

Doped Mesoporous Carbons Derived from Transition Metal Iron and Chitosan as Efficient Non-Precious Cathode Catalysts for Oxygen Reduction Reaction in Alkaline Electrolyte

Fang Dong¹, Enguang Zhang¹, Qiaowei Tang¹, Qinqing Guo^{2*} and Jinli Qiao^{1*}

¹College of Environmental Science and Engineering, Donghua University,
2999 Ren'min North Road, Shanghai 201620, China

²College of Material Science and Engineering, Taiyuan University of Technology,
Taiyuan 030024, Shanxi, China

E-mail address: *qiaojl@dhu.edu.cn, guoqingping6502@163.com

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Abstract. In this work, a series of mesoporous carbonaceous materials (MCs), which are simultaneously doped with N and Fe-containing species, were prepared by polymerization of potassium hexacyanoferrate-mediated chitosan on SiO₂ nanospheres. The SiO₂ template was carbonized and etched with NaOH. The electrochemical properties of the MCs as nonprecious-metal electrocatalysts for oxygen reduction reaction (ORR) are characterized, which was performed using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) employing a rotating disk electrode (RDE). The results show that chitosan with well-dispersed K₄Fe(CN)₆ nanoparticles prepared by annealing at 800°C (CTS-Fe-800) exhibits the highest catalytic performance in terms of ORR among the catalysts studied, where the onset potential at 0.91V, half-wave potential at 0.82 V and average transferred electron number of 3.49, were achieved in alkaline media.

Introduction

Faced with the increasingly serious energy crisis, fuel cells, as a clean and efficient power source, have become the most promising energy conversion devices and attracted significant attention during the last decades. Oxygen reduction reaction (ORR) at the cathode of fuel cells plays a decisive role in determination of the performance, and electrocatalysts with high-performance ORR are essential for practical applications. Pt-based materials are widely recognized as superior electrocatalysts for ORR [1], however, they are hindering this technology's commercialization because of their expensive and scarce nature [2]. Therefore, overcoming the challenge is undoubtedly of particular importance. A promising approach to solve this problem is to introduce non-noble metals such as Fe, Co [3] or their compounds into the nitrogen-doped carbon material since the N-doped carbon can exhibit good electrocatalytic activities to the ORR [4] and incorporation of a metal can significantly improve the catalytic efficiency [5].

Extensive efforts have been devoted to develop cheap and earth abundant alternative electrocatalysts [6]. In fact, certain types of N-containing transition metal catalysts have shown high activity for oxygen reduction in alkaline media [7, 8], however, compared to Pt-based catalysts for practical application in fuel cells, both the ORR activity and stability of these catalysts have to be significantly improved.

It is believed that the high surface area, high porosity, and appropriate pore structure of the catalyst generally leads to a high catalytic activity for ORR [9]. In this paper, we choose the template method for the synthesis of transition metal Fe and N co-doped mesoporous carbon as

non-noble metal catalysts. Nanoscale SiO₂ was used as a sacrificial support to produce pores, while chitosan (CTS) was used as the source of both N and C.

Experimental

Catalyst preparation. For obtaining the mesoporous carbon materials, the chitosan solution was prepared at first as follows: 5 mL glacial acetic acid was dissolved in 200 mL deionized water to get a 4 M CH₃COOH solution. Then, 0.76 g chitosan was dissolved in the above solution under magnetic stirring to form a uniform solution.

