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Article

Effect of pyrolysis conditions on nitrogen-doped ordered mesoporous carbon electrocatalysts

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ABSTRACT

Pt is the most effective and widely used electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells; however, its scarcity and high cost pose a great challenge to the commercialization of the fuel cell technology. N-doped carbon materials have been regarded as one of the most promising Pt-alternative catalysts. In this work, the N-doped ordered mesoporous carbon was synthesized by the nanocasting method using SBA-15 as the template. The effect of the pyrolysis conditions (pyrolysis temperature, pyrolysis duration, and ramp rate) on this material was investigated. N₂ adsorption-desorption isotherms, X-ray photoelectron spectroscopy, and Raman spectroscopy were used to investigate the intrinsic properties of the resultant materials. Cyclic voltammetry and rotating ring-disk electrode were used to investigate the electrochemical behavior for ORR in an alkaline medium. It was found that the resultant mesoporous carbon materials exhibit high electrical conductivity, high specific surface area, and unique pore structure. The pyrolysis temperature was the most important parameter in determining the thermodecomposition of the carbon precursor, and the microstructure, elemental composition, and chemical configuration of the resultant mesoporous carbon materials. To achieve reasonable electrocatalytic activity and selectivity, a high pyrolysis temperature above 800 °C is required for effective N doping to form active sites and for graphitization to facilitate charge transfer, whereas the pyrolysis duration and ramp rate have a much less significant effect. This indicates that both the surface composition/structure and consequent electrochemical properties are more dependent on the thermodynamics than the kinetics during the pyrolysis process. Finally, the optimal N-doped ordered mesoporous carbon catalyst showed superior electrochemical activity for ORR than the commercial Pt catalyst and is promising for fuel cell and metal–air battery applications.

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1. Introduction

Oxygen reduction reaction (ORR) is one of the most important reactions in both fuel cells and metal–air batteries [1].

Pt is the most effective electrocatalyst for the ORR [1–3]. However, its scarcity and high cost has long been the main issue hampering the commercialization of fuel cells [4–6]. In the past decades, enormous efforts have been made to investigate al-

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ternative non-precious-metal catalysts [7,8].

Among the potential candidates, carbon-based catalysts have attracted intensive attention [9]. N-doping can effectively alter the electronic and geometrical properties and thus improve the electrochemical performance of carbon catalysts [10]. Both the content and chemical configuration of the nitrogen dopant on the surface are of great importance in the electrocatalytic activity of the carbon catalyst. Effective N-doping can be achieved by either etching the carbon material in a N-containing gas [11,12] or direct pyrolysis of N-containing carbon sources such as melamine [13], polypyrrole [14–16], and polyaniline [17,18]. In both methods, the pyrolysis conditions are known to have a significant effect on the composition and structure of the resultant carbon. Jaouen et al. [19,20] investigated the effect of heat treatment on the activity and structure of carbon black etched by NH_3 .

In previous work, we synthesized N-doped ordered mesoporous carbon (NOMC) by a modified nanocasting method, and the NOMC had high specific surface area, uniform pore structure, and excellent electrocatalytic activity [21]. The pyrolysis conditions are known to have a significant effect on the catalyst. However, this effect has not been explicitly investigated. In this work, the effects of the pyrolysis conditions, including the pyrolysis temperature, pyrolysis ramp rate, and duration, on the intrinsic properties and electrocatalytic activity of the NOMC catalyst were extensively investigated.

2. Experimental

2.1. Preparation of SBA-15

The details of the SBA-15 synthesis have been described elsewhere [22]. Typically, 4.0 g Pluronic P123 (Aldrich Chemistry, German) was dissolved in a mixture of 126 mL deionized water and 20 mL hydrochloric acid (37 wt%, Sinopharm Chemical Reagent Company Limited, Shanghai), and then 9.2 mL tetraethyl orthosilicate (Guangzhou Chemical Reagent Factory, Guangzhou) was added and the solution was stirred for 20 h at 35 °C. The slurry was hydrothermally treated at 110 °C for 12 h. Finally, the product was filtered, dried, and then calcined at 550 °C for 6 h in air to remove the organic template.

