Effect of carbonization temperature of carbon felt on removal of methylene blue: carbon felt as the cathode of Electro-Fenton system

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Abstract—The surface properties of carbon fiber have been regarded as the critical factor for 2-electron oxygen reduction (ORR) and degradation of organic pollution in Electro-Fenton process. The aim of this work was to investigate the effect of carbonization temperature on the performance of carbon felt as the cathode for degradation methylene blue (MB). This work was adopted carbon felt that obtained at the carbonization temperature of 1050, 1600, 2000 °C respectively, comparison of the electrogeneration of H\textsubscript{2}O\textsubscript{2} and MB removal rate at pH 3. Compared with CF-B and CF-C, high-yield H\textsubscript{2}O\textsubscript{2} production (38.9 mg L\textsuperscript{–1}, 1.3 mg h\textsuperscript{–1} cm\textsuperscript{–2}) and high-degradation rate of MB (96.7%, kinetics constant: 0.0623 min\textsuperscript{–1}) in CF-A system have been achieved. The hydrophilic was carried by water contact angle test, indicated that the inert of surface: CF-C > CF-B > CF-A. The disorder degree of surface was characterized by Raman spectroscopy, and in combination with CV and LSV tests, revealed the ORR catalysis properties of different types cathode. This study suggested that lower temperature of carbonization was in favour of carbon felt as the Electro-Fenton cathode to degenerate organic pollution.

1. Introduction
In recent, the removal of micropollutants has been becoming the focus on wastewater treatment. This is due to these kinds of pollutants such as pesticide, antibiotic, dye; even if its are of low-concentration existed in nature water, however, they may have potential impacts on the safety of environment [1,2]. As an environmentally friendly technology for degradation of organic pollution, Electro-Fenton process can generate ·OH indirectly via oxygen reduction reaction (ORR) and Fenton reaction (eq (1) and (2)).

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\begin{align*}
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2 & E^0 = +0.695 \text{ V/SHE} \quad (1) \\
Fe^{2+} + H_2O_2 & \rightarrow Fe^{3+} + H_2O + \cdot OH \quad (2)
\end{align*}
\]

The properties of cathode surface are of vital significance for pollution removal. That's because the H\textsubscript{2}O\textsubscript{2} production rate is an important condition of the ·OH yield [3]. In view of the advantages of anti-corrosion, higher hydrogen evolution potential, environmental friendliness and so on.
Carbonaceous materials such as activated carbon fiber [4], graphite fiber [5, 6], biomass derived carbon foam [7], were extensively used for the cathode of Electro-Fenton system. In general, defects, functional groups, and microcrystalline edge could be the active sites of the carbon structure [8, 9]. Thus, many studies enhanced the catalytic action via introduced defects to the sp2-hybridized surface of carbonaceous materials [10-12]. However, carbon fiber is a carbonaceous materials which originally existed defects, which attribute to N and O escapes and graphitization of C in fiber were incomplete [13]. Usually, the defect degree of carbon fiber depended on carbonization temperature of technological process.

The purpose of this work was to compare the electrogeneration yield of H2O2 and methylene blue (MB) degradation rate of three kinds carbon felt. The properties of carbon fiber surface were characterized by Raman spectroscopy and contact angle technique. Meanwhile, the electrochemical activity measured by linear voltammetry sweep (LSV) and cyclic voltammetry (CV) tests. This work was verified that the carbonization temperature has a significant effect on the surface catalysis performance of carbon felt.

2. Methods and materials

2.1. Chemicals and pre-treatment

In this work, unless otherwise specified, all chemicals are analytical-grade reagents and purchased from Sinopharm Chemical Reagent Co., Ltd. Carbon felts (2×3 cm², 0.15 g) were obtained from Gansu HaoShi Fiber Co., Ltd. Table 1 shown the label of sample and carbonization process. Carbon felts were ultrasonically washed in absolute ethyl alcohol for 30 min, and then dried in drying oven at 80 °C for 24 h.

