Non Noble Metal Catalyst for Oxygen Reduction Reaction and Its Characterization by Simulated Fuel Cell Test

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In this work nitrogen doped multi-layer graphene and porous carbon are prepared by the pyrolysis of glycine as precursor. The morphology of the product is controlled by the catalyst used. The nitrogen doped multi-layer graphene exhibits a high onset potential and four-electron pathway for oxygen reduction reaction (ORR) in alkaline solution as well as much enhanced stability compared with commercial Pt/C catalyst. In a simulated fuel cell test the nitrogen doped multi-layer graphene shows comparable performance with Pt/C catalyst in alkaline environment. The ORR activity of the as-prepared carbon material is found to be related with graphitization degree and graphitic-N.

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The oxygen reduction reaction (ORR) at the cathode is an important process in fuel cells (FCs). The complicated intermediates and reaction barriers of the ORR greatly influence the energy conversion efficiency of fuel cells. The Pt and Pt-based materials have been proved to be the best electrocatalysts to catalyze the ORR, however, the high cost and low stability of Pt become the bottle neck for the large-scale commercial application of FCs.1,2 Consequently, extensive researches have been focused on highly efficient and cost-effective electrocatalysts using earth-abundant elements as ORR catalysts, including non-precious-metal and metal free catalysts.2-4

Traditional non-precious-metal catalysts have shown appealing performance in proton exchange membrane fuel cells (PEMFC) which is the most promising candidate for electric vehicles. However, the stability is still a big problem to be overcome. The active sites of such catalyst can be described as iron chelated with nitrogen forming FeN4, FeN2+, or FeN2.5 The existence of iron in the active site is considered to be one of the main factors of the low stability.6 Some research replaced Fe with Co or Ni, but with much inferior activity.7 So a new group of catalysts for ORR have emerged as metal free catalysts in which there is no metal. Such kind of catalyst shows no activity in acidic media, which is the working environment of PEMFC. However, due to their potential application in alkaline membrane fuel cells (AMFC), great interest has been put in this group of catalysts.5 The metal free catalysts are heteroatom-doped (such as N, B, P, S, and I) carbon materials, the ORR activity is explained by their unique electronic and structural features.8-12 Among the different heteroatom-doped carbon materials, nitrogen-doped carbon (NC) materials, including N-doped carbon nanotubes, carbon nanospheres, carbon nanosheets and graphene, have been proved to show comparable ORR activity with Pt-based catalysts in alkaline media.13-18 The introduction of N atoms into carbon can modify the electronic structure and introduce defects into the carbon structure, thus increasing the catalytic activity.17 Due to the difference in the electronegativity of nitrogen (3.04) in comparison to carbon (2.55), the N-species can facilitate the O2 adsorption and weaken the O-O bond effectively.18 The N-containing defects can attract the protons through electrostatic attraction and act as the active sites for ORR as reported by previous study.19 Besides N-doping, the graphitization degree of the carbon materials is another important factor in determining the ORR activity. The higher electric conductivity of higher graphitized carbon has been recognized to promote the mass/electron transfer during ORR.20 The third factor determining the ORR activity is the specific surface area and porous structure, which is the host of active sites and are necessary to improve the ORR activity.21

NC materials are generally prepared via two procedures: post-treatment of the carbon materials with nitrogen source or in situ direct-doping during the carbonization of nitrogen-rich carbon precursor. The preparation often use chemical precursors, including thiourea, melamine, phenylisulfide/ammonia, polyacrylonitrile, etc.15,22-24 and the preparation strategies are usually complicated.25,26 There are some clean preparation methods such as plasma etching and chemical vapor deposition (CVD), but are comparatively complicated and demand strict synthesis conditions.21,27,28 Recently, pyrolysis of metal organic frameworks (MOFs) and covalent organic frameworks (COFs), as well as some environmentally friendly biomass materials such as seaweed, cornstalk, animal blood and eggs have been recognized as promising approach to prepare porous NC catalysts for ORR.29-33 When 3D porous NC materials are aimed, the use and removal of the template make the multi-step preparation complicated and costly.11 Therefore, it is urgent to develop a green, facile and highly efficient route to synthesize NC materials with high ORR activity.

