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# Abstract

In this work, the active carbon fibers (ACFs) was modified by nitrogen doped porous carbon (NPC) and carbon nanotubes (CNTs) to prepare a novel modified electrode as cathode. The effect of different amount of CNTs mass ratio to NPC modified ACFs on H<sub>2</sub>O<sub>2</sub> production and EEC were investigated and the optimal CNTs mass ratio to was 1:7. It was observed that  $H_2O_2$ production with NPC-CNTs/ACF as cathode (1554.55 mg L<sup>-1</sup>) was much larger than with raw ACF as cathode (59.96 mg L<sup>-1</sup>). The detection results of SEM, XPS, LSV and Raman showed a higher electrochemical performance and abundant pyridine N and oxygen containing functional groups on the cathode after modifying, which exposes more defects and oxygen active sites to speed up the oxygen reduction reaction (ORR) and improve the electrocatalytic activity of the electrode. The  $H_2O_2$  production could also achieve a balance in a high state of  $H_2O_2$  produciton (around 1550 mg L<sup>-1</sup>) with low EEC (< 30.08 kWh kg<sup>-1</sup>) in consecutive 6 runs. Moreover, The TOC removal rate of PPCPs (tetracycline hydrochloride and diclofenac sodium) by electro-Fenton on the modified cathode was over 100 % in 50 min, while the total organic carbon removal of tetracycline hydrochloride and diclofenac sodium reached 69.5 % and 79.2 % respectively, at 2 h, which was more the four and five times that on the unmodified one (9.60 % and 16.27 %). Such loaded cathode with high efficiency and significant increase of H<sub>2</sub>O<sub>2</sub> generation, and degrade organic pollutants by EF with high efficiency and low energy consumption.

Keywords: Electro-Fenton process; Carbon fiber; Hydrogen peroxide; Oxygen reduction reaction

#### 1. Introduce

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Recent years, advanced oxidation processes (AOPs) can oxidize the refractory organic compounds in water into low-toxic/non-toxic small molecular substances, and directly mineralize products to CO<sub>2</sub> or H<sub>2</sub>O[1, 2]. In various AOPs, the H<sub>2</sub>O<sub>2</sub> can be decomposed to produce hydroxyl radicals (·OH) with strong oxidation ability, which are non-selective and widely used to remove refractory organic pollutants in water environment[3]. As a new advanced oxidation technology, electro-Fenton process has been attracting more and more people's attention due to its advantages of rapidity, high efficiency, environmental friendliness and simple operation[4]. EF as a efficient technology for AOPs, can be continuous in situ at the cathode surface to produce H<sub>2</sub>O<sub>2</sub>, solves the problem of collection and transportation storage[5]. It also can produce a large number of ·OH enhanced oxidation capacity when using iron as a catalyst in system[6, 7]. In EF process, the concentration of H<sub>2</sub>O<sub>2</sub> is the source of the strong oxidant (·OH) in the system, which determines the ability of EF process to oxidize and degrade pollutants. The basic principle of EF reaction is that H<sub>2</sub>O<sub>2</sub> is generated by oxygen reduction reaction (ORR) of two electrons on the surface of suitable cathode material by dissolved oxygen as shown in formula (1). In the EF system, Fe<sup>2+</sup> can achieve effective reduction at the cathode as shown in equations (2)[8].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+}OH + OH^-$$
(2)

 $H_2O_2$  as a powerful oxidant, has many functions and wide applications. Theoretically, the generation of  $H_2O_2$  plays a major role in the EF process and determines the removal performance[9].  $H_2O_2$  concentration is a principal element affecting the performance of EF treatment of pollutants. Therefore, it is very important to choose suitable EF cathode materials[10]. The proper selection and use of the cathode material not only improves the efficiency of EF, but also saves the wastewater treatment costs. Cathodes with high production of  $H_2O_2$  are very recommendable. Carbonaceous materials, such as graphite[11], graphite felt (GF)[12], reticulated vitreous carbon (RVC)[13]. Activated carbon fibers (ACFs)[14], gas diffusion electrodes(GDE) and carbon sponge[15] are extensive used as cathode materials due to their good chemical stability, electrical conductivity and corrosion resistance. As one of the most

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widely used commercial electrode materials, ACFs has high quality properties, larger activitie Online Onl

