Effect of Annealing Temperature on Oxygen Reduction Reaction (ORR) Activity of Nitrogen and Sulfur Co-doped Mesoporous carbons

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Abstract. In this work, we have synthesized N and S co-doped mesoporous carbons as highly efficient electrocatalysts to investigate the influence of annealing temperatures on electrocatalytic activity of N and S co-doped mesoporous carbon for oxygen reduction reaction (ORR) in alkaline media. The catalysts were prepared through silica hard template method, thermal annealing of ferrous chloride ($FeCl_2$ $4H_2O$) and polyquaternium-46 (PQ) in nitrogen. Results of electrochemical characterizations for ORR were studied by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) employing rotating disk electrode (RDE) technique. The peroxide yield ($H_2O_2\%$) and electron transfer number (n) on the mesoporous carbon catalyzed electrode were investigated via the rotating ring-disk electrode (RRDE) experiments to study the ORR catalytic pathway of the catalysts. It is found that the temperature of the heat treatment is a significant parameter in synthesizing the high performance ORR catalysts. Of the three catalysts, $FeCl_2$-PQ-800°C showed superior catalytic activity with onset potential at 0.965 V and half-wave potential at 0.807 V. The corresponding electron transfer number was greater than 3.81, indicating that the ORR process proceeds mainly via a four-electron mechanism.

Introduction

Mesoporous carbon materials have been used for numerous applications such as adsorption [1], separation [2], supercapacitor [3] and oxygen reduction reaction (ORR) [4]due to their preeminent textural characteristics, high specific surface area, mechanical stability and porous structure. To date, extensive research efforts have been made to investigate the influence of experimental parameters on the catalytic activity of the ORR, such as the nitrogenated ligand in the precursor complex, chemical doping of mesoporous carbon, and duration of calcination [5]. Moreover, it has been demonstrated that temperature of annealing treatment plays an important role in the doping level of nitrogen and different binding configurations of the N-doping, such as pyridinic-N, pyrrolic-N and graphitic-N [6]. Besides, it has been reported that the electrocatalytic activity of N-doped graphene and S-doped graphene are both strongly dependant on the annealing temperature [7,8]. Herein, we report the N and S co-doped mesoporous carbon catalysts which was synthesisze via a green synthetic route with nanoscale SiO_2 as the sacrificial template and polyquaternium-46 (Luviquat^{TM} HOLD) as precursor of both nitrogen and sulfer source. After first-time graphitization, the silica was removed by excess amounts of NaOH, and unreacted metallic iron and iron compounds were acid-leached before second-time annealing treatment. The two-step of the graphitization was carried out at different temperatures from 700 to 900°C to obtain the simultaneous optimization of both porous structures and surface functionalities of N and S co-doped carbon under N_2 atmosphere. The electrocatalytic activities were studied by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) employing rotatingring-disk electrode (RRDE).

Experimental

Catalyst preparation. For the preparation of template SiO_2 solution: silica of 500 nano-scale, as the starting materials, was mixed with hydrochloric acid solution (1 M) and sonicated for 10 min, resulting in the homogeneous of binary SiO_2 solution. Then 11.2 g polyquaternium-46 solution (20 wt. %, Sigma–Aldrich) was added into the above SiO_2 solution under magnetic stirring. A solution of $FeCl_2\cdot4H_2O$ stirred for 5 min and further sonicated for 20 min was added into this mixture under stirring for more than 3 h. The resulting viscous solution was dried at 85^oC for 48 h. The solid was ground to a fine powder in an agate mortar, and then pyrolyzed for 1 h at 700, 800 and 900^oC under a nitrogen atmosphere, with temperature ramp rate of 20^oC min^{-1}. The excess amount of sodium hydroxide (NaOH) (4 M) was added to vacate the silica for 48 h and the resulting powder was washed by deionized water to neutralize it, and dried overnight. The final catalyst samples were obtained by exposure to acid-leaching using sulphuric acid (0.5 M) at 85^oC for 8 h to remove the unreacted metallic iron. After dried overnight, the resulting powder was re-pyrolyzed for 1 h at 700, 800 and 900^oC under a nitrogen atmosphere, with temperature ramp rate of 20^oC min^{-1}, respectively.