Table 1 The label and properties of carbon felts

| Sample  | Carbonization temperature | Carbonization time |
|---------|---------------------------|--------------------|
| CF-A    | 1050 °C                   | 36 h               |
| CF-B    | 1600 °C                   | 37 h               |
| CF-C    | 2000 °C                   | 40 h               |

2.2. Electrolysis

The production of H2O2 and degradation of MB were used an electrochemical workstation (CHI660D, Shanghai) carried out in 200 ml undivided cell, platinum wire and saturated calomel electrode (SCE) were used for the counter electrode and reference electrode, respectively. The supporting electrolyte was 0.05 M Na2SO4 aqueous (pH 3, adjusted pH value employed by 0.1 M NaOH and H2SO4). The whole reaction under a magnetic agitation speed of 350 rpm, and aerated to the cell with 0.4 L min⁻¹ O2 flow rate. Ferrous sulfate (FeSO4·7H2O) was used for supplying Fe²⁺ ions, and the initial concentration of MB and Fe²⁺ were 100 mg L⁻¹ and 0.25 mM. Fig. 1 demonstrated the equipment of electrochemical experiment in this study.
2.3. **Analytical methods**
The concentration of H$_2$O$_2$ measured by the potassium titanium (IV) oxalate method of 400 nm wavelength, on a ultraviolet–visible spectrophotometer (Cary 100, Agilent). The absorbency of MB measured at the wavelength of 664 nm. At oxygen saturation, linear voltammetry sweeps were tested in a three electrode cell system at the range of 0 - 1.4 V, and the scan rate of 10 mV s$^{-1}$. Cyclic voltammetry was tested in 1M KCl and 10 mM K$_3$[Fe(CN)$_6$] mixed solution, and also the scan rate of 10 mV s$^{-1}$. The Raman spectrum of electrodes surface characterized by a thermo scientific DXR micro focused Raman spectrometer (Thermo Fisher Scientific, Germany). The contact angle of water on cathode surface was carried out using a contact angle meter (OCA25, Germany), using the SNS 021/011 nozzle, the water droplet volume was 3 uL, and the water droplets speed was 5 uL min$^{-1}$.

3. **Results and discussions**

3.1. **Raman spectrometer and contact angle of water**
Raman spectrometer was carried out to explore the surface condition of cathode. Fig. 2(a) and (b) verified the degree of graphitization of carbon fiber surface. In view of D peak located in nearby 1360 cm$^{-1}$ was caused by the defects of sp$^2$ carbon edge, functional groups, and structure disorders, etc.; but G peak was originated in the vibration modes E$_{2g}$ of graphite unit cell, which was the evidence of sp$^2$ hybridize carbon in microcrystalline planes. The ratio of peaks area of D and G were used for describing surface defects degree [14]. Table 2 shown that the fitting information of peaks. As expected, the value of I$_D$/I$_G$ of CF-B and CF-C much lower than CF-A, which attributed to high temperature graphitization made for C atoms rearrangement and graphite microcrystalline growth. However, the lower degree of defects to the disadvantage of electrocatalysis [15]. In addition, as shown in Fig. 2(c), demonstrated the contact angles on cathode, at 0, 10, 20 s, respectively. The contact angle of CF-C as high as 143.4° at 0 s, meanwhile, the contact angle of CF-A was only 125.1°. After 20 s of residence, the contact angles of CF-A, CF-B and CF-C were 105.8°, 123.7°, 135.7°, respectively. The better surface hydrophilic property in favour of the electron transferred at the interface of electrolyte and electrode surface, and thus, accelerated ORR kinetics.
Fig. 2 (a) Raman spectrum of CF-A, CF-B and CF-C. (b) Fitting of D and G peaks of Raman spectrum. (c) Contact angle of water of cathode surface.

Table 2 The fitting results of Raman spectrum

| Sample | D band | G band |
|--------|--------|--------|
|        | Center | FWHM   | I_Area | Center | FWHM | I_Area | ID/IG |
| CF-A   | 1356.39| 279.69 | 23.97  | 1588.46| 103.60| 8.33 | 2.88 |
| CF-B   | 1355.41| 226.96 | 17.67  | 1600.31| 107.15| 8.91 | 1.98 |
| CF-C   | 1345.53| 47.32  | 25.62  | 1583.52| 52.68 | 28.52| 0.90 |

3.2. Electrogeneration of H₂O₂

Fig. 3(a) shown that the H₂O₂ electrogeneration of three samples. Among these cathodes, CF-A has the highest rate of H₂O₂ production, and achieved 38.9 mg L⁻¹ after 60 min of electrolysis. Compared with CF-A, CF-B and CF-C demonstrated relatively low H₂O₂ concentration. The yield of CF-B and CF-C after 60 min electrolysis were 10.9 mg L⁻¹ and 4.4 mg L⁻¹, respectively. The H₂O₂ yield is of vital significance of pollution degradation, due to its decide the generation rate of ·OH in Electro-Fenton chain reaction. Furthermore, as shown in Fig. 3(b), we calculated the current efficiency (CE) of whole electrolysis reaction via using eq (3). Obviously, the CE of CF-A better than CF-B and CF-C, which indicated that higher 2-electron ORR selectivity of CF-A. Because of the hydrophilicity of cathode surface enhanced with electrolysis process, and thus, the CE of CF-A system was improved with the extension of electrolysis time.