In recent years,nitrogen doped porous carbons (NPC) prepared by metal organic frameworks (MOFs) is favored by many researchers because that it has abundant pore structures to offer more electrocatalytic active sites, and has excellent defects and electrical activity to promote ORR by EF [17]. In particular, as an ideal precursor, nitrogen-rich MOFs can induce positively charged and activated adjacent atoms by doping nitrogen atoms into the carbon plane, thus producing homogeneous nitrogen-doped porous carbon. In addition, the alkalinity of carbon and ability to provide electrons is enhanced by nitrogen. And recently, the use of carbon nanotubes (CNTs) for the reduction of dissolved oxygen has aroused great interests in scientific research. CNTs are one-dimensional nanomaterials with a light weight, high specific surface area and many defects and traps on the surface[18]. CNTs have attracted much attention with their inequable mechanical, electrical and chemical properties [19, 20]. Therefore, ACFs modified by porous carbon and CNTs may have the advantages of both to further improve the electrochemical performance of ACFs.

In this study, the NPC was carbonized from ZIF-8 which a MOFs rich in nitrogen as precursor, NPC were used to modify the ACF electrode to improve the  $H_2O_2$  generation in situ in the EF system, the performance of this EF process was assessed with common antibiotics, tetracycline hydrochloride and diclofenac sodiumand to study the degradation performance and stability of organic pollutants.

## 2. Experimental

#### 2.1 The preparation of porous carbon and cathode

Synthesis of ZIF-8: ZIF-8 was synthesized by mixing 10.55 g 2-methylimidazole powder with 0.65 g hexahydrate zinc nitrate and continuously stirring for 24 h. Carbonization of ZIF-8:

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 After stirring, purify with methanol for 3 times, dry in a vacuum oven at 50 °C for 12  $h_{DB1:10}$  for  $h_$ 

Modification of ACF: The ACF electrode material was immersed in acetone solution and ultra-pure water for multiple ultrasonic cleaning and dried 24 h at 80 °C to remove the stains and grease on the original ACF. Take a suitable amount of NPC (0.05-0.30 g), carbon nanotubes (0.3-1.5g), polytetrafluoroethylene (0.5ml), ultra-pure water (10ml) and isopropanol (0.5ml) were mixed in ultrasonic bath for 10 min. The ACF was immersed in the mixed solution and ultrasonic instrument was used for 30 min. After that, the electrode was taken out and the remaining mixture was evenly coated on both sides of the electrode. The electrode samples were dried for 24 h at 80 °C and calcined for 60 min at 360 °C. After cooling, the modified electrode was prepared. The mass ratio of the NPC to CNTs in the mixture were 1:1, 1:3, 1:5, 1:7, 1:9 and the modified electrodes corresponding to the mass ratio of NPC to CNTs in the mixture were labeled as ACF-(1:1), ACF-(1:3), ACF-(1:5) ACF-(1:7) and ACF(1:9), respectively.

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# 2.2 Characterization and analytical methods

The surface morphology and microstructure of ACF samples are observed with Q45 environmental Scanning Electron Microscope (SEM), and the physicochemical properties are analyzed. Aiming to measure the hydrophobicity of ACF, the contact angle of water on the material surface was determined by contact goniometer (Dataphysics, OCA15, Germany). X-ray diffraction (XRD) analysis was carried out utilizing a Philips-12045 B/3 diffractometer at 40 kV of tube voltage and 30 mA of current to identify the electrode at the scan rate of 6° min<sup>-1</sup>. The surface elemental composition was analyzed by X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, England). The specific surface area of the electrode was determined by nitrogen adsorption in a constant volume adsorption apparatus (BET, Autosorb-IQ-MP, America). The research on the electrochemical properties of stone ink felt is carried out in the electrochemical working station (CHI660E, Shanghai chenhua). The ACF is the working electrode, the platinum plate is the positive electrode, and the filling and glycerine electrodes are the reference electrodes,

the working electrode is separated from the anode by 1.0 cm, and 0.05M Na<sub>2</sub>SO<sub>4</sub> of 0.1 L servekew Article Online as the supporting electrolyte. Used linear sweep voltammetry (LSV) to analyze the electrochemical response of ACF samples. The scanning rate was 0.05 V·s<sup>-1</sup>. The ORR activity of ACF electrode was investigated by rotating disk electrode (RDE) at a scanning rate of 0.01 V s<sup>-1</sup>. For the ACF-NPC electrode, 10 mg NPC with 0.5 mL ethanol and 10  $\mu$ L 5 wt % Nafion was mixed, then drop 0.01 mL of the mixture onto the glass carbon electrode until dry to room temperature. Through the slope of kouteckk-levich plot, the formation mechanism of H<sub>2</sub>O<sub>2</sub> is calculated, and the calculation formula is as follows :