Electrochemical testing. For working electrode preparation, 2 mg $FeCl_2$-PQ-T (T = 700, 800, 900^oC) catalyst was dispersed in 400 μL isopropyl alcohol (Sinopharm Chemical Reagent Co., Ltd). 100 μL 0.5% Nafion (diluted with methanol) was added into the mixture to prepare the catalyst ink. Then the12.4 μL ink was applied onto a clean glassy carbon (GC) disk with a sectional area of 0.2475 cm^2. The overall loading was 200 μg cm^{-2}.

The electrochemical analysis was performed by CV, LSV, RDE and RRDE measurements on a CHI Electrochemical Station (Model 750b). The electrochemical experiment was carried out in a conventional three-electrodes cell, where O_2-saturated KOH aqueous solution (0.1 M) was used as electrolyte. GC disk was used as working electrode. A platinum wire and saturated calomel reference electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials were referred to reversible hydrogen electrode (RHE) in this work. The CV and LSV curves were obtained in the O_2 -saturated KOH (0.1 M) solution at the scanning rate of 50 mV s^{-1} and 5 mV s^{-1}. The RRDE curves were measured with the scanning rate of 5 mV s^{-1} and working electrode rotation speed of 1600 rpm.

Results and Discussion

Cyclic voltammetry. As shown in Fig. 1, in the case of a N_2-saturated solution, the cyclic voltammogram only presents a featureless voltammetric curve in the potential range of 0.5 V to 1.2 V, which is ascribed to the typical double-layer capacitive current of porous carbon materials. When O_2 was purged into the solution, a distinct cathodic current with the peak potential (E_p) at 0.78 V vs. RHE, and the peak current density (I_p) of 3.61 mA cm^{-2} can be clearly observed, indicating that this Fe-PQ-800^oC catalyst has a very high catalytic activity towards the ORR.

Linear sweep voltammetry. To further evaluate the electrocatalytic activity of $FeCl_2$-PQ-T (T = 700, 800 and 900^oC) for the ORR, LSV measurements were performed in O_2-saturated KOH (0.1M) solution by RDE technique. From the polarization curves showed in Fig. 2, it can be seen that the onset potential, half-wave potential and diffusion limit current density changed significantly by comparison of three different prepared catalysts. For $FeCl_2$-PQ-800^oC, it showed a much better performance with onset potential (E_{onset}) of 0.965 V and half-wave potential ($E_{1/2}$) of 0.776 V, which are 17 mV and 6 mV positive shifts more than that of $FeCl_2$-PQ-700^oC, respectively. As for $FeCl_2$-PQ-900^oC, the E_{onset} and $E_{1/2}$ values were detected at 0.959 V and 0.818 V, which are 11 mV and 48 mV positive shifts more than that of $FeCl_2$-PQ-700^oC, respectively. In addition, $FeCl_2$-PQ-800^oC shows the limited current density of 6.6 mA cm^{-2}, which is enhanced greatly compared to $FeCl_2$-PQ-900^oC (5.7 mA cm^{-2}), along with a better-defined diffusion-limiting current plateau. These results agreed with the previous discussions on grapheme oxides, demonstrating that porous nanosheets subjected to annealing under NH_3 or H_2S atmosphere at different temperatures show different degree of reaction [7]. Thus, it is reasonable to refer that the resulted abundant functional groups such as carbonyl, carboxyl, lactone and quinone at the edges and in the plane were

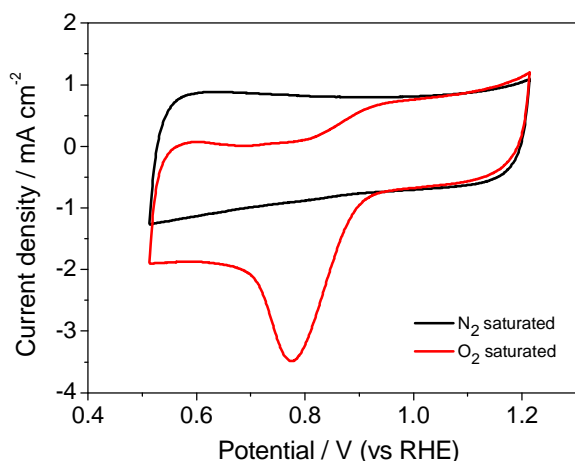favorable for the binding of nitrogen and sulfur when annealed at $800^{o}C$.

