Effect of particle size of carbon catalyst on oxygen reduction activity for fuel cell applications

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Abstract. Graphite powders with particle sizes of 40, 100, 400, and 1000 nm were used as cathode catalysts. The influence of graphite particle size on the electrocatalytic behavior towards the oxygen reduction reaction (ORR) was investigated. The catalytic activity and kinetics of the ORR, and methanol tolerance were tested in alkaline solutions with saturated oxygen via cyclic voltammetry (CV), rotating disk electrode (RDE) and amperometric i-t curve techniques. Experimental results show that the ORR process of the graphite catalyst with a particle size of 40 nm was close to the four-electron pathway at -0.6 V, exhibiting the best ORR activity. This is ascribed to a greater number of edge defects as ORR active sites in the carbon material. The number of sites can be characterized with X-ray diffraction (XRD) and Raman spectroscopy. Additionally, these graphite catalysts have been demonstrated a superior tolerance to methanol than the commercial 20 wt.% Pt/C electrode in alkaline solutions.

1. Introduction
Fuel cells have been regarded as one of energy conversion devices for the future renewable energy systems. Pt-based materials are known to be the best candidate for the electrocatalysts in an alkaline fuel cell cathode, even though the kinetics of the oxygen reduction reaction (ORR) is sluggish and causes electrocatalytic performance losses in energy conversion devices [1-3]. The search and development of non-precious metal catalysts (NPMCs) are a continuous subject to handle [4–6]. Among a variety of NPMCs, carbon-based nitrogen containing composites have been widely considered as the most promising candidate materials [7-11].

Nitrogen-doped carbon catalysts are a sort of sp² hybridization carbon-based catalytic materials. There are π electrons that can freely migrate on the surfaces of these doped carbon materials, which can promote the oxygen electrocatalysis [12]. Studies have shown that non-doped carbon-based materials have a certain catalytic performance in alkaline electrolytes, indicating that the intrinsic defects of carbon play a vital role in improving ORR activity [13, 14]. F. Peng et al. [15, 16] have found that the edge defects in carbon materials have good ORR performance under alkaline conditions and are important active sites through experiments and theoretical calculations. In addition, by transversely and longitudinally comparing potentials and current densities of oxygen reduction peaks of non-doped and doped carbon materials, we can find that there are some differences between the
catalytic properties of various non-doped carbon materials, as well as the ORR activity of doped carbon-based catalysts has different degrees of improvement, comprehensively explaining that the importance of selection and modification of carbon-based materials [7-11]. It is necessary and should be given a certain consideration to study the non-doped carbon materials for the sake of effectively enhancing the ORR activity of the doped carbon-based catalysts.

Herein, the relationship between the concentration of edge defect and electrocatalytic performance is explored. For this purpose, graphite powders with different particle sizes are used as the cathode catalytic materials of fuel cells. The content of edge defect can be assessed by means of X-ray diffraction (XRD) and Raman. The catalytic activity and kinetics of ORR, and the resistance to methanol were characterized using cyclic voltammetry (CV), rotating disk electrode (RDE), and amperometric i-t curve techniques.

2. Experimental procedure

2.1. Pretreatment of graphite powder catalysts
Graphite powder catalysts with particle sizes of 40, 100, 400, and 1000 nm purchased from Dalian Meilun Biology Co. were dispersed into the degreasing solution containing sodium phosphate, and stirred simultaneously to effectively remove the grease on the surface of graphite powders. Afterwards, the mixture was separated by vacuum filtration (Shanghai Lingde Instrument Co., C300A). Then the graphite powders were repeatedly rinsed with deionized water until neutral PH was reached, and dried in a vacuum oven.

2.2. Characterization
The phase structure of the graphite powder catalysts was examined by X-ray diffraction (XRD) using Co-Kα radiation (λ=0.179 nm) at the scale of 20°–100°. The composition and structure of the catalysts were characterized using Raman spectroscopy with the Red Light laser line at 632.8 nm (InVia). The specific surface area (SSA) of samples was measured by Brunauer-Emmett-Teller (BET, AUTO SORB-1-MP, USA).

