrolyte fuel cells (PEFCs) for direct conversion of the chemical energy into electricity.^{1,2} Hence, ORR electrocatalysts with high efficiency are essential for large-scale applications in fuel cells.^{3,4} To date, Pt-based materials are known as the most efficient ORR catalysts;⁵⁻⁷ however, Pt-based materials suffer from many problems in commercial application including prohibitive cost, finite reserves, low durability and CO poisoning effects of Pt.^{8,9} Consequently, it is critical to develop energetically high-efficient nonprecious metal catalysts for ORR to achieve the substitution of Pt-based catalysts. In recent decade, the nonprecious metal catalysts, especially, Fe, N co-doped carbon-based catalysts (FeN_x/C) with excellent electrocatalytic performance for ORR have been well realized to be promising candidates to Pt-based ones.^{10,11} However, these catalysts were usually synthesized through a pyrolysis at high temperature under atmospheric condition with large consumption of chemicals and electricity. Obviously, such environmentally unfriendly synthesis protocol is time-, energy-, and chemical-consuming. On the other hand, due to the specialty of sealed ultrahigh pressure (UHP) environment, the UHP technique

possesses some unique advantages in preparation and performance improvement of materials. For instance, UHP can effectively modulate phase transformations, morphology, lattice structure, microstructure, etc., influencing optical, electrical, and thermal performances in materials.^{12,13}

In this work, to deal with the problems in traditional synthesis of heteroatom-doped catalysts, for the first time, UHP technique was adopted for highly efficient synthesis of FeN_x/C with high ORR electrocatalytic activity.^{2,14,15} Such high efficient synthesis can be done in short time (down to 5min) with little consumption of chemicals (such the nitrogen precursor) and energy (electricity) due to the fast and high efficient doping of heteroatoms. In this way, the obtained FeN_x/C catalysts with high ORR electrocatalytic activity possess one of the best price/performance ratio and make the method the most environmentally friendly.





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^{a.} State Key Laboratory of Electroanalytical Chemistry & Jilin Province Key Laboratory of Low Carbon Chemical Power, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. E-mail: weilinxu@ciac.ac.cn

^b Department of Materials Science and Engineering, Changchun University of Science and Technology, 7989 Weixing Road, Changchun, 130022, P. R. China.

^c State Key Laboratory of Superhard Materials, Jilin University, 2699 Qianjin Street, Changchun, 130012, P. R. China.

^d University of Chinese Academy of Sciences, Beijing, 100049, P. R. China

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Fig. 1 Scheme for UHP synthesis:(a) precursor processing and (b) UHP synthesis at controllable high temperature and the schematic diagram of pressure cavity in cubic anvil high-pressure apparatus, and assembled chamber (1-steel plate, 2-graphite heater, 3-dolomitic cylinder, 4-molybdenum box, 5-sample, 6-pyrophyllite).

2. Experimental Procedures

2.1 Materials

The carbon black BP2000 (BP) was purchased from Asian-Pacific Specialty Chemicals Kuala Lumpur. Urea (CH₄N₂O, >99%), ferric chloride hexahydrate (FeCl₃·6H₂O, >99%) and Potassium hydroxide (KOH, >85%) were purchased from Sinopharm Chemical Reagent Co. LTD. Nafion solution (5wt.%) was obtained from Sigma-Aldrich. All the chemicals were used as delivered without further treatment. Deionized water with the specific resistance of 18.2mΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration. Rotating ring-disk electrode of glassy carbon (RRDE, 4mm in diameter) was purchased from CH Instruments, Inc, USA.