Fig. 1 Cyclic voltammograms of FeCl$_2$-PQ-800°C in N$_2$- and O$_2$-saturated 0.1M KOH; Scan rate: 50 mV s^{-1}.The overall loading of the mixed catalyst: 200 μg cm^{-2}.
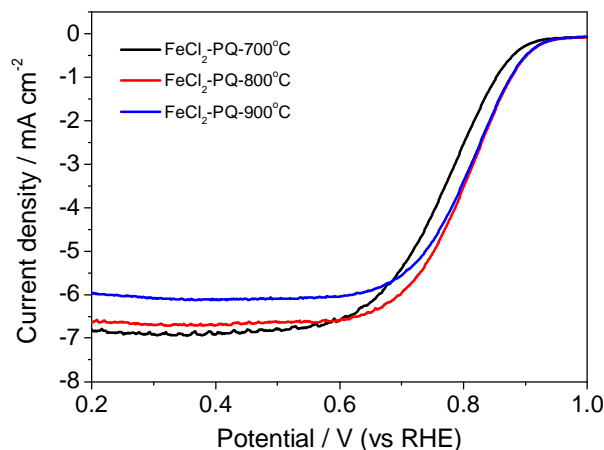
Fig. 2 Polarization curves of FeCl$_2$-PQ-T (T = 700, 800 and 900°C) in O$_2$-saturated 0.1M KOH solution. Potential scan rate: 5 mV s^{-1}. Electrode rotation rate: 1500 rpm.

RRDE measurements. RRDE measurements were performed to monitor the peroxide yield ($H_2O_2\%$) and electron transfer number (n) on the FeCl$_2$-PQ-T (T = 700, 800 and 900°C) catalyzed electrode to further study the ORR catalytic pathway of the catalyst. The $H_2O_2\%$ yield was determined based on the disk current (I_d) and ring current (I_r) via the following equation:

$$H_2O_2\% = 100 \times \frac{2I_r / N}{I_d + I_r / N} \tag{1}$$

The electron transfer number (n) was thus obtained based on the following equation:

$$n = \frac{4I_d}{I_d + I_r / N} \tag{2}$$

Where N = 0.36 is the current collection efficiency of the Pt ring, which was calibrated in 0.1 M KOH with a10 mM K$_3$Fe(CN)$_6$ electrolyte.

From Fig. 3(a), it can be found that the $H_2O_2\%$ yield was about 10% over the potential range of 0 V to 0.8 V, while the n was nearly 3.81. Furthermore, the $H_2O_2\%$ yield was decreased generally with potential increasing, even there was little peroxide could be detected between 0.65 V to 0.8 V. In brief, the whole tested potential range suggests that the O$_2$ is mostly reduced to water rather than peroxide. As shown in Fig.3(b), on the FeCl$_2$-PQ-800°C, the H$_2$O$_2$% yield was detected to be less than 10% which is much lower than that of FeCl$_2$-PQ-700°C, implying a high ORR activity compared with FeCl$_2$-PQ-700°C. The electron transfer number of FeCl$_2$-PQ-800°C was nearly 3.90, which suggests that about 95% O$_2$ was reduced to H$_2$O and other O$_2$ was reduced to H$_2$O$_2$. For FeCl$_2$-PQ-900°C, however, it showed the highest H$_2$O$_2$% yield and lowest electron transfer number among the three kinds of catalysts. The peroxide yield on FeCl$_2$-PQ-900°C electrode was found nearly 11%, and it sharply increased while the potential was above 0.8 V. Meantime, the electron transfer number of FeCl$_2$-PQ-900°C was about 3.80, indicating that nearly 10% O$_2$ was reduced to H$_2$O$_2$ through 2e$^-$ transfer process. The above results implying that when temperature is 700°C or 900°C, it has low ORR activity result from fewer accessible active sites, compared with graphitization at 800°C.