2.3. Electrochemical measurements
An electrochemical workstation (Shanghai Chen Hua Instrument Co., Ltd., CHI760E) with standard three electrodes was used to carry out electrochemical tests at ambient temperature. These tests were done on the glassy carbon electrode (GCE) with a diameter of 3 mm as the RDE which was used to load the graphite catalysts. The GCE was polished successively with 0.30 and 0.05 μm alumina powders, and then vibrated ultrasonically in deionized water for 30 s. For preparing working electrode, the graphite powder was dissolved in a mixed solution of deionized water and isopropanol with volume ratio of 3:1, and the concentration was 5 g/L. Then 10 wt.% Nafion solution was added into the mixture, which was vibrated ultrasonically for 30 min to form a homogeneous catalyst slurry. Finally, the 10 μL catalyst slurry was dripped onto the GCE and dried naturally at ambient temperature. Pt wire and Ag/AgCl filled with saturated KCl solution act as counter and reference electrodes, respectively. The CV measurement was performed in O₂- and N₂-saturated 0.1 M KOH electrolyte. The potential and scanning rate were set in the range of -1.0 to 0 V (vs Ag/AgCl), and 50 mV·s⁻¹, respectively. Linear sweep voltammetry (LSV) measurement was carried out at different rotation rates in 0.1 M KOH electrolyte with saturated oxygen at a scanning rate of 10 mV·s⁻¹. Methanol selectivity was evaluated via testing the current response at -0.35 V using chronoamperometry. The scanning and rotation rates were fixed at 10 mV·s⁻¹ and 1800 rpm, respectively. The electrochemical impedance spectroscopy (EIS) in the frequency range of 100 kHz-0.01 Hz was measured by the excitation signal disturbance with an amplitude of 5 mV.
3. Results and discussion

3.1. XRD patterns and Raman spectra

Figure 1 shows the XRD patterns of graphite powder catalysts with particle sizes of 40, 100, 400, and 1000 nm. The diffraction peaks located at $2\theta \approx 31.02^\circ$, $49.47^\circ$, $52.16^\circ$, $64.46^\circ$, $70.78^\circ$ and $93.11^\circ$ are corresponding to the (002), (100), (101), (004), (103) and (110) crystal planes of graphite phases (JCPDS # 00-008-0415), respectively. In all XRD patterns, the sharp diffraction peaks can be observed. As the particle size decreases, the intensity of each diffraction peak decreases. This is due to the fact that there are more structural defects and larger internal stress in the graphite catalyst with a smaller particle size.

![XRD patterns of graphite powder catalysts](image1)

Figure 1. (a) Entire and (b) partial XRD patterns of the graphite powder catalysts with particle sizes of (I) 1000, (II) 400, (III) 100 and (IV) 40 nm, respectively.

![Raman spectra of graphite powder catalysts](image2)

Figure 2. Raman spectra of the graphite powder catalysts with particle sizes of (I) 1000, (II) 400, (III) 100 and (IV) 40 nm, respectively.

![Nitrogen adsorption-desorption isotherms](image3)

Figure 3. $N_2$ adsorption-desorption isotherm plots of the graphite powder catalysts with particle sizes of 40 and 1000 nm, respectively.

The microstructural changes of graphite powder catalysts with various particle sizes have been characterized by Raman spectroscopy, as shown in Figure 2. The two Raman peaks located at 1337 and 1564 cm$^{-1}$ corresponding to D and G bands, respectively. The D band is attributed to the first-
order scattering of sp$^2$-hybridized disordered carbon material [17]. The G band is caused by the $E_{2g}$ vibration mode of the sp$^2$ carbon material, which is used to explain the degree of graphitization [18]. The intensity ratio of D and G bands labeled $I_D/I_G$ is calculated to evaluate quantitatively the disordering degree of graphite powder catalysts, and that is to characterize the number of structural defect sites. The $I_D/I_G$ value of carbon catalysts with particle size ranging from 1000 to 40 nm varies from 0.096 to 0.279. The increase in the $I_D/I_G$ ratio demonstrates the increase in the number of defects, further indicating that the larger surface area can provides more edge defects, in good agreement with the XRD results.

N$_2$ adsorption-desorption isotherm plots are shown in Figure 3. Before measurement, the samples were degassed at 150 ºC for all night. The calculated SSA values were determined as 3.9 m$^2$/g and 0.4 m$^2$/g using BET method for the graphite powders with particle sizes of 40 and 1000 nm, respectively.