2.2 Preparation of Fe, N co-doped carbon materials

Firstly, the N (urea) and Fe (FeCl₃·6H₂O) precursors were mixed homogeneously with carbon support (BP2000 (BP)) by refluxing for 7 hours at 80°C, as shown in Figure 1a; secondly, for the UHP experiments (Fig. 1b, Fig. S1), the obtained mixture containing carbon and chemical precursors was pressed tightly to be a ϕ 10.5×2 mm cylinder by cold compression, and then was assembled into the sample chamber of cubic anvil high-pressure apparatus(SPD 6×1200), on which a graphite box was used as the heating unit, following by preparation at 760°C and under the pressure of 0.85-3.5GPa for 5min. The sample chamber was sealed by the UHP exerted from six directions and then heated up rapidly with rate of 12°C/second as shown in Fig. 1b. The pressure was calibrated by the change in resistance of standard substances. The synthesis temperature was measured by a Pt RH/Pt Rh6 thermocouple placing near the sample. Finally, the as-prepared catalysts were cracked and ground thoroughly for further the electrochemical and physical characterization.

During the pyrolysis in such sealed chamber, nothing will be leaked out and all the components from the pyrolysis of chemical precursors will be trapped inside. In this way, a tiny amount of precursor can induce highly efficient doping of heteroatoms in short time and then the consumption of chemicals and energy can be reduced hugely, making it a green and environmentally friendly method to replace traditional pyrolysis, in which the gas flow under atmospheric condition usually leads to a huge consumption or wasting of large amount of chemicals and energy.

2.3 Physical and electrochemical characterization of catalysts

The phase of as-prepared catalysts was identified by X-ray diffraction (XRD, D/MAX 2500) with Cu-K α radiation. X-ray photoelectron spectroscopic (XPS) measurements were performed on AXIS Ultra DLD (Kratos company) using a monochromic Al X-ray source. The microstructures were obtained using a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100FS). The final N content was determined by element analysis (EA) using varioEL cube (elementaranalysensystemeGmbh). The final Fe

content was obtained from ICP-MS (ICAP-6000, Thermo Fisher Scientific). The Brunauer-Emmett-Teller (BET) surface areas and pore volumes were obtained from 77K N_2 sorption isotherms using ASAP 2020 instrument.

The ORR activity of as-prepared catalysts was evaluated by voltamperometry on a glassy carbon electrode. Fabrication of the working electrodes was done by pasting catalyst inks on a glassy carbon rotating disk electrode (4mm in diameter). Its apparent surface area (0.1256cm²) was used to normalize the ORR activity of the catalysts. The ink was formed by mixing 5mg of the catalysts, 50µL of a 5wt.% Nafion solution in alcohol, and 950µL of ethanol in a plastic vial under ultra-sonication. A 10-µL ink was dropped on the surface of the glassy carbon rotating disk electrode, yielding an approximate catalyst loading of 0.39mg·cm⁻². For comparison, a commercially available platinum/carbon (Pt/C) catalyst, nominally 20wt.% on carbon black from E-TEK was used. The platinum-based ink was obtained by mixing 1mg catalyst, 50µL of a 5wt.% Nafion solution in alcohol, 950µL of ethanol. Then, a 15-µL platinum ink was dropped on the glassy carbon rotating disk electrode, yielding an approximate loading of 0.015mg or 24ug Pt cm⁻². The electrolyte was 0.1M KOH solution; the counter and the reference electrodes were a platinum wire and a SCE electrode (Fig. S2), respectively. The potential of the electrode was controlled by an EG&G (model 273) potentiostat/galvanostat system. Cyclic voltammetry was performed from 0.2 to -1.2V at $50 \text{mV} \cdot \text{s}^{-1}$ after purging the electrolyte with O2 or N2 gas for 30min. Voltamperometry measurements were performed by using a RRDE at a rotating speed of 1600rpm in an O₂ saturated electrolyte from 0.2 to -1.2V (vs SCE) at a sweep rate of 5mV/s. The measured potentials vs SCE were converted to a reversible hydrogen electrode (RHE) scale by the Nernst equation.

For the calculation of H_2O_2 yields of as-prepared catalysts in 0.1M KOH, based on both ring and disk currents from RRDE, the $HO_2^-\%$ generated from ORR and the electron transfer number (n) were estimated by the following equations:

$$HO_{2}^{-}\% = 200 \times \frac{i_{R}/N}{i_{D} + i_{R}/N}$$
(1)
$$n = 4 \times \frac{i_{D}}{i_{D} + i_{R}/N}$$
(2)

where i_D is the disk current density, i_R is the ring current density and N is the current collection efficiency of the Pt ring disk. N is 0.37 from the reduction of K_3 Fe[CN]₆. All the current densities have already been normalized to the electrode surface area.