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{\frac{1}{Bw^2}}$$
(3)

$$B = 0.62nFv^{\frac{1}{6}}C_{0_2}D_{0_2}^{\frac{2}{3}}$$
(4)

Where J and  $J_k$  are the detected current density and kinetic current density, respectively (mA cm<sup>-2</sup>), w is the angular velocity (rad s<sup>-1</sup>), F is the Faraday constant (C mol<sup>-1</sup>), n is the electron transfer numbers,  $C_{0_2}$  is the bulk concentration of O<sub>2</sub> (mol cm<sup>-3</sup>), v is the kinematic viscosity (cm<sup>2</sup> s<sup>-1</sup>), and  $D_{0_2}$  is the diffusion coefficient of O<sub>2</sub> in the electrolyte solution (cm<sup>2</sup> s<sup>-1</sup>).

# 2.3 Electro-generation of H<sub>2</sub>O<sub>2</sub>

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The electrocatalytic experiment of  $H_2O_2$  was carried out in a two-electrode single-chamber reaction system. 0.05 M Na<sub>2</sub>SO<sub>4</sub> solution with a volume of 0.15 L was used as the supporting electrolyte. And there is no additional aeration is provided . The anode adopts modified ACF and unmodified ACF (2 cm × 2.5 cm), the anode adopts platinum sheet (1 cm × 2 cm) and the anode and cathode are separated by 1.0 cm. dc power supply to provide output constant current mode, the whole experiment under the condition of room temperature (25°C). 0.5 mL of the reaction was sampled from the solution every 10 min . The concentration of  $H_2O_2$  was determined by potassium oxalate spectrophotometer (UNICO, WFJ7200) at  $\lambda = 420$  nm. The current efficiency (CE) of  $H_2O_2$  production was calculated as follows:

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where n is the number of electrons transferred during the reaction process of oxygen reduction to  $H_2O_2$ , F is Faraday's constant (96485 C mol<sup>-1</sup>),  $C_{H2O2}$  is the mass concentration of  $H_2O_2$  (M), V is the solution volume (L) of the reaction system, I is the current intensity (A), and t is the time(s).

The electric energy consumption (EEC, kW h kg<sup>-1</sup>) was measured by formula:

 $CE = \frac{nFC_{H_2O_2}V}{\int_{0}^{t} Idt} \times 100\%$ 

$$EEC = \frac{1000UIt}{CV} \tag{6}$$

where U is the voltage (V), I is the applied current (A), t is the electrolysis time (h), C is the concentrated  $H_2O_2$  (mg L<sup>-1</sup>), and V is the solution volume (L).

# 2.4 Degradation of PPCPs by EF

The two typical PPCPs (tetracycline hydrochloride and diclofenac sodium) were chose for EF degradation research. The degradation of diclofenac which initial concentration was 50 mg L<sup>-1</sup> by the EF process in the reactor, the solution contains  $0.05m Na_2SO_4$  as the supporting electrolysate, used 0.1 M H<sub>2</sub>SO<sub>4</sub> and NaOH to adjust the dissolved solution to pH=3, and FeSO<sub>4</sub> of 0.4 mM is added to provide Fe<sup>2+</sup> catalyst. During the reaction process, the removal rate of pollutants and the removal rate of TOC in solution were determined by sampling.

Tetracycline was quantitatively analyzed by high performance liquid chromatography. The chromatograph was Waters uplc-hclass ultra-high performance liquid and the chromatograph column was reversed phase C18 chromatographic column (1.7m, 2.1mm ×50mm), and the detector was ACQUITY UPLC TUV detector. The mobile phase of tetracycline hydrochloride was acetonitrile (A) and 0.1% formic acid aqueous solution (B). The mobile phase A/B gradient was  $0 \sim 5$  min and  $5\% \sim 17\%$  A.5 ~ 6 min, 30% A;6 ~ 10 min, 85% A;10 ~ 11 min, 5% A, kept for 1 min, A total of 12 min. Flow rate of 0.3 mL min <sup>-1</sup>, column temperature of 35 °C, sample room 10 °C temperature, sample volume  $10\mu$ L, the peak time of about 4.54 min, uv detection wavelength of 270 nm.The standard curve equation is c =  $1.539 \times 10^{-5}$  A, R<sup>2</sup> = 0.999. Sodium