Herein, in this work we synthesized N-doped multi-layer graphene and porous carbon by a one-step and template-free pyrolysis of glycine and transition metal salts, in which glycine serves as both carbon and nitrogen source. Glycine is graphitized during the pyrolysis with Fe3+ or Co2+ as the graphitization catalysts. The morphology of the product is determined by the transition metal used. The as prepared catalyst shows comparable ORR performance to commercial Pt/C catalyst in alkaline media.

Experimental

All chemicals were of analytical grade and used as received from Aladdin Industrial Inc. All water was ultra-pure water with the
impedance of 18.3 MΩ from HITECH laboratory water purification system.

**Synthesis.**—In a typical synthesis, glycine and transition metal salt (FeCl₃ · 6H₂O/OCoCl₂ · 6H₂O/NNiCl₂ · 6H₂O) were mixed with the mass ratio of 1:2 by 50 ml of ultra-pure water. The mixture was stirred for 24 h, and then heated to evaporate the solvent. The resultant powder was placed into a quartz boat and pyrolyzed in a tube oven at 950 °C for 1 h under N₂ condition with the heating rate of 5 °C min⁻¹. After cooling to room temperature and ground, the product was washed with 1 mol L⁻¹ HCl, ultra-pure water and ethanol repeatedly to remove the impurities. The as-prepared samples were labeled as NCFe-950, NCCo-950 and NCNi-950 depending on the transition metal salt used. For comparison, NC-950 was synthesized under the same conditions without transition metal salts.

The preparation and catalytic performance of NCFe-950 is optimized by the following parameters: acid-leaching, pyrolysis temperature, precursor ratio and pyrolysis atmosphere. (1) The NCFe-950 without acid-leaching (1 M HCl) was denoted as NCFe-950-0. (2) The pyrolysis temperatures were 750, 850 and 1050 °C with fixed mass ratio of 1:2 between glycine and FeCl₃ · 6H₂O, the products were denoted as NCFe-750, NCFe-850 and NCFe-1050; (3) The mass ratio between glycine and FeCl₃ · 6H₂O were 2:1, 1:1 to 1:4 with fixed pyrolysis temperature at 950 °C, the products were denoted as NCFe-950-1, NCFe-950-2 and NCFe-950-3. (4) Ammonia was used as a substitute for nitrogen during the pyrolysis; the product was denoted as NCFe-950-NH₃.

**Materials characterizations.**—Powder X-ray diffractometer (XRD) patterns were measured by Rigaku-D-Max-III A (Cu Kα1, λ = 1.54056 Å radiation). The diffraction peaks were recorded in the 20 range of 10–70° with a measuring rate of 10 degree per minute. A Renishaw-Laser Micro-Raman Spectrometer was used to acquire Raman spectra. Surface morphology was obtained by a JEM-2100F field emission scanning electron microscopy (FE-SEM) operated at 20 kV. Transmission electron microscopy (TEM) images were investigated using JEM-2100HR high resolution electron microscope operated at 200 kV. The elemental composition and chemical state of the samples were studied with an X-ray photoelectron spectroscopy (XPS) instrument (ESCA- Lab 250, Thermo VG) with Al Kα radiation.

**Electrochemical characterizations.**—Electrochemical analysis was conducted with a three-electrode system using 0.1 mol L⁻¹ KOH electrolyte at 25°C. A glassy carbon electrode (RRDE, Pine Research instrument, 0.247 cm²), a platinum foil (1.0 × 1.0 cm²) and Ag/AgCl (saturated KCl) were used as working electrode, counter electrode and reference electrode, respectively. The catalyst ink was prepared by adding 10.0 mg of finely ground catalyst powder and 10 μL 5 wt% Nafion solution (DuPont Co. Ltd) into 0.5 mL ethanol. After ultrasonic stirring for 30 min, 10 μL prepared ink was deposited onto the glassy carbon and followed by drying naturally. The loading of as-prepared catalysts on carbon glass in the RDE test is 1 mg cm⁻². Commercial 46.6wt% Pt/C catalyst (Johnson Matthey, JM) was tested as a benchmark. Cyclic voltammograms (CV) was recorded at the sweep rate of 100 mV s⁻¹, and the potential range was between 1.1 and 0.1 V. Linear sweep voltammetry (LSV) was performed with a sweep rate of 10 mV s⁻¹, and the rotating speed was from 400 to 2500 rpm. The potential of ring was set at 1.2 V vs. RHE in the RRDE measurements.