Further from Table 1, the FeCl$_2$-PQ-800°C gives the best onset potential, peak potential, peak current density, limited current density and electron transfer number compared to those of FeCl$_2$-PQ-700°C and FeCl$_2$-PQ-900°C. This is probable due to more active sites and porous structure formed at 800°C. All the experiments including the composition, morphology, and microstructure of

the as-prepared $FeCl_2$-PQ-T catalysts characterized using XRD, EDS, XPS and nitrogen sorption analysis are in progress and the results will be reported in our further work.
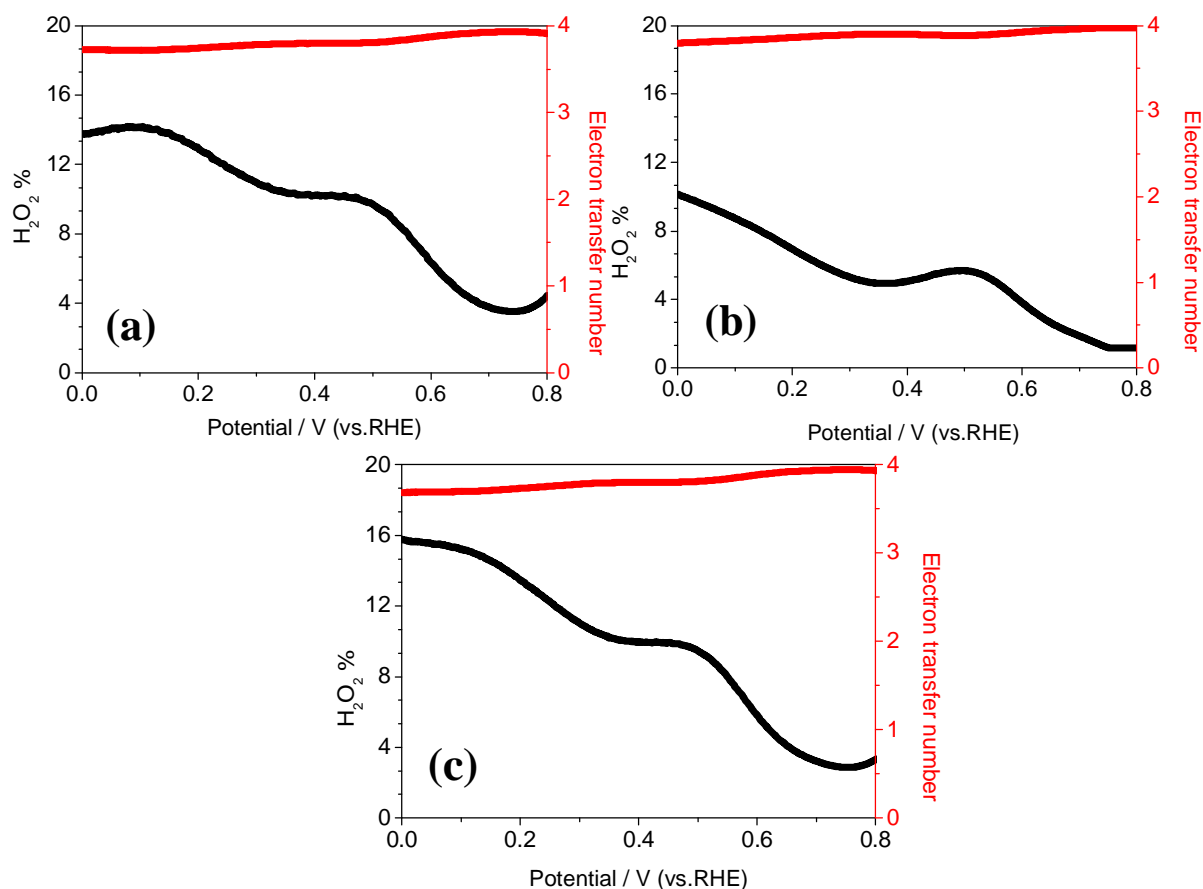

Fig. 3 Percentage of H_2O_2 produced and the electron transfer number of $FeCl_2$-PQ-700°C (a), $FeCl_2$-PQ-800°C (b) and $FeCl_2$-PQ-900°C (c) with a rotation rate of 1600 rpm.