\[
CE \ (%) = \frac{n F C V}{\int_0^t I dt} \times 100\%
\]  

Where n is the number of electron transfer, F is the Faraday constant (96486 C mol⁻¹), C (mol L⁻¹) is the concentration of H₂O₂ production, V is the volume (L) of electrolytic cell, I is the current of electrolysis process (I), t is the electrolysis time (s).
Fig. 3 (a) Effect of cathode types on H$_2$O$_2$ production. (b) Current efficiency. Conditions: pH 3, 0.05 M Na$_2$SO$_4$, O$_2$ flow rate was 0.4 L min$^{-1}$, $E = -0.6$ V (vs.SCE); (c) CV curves of CF-A, CF-B, CF-C in 10 mM [K$_3$Fe(CN)$_6$] solution (1.0 M KCl as the supporting electrolyte) at the scan rate of 0.01 V s$^{-1}$. (d) LSV curves of CF-A, CF-B, CF-C in 0.05 M Na$_2$SO$_4$ (pH 3, oxygen saturation) at the scan rate of 0.01 V s$^{-1}$ with a slight magnetic stir.

The cyclic voltammetry of Fe$^{3+}$/Fe$^{2+}$ system was used for calculating the activity area of cathode, because the activity area was directly proportional to CV peaks current of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4+}$ that was employed by the ferrocyanide redox system. As can be seen in Fig. 3(c), a clear distinction of current peaks between CF-A, CF-B, and CF-C, and the highest of CF-A current peak indicated the maximum value of electroactive area. The actual area of electrode electroactive surface can be calculated by Randles-Sevcik equation (eq. (4)) [7], and the electroactive area of CF-A, CF-B and CF-C were 104.9, 83.6 and 21.2 cm$^2$ respectively. In addition, LSV was performed to confirm the the ORR activity of three types electrode. As shown in Fig. 3(d), CF-A exhibited that the highest current response, two peaks was corresponded to 2-electron transfer of ORR [10], which indicated that the most excellent activity for surface catalysis and its were similar to CV test results.

$$I_p = 2.69 \times 10^5 \times AD^{1/2}n^{3/2} \gamma^{1/2}C$$ (4)

Where $I_p$ is the peak current (A), $A$ stands for cathode area (cm$^{-2}$), $D$ is the diffusion coefficient of the ferrocyanide molecule (cm$^2$ s$^{-1}$), $n$ is the number of electron transfer in the redox reaction, $\gamma$ is the scan rate of CV experiment (V s$^{-1}$), $C$ is the concentration of the probe molecule (mol cm$^{-3}$).

3.3. Degradation of MB

In this section, comparison of MB degradation rate were carried out. Significantly, the highest removal rate of pollution was obtained by CF-A electrode. After 60 min of electrolysis, the absorbancy removal efficiency of CF-A, CF-B and CF-C electrolysis system were 96.7%, 88.4% and 37.7%, respectively. Furthermore, the removal of absorbancy was fitted for a pseudo first-order kinetics, and the kinetic rate constant of CF-A, CF-B and CF-C were 0.0623, 0.0374 and 0.0079 min$^{-1}$, respectively. The degradation behavior was similar with previous literature [7,17].
Fig. 4. (a) Effect of cathode type on MB degradation. (b) The first-order kinetics fitting of degradation process. Conditions: 100 mg L⁻¹ MB, 0.25 mM Fe²⁺ dosage, pH 3, 0.05 M Na₂SO₄, O₂ flow rate at 0.4 L min⁻¹, E = −0.6 V (vs.SCE)

4. Conclusions

Taken together, this work demonstrated that three types carbon felt of different carbonization temperature were used for the cathode of Electro-Fenton process. Characterized by Raman spectrometer, CF-A performed the highest disorder degree, which made for CF-A surface emerged the catalysis stem for ORR. Obviously, the higher carbonization temperature made for the perfect crystal structure of carbon fiber, but decreased the surface catalysis activity. At the conditions of pH 3, 0.05 M Na₂SO₄, and 0.4 L of O₂ flow rate, the H₂O₂ yield of CF-A can be reached 38.9 mg L⁻¹ (1.30 mg h⁻¹ cm⁻²), and achieved 96.7% removal efficiency of 100 mg L⁻¹ MB. This study can provide a reference for selectivity of carbon fiber cathode in Electro-Fenton technology.

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