The percentage of HO₂-released during ORR (HO₂⁻ %) and the electron transfer number (n) were calculated according to the following equations:

\[
\% \text{HO}_2^- = 200 \times \frac{I_p}{I_p + (I_R/N)} [1]
\]

\[
n = \frac{4I_p}{I_p + (I_R/N)} [2]
\]

Where \( I_p, I_R \) and \( N \) are ring current, disk current and current collection efficiency (\( N = 0.37 \)), respectively.

The Koutecky-Levich (K-L) equation was used to calculate the electron-transfer number (n):

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B \nu^{1/2}} + \frac{1}{J_K} [3]
\]

\[
B = 0.2nFCE(\alpha D_0)^{1/2} \nu^{-1/6} [4]
\]

In which J, J_L and J_K are the measured current density, kinetic current density and diffusion limited current density, respectively. \( \alpha \) is the rotation speed of the electrode, \( n \) is the electron transfer number, F is Faraday constant (96485 C mol⁻¹), \( D_0 \) is bulk concentration of oxygen (1.2 × 10⁻⁵ mol cm⁻³), \( \nu \) is the diffusion coefficient of oxygen (1.9 × 10⁻⁵ cm² s⁻¹), \( \nu \) is the kinetic viscosity (0.01 cm² s⁻¹). The constant 0.2 is adopted when rotation speed is expressed in rpm.

**Results and Discussion**

**Physical characterizations: morphology, crystallography, surface area, surface chemical status.**—The morphology and structure of the as-prepared NC were investigated by SEM and TEM as shown in Fig. 1. From the TEM images of Figs. 1a, 1b and 1c, it is clear that NC-950 is a kind of amorphous carbon, because even in the HRTEM image of Fig. 1c no graphite lattice fringes can be observed. This result proves glycine cannot be graphitized without transition metal salt which works as graphitization catalyst during the pyrolysis. It is also noted that NC-950 shows no special morphology, which is just a block of amorphous carbon. The morphology changed greatly when FeCl₃ is used during the pyrolysis with the product of NCFe-950. A typical graphene structure is resulted, as shown in the SEM image of Fig. 1d the carbon sheets of NCFe-950 are interconnected into a 3D network forming a porous architecture. The TEM images of NCFe-950 in Figs. 1e, 1f and 1g show layers of graphene sheets with wrinkled features. The HRTEM image (Fig. 1h) of NCFe-950 reveals clear lattice fringes, proving NCFe-950 is well graphitized with the presence of Fe catalyst. The layer number of NCFe-950 are observed to be ~10 layers with an average adjacent interlayer distance of 0.334 nm. The elemental distribution in NCFe-950 is studied by energy-dispersive spectrometry (EDS) mapping as shown in Fig. 1i, which indicates that C, O and N are uniformly distributed in multi-layer graphene. This is a direct proof of the successful doping of nitrogen into the graphene structure. It is found the graphitization catalyst can greatly influence the morphology of the product. As discussed above multi-layer graphene is resulted when Fe is used, while when Co is used as graphitization catalyst a kind of porous structure is found. The TEM images (Figs. 1 and 1k) show the porous structure of NCCo-950. HR-TEM image in Fig. 1l reveals the details of the structure, in which the nanosipes is enclosed by concentric graphitic shells. The outer diameter of the quasi-spherical graphitic shell is 15–20 nm, and the inner diameter is 5–10 nm. In conclusion, this work prepared a nitrogen doped multi-layer graphene from a uniform precursor. The graphitization catalyst determines the morphology of the product, Fe catalyst leads to multi-layer graphene while Co catalyst leads to porous carbon.