3.2. Electrochemical characterization

The EIS measurement was conducted in 0.1 M KOH solution with saturated oxygen to investigate the ORR kinetics of catalysts. Figure 4 shows the Nyquist curves of graphite powder catalysts with different particle sizes. The high-frequency region is a semicircle controlled by the interface charge transfer dynamics, and the diameter of the arc represents the charge transfer resistance. It can be seen from the Figure 4 that the curve in the high-frequency region is a non-standard semicircle and there is no oblique line in the low-frequency region, indicating that the ion transport is controlled by both electron transfer and diffusion in the electrochemical reaction. The catalyst with a particle size of 40 nm possesses the smallest semicircle diameter. It is clear that the charge transfer resistance in the electrochemical reaction is the least, which will result in the fastest rate of ORR in all catalysts.

The ORR performance of the graphite powder catalysts with different particle sizes are presented in Figure 5. It can be observed that the featureless voltammetric curves are obtained in 0.1 M KOH electrolyte saturated with N$_2$ (dashed line). However, when the oxygen is dissolved in the solution, there are obvious oxygen reduction peaks in the same potential range (solid line). The reduction peak potential of the graphite catalyst with a particle size of 40 nm is located at -272.9 mV vs. Ag/AgCl, and the potentials of other samples are basically the same, all of which are -293.0 mV vs. Ag/AgCl. The current density of reduction peak decreases with the increase of graphite particle size. The current densities of the four samples are -0.934 (40 nm), -0.550 (100 nm), -0.432 (400 nm) and -0.396 (1000 nm) mA·cm$^{-2}$, respectively. It can be known from the CV experimental results that the ORR activity of the graphite powders with a particle size of 40 nm with larger SSA (see Figure 3) is better than that of
the graphite powders with a particle size of 1000 nm. This is due to the more edge sites with a higher charge density [19]. Hence, this also means that the ORR performance of the graphite powders is indirectly dominated by the particle size.

Figure 5. CV curves of the graphite powder catalysts with particle sizes of (a) 1000, (b) 400, (c) 100 and (d) 40 nm respectively in N\textsubscript{2}- (dash line) and O\textsubscript{2}-saturated (solid line) 0.1 M KOH solution at a potential scanning rate of 50 mV·s\textsuperscript{-1}.

Figure 6. The graphite powder catalysts with particle sizes of (I) 1000, (II) 400, (III) 100 and (IV) 40 nm respectively: (a) The test curves for the selectivity of catalysts form ethanol oxidation in O\textsubscript{2}-saturated 0.1 M KOH solution injected 3 M methanol at scanning and rotation
rates of 10 mV·s⁻¹ and 1800 rpm, and constant potential of -0.35 V. The commercial 20 wt.% Pt/C electrode as contrastive experiment; (b) The RDE polarization curves in O₂-saturated 0.1 M KOH solution at scanning and rotation rates of 10 mV·s⁻¹ and 1800 rpm, respectively.

For the practical application in the field of fuel cells, the tolerance to the presence of methanol should also be assessed by chronoaamperometric method. This is due to the possibility that the molecules of fuels (for example, methanol) may permeate from the anode to the cathode through the proton exchange membrane, affecting seriously the performance of the cathode catalysts [20, 21]. Figure 6a shows the current-time response curves of graphite powder catalysts with various particle sizes and Pt/C electrode. The attenuation degree of current density gradually decreases with the increase of graphite catalyst particle size when the 3 M methanol is added to the 0.1 M KOH electrolyte with saturated oxygen. The result explains significantly that the ability to resist methanol of catalysts gradually enhance. And yet, Pt/C electrode shows a larger current response to methanol oxidation, showing that it has an inferior resistance to methanol performance.