2.2. Preparation of N-doped ordered mesoporous carbon

Newly distilled pyrrole (PY, 1.20 mL, 99%, Xiya Reagent, Shandong) together with 1.0 g SBA-15 was added into a vacuum container, which was then kept in an oven at 133 °C for 2 h. The obtained light-yellow powder was added to 40 mL 2.0 mol/L FeCl_3 (Sinopharm) aqueous solution, which was then vigorously stirred for 24 h at room temperature for polymerization. The product was filtrated and thoroughly washed with deionized water to remove the metal salt. After drying, the obtained black power was pyrolyzed at high temperature (600, 800, 900, or 1000 °C) for a given duration (1, 2, or 3 h) in argon (99.999%, Zhuozheng Gases Company Limited, Guangdong) with a certain pyrolysis ramp rate (10 or 30 °C/min). Finally, the silica template was removed in 10 mol/L NaOH at 120 °C

for 24 h, followed by rinsing with deionized water. The NOMC catalyst samples were denoted as C-PY-Temp-Duration-Rate.

2.3. Characterization

X-ray photoelectron spectroscopy (XPS) was carried out with a Physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray at a power of 350 W. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 S-TWIN microscope operated at 200 kV. Raman spectra of the samples were performed on a LabRAM Aramis spectrometer with a 632.81 nm helium-neon laser. Nitrogen adsorption-desorption isotherms were measured at −196 °C using a Micromeritics TriStar II 3020 analyzer. Before adsorption measurements, each sample was outgassed under vacuum for 3 h at 200 °C. The total surface area (A_{BET}) was analyzed by the well-established Brunauer-Emmett-Teller (BET) method, the microporous surface area (A_{MP}) was obtained by the micropore (MP) method (t -plot method), and the pore size distribution (D_{BJH}) was analyzed by the Barrett-Joyner-Halenda method.

2.4. Electrochemical characterization

The electrochemical behavior of the catalyst was characterized by cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) using a three-electrode cell with a Zennium electrochemical workstation (Zahner) at room temperature (25 °C). A platinum wire and double junction Ag/AgCl reference electrode (PINE) were used as the counter and reference electrode, respectively. The working electrode was a rotating ring-disk electrode (RRDE; glassy carbon disk: 5.0 mm in diameter; platinum ring: 6.5 mm inner diameter and 7.5 mm outer diameter). The thin-film electrode on the disk was prepared as follows. First, 10 mg of the catalyst was dispersed in 1.0 mL Nafion/ethanol (0.84 wt% Nafion) by sonication for 120 min. Then, 10 μL of the dispersion was transferred onto the glassy carbon disk using a pipette, giving the catalyst loading of 0.50 mg/cm². For comparison, we also measured the electrocatalytic activity of the commercial 40 wt% Pt/C catalyst (HiSPEC4000, Johnson Matthey) for the ORR with metal loading of 20 $\mu\text{g}/\text{cm}^2$.

The electrolyte solution was first bubbled with Ar for 60 min. Then, a CV test was conducted at 20 mV/s in the potential range 0–1.23 V (vs. reversible hydrogen electrode, RHE) for 20 cycles. Unless otherwise specified, the LSV curve was collected by scanning the disk potential from 1.2 V down to 0 V at 5 mV/s in O_2 saturated electrolyte solution under 1600 r/min, from which the ORR polarization curve was determined by subtracting the capacitive current. During the collection, the potential of the ring was set to 0.5 V (vs. RHE) in alkaline solution to determine the yield of H_2O_2 .

The electron-transfer number (n) and H_2O_2 yield ($\text{H}_2\text{O}_2\%$) in the ORR were calculated from [23,24]

$$n = \frac{4|i_d|}{|i_d| + i_r / N} \quad (1)$$

$$H_2O_2(\%) = \frac{2i_r / N}{|i_d| + i_r / N} \times 100 \quad (2)$$

where i_d is the disk current, i_r is the ring current, and N is the collection efficiency (20.50%).

3. Results and discussion

Figure 1 shows the N_2 adsorption-desorption isotherms of the carbon materials synthesized under various pyrolysis conditions. All of the curves are similar and show the typical type-IV isotherm. The inset figure shows that the pore diameter is essentially in the range of 2–10 nm, indicating the mesoporous structure of the synthesized carbon materials.

The key pore parameters extracted from the isotherms are listed in Table 1. Next, the effect of the pyrolysis temperature is discussed based on the pore structure. The surface area of the micropores is much smaller than the total surface area, indicating that the pores in the synthesized carbon materials are mainly mesopores. Moreover, micropores are only present at pyrolysis temperatures above 600 °C, which is strongly indicative of the onset of decomposition of the carbon source. Accordingly, increasing the pyrolysis temperature promotes the decomposition process, which yields more micropores and enlarges the microporous surface area. A similar trend is also seen for the total BET specific surface area, which increases from 700 to 888 m^2/g with increasing pyrolysis temperature from 600 to 900 °C. A further increase to 1000 °C results in a decrease of the surface area, which can be attributed to the collapse of the carbon framework at high temperature. It is concluded that the pyrolysis temperature is detrimental to the thermochemical decomposition of the carbon precursor, and therefore the micropore structure of the resultant carbon. Accordingly, it is expected that micropores continue to develop as decomposition proceeds with increasing pyrolysis duration. The results in Table 1 confirm this deduction. The microporous surface area increases from 74 to 131 m^2/g when the pyrolysis

Table 1

Pore features of SBA-15 and the as-synthesized carbon materials.