3. Results and discussion

To assess the ORR activities of the catalysts obtained under different conditions, linear sweep voltammetry (LSV) tests were performed on a rotating ring disk electrode(RRDE) in O₂-saturated 0.1 M KOH. Based on the half-wave potential ($E_{1/2}$) obtained from LSV curves, the synthesis process was optimized by varying the synthesis temperature (Fig. S3), time (Fig. S4), weight ratio between carbon and urea (Fig. S5), and pressure (Fig. 2a). The optimal catalyst obtained (under the optimal synthesis conditions: pressure = 1GPa, pyrolysis temperature = 760 °C and time = 5 min, mass ratio between BP and urea=1:0.5) finally with Fe 4.7wt% (ICP-MS) and N 1.67 wt%(elementary analysis) was named as BP-NFe. For comparison, the BP, BP-Fe (without urea) and BP-N (without

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FeCl₃·6H₂O) were also obtained by UHP method. The traditional pyrolysis method with gas flow under atmospheric condition was adopted to obtain another FeN_x/C (named as P-BP-NFe) at 760°C for 5min under atmospheric pressure based on the same amount of raw materials as that for the synthesis of optimal BP-NFe under UHP.

Specially, as for the pressure-dependence of ORR performance of catalysts, as shown in Fig. 2b, the half-wave potential $(E_{1/2})$ obtained from LSV curves increases initially with the pressure increase, while after a maximum at 1GPa, the $E_{1/2}$ decreases inversely with the further increase of pressure. The effect of pressure on ORR performance of the catalysts also could be revealed by the pressure-dependent variation of the diffusionlimiting current as shown in Fig. 2c. Similarly, the limiting current (Ilimit) increases first with the increase of pressure probably due to the content increase of N doped on carbon, after a maximum at 1 GPa, the limiting current decreases inversely with the pressure although the content of N doped on carbon increases (Fig. 2b). The negative shift of $E_{1/2}$ or the decrease of limiting current after the maximum probably could be attributed to the compact structure formed at higher pressure, such compact structure decreases the accessibility of oxygen to the Fe, N-based active sites, and then leads to the decrease of both $E_{1/2}$ and I_{limit} although the total content of N doped on carbon increases continuously with the pressure. Such results indicate that there is an optimal content of N doped on carbon or an optimal pressure in such UHP experiments.¹⁶ Moreover, as shown in Fig. 2a,b,c, the P-BP-NFe possesses the lowest content of N doped, lowest $E_{1/2}$ or ORR activity but with largest limiting current. This fact indicates that the amount of exposed active sites on P-BP-NFe is much larger than that on UHPbased catalysts although the content of N doped on P-BP-NFe is lower than that on UHP-based catalysts. It further indicates that the intrinsic activity of the exposed active sites on BP-NFe is much higher than those on P-BP-NFe.



Fig. 2 (a) LSV curves of P-BP-NFe and the FeN_x/C obtained by varying the UHP in O₂ saturated 0.1M KOH with a scan rate of 5mV/s and a rotation speed of 1600rpm. (b) Synthesis pressure dependences of $E_{1/2}$ and the content of N-doped on carbon. (c) Synthesis pressure dependences of the limiting current (I_{limit}). The green points in (b,c) are the values for P-BP-NFe and BP-NFe catalysts. (d) LSV curves for BP, BP-N, BP-Fe and BP-NFe. (e) and (f) are the potential-dependent number of electrons and H_2O_2 yields on these catalysts. The loadings of catalysts are 0.39mg/cm².