The CTS-Fe catalyst was prepared by homogeneously dispersing potassium ferrocyanide (Sinopharm Chemical Reagent Co) and chitosan (Sinopharm Chemical Reagent Co) precursors onto the surface of SiO₂ (Hangzhou Wanjing New Material Co, Ltd, 15 ± 5 nm). In a typical synthesis process, the pre-synthesized chitosan solution was added into a calculated amount of SiO₂ solution (silica amount: 5 g) under magnetic stirring. Then, a solution of K₄Fe(CN)₆ was added under stirring for 15 minutes. The resulting solution was further heated in 85°C water bath for 4 hours to mix sufficiently. After heated, the resulting viscous solution was filtration to obtain the light green solid CTS-Fe/SiO₂, and then dried overnight at 85°C. The solid (CTS-Fe/SiO₂) was ground to a fine powder in an agate mortar and pyrolyzed at 700, 800, and 900°C, respectively, for 1 hour under a nitrogen atmosphere, with temperature ramp rates of 5°C/min. The SiO₂ was leached out using excess amounts of 5 M sodium hydroxide (NaOH) for 48 hours and dried for overnight. Then the final catalyst samples were obtained and denoted as CTS-Fe-700, CTS-Fe-800, CTS-Fe-900, respectively.

Electrochemical testing. 5.0 mg of CTS-Fe-x (x =700,800,900) catalyst was dispersed in a mixed solution containing 800 μL isopropyl alcohol (Sinopharm Chemical Reagent Co, Ltd) and 200 μL 0.5% Nafion (diluted with methanol) to prepare the catalyst ink. Then 5 μL of ink was applied onto a clean glassy carbon (GC) disk three times, with a sectional area of 0.2475 cm² (5.6 mm diameter). Then GC disk was ready to work after air-drying with the overall loading of 300 μg cm⁻². The current densities reported here all use the geometric area of the carbon electrode and all potentials were referred to a reversible hydrogen electrode (RHE).

Electrochemical analysis for the synthesized catalysts was performed by CV, LSV and RDE measurements using a CHI Electrochemical Station (Model 750b) and a conventional three electrode cell filled with 0.1 M KOH electrolyte saturated in O₂ at room temperature. The measurements were carried out using RDE (Pine 5908 Triangle Drive Raleigh, NC21617) by CV and LSV at a slow scan rate of 50 mV s⁻¹ and 5 mV s⁻¹, respectively, at a rotation speed of 300, 600, 900, 1200 , 1600 rpm, respectively, to determine the Koutecky– Levich plots.

Results and Discussion

Cyclic voltammetry. CV curves were employed to compare the electrocatalytic activity of CTS-Fe-700, CTS-Fe-800, and CTS-Fe-900 for ORR in N₂- or O₂-saturated 0.1 M KOH solution, as shown in Fig. 1. It can be seen that the CV curves of CTS-Fe-700, CTS-Fe-800, and CTS-Fe-900 are essentially featureless in the N₂ saturated solution, whereas the three catalysts exhibit significant cathodic oxygen reduction peaks in the O₂-saturated electrolyte. Compared with CTS-Fe-700 and CTS-Fe-900, CTS-Fe-800 displayed a more pronounced ORR peak, a more positive peak potential (0.73 V vs. 0.71 V vs. 0.66 V) and a higher corresponding current density (−2.1 mA cm⁻² vs. −2.6 mA cm⁻² vs. −4.1 mA cm⁻²).

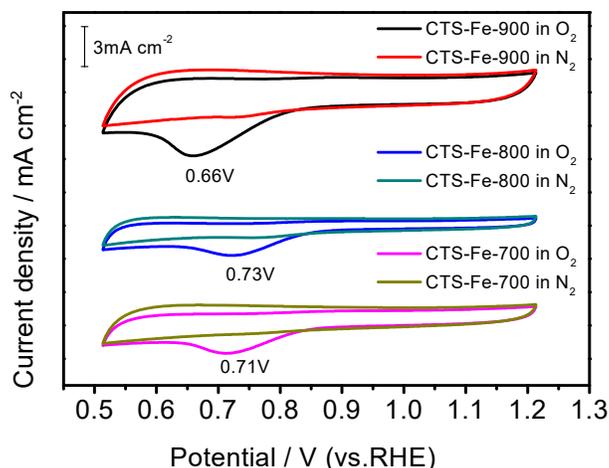


Fig.1 CV curves of CTS-Fe-700, CTS-Fe-800, CTS-Fe-900 in N₂- and O₂-saturated 0.1 M KOH solution (scan rate: 50 mV s⁻¹). The overall loading of the mixed catalyst: 80 μg cm⁻².