The XRD patterns of the NC samples are compared in Fig. 2a. In case of the nitrogen doped multi-layer graphene (NCFe-950) and porous carbon (NCCo-950), the characteristic diffraction peaks corresponding to the (002) and (101) basal plane of graphitic carbon can be indexed at the 2θ of 24.5–27° and 43.5°, respectively. While for NC-950 only a broad (002) peak can be found, which works as a direct proof of the amorphous nature of carbon. The shape of the (002) peak clearly proves the effect of transition metal in the pyrolysis of the precursor: transition metal works as the catalyst for graphitization. The obvious shift of the (002) diffraction peak of NCFe-950 and NCCo-950 compared to NC-950 clearly proves the effect of transition metal in the pyrolysis of the precursor: transition metal works as the catalyst for graphitization. The shift of the (002) diffraction peak of NCFe-950 and NCCo-950 compared to NC-950 also works as a proof of the formation of graphitic crystalline structure due to decreased d-spacing. It is noted that NCFe-950 shows a much sharper (002) peak compared with NCCo-950, indicating higher degree of graphitization resulting from the Fe catalyst compared to Co catalyst.
The graphitic and disordered properties of the NC materials are investigated by Raman spectroscopy. As shown in Fig. 2b, two distinct peaks of D band (\(\sim 1356 \text{ cm}^{-1}\)) and G band (\(\sim 1595 \text{ cm}^{-1}\)) as well as a weak 2D band (\(\sim 2590–3060 \text{ cm}^{-1}\)) are found in three samples. The D and G band are associated with the disordered carbon and sp\(^2\)-bonded graphitic carbon, respectively. The intensity ratio of the D to G band (\(I_D/I_G\)) is used to evaluate the degree of defect.\(^{25}\) The ratio value of NCFe-950 is 0.89, which is lower than that of NC-950 (1.12) and NCCo-950 (1.18). This result proves that NCFe-950 has a higher graphitization degree than NC-950 and NCCo-950, which is in accordance with the relatively higher intensity of (002) peak in XRD. The difference between the \(I_D/I_G\) of NCFe-950 and NCCo-950 also proves more defect of NCCo-950.

The specific surface areas are studied by the nitrogen adsorption-desorption technique as shown in Fig. 2c. The \(N_2\) adsorption-desorption curves of NCFe-950 and NCCo-950 show a characteristic of type IV isotherms, indicating the existence of mesopores in the sample. A hysteresis loop is also observed at higher relative pressures (\(P/P_0 = 0.4\) to 0.95), which is commonly related to the capillary condensation in mesopores.\(^{34}\) Due to the amorphous structure of NC-950 (Figs. 1a–1c), there is no significant \(N_2\) adsorbed on its surface. The Brunauer-Emmett-Teller (BET) surface area derived from \(N_2\) isotherms increased dramatically from NC-950 (24.5 m\(^2\) g\(^{-1}\)) to NCFe-950 (307.4 m\(^2\) g\(^{-1}\)) and NCCo-950 (457.8 m\(^2\) g\(^{-1}\)). The higher BET surface area of NCCo-950 compared to NCFe-950 is explained by the porous structure as shown in Figs. 1j–1l.