Sample	A_{BET} (m^2/g)	A_{MP} (m^2/g)	D_{BJH} (nm)	V (cm^3/g)
SBA-15	823	133	5.2	1.20
C-PY-600-3-30	700	5	3.8	0.63
C-PY-800-3-30	840	50	4.1	0.83
C-PY-900-3-30	888	131	4.1	0.82
C-PY-1000-3-30	740	88	4.6	0.75
C-PY-900-1-30	691	74	4.4	0.71
C-PY-900-2-30	837	79	4.4	0.87
C-PY-900-3-10	822	114	4.4	0.79

Table 2

Elemental composition of the as-synthesized carbon materials measured by XPS.

Sample	C (%)	N (%)	O (%)	Fe (%)	N:C
C-PY-600-3-30	84.48	10.16	4.40	0.06	0.120
C-PY-800-3-30	89.81	5.91	3.76	0.09	0.066
C-PY-900-3-30	92.11	3.78	3.78	0.05	0.041
C-PY-1000-3-30	92.97	2.58	3.50	0.17	0.028
C-PY-900-1-30	89.35	4.55	4.95	0.21	0.051
C-PY-900-2-30	91.73	3.73	4.03	0.15	0.041
C-PY-900-3-10	91.25	3.71	4.48	0.20	0.041

duration increases from 1 to 3 h. Finally, the effect of pyrolysis ramp rate was investigated. All of the pore parameters are similar when the pyrolysis ramp rate increases from 10 to 30 °C/min. This result seems to contradict the general belief that the ramp rate should be selected as slow as 5 °C/min. Our finding suggests that the pore features are more dependent on the thermodynamics than the kinetics of the thermodecomposition of the carbon precursor.

XPS survey spectra were collected to determine the elemental composition, and the quantitative results are listed in Table 2. The N content decreases with increasing pyrolysis temperature and duration, while the ramp rate has a negligible effect on the elemental composition. The pyrolysis temperature has the largest effect on the N content and elemental composition.

Fig. 1. N_2 adsorption-desorption isotherms and pore size distributions (inset) of the as-synthesized carbon materials under different pyrolysis conditions. (a) Pyrolysis temperature 600, 800, 900, and 1000 °C, pyrolysis duration 3 h, and ramp rate 30 °C/min; (b) Pyrolysis duration 1, 2, and 3 h, pyrolysis temperature 900 °C, and ramp rate 30 °C/min; (c) Ramp rate 10 and 30 °C/min, pyrolysis temperature 900 °C, and pyrolysis duration 3 h.

Fig. 2. N 1s peak and the peak fitting results of the C-PY-Temp-3-30 materials. (a) C-PY-600-3-30; (b) C-PY-800-3-30; (c) C-PY-900-3-30; (d) C-PY-1000-3-30.

tion. For example, the N content dramatically decreases from 10.16% to 2.58% with increasing pyrolysis temperature. Furthermore, the N content decreases from 4.5% to 3.7% when the pyrolysis duration increases from 1 to 2 h, and then levels off with further increasing pyrolysis duration. This finding is similar to the effect of the pyrolysis conditions on the micropore features (vide supra). This strongly indicates that the decomposition of the N-containing functional groups results in the formation of micropores.

Figure 2 shows the high-resolution N 1s XPS spectra and curve fitting of the synthesized materials. The quantitative results of each species are listed in Table 3. The N 1s spectra can be deconvoluted into four peaks at 398.4 ± 0.2 , 400.1 ± 0.1 , 401.0 ± 0.1 , and $401.5\text{--}404$ eV, corresponding to pyridinic nitrogen, pyrrolic nitrogen, graphitic nitrogen, and nitrogen-oxide groups, respectively [25,26]. Increasing the pyrolysis temperature converts pyrrolic nitrogen into other types of nitrogen upon pyrolysis [27], predominantly into graphitic nitrogen [28]. This result indicates that a higher pyrolysis temperature promotes the incorporation of the nitrogen dopant into the framework of graphene, and has a significant effect on

the electrochemical performance, as discussed below.