The above results indicate that the UHP in appropriate range indeed can improve the ORR performance of the catalysts, probably due to its significant effect on the doping efficiency of heteroatoms and the microstructure of active sites on carbon. Significantly, as shown in Fig. S6, the ORR performance of the obtained optimal BP-NFe is even better than the commercial Pt/C with Pt 20 wt% indicated by the huge difference of $E_{1/2}$ (0.87 V for BP-NFe vs 0.81V for Pt/C) and on the same level as other reported best Fe-N-based catalysts (Table S1) in alkaline.¹⁷⁻²³ As for the advantages of the UHP method over traditional pyrolysis under atmospheric conditions, as shown in Fig. 2, the ORR catalytic activity of optimal BP-NFe is much higher than that of P-BP-NFe, which was obtained with the consumption of the same amount of chemicals as but much more energy than that for BP-NFe obtained from UHP.

To deeply understand the high ORR catalytic activity of the optimal BP-NFe, the ORR catalytic activity of BP, BP-Fe (without urea) and BP-N (without Fe) obtained by UHP method were also studied. As shown in Figure 2d, the pure carbon BP shows a very low ORR activity. While after the sole doping of N- (BP-N) or Fe-(BP-Fe) on carbon, the ORR activity was improved more or less indicated by the increase of onset potential and limiting current. As expected, after the co-doping of N and Fe on carbon, the ORR performance on BP-NFe was improved significantly due to the wellknown synergistic effect between N and Fe.^{24,25}The electron transfer numbers (n) and H₂O₂ yields for these catalysts were also plotted in Fig. 2e,f based on RRDE data. It shows that the H₂O₂ yield on the optimal BP-NFe is the lowest (<10%) among these catalysts in a wide potential range while with the largest n of ~3.9, very close to that of Pt/C (n~4). This result indicates that the BP-NFe catalyst in alkaline medium is a direct four-electron process with water as the main product from ORR.²¹



Fig.3 (a) TEM and (b) HRTEM images of BP-NFe. The white circles indicate the distribution of Fe nanoparticles in (a). (c) Nitrogen adsorptiondesorption isotherms, the inset is pore-size distributions; (d) Synthesis pressure dependence of the Brunauer-Emmett-Teller (BET) surface area.

To further understand the origin of high ORR activity and the effect of UHP on BP-NFe, the sample was characterized with different techniques. Fig. 3a,b show the typical TEM images of BP-NFe. The iron nanoparticles and the amorphous porous carbon structure with thin-layer graphene-like nanosheets can be seen clearly. Along with the XRD analysis(Fig. S7), interestingly, it was found that the iron nanoparticles on BP-NFe mainly exist in the form of Fe_3O_4 nanoparticles (Fig. 3b). The pressure-dependent

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porous nature of catalysts was further assessed by nitrogen adsorption-desorption analysis as shown in Fig. 3c,d. Fig. 3c shows clearly that the average size of mesopores decreases and the percentage of micropores increases gradually with the pressure increase. Correspondingly, the BET surface area also decreases gradually with the increase of pressure as shown in Fig. 3d. Obviously, the observed decreases of pore size and BET surface area at higher pressure could be attributed to the UHP-induced formation compact structure. Such compact structure can prohibit the accessibility of oxygen to the active sites, just like that shown in Fig. 2.

Furthermore, high-resolution XPS was employed to investigate the chemical states of doped N and Fe atoms. As shown in Fig. 4a, the doped N atoms mainly exist in four different bonding states. The peaks at 398.3, 400.1, and 401.1eV correspond to pyridinic (33.04%), pyrrolic (26.64%) and graphitic (8.82%) N, respectively,² while the peak at 399.5 eV is indexed to the Fe-N bond (31.50%). $^{\rm 26}$ Generally, the active centers based on Fe-N bond can highly activate the ORR process by the significant decrease of oxygen adsorption energy and extension of the O-O bond.²⁸⁻³⁰ Such observation can explain the observed synergistic effect between doped N and Fe during the ORR process as shown in Fig. 2. In addition, the existence of high contents of pyridinic N also can partially explain the observed high ORR activity since it has been known that pyridinic N is the main active component with highest ORR activity among different N forms in N-doped metal free catalysts.^{24,31} By comparing the N-based chemical states between BP-NFe and P-BP-NFe, as shown in Fig. S8 and Table S2, it can be seen that the UHP can enhance the formation of highly active sites of Fe-N_x(from 23.58% to 31.50%) and pyridinic N (from 20.75% to 33.04%), confirming the significant role of UHP for the selective formation of highly active sites.