The elemental compositions of the NC materials are studied with XPS. In XPS survey spectra, the peaks at around 284, 400 and 532 eV are indexed to C1s, N1s and O1s, respectively, confirming the existence of nitrogen doped carbon. There is no Fe2p or Co2p signal in the full scan spectra. Since the samples are washed with acid, the XPS results prove the successful removal of the metal species on the surface, which is consistent with the XRD result. The effect of acid washing to the NCFe-950 sample is compared with XPS. The obvious Fe2p peak of the sample before acid washing disappears after acid washing, which works as a direct proof of the removal of the surface metal. The doped nitrogen can lead to the formation of positively charged sites in the carbon matrix, which favors the ORR process. So the high-resolution N1s spectra are studied in detail as shown in Fig. 2d. The N1s peak is deconvoluted into four types of nitrogen functionalities at 398.7 \(\pm 0.3\) eV, 400.1 \(\pm 0.3\) eV, 401 \(\pm 0.3\) eV and 402–405 \(\pm 0.3\) eV, corresponding to pyridinic-N, pyrrolic-N, graphitic-N and N-oxide of pyridinic-N, respectively.\(^{35,36}\) The graphitic-N is considered to be the most efficient active site. Table I summarizes the total nitrogen content and the proportion of the four types of nitrogen functionalities. The pyridinic-N and graphitic-N are the dominant nitrogen species in all NC samples, which are doped at the edge sites and the in-plane sites of the graphitic carbon. The total N content of NC-950
Figure 2. (a) XRD patterns, (b) Raman spectra, (c) N\textsubscript{2} adsorption/desorption isotherm and (d) High resolution N1s spectra of NC-950, NCFe-950 and NCCo-950.

(5.91 at.%) is much higher than that of NCFe-950 (1.56 at.%) and NCCo-950 (3.12 at.%), implying the loss of nitrogen during the pyrolysis with transition metal. The relative content of pyridinic-N is largely decreased from NC-950 (31.68 at.%) to NCFe-950 (20.95 at.%) and NCCo-950 (26.15 at.%). Since pyridinic-N is at the edge sites, the higher graphitization degree may lead to the reduction of the edge nitrogen. The proportion of graphitic-N in NCFe-950 (54.05 at.%) increases compared with NC-950 (48.09 at.%), while the value of NCCo-950 (37.31 at.%) decreases compared with NC-950. The presence of Fe may facilitate the doping of the in-plane nitrogen.

**Electrochemical characterizations: ORR activity and stability.**

The ORR activities are preliminarily tested by cyclic voltammograms (CV) in 0.1 M KOH aqueous solution. Both NCFe-950 and NCCo-950 show obvious cathodic peak compared with NC-950, proving the ORR activity. The peak position of NCFe-950 (0.772 V vs. RHE) is more positive than that of NCCo-950 (0.745 V vs. RHE), together with the positive shift of onset potential. The CV results prove higher ORR activity of NCFe-950 than that of NCCo-950. The ORR is further studied with RDE and RRDE to get more kinetic details. The commercial Pt/C catalyst (46.6 wt%) is tested under the same conditions for comparison. From Fig. 3a, the crucial parameters of ORR such as onset potential (E\textsubscript{o}) and half-wave potential (E\textsubscript{1/2}) can be determined to compare the activity. NCFe-950 show comparable activity (E\textsubscript{o} = 0.965 V vs. RHE, E\textsubscript{1/2} = 0.83 V vs. RHE) with that of Pt/C (E\textsubscript{o} = 1.0 V vs. RHE, E\textsubscript{1/2} = 0.84 V vs. RHE). The ORR activity increases in the sequence of NC-950 < NCNi-950 < NCCo-950 < NCFe-950. It can be concluded that the transition metal greatly influences the ORR activity. The Tafel plots are used to compare the kinetics of ORR as shown in Fig. 3b. Two linear regions are observed in all Tafel plots at the low and high overpotential regions with different slope values. The Tafel slopes of NCFe-950 are 84.4 and