The LSV polarization curves of graphite catalysts in oxygen reduction process were obtained by the RDE experiment in saturated oxygen 0.1 M KOH solution to further explore the electrocatalytic the ORR activity, as shown in Figure 6b. The onset potential of oxygen reduction is one of the important parameters to evaluate the ORR activity of the catalyst. Oxygen molecules can be adsorbed on the surface of catalyst, which is the key to control the onset potential [22]. The onset potentials of the graphite catalysts with particle sizes of 1000, 400, 100 and 40 nm were gained via the RDE voltammograms, as can be seen in Table 1. It is known from the Table that the catalyst with a particle size of 40 nm has the highest onset potential, illustrating that it has the rapidest reaction kinetics. In addition to onset potential, the positive shift of half-wave potential and the enhanced limiting diffusion reduction current also show that the electrocatalytic ORR activity of the catalyst with a particle size of 40 nm is highest in all catalysts. The results are due to the fact that there are more edge defects in the catalyst material, which is conducive to adsorption of oxygen in large area to promote the catalytic activity, and then accelerate the process of oxygen reduction.

Table 1. The reduction kinetic parameters of the graphite powder catalysts respectively with particle sizes of 1000, 400, 100, and 40 nm.

| Particle size (nm) | 1000  | 400   | 100  | 40   |
|-------------------|-------|-------|------|------|
| Onset potential (V vs. Ag/AgCl) | -0.12 | -0.11 | -0.09 | -0.06 |
| Half-wave potential (V vs. Ag/AgCl) | -0.49 | -0.47 | -0.34 | -0.28 |
| Number of electron transferred (n) | 2.01  | 3.26  | 3.34  | 3.50  |

The RDE voltammetry measurement was performed to further gain insight into the kinetics of the ORR. As an example, a series of the RDE voltammograms of the ORR on the graphite powder catalyst with a particle size of 40 nm in the same electrolyte at different rotation speeds and a scanning rate of 10 mV·s⁻¹ were given in Figure 7a. It can be observed that the limiting diffusion current increases gradually with the increase of rotation rate in the diffusion-controlled region, which is owing to the shorter diffusion distance at a higher rotation rate. The following Koutecky–Levich (K-L) equations (1) and (2) are used to analyze the kinetics.

\[ J^{-1} = J_L^{-1} + J_K^{-1} = (B\omega^{1/2})^{-1} + J_K^{-1} \]  
\[ B = 0.62nFCE_0(D_o)^{2/3} \eta^{-1/6} \]

where \( J \) is the measured current density (mA·cm⁻²), \( n \) is the number of electron transferred per O₂ in the process of oxygen reduction, \( F \) is Faraday constant (96485.3 C·mol⁻¹), \( C_0 \) and \( D_o \) are the oxygen bulk concentration (1.21×10⁻⁶ mol·cm⁻³) and the diffusion coefficient (1.9×10⁻⁵ cm²·s⁻¹), respectively,
in 0.1 M KOH electrolyte, \( v \) is the dynamic viscosity of electrolyte (0.01 cm\(^2\)·s\(^{-1}\)), \( \omega \) is the angular rate of electrode \( (\omega = 2\pi N, \text{rad} \cdot \text{s}^{-1}, N \text{ is the linear rotation rate}) \) [23, 24]. Based on the RDE data in Figure 7a, the K-L curves \( (J_1^{1/2} \text{vs.} \omega^{1/2}) \) at different potentials are obtained, as shown in Figure 7b. The calculated \( n \) values of the catalysts with particle sizes of 1000–40 nm were in the range of 2.01–3.50 at -0.6 V vs. Ag/AgCl (see Table 1) by the slope obtained from the linear fitting K-L curves and equations (1) and (2).

Figure 7. (a) The RDE polarization curves of the graphite powder catalyst with a particle size of 40 nm at different rotation rates in \( \text{O}_2 \)-saturated 0.1 M KOH electrolyte at a scanning rate of 10 mV·s\(^{-1}\); (b) Corresponding K-L curves at various potentials.

4. Conclusions

In this paper, the electrocatalytic behavior towards the ORR of pure graphite powders with different particle sizes in alkaline electrolytes had been studied. Results from XRD and Raman measurements showed that the edge defect density increases as the particle size decreases. The graphite powder catalyst with a particle size of 40 nm had the best catalytic performance for the ORR according to the highest onset and half-wave potentials, limiting diffusion current density, and number of electron transferred. The selectivity for methanol oxidation of graphite catalyst enhanced with the increase of graphite particle size and was superior to that of marketizational Pt/C electrode. These results demonstrate that the original carbon materials play an important role in enhancing electrocatalytic activity for the ORR of the doped carbon-based catalysts.

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