Fig.4 High-resolution XPS spectra of N 1s (a) and Fe 2p (b) of the BP-NFe catalyst. (c) Raman spectra of the P-BP-NFe and the BP-NFe catalysts. (d) The durability of BP-NFe in O₂-saturated 0.1M KOH.

The Fe 2p spectrum of BP-NFe shown in Fig. 4b could be divided into two peaks at 710.4 and 711.3 eV, which can be assigned to the binding energies of the $2p_{3/2}$ orbitals of Fe²⁺ and Fe³⁺ species, confirming the observation of Fe₃O₄ from the HRTEM (Fig. 3b) and XRD (Fig. S7). Furthermore, from the atomic ratio of Fe³⁺/Fe²⁺=2 in Fe₃O₄ and the contents of Fe²⁺ and Fe³⁺ shown in Table S2, the content of Fe²⁺ in the form of Fe-N_x in the BP-NFe was deduced to be about 6.9%. By comparing it with that (1.0%) on P-BP-NFe as

shown in Fig. S8 and Table S2, one can see that the UHP can enhance the formation of $Fe\text{-}N_x$ on carbon support, consistent with the conclusion made from N-based component.

Fig. 4c shows the Raman spectra of the P-BP-NFe and BP-NFe catalysts, moreover, Raman spectra of all catalysts prepared is also summarized in Fig. S9, including the P-BP-NFe and BP-NFe with synthesis pressure from 0.85 to 3.5 GPa. It shows clearly that the UHP can lead to the graphitization of carbon to generate graphene-like nanosheets with the intensity increase of I_G , consistent with the observation from the HRTEM image (Fig. 3b). No significant shifts or line broadening suggests that the carbon structure is mostly retained after the UHP process. It is well known that the carbon graphitization in the catalysts can enhance the electronic conductivity and corrosion resistance in electrocatalysis,^{2,32} which then also contribute in part to the observed high ORR performance.

The durability or stability of the optimal catalyst was assessed based on the US Department of Energy's accelerated durability test protocol by cycling the catalyst between 0.6 and 1.15V at 200 mV/s in O₂ saturated 0.1M KOH. As shown in Fig. 4d, the BP-NFe shows a slight decrease of limiting current and a 14mV negative shift of $E_{1/2}$ but without negative shift of onset potential after 10000 cycles. The slight decrease of limiting current probably could be attributed to the loss of catalyst from the electrode surface, while the slight decrease of E1/2 represents a deterioration of ORR activity for BP-NFe, which may be ascribed to the collapsing of local N- or Fe-based active sites, further impacting the diffusion-limiting current. For comparison, the durability commercial Pt/C was also tested. As shown in Fig. S10, due to the migration/aggregation of Pt nanoparticles caused by continuous potential cycling and subsequent loss of the specific catalytic activity, the Pt/C displays a much larger negative shift (24 mV) of $E_{1/2}$ after 5000 cycles. Such difference thus indicates an excellent long-term operation stability of BP-NFe during the ORR process. As expected, such catalyst also shows no response to CO and methanol (Fig. S11).^{16,33}

4. Conclusions

In summary, for the first time, ultrahigh pressure (UHP) synthesis was adopted as a green synthesis of highly efficient FeN_x/C electrocatalysts for ORR with much less consumption of chemicals and energy compared with tradition atmospheric pyrolysis. The obtained optimal catalyst BP-NFe with a remarkable durability shows superhigh ORR performance. It was further found that the UHP can efficiently enhance the doping efficiency of heteroatoms on carbon, the graphitization of carbon, and the selective formation of highly active sites of pyridinic N and Fe-Nx for ORR. The UHP-based synthesis protocol with much less consumption of chemicals and energy makes the obtained optimal catalyst possess the best performance/price ratio. Such work for the "green" synthesis of highly efficient catalysts opens a new direction for us to explore highly efficient function materials for energy or industrial process.

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