| Table I. Fitting results of the XPS N1s peaks for the different samples. |
|---|---|---|---|---|
| Samples | Total N content (at.%) | pyridinic-N (398.7 ± 0.3 eV) Proportion(at.%) | pyrrolic-N (400.1 ± 0.3 eV) Proportion(at.%) | graphitic-N (401 ± 0.3 eV) Proportion(at.%) | N-oxide of pyridinic-N (402-405 ± 0.3 eV) Proportion(at.%) |
| NC-950 | 5.91 | 31.68 | 12.4 | 48.09 | 7.82 |
| NCFe-950 | 1.56 | 20.95 | 14.19 | 54.05 | 10.81 |
| NCCo-950 | 3.12 | 26.15 | 18.08 | 37.31 | 18.46 |
115.9 mV dec$^{-1}$ in the two overpotential ranges, respectively, which is nearly the same as the Pt/C. The origin of the double Tafel slopes of Pt/C is explained by the site blocking effect of the adsorbed intermediates at low overpotential region. The similar Tafel behavior of NCFe-950 proves similar characteristics. The deviation of Tafel slope from 115.9 mV dec$^{-1}$ to 84.4 mV dec$^{-1}$ is explained by the site-blocking effect of OOH at high potentials, where the ORR rate is determined by the first electron reduction of oxygen to form adsorbed intermediates (OOH) on the surface of the catalyst. The binding energy of OOH during adsorption and desorption determines the catalytic activity of the catalyst.37

The intermediates during ORR is studied by RRDE. The peroxide yields (%HO$_2^-$) of different catalysts are derived from the ring current and disk current according to Equations 1 and 2. The NCFe-950 exhibits the lowest %HO$_2^-$ compared with NCCo-950 and NC-950, although slightly higher than Pt/C, suggesting the highest activity in this series. The electron transfer number (n) is a direct parameter of the ORR. The n value of NCFe-950 is calculated to be 3.83–3.95 in the diffusion controlled region (Fig. 3c), which is close to that of Pt/C (ca. 4.0), revealing a four-electron pathway of ORR. In contrast, the n values are 3–3.13 and 3.14–3.5 for NC-950 and NCCo-950, respectively. The electron transfer number (n) can be also quantified on the basis of the LSV at different rotating rates (400–2500 rpm) based on the Koutecky-Levich (K-L) Equations 3 and 4. Fig. 3d shows the curves of NCFe-950. The K-L plots exhibit good linearity at different potentials. The average n values based on the slope of the fitted K-L plots are calculated to be 3.37, 4.01 and 3.97 for NCCo-950, NCFe-950 and Pt/C, respectively. The n values are similar with the results of RRDE. It can be concluded from above electrochemical tests that NCFe-950 shows similar ORR performance with Pt/C catalyst in terms of onset potential, half-wave potential, peroxide yield and number of electrons transferred.

The ultimate aim of a catalyst is to be applied in a fuel cell, so a MEA test is necessary. Due to the lack of anion exchange membrane, we used a simulated test to study the MEA performance of the catalysts. A real MEA is mainly composed by three parts: anode, membrane and cathode. Hydrogen gas is inflowed into the anode and oxygen gas to the cathode. Since the anode is the hydrogen oxidation reaction with the potential of 0 V, we monitored the potential-current curve of the cathode to simulate the MEA performance. The catalyst is prepared into a square of 1 cm$^2$ on carbon paper, which is immersed into O$_2$-saturated 0.1 M KOH solution with O$_2$ continuously bubbled onto the surface of the solution. The loading of the as prepared catalysts on carbon paper in the simulated fuel cell tests is about 1.2 mg cm$^{-2}$. The simulated fuel cell test was carried out in a three-electrode system. The counter electrode, reference electrode and catalyst ink are the same as those of in ORR test. A carbon paper with one centimeter of width is employed as the work electrode. The results are iR-corrected with the impedance value from the high frequency value of the EIS spectrum. The simulated fuel cell polarization
Stability is another important parameter for fuel cell catalyst. In this work we used acceleration test to study the electrochemical stability of the catalysts: the working electrode was cycled for 10000 cycles in the potential range from 1 to 0.6 V vs. RHE in 0.1 M KOH. As shown in Fig. 5a, for NCFe-950 there is no change in the ORR onset potential ($E_0$) and half-wave potential ($E_{1/2}$) after the acceleration test, only slight decrease in diffusion limiting current density happens. However, for the Pt/C catalyst, there are 35 mV and 30 mV loss in $E_0$ and $E_{1/2}$, respectively. These results prove that NCFe-950 exhibits much better catalytic stability toward ORR than the commercial Pt/C catalyst in alkaline media. The unstability of Pt/C catalyst comes from the fall off, aggregation or poison of Pt metal. While NCFe-950 is a metal free catalyst, the active site is nitrogen doped carbon, the elimination of the unstable factors leads to much improved stability.