Figure 3 shows the Raman spectra of the catalysts used to evaluate its crystalline structure and defects. The peaks at 1327 and 1583 cm^{-1} correspond to the D and G band, respectively. The D band is related to disorder or defects in the graphitic structure because of sp^3 hybridized carbons, and the G band is related to the graphitic structure of sp^2 hybridized carbons [29,30]. The ratios of the intensity of the D band to that of the G band (I_D/I_G ratios) are 1.42, 1.32, 1.28, and 1.27 for the carbon materials prepared at 600, 800, 900, and 1000 °C, respectively, indicating that the graphitic degree increases with increasing pyrolysis temperature.

Fig. 3. Raman spectra of the C-PY-Temp-3-30 materials.

Table 3

Content of each N-component (%) in C-PY-Temp-3-30.

Sample	Pyridinic	Me-N	Pyrrolic	Graphitic	O-N
C-PY-600-3-30	36.40	9.88	49.48	—	4.25
C-PY-800-3-30	28.16	12.89	—	48.05	10.90
C-PY-900-3-30	24.81	9.73	—	53.08	12.38
C-PY-1000-3-30	15.37	8.14	—	63.52	12.98

Fig. 4. CV curves of the C-PY-Temp-3-30 materials in Ar-saturated 0.10 mol/L KOH solution.

Figure 4 shows the CV curves of the carbon materials prepared at different temperatures. The CV curve of C-PY-600-3-30 is different to those of the carbon materials synthesized at higher temperatures. This curve is highly distorted and shows a pair of irreversible peaks. The distorted shape can be attributed to the high ohmic resistance of C-PY-600-3-30 because of the low degree of crystallinity, as evidenced by Raman results. For the three carbon materials synthesized at higher temperatures (800, 900, and 1000 °C), the curves are similar in shape with broad redox peaks at 0–0.8 V, and the current continues to decrease with increasing pyrolysis temperature. First, the large capacitance current reveals the high specific surface area of the carbon materials (vide supra). Second, the broad peaks in the potential range 0–0.8 V are

relatively symmetrical in curve shape, indicating fast electron transfer processes in this range. The redox peaks should result from the adsorption of hydroxyl ions on the carbon surface. Third, the decrease in the capacitive current can be understood as a result of the increased decomposition of the functional groups at higher pyrolysis temperatures, as previously mentioned. In addition, no well-defined iron redox peaks are observed in all of the CV curves, indicating that no electrochemically detectable Fe is present on the surface of the carbon materials.

Figure 5 shows the ORR polarization curves and the H_2O_2 yield in O_2 -saturated 0.10 mol/L KOH solution. The pyrolysis temperature was found to have a significant effect on the electrocatalytic activity and selectivity. First, the electrocatalytic activity continues to improve with increasing pyrolysis temperature, and the two catalysts pyrolyzed at 900 and 1000 °C outperform the commercial 40 wt% Pt/C catalyst. Second, increasing the pyrolysis temperature lowers the H_2O_2 yield, thereby favoring the 4-e reduction of oxygen and the stability of the catalyst. As such, the catalysts pyrolyzed at 900 and 1000 °C show a higher electron transfer number (~ 3.8) than those pyrolyzed at lower temperatures. Such an effect is understandable by considering the above-mentioned findings. Therefore, a high pyrolysis temperature is essential for effective doping of N to form the active sites and for graphitization to facilitate charge transfer.

Finally, the effect of pyrolysis duration and ramp rate on the electrochemical behavior was investigated. Figure 6 shows the CV and ORR polarization curves of the carbon materials. Both the pyrolysis duration and ramp rate did not significantly affect the CV and polarization performance. This finding is not surprising because these two pyrolysis parameters do not play an

Fig. 5. RRDE results of the C-PY-Temp-3-30 materials in O_2 -saturated 0.10 mol/L KOH solution. (a) ORR polarization curves; (b) Electron transfer number and H_2O_2 yield.

Fig. 6. CV (a, c) and ORR polarization (b, d) curves of the carbon materials synthesized with different pyrolysis durations (a, b) and ramp rates (c, d) in 0.10 mol/L KOH solution.

important role in determining the composition and structure of carbon materials. This further confirms the above conclusion that both the surface composition/structure and consequent electrochemical properties are more dependent on the thermodynamics than the kinetics during the pyrolysis process.