diclofenac was quantitatively analyzed by high performance liquid chromatography (HPL Criew Article Online miliford-ma 1,757, USA), chromolith rp-18e C18 column (1.7 m, 2.1 mm x 100 mm) and Perkin Elmir 785 A uv detector. The mobile phase of diclofenac sodium was acetonitrile, 0.02 M ammonium acetate solution (containing 0.1% acetic acid), and the proportion of the two was 40%: 60%. Flow rate 0.5 mL min <sup>-1</sup>, column temperature of 30 °C, sample volume 10 mu L, the peak time is about 5.5 min, uv detection wavelength of 275 nm. Its standard curve is c = 4.627  $\times 10^{-5}$  A, R<sup>2</sup> = 0.999.

The removal efficiency of these contaminants is calculated as follows:

$$\eta = \frac{Co - Ct}{Co} \times 100\% \tag{7}$$

Where and are respectively the initial pollutant concentration and the residual pollutant concentration at a given time. The mineralization of pollutants by an electrochemical Fenton system is determined by a total organic carbon (TOC) analyzer (Liqui TOC II, Elementar, Germany). TOC was tested by sampling from the solution at 180 min after EF reaction. Electron spin resonance (ESR) spectroscopy was used measure ·OH. In the meantime, the ESR spectra was created by Bruker EMX ESR Spectrometer (Billerica, MA).

# 3. Results and discussion

#### 3.1 Nitrogen doped porous carbon optimization



 The modification of ACF can obviously change the generation of  $H_2O_2$ , and the loading of NPC and CNTs on ACF had a great effect on the electrocatalytic activity of cathode, which distinctly improves the ability of generating  $H_2O_2$  in situ. Fig.1 shows the production of  $H_2O_2$  obtained by modifying the cathode with different proportions of NPC to CNTs (ACF, ACF-(1 : 1), ACF-(1 : 3), ACF-(1 : 5), ACF-(1 : 7) and ACF-(1 : 9). The yield of  $H_2O_2$  increased as the NPC to CNTs increased up to 1 : 7, but the further increase of the ratio reduces the formation of  $H_2O_2$ . For the cathode with a mass ratio of NPC to CNTs, the maximum concentration of  $H_2O_2$  come up to 1434.55 mg L<sup>-1</sup>, and that obtained by unloaded NPC cathode was 59.96 mg L<sup>-1</sup>, the yield of  $H_2O_2$  of modified electrode ACF-(1:7) was increased by nearly 30 times. In addition, ACF-(1:7) had the highest yield of  $H_2O_2$  increased as the mass of NPC to CNTs increased up to 1:7, the increase in mass reduces the yield of  $H_2O_2$ , which might be the excessive load of NPC increases the resistance of the cathode electrode and reduced the CE. Thus, it is implied that the active carbon filer electrodes modified by porous carbon is potential electrode to efficiently generate  $H_2O_2$  in EF process.

# 3.2 The electrochemical analysis of cathode



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> Fig. 2 The LSV of different cathode materials(a) and the blank LSV (b). Conditions:  $0.05 M_{DOF: 10.1039/DONJ02360D}$ Na<sub>2</sub>SO<sub>4</sub>, pH=7, potential window 0 ~ -1.6V (vs. SCE), scan rate is 0.05 V·s<sup>-1</sup>.

Aiming to study the impact of NPC affects  $H_2O_2$  electrochemical generation on the electrocatalytic activity of cathode for oxygen reduction reaction (ORR), saturated calomel electrode was used as reference electrode, LSV measurement was carried out. In Fig. 2a, the current response for ORR of modified cathode was enhanced than that of other electrode. As a comparison, in Fig.2b, a blank voltammogram to prove that the cathodic currents flowing are actually due to the ORR. The results show that the introduction of NPC improved the conductivity of the cathode, at the same voltage, the modified electrode has the higher current density. There is an obvious negative shift constantly as NPC content increased, and the electrode showed the strongest current response when the mass of CNTs:NPC was 1:7. However, the potential decreased with the load increased further, which is consistent with the  $H_2O_2$  trend of the above mentioned. It makes sense, that NPC can improve the electrocatalytic activity of O<sub>2</sub> reduction and produce higher selectivity and concentration of  $H_2O_2$ , suggesting that the excessive NPC also reduces current efficiency owing to the stable three phase interface destabilize [21-23].