**Optimization of the preparation parameters.**—In case of the optimization of the catalyst, the following parameters are concerned: the effect of acid-leaching, pyrolysis temperature, precursor ratio and protection atmosphere. Since NCFe-950 is proved to be the best catalyst, the optimization tests all use FeCl₃ as the graphitization catalyst of glycine. Fig. 6a shows the effect of acid-leaching, the 110 mV shift in the $E_{1/2}$ from NCFe-950-0 to NCFe-950, together with the no shift of onset potential prove that acid-leading will not influence the nature of the active site, but can greatly change the diffusion property of the electrode. The direct effect of acid-leaching is the removal of Fe from the catalyst, this process may generate micro or meso holes in the catalyst structure, improving the diffusion property. Fig. 6a compares the effect of the pyrolysis temperature which is reported to play a crucial role in the electrocatalytic activity of catalysts. The catalysts were prepared at different pyrolysis temperatures from 750 to 1050°C, denoted as NCFe-750, NCFe-850, NCFe-950 and NCFe-1050, respectively. The influence of temperature is obvious: the activity increases with temperature from 750 to 950°C, with a slight decrease at 1050°C. So 950°C is the best pyrolysis temperature. The simulated test can also be used to compare the catalysts. For example, NCFe-950 shows a current density of $\sim 44$ mA cm$^{-2}$ at 0.7 V, which is very close to Pt/C. The results are in good agreement with the RDE results. The simulated test is in-between the fuel cell MEA test and the pure half cell RDE test. A diffusion electrode is used, and the main difference to the MEA test is that in a MEA O₂ diffuse through the three-phase boundary while in the simulated test O₂ diffuse through the O₂ saturated KOH solution.

![Figure 4](image)

The simulated fuel cell polarization plots (solid line) and power-density curves (dash line) of different samples are compared in Fig. 4. Due to the limited supply of O₂, even for Pt/C catalyst the current density at 0.7 V can only reach $\sim 55$ mA cm$^{-2}$. So there must be a coefficient between the simulated test and a real MEA test. Despite of this, the simulated test can also be used to compare the catalysts. For example, NCFe-950 shows a current density of $\sim 44$ mA cm$^{-2}$ at 0.7 V, which is very close to Pt/C. The results are in good agreement with the RDE results. The simulated test is in-between the fuel cell MEA test and the pure half cell RDE test. A diffusion electrode is used, and the main difference to the MEA test is that in a MEA O₂ diffuse through the three-phase boundary while in the simulated test O₂ diffuse through the O₂ saturated KOH solution.

![Figure 5](image)

The simulated fuel cell polarization plots (solid line) and power-density curves (dash line) of different samples are compared in Fig. 4. Due to the limited supply of O₂, even for Pt/C catalyst the current density at 0.7 V can only reach $\sim 55$ mA cm$^{-2}$. So there must be a coefficient between the simulated test and a real MEA test. Despite of this, the simulated test can also be used to compare the catalysts. For example, NCFe-950 shows a current density of $\sim 44$ mA cm$^{-2}$ at 0.7 V, which is very close to Pt/C. The results are in good agreement with the RDE results. The simulated test is in-between the fuel cell MEA test and the pure half cell RDE test. A diffusion electrode is used, and the main difference to the MEA test is that in a MEA O₂ diffuse through the three-phase boundary while in the simulated test O₂ diffuse through the O₂ saturated KOH solution.