4. Conclusions

N-doped ordered mesoporous carbon was synthesized for the oxygen reduction reaction in fuel cells. The effects of the pyrolysis conditions, including pyrolysis temperature and duration, and ramp rate, on the resultant carbon materials were extensively investigated. The results reveal that the pyrolysis temperature plays an important role in determining the microstructure, composition, and electrocatalytic activity. In comparison, both the pyrolysis duration and ramp rate have less significant effects. The above findings strongly indicate that both the surface composition/structure and consequent electrochemical properties are more dependent on the thermodynamics than the kinetics during the pyrolysis process.

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Graphical Abstract

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Effect of pyrolysis conditions on nitrogen-doped ordered mesoporous carbon electrocatalysts

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We have investigated the effect of pyrolysis conditions on nitrogen-doped ordered mesoporous carbon electrocatalysts. The pyrolysis temperature was found to determine the microstructure, composition, and electrocatalytic activity for the oxygen reduction reaction.

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热解条件对氮杂有序介孔炭材料电催化性能的影响

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摘要: 氧还原反应是燃料电池及金属空气电池中极其重要的电化学反应之一, 贵金属铂基催化剂被认为是最有效的氧还原反应电催化剂。然而, 贵金属铂的资源稀缺以及高成本问题阻碍了相关技术的大规模应用, 探索发展廉价高效的贵金属替代型催化剂是推动燃料电池发展的根本解决方案。近年来, 人们在非贵金属催化剂开发方面取得了显著进展, 其中新型纳米结构掺杂炭材料研究尤为活跃。氮杂有序介孔炭材料由于其高比表面积和独特的孔结构, 在燃料电池技术上具有广泛的应用前景。在氮杂有序介孔炭材料的制备过程中, 热解条件对炭材料组成、结构及电催化性能有着重要影响。然而, 目前尚未见对氮杂炭材料制备过程中热解条件的影响进行系统研究。

本文采用我们发展的蒸汽化-毛细管冷凝法, 以SBA-15为硬模板浸渍前驱体吡咯, 制备出具有高比表面积和独特孔结构的氮杂有序介孔炭材料, 系统研究了热解条件(包括热解温度、热解时间和升温速率)对炭材料组成、结构及电催化性能的影响, 采用N₂吸附-脱附等温线、X射线光电子能谱(XPS)及Raman光谱等方法考察了氮杂有序介孔炭材料的结构和组成, 采用循环伏安法与旋转圆盘电极研究了其电化学行为与氧还原反应电催化活性及选择性。

N₂吸附-脱附等温线显示, 氮杂炭材料对应IV型吸附-脱附等温线, 孔径主要分布在2–10 nm, 表明所制材料具有介孔结构。随着热处理温度升高, 氮杂有序介孔炭材料比表面积先增加而后降低, 热处理时间的延长有利于比表面积增大, 但升温速率对所制炭材料比表面积没有明显影响, 当升温速率为30 °C/min, 900 °C焙烧3 h时, 氮杂有序介孔炭材料的比表面积达到最大值888 m²/g。XPS测试结果表明, 随着热处理温度升高, 氮杂有序介孔炭材料中含氮基团的分解进一步加深, 使N含量逐渐降低。延长热处理时间亦然, 而升温速率的改变对N含量无明显影响。在热处理温度较低时(600 °C), 所得材料中N主要以吡咯氮和吡啶氮的形式存在; 当温度达到800 °C以上, 吡咯氮转化为吡啶氮和骨架氮, 且主要以骨架氮形式存在, 说明氮杂有序介孔炭材料的石墨化程度逐渐升高。

Raman光谱结果显示,随着热处理温度升高, I_D/I_G 逐渐降低,进一步印证了温度对石墨化程度的影响.

电化学测试结果表明,随着热处理温度升高,氮杂有序介孔炭材料的氧还原反应电催化活性逐渐升高,但是当热处理温度从900℃升至1000℃时,氧还原反应活性增加很小;升温速率与热处理时间对氧还原反应电催化活性的影响均不明显.与商品Pt/C催化剂相比,900℃以上所制催化剂均表现出更优异的氧还原电催化活性与选择性.由此可见,热处理温度是决定碳源热化学行为的关键因素,进而决定炭材料表面组成与结构.电化学研究结果表明,800℃以上进行热处理碳化,所生成石墨化微晶可有效促进电子传递,降低欧姆极化损失,同时,较高的处理温度可促进骨架氮掺杂,从而构建出高效氧还原反应活性位点.因此,氮杂型炭催化剂的组成、结构与电化学性能更多地受控于热处理过程中的热力学,而非热解动力学过程.

关键词: 电催化剂; 氮掺杂炭; 有序介孔材料; 氧还原反应; 热解条件

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