The results strongly indicate that the temperature have a significant effect on improving the ORR catalytic activity, and the catalyst annealed at 800°C has a higher performance towards ORR. Since the catalytic activity of pure oxidized iron species for ORR is low, the high activity of CTS-Fe-800 could be attributed to a synergetic effect between the doped N and K₄Fe(CN)₆.

RDE measurements. The effect of the pyrolysis temperature in the range of 700~900°C on the ORR activity of the CTS-Fe-x catalyst was also studied using RDE technique. The polarization curves in Fig. 2(a) show that the CTS-Fe-800 exhibits a higher ORR activity than CTS-Fe-700 and CTS-Fe-900 in terms of both onset potential and half-wave potential, as well as the current density over the whole potential range. These results imply that CTS-Fe-800 has a better catalytic activity for ORR than the other samples, confirming that the temperature is one of the main factors for its excellent electrocatalytic activity.

For clarifying the pathway and kinetic process of the ORR, polarization curves of the CTS-Fe-800 catalyst were recorded using the RDE technique at different rotation rates (300, 600, 900, 1200 and 1600 rpm) in O₂-saturated solution with a scan rate of 5 mV s⁻¹ (Fig. 2(b)). The curves show an increase in the catalytic current density with rotation rates because of the enhanced diffusion of electrolytes. Then the Koutecky–Levich plots for the ORR at different potential for CTS-Fe-800 can be obtained. The slope of the plots allows us to check the consistency with the theoretical values according to the Eq. 1:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_f} + \frac{1}{j_d} \quad (1)$$

Where j is the measured current density at given potential, j_k is the activation controlled current density, j_f is the effect of Nafion ionomer inside the catalyst layer on the measured current density, and j_d is the O₂ diffusion limiting current density. Due to the j_f may be negotiable if the equivalent Nafion ionomer thickness is much small ($j_f \rightarrow \infty$), therefore, its reciprocal can be negligible. In this case, Eq. 1 can be simplified to Eq. 2:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \quad (2)$$

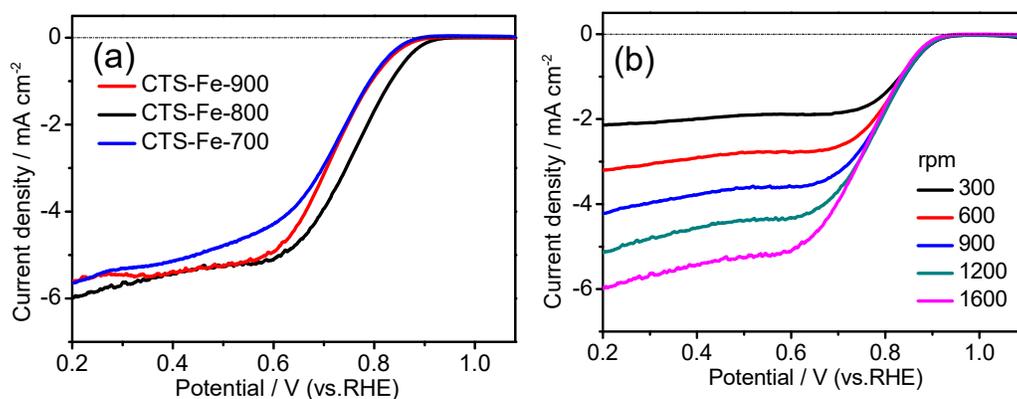


Fig. 2 (a) Polarization curves of CTS-Fe-700,-800,-900 in O₂-saturated 0.1 M KOH, scan rate: 5 mV s⁻¹, rotation rate: 1600 rpm. (b) Polarization curves of CTS-Fe-800 in O₂-saturated 0.1 M KOH at different rotation rates.