3.3 Characterizations of cathodes

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Fig. 3 The SEM of ACF (a, b) and ACF (1:7) (c, d).

In order to study the relationship between the change of properties of ACF by NPC loading and the production of high H<sub>2</sub>O<sub>2</sub>. And analyzed the influence of modification process on electrocatalytic activity of the materials. The SEM images of ACF and ACF- (1:7) were shown in Fig.4. The morphology and characteristics of the electrode were significantly affected. The unmodified ACF was composed of about 10 microns of smooth and neat carbon fiber. After modification, there are many particles on the modified ACF fiber, which is completely different from the cleaned ACF fiber, the surface of carbon fiber become rough, which significantly changes the surface characteristics of the cathode material. Such a structure can effectively increase the BET of the material (increase from 2.565  $m^2/g$  to 6.58  $m^2/g$ ) and promote the diffusion of O<sub>2</sub> on the surface, which was beneficial to the catalytic reaction[24, 25]. Compared with ACF, the number of micropores and mesopores in NPC loaded ACF increased, the cathode modification resulted in about 2.6 times (increase from 3.005 nm to 6.955 nm) and more than 23 times (increase from 0.004 mL g<sup>-1</sup> to 0.097 mL g<sup>-1</sup>) increase in surface area and pore volume, respectively. An electrode loaded with a specific three-dimensional structure facilitates the diffusion of gas molecules through pores near the surface of the carbon material for further reaction. The dynamic equilibrium of solid, gas and surface oxygen increases the solubility of O2

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in solution[26-27]. The loading of NPC and carbon nanotubes in the cathode speeds up the watche online electron transfer rate, and increases the BET surface area and electroactive surface of the cathode. The result is a faster rate of diffusion of  $O_2$  molecules and the active site ORR increased on the cathode. Fig. 5 shows the ACF and ACF (1:7) contact Angle, the respective initial contact angle of ACF(1:7) (115°) was smaller than that of raw ACF (135°), which indicated the better wettability of modified electrode although surface energy of them were still very low [28]. The reaction process facilitate because the better wettability of the prepared materials enhanced and the electron and mass transfer between the cathode and  $O_2$  were accelerated, benefiting H<sub>2</sub>O<sub>2</sub> production[28].



Fig. 4 The contact angle of ACF (a), ACF (1:7) (b).





**Fig. 5** XPS spectrum of the C1s (a) and N1s (b), Raman spectra (c) and XRD (d) of ACF(1:7), Electrochemical impedence spectroscopy(EIS) of ACF(1:7) and ACF (e).

Table 1 The atomic percentage in the samples

Sample		C1s	O1s	O/C	N1s
ACF	At %	88.10	6.30	0.08	0.15
ACF (1:7)	At %	70.75	12.42	0.23	3.20

In order to further explore the affect of the surface chemical state for high redox activity, XPS, Raman spectra (c) and XRD analysis was performed on the different electrodes (as shown in Fig. 5). The atomic percentage in the samples (ACF and ACF (1:7)) was detected, and the