Stability is another important parameter for fuel cell catalyst. In this work we used acceleration test to study the electrochemical stability of the catalysts: the working electrode was cycled for 10000 cycles in the potential range from 1 to 0.6 V vs. RHE in 0.1 M KOH. As shown in Fig. 5a, for NCFe-950 there is no change in the ORR onset potential ($E_0$) and half-wave potential ($E_{1/2}$) after the acceleration test, only slight decrease in diffusion limiting current density happens. However, for the Pt/C catalyst, there are 35 mV and 30 mV loss in $E_0$ and $E_{1/2}$, respectively. These results prove that NCFe-950 exhibits much better catalytic stability toward ORR than the commercial Pt/C catalyst in alkaline media. The unstability of Pt/C catalyst comes from the fall off, aggregation or poison of Pt metal. While NCFe-950 is a metal free catalyst, the active site is nitrogen doped carbon, the elimination of the unstable factors leads to much improved stability.

**Optimization of the preparation parameters.**—In case of the optimization of the catalyst, the following parameters are concerned: the effect of acid-leaching, pyrolysis temperature, precursor ratio and protection atmosphere. Since NCFe-950 is proved to be the best catalyst, the optimization tests all use FeCl₃ as the graphitization catalyst of glycine. Fig. 6a shows the effect of acid-leaching, the 110 mV shift in the $E_{1/2}$ from NCFe-950-0 to NCFe-950, together with the no shift of onset potential prove that acid-leading will not influence the nature of the active site, but can greatly change the diffusion property of the electrode. The direct effect of acid-leaching is the removal of Fe from the catalyst, this process may generate micro or meso holes in the catalyst structure, improving the diffusion property. Fig. 6a compares the effect of the pyrolysis temperature which is reported to play a crucial role in the electrocatalytic activity of catalysts. The catalysts were prepared at different pyrolysis temperatures from 750 to 1050°C, denoted as NCFe-750, NCFe-850, NCFe-950 and NCFe-1050, respectively. The influence of temperature is obvious: the activity increases with temperature from 750 to 950°C, with a slight decrease at 1050°C. So 950°C is the best pyrolysis temperature. The simulated test can also be used to compare the catalysts. For example, NCFe-950 shows a current density of $\sim 44$ mA cm$^{-2}$ at 0.7 V, which is very close to Pt/C. The results are in good agreement with the RDE results. The simulated test is in-between the fuel cell MEA test and the pure half cell RDE test. A diffusion electrode is used, and the main difference to the MEA test is that in a MEA O₂ diffuse through the three-phase boundary while in the simulated test O₂ diffuse through the O₂ saturated KOH solution.

![Figure 5](image)

The LSV curves of (a) NCFe-950 and (b) Pt/C for ORR in O₂-saturated 0.1 M KOH before and after 10000 cycles.

### References

- J3008-J3015 (2018) J3013
- J3008-J3015 (2018) J3013
catalyst pyrolyzed in NH$_3$ shows a slight improvement in ORR activity proved by a 20 mV higher half-wave potential than that pyrolyzed in N$_2$. This clearly indicates that the addition of NH$_3$ treatment is effective to increase density of active sites as evidenced by more positive $E_{1/2}$. This phenomenon is the same with previous report. During the high-temperature treatment of NCFe-950 in the presence of NH$_3$, the defects and micropores are further increased caused by the NH$_3$ partly gasifies the carbon support. Those extra defects and micropores are beneficial to host catalytic sites, thus facilitating the oxygen reduction process.

Conclusions

This work prepares nitrogen doped multi-layer graphene and porous carbon via a one-step pyrolysis of glycine. The morphology of the product is determined by the catalyst used. Among the prepared catalysts the nitrogen doped multi-layer grapheneshows the highest ORR activity, with similar onset potential and half-wave potential than the P/C catalyst. The kinetic parameters such as rate determining step and electron transfer number are also similar with P/C catalyst. Much improved stability is found compared with P/C catalyst, which is explained by the elimination of the unstable factors in the nitrogen doped carbon. The total N content can be controlled by preparation methods. The highest ORR performance is found in NCFe-950 with the highest content of graphitic-N. The relative content of graphitic-N is a determining factor for the ORR activity compared with the total N content. The graphitization degree also determines the ORR activity, which is explained by the higher electric conductivity with higher graphitization degree.

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