Then the j_d can be expressed as Eq. 3:

$$j_d = 0.2nFC_{O_2}D_{O_2}^{\frac{2}{3}}\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}} \quad (3)$$

Where n is the overall electron transfer number per molecule of O₂ reduced, ω is the electrode rotation rate (rpm), F is the Faraday's constant ($F = 96485\text{C mol}^{-1}$), C_{O_2} is the concentration of dissolved oxygen, D_{O_2} is the diffusion coefficient of oxygen in the bulk solution, ν is the kinematic viscosity of the solution. □

With CTS-Fe-800 as typical candidate, Fig. 3 (a) shows the Koutecky-Levich plots at 0.68, 0.70, 0.74, 0.76, 0.78 V vs RHE, respectively. By calculating the slopes of the Koutecky-Levich plots, n value of 3.50, 3.13, 3.58, 3.81 and 3.42 were obtained, respectively. It can be seen that the values of n for oxygen reduction depend on the high positive over potentials with an average value of 3.49. This indicates that the mixed 2 e⁻ and 4 e⁻ transfer process took place and, the reduction of O₂ produces both HO₂⁻ and OH⁻ in the final product on CTS-Fe-800 electrode, but the latter is dominant.

To further investigate the ORR catalytic pathway of the catalyst, rotating ring-disk electrode (RRDE) measurements were also performed to monitor the peroxide yield on the CTS-Fe-800 catalyzed electrode. The peroxide percentage ($H_2O_2\%$) was determined from RRDE measurements based on the disk current (I_d) and ring current (I_r) via Eq. 4:

$$H_2O_2\% = 100 \times \frac{2I_r / N}{I_d + I_r / N} \quad (4)$$

The electron transfer number (n) was based on Eq. 5:

$$n = \frac{4I_d}{I_d + I_r / N} \quad (5)$$

Where $N = 0.36$ is the current collection efficiency of Pt ring, which is calibrated in 0.1 M KOH with a 10 mM K₄Fe(CN)₆ electrolyte.

As shown in Fig. 3(b), the $H_2O_2\%$ yield on the CTS-Fe-800 electrode is found to be less than 20% over the potential range of 0 V to 0.85 V. The corresponding electron transfer number is higher than 3.6, suggesting the nearly complete reduction of oxygen to water.

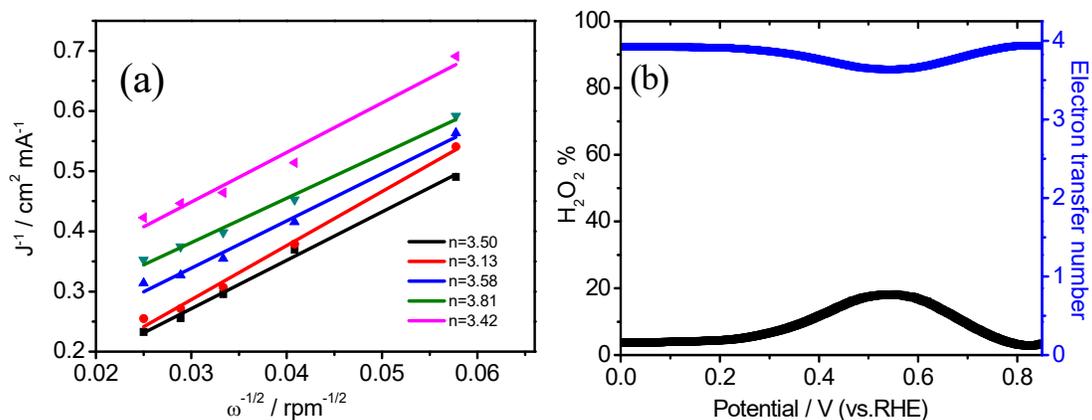


Fig. 3 (a) Koutecky–Levich plots at different electrode potential, which is obtained from RDE polarization curves of CTS-Fe-800 at different rotation rates for ORR in O_2 -saturated 0.1M KOH solution. Scan rate: 5mVs^{-1} and catalyst loading: $80\mu\text{gcm}^{-2}$. (b) Percentage of H_2O_2 produced and the electron transfer number of CTS-Fe-800 (1600 rpm).

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