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carbon contents were 88.10 % and 70.75 %, while the contents of oxygen were 6.30 % and 12 4% we Article Online DOI: 10.1039/DONJ02360D %, respectively (Table 1). The O/C atomic and N1s ratios increased form 0.08 and 0.15 to 0.23 and 3.20, which indicates the raise of oxygen-containing functional groups [29]. In Fig. 5a, the main peak at 284.6–284.7 eV is corresponded to graphitized carbon (C=C). Carbon is coordinated to a single oxygen in hydroxyl groups or others (C-OH, C-O-R, 286.2 eV), and carboxyl or ester groups (-COOH or -COOR, 289.2 eV)[29-31]. These results corresponded to previously reported literature. In Fig. 5b, the maximum peak centered at 400.9-401.1 eV was corresponded to the graphitic nitrogen, the peak at 398.4 eV was indicated to pyridinic nitrogen and at 399.4 eV was indicated to pyrrolic nitrogen[32, 33]. Due to the presence of graphite nitrogen, the ORR of ACF (1:7) is accelerated because graphite nitrogen can accelerate the electron transfer between the carbon surface and the oxygen molecule. [33]. Fig. 5c shows the Raman spectrum of ACF(1:7), shown the significant characteristic peaks of carbon materials. For ACF (1:7), the peak at around 1350 cm<sup>-1</sup> corresponding to the D band which was typical for disordered graphite, this was attributed to vibrations of carbonatoms with dangling bonds in plane terminations, and another peak at around 1595 cm<sup>-1</sup> corresponding to the G band was ascribed to an Eg vibration mode of sp<sup>2</sup>-bonded carbon atoms in a 2D hexagonal lattice [34]. The XRD pattern of ACF-HPC-40 (Fig. 5 d) shows two weak peaks near  $25^\circ$ ,  $34^\circ$ ,  $47^\circ$  and  $56^\circ$ , which are respectively the (002), (004) and (101) planes of carbon. This conclusion confirms the existence of  $sp^2$  carbon, and it is precisely because of this structure that the electron transfer rate of NPC is greatly accelerated, because this structure contains a large number of free-moving  $\pi$  electrons[35]. Electrochemical impedance was used to study the electrical conductivity of ACF and ACF (1:7) electrodes. Fig. 5e shows that each Nyquist plot includes a semicircular part and a linear part. Compared with ACF, the EIS of the ACF (1:7) electrode is composed of a slightly lower semicircle in the high-frequency region and a more vertical line at low frequency, which shows that the cooperative effect of the catalytic layer and the photo-electricity has a lower charge transfer resistance and faster ion diffusion speed. The introduction of electron hole pairs can improve the electrical conductivity of ACF (1:7), thereby improving the separation efficiency of photocarriers. Therefore, the ACF (1:7) electrode has a higher electricity than ACF electrode.

# 3.3 Performance of the modified cathode for H<sub>2</sub>O<sub>2</sub> production

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**Fig. 6** The effects of (a) air flow rate, (b) current density and (c) pH on the H<sub>2</sub>O<sub>2</sub> generation for ward of the DOI: 10.1039/DONJ02360D ACF (1:7).

For further understanding the performance of modified cathode, we explored the influence factors of H<sub>2</sub>O<sub>2</sub> electro-generation including air flow rate, current density and pH, and then the results can be seen in Fig. 6. Fig. 6 reveal the impact of air flow rate, current density and pH on the H<sub>2</sub>O<sub>2</sub> yield using the ACF-(1:7) electrode. In Fig. 6a, the H<sub>2</sub>O<sub>2</sub> accumulations were 255.80, 1255.58, 1455.05 mg L<sup>-1</sup> at air flow rate from 0 to 0.60 L min<sup>-1</sup>, when the current density is 20 mA cm<sup>-2</sup>. Because before the aeration, the amount of dissolved oxygen in the water is low just about  $8-10 \text{ mg } L^{-1}$ . So dissolved oxygen in the solution increases by enhance the air flow rate, and the increase of O2 can accelerate the mass transfer rate between the electrolyte and the cathode surface, which improved ORR reaction rate and was conducive to the  $H_2O_2$  production [12, 36]. But, the electro-generated  $H_2O_2$  change was not obvious when air flow rate increased further to  $0.80 \text{ L min}^{-1}$ , which can be explained by that the excess gas can not be able to attach the electrode in time at a higher flow rate. Thus, the value of air flow will become less useful for a higher  $H_2O_2$ production [35]. In terms of current efficiency (CE) and EEC, the former obtained results followed the same tendency with  $H_2O_2$  generation as the air flow rate increased, while the later showed opposite trends (insert Fig. 6a). It can be demonstrated that 0.60 L min<sup>-1</sup> was the optimized velocity, promoting a high H<sub>2</sub>O<sub>2</sub> generation rate of 52.83 mg h<sup>-1</sup> cm<sup>-2</sup> and the lowest EEC (42.77 kWh g<sup>-1</sup>).