Table 1 Comparison of electrochemical data of $FeCl_2$-PQ-T (T=700, 800 and 900°C)

Catalyst	E_p (V)	I_p (mA cm^{-2})	i_d (mA cm^{-2})	E_{onset} (V)	$E_{1/2}$ (V)	n
$FeCl_2$-PQ-700°C	0.73	3.22	7.1	0.948	0.770	3.81
$FeCl_2$-PQ-800°C	0.78	3.61	6.6	0.965	0.807	3.90
$FeCl_2$-PQ-900°C	0.76	2.74	5.7	0.959	0.818	3.80

*the i_d, E_{onset} and $E_{1/2}$ were measured at 1500 r/min.

Morphology and structural characterization. The microstructures of the $FeCl_2$-PQ-800°C was characterized by scanning electron microscopy (SEM) to explan its highest electrochemical properties for the oxygen reduction. Fig. 4(a) and (b) show the distribution of pores in the catalyst. We can clearly see a sponge-like structure with interconnected mesopores (2~50 nm)and macropores (>50 nm) system resulting from combined effect of the medi-template and metal salt. In terms of the results obtained from Fig. 4, the superior ORR performance of $FeCl_2$-PQ-800°C may be closely related to its hierarchical porous structure.

Conclusions

The calcination temperatures play a critical role in synthetising the mesoporous carbon materials via hard template method for the oxygen reduction reaction. After annealing at different temperatures
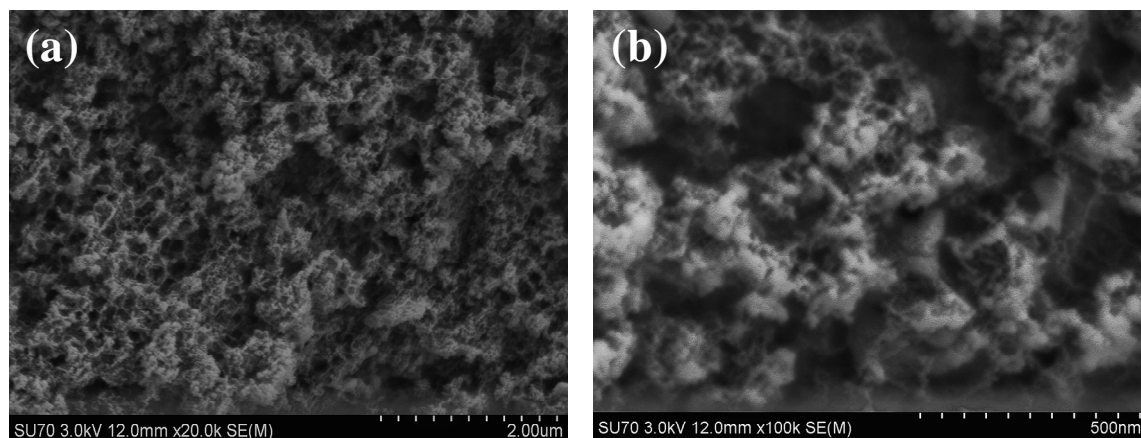
Fig. 4 SEM images of FeCl$_2$-PQ-800°C catalyst, showing the highly porous structure. Scale bars: (a) 2.00 um and (b) 500 nm.

ranging from 700 to 900°C, three distinct catalystswere obtained and investigated. Through the analysis of electrochemical characterization and distribution of porous, it can be concluded that the optimum heat-treatment temperature is 800°C and the FeCl$_2$-PQ-800°C was the best performing catalyst, for which the onset potential at 0.965 V and half-wave potential at 0.807 V were obained, along with the ORR electron transfer number greater than 3.81.

Acknowledgements

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