The effects of current density are also important for  $H_2O_2$  concentration, which are shown in Fig. 6b. At current density values of 8 mA cm<sup>-2</sup>, 12 mA cm<sup>-2</sup>, 16 mA cm<sup>-2</sup>, 20 mA cm<sup>-2</sup>, 24 mA cm<sup>-2</sup> and 28 mA cm<sup>-2</sup>, potential in the range of 0.1-0.13V, the accumulation of  $H_2O_2$  increased significantly with the increase of current density. When the current density was 20 mA cm<sup>-2</sup>, the concentration of  $H_2O_2$  reached the maximum value of 1554.55 mg L<sup>-1</sup> in 1 h. As the current density increases to 28 mA cm<sup>-2</sup>, the  $H_2O_2$  concentration decreases to 1409.66 mg L<sup>-1</sup> for 60 min. The results show that CE shows an opposite trend. The current utilization rate of the reaction generated by  $H_2O_2$  reached the highest when the current density was 20 mA cm<sup>-2</sup>, and the current

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efficiency was 53.42%. As current density increase the electron transfer ware accelerated and the warticle Online ORR be promote[29]. Also, the anodic oxidation would be enhanced, resulting in a higher dissolved oxygen. Without aeration, the cathode can only use the  $O_2$  produced by the anode. At higher current densities, some side reactions such as hydrogen evolution on the cathode(Eq. (6)), which is not conducive to the accumulation of H<sub>2</sub>O<sub>2</sub>[30, 31]. Similar phenomena were observed in literature[32].

$$2 \operatorname{H}^{+} + 2 \operatorname{e}^{-} \to \operatorname{H}_{2} \tag{6}$$

Fig. 6c shows that the formation of H<sub>2</sub>O<sub>2</sub> is affected by pH. Set the air flow rate to 0.6 L min<sup>-1</sup>, current density is 20 mA cm<sup>-2</sup>. The experiment investigated the impact of pH from 3 to 9 on the production of  $H_2O_2$  by ACF-(1:7). When solution pH increases from 3 to 7, the concentration of H<sub>2</sub>O<sub>2</sub> also increases from 1072.99 mg L<sup>-1</sup> to 1554.55 mg L<sup>-1</sup> at 60 min of electrolysis. But the concentration of H<sub>2</sub>O<sub>2</sub> for 60 min decreases to 1443.04 mg L<sup>-1</sup> at pH 9. At pH value of 7, the electricity generation rate, CE and EEC of  $H_2O_2$  reach the optimal state. At this time, the  $H_2O_2$ production rate was the highest and the energy consumption was the lowest. The electrochemical reaction of H<sub>2</sub>O<sub>2</sub> at the cathode is shown in the equation (1) Given, oxygen on the cathode surface protons and electrons reduction to produce  $H_2O_2$ . Protons are more likely to participate in the reaction in a relatively acidic environment, which is conducive to the production of  $H_2O_2$ . When the system is relatively alkaline,  $H_2O_2$  mainly exists in the form of  $HO_2^{-1}$ , and a large amount of H<sub>2</sub>O<sub>2</sub> would be lost due to the catalytic decomposition of H<sub>2</sub>O<sub>2</sub> by HO<sub>2</sub><sup>-1</sup> in an alkaline environment (especially when pH is greater than 9). Reduction of hydrogen peroxide at the cathode (Eq. (7)) and reduction of oxygen by four electrons directly generated water (equ (8)) when the concentration of protons in the system is too high [33]. So the highest H<sub>2</sub>O<sub>2</sub> accumulation in this system was achieved when the solution was neutral. In conclusion, the modified electrode can obtain higher CE and lower EEC at pH 7.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
 (7)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{8}$$

3.4 The ORR activity and stability of the modified cathode

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The oxygen reduction pathway of ACF was studied by rotating disk electrode (RDE), underew Article Online the condition of pH 7 and oxygen saturation. Further analysis of the measured data of the rotating disk was consistent with the literature [5,6], As shown in Fig. 7a, that the reduction current increases with the increase of the rotating speed along with the shortening of the diffusion layer [37]. The curves of steady-state diffusion plateau currents analyzed through Koutecky-Levich plots (inset in Fig. 7a ) proved the electron number during the electrochemical processes, which was 2.05, showing the reaction was two-electron ORR processes[38, 39]. The results of the rotating disk experiment show that the electron transfer rate under the composite ORR mechanism is accelerated due to the presence of NPC. Therefore, NPC introduction simply accelerated the rate of the electron transfer rather than changing the ORR mechanism, which was consistent with the results of  $H_2O_2$  production in Fig. 1.





Fig. 7 The ORR activity (a) and stability test (b) of modified electrode.Conditions: ACF (1:7), 0.05 M Na<sub>2</sub>SO<sub>4</sub>, pH=7, current density 20 mA ⋅ cm<sup>-2</sup>.

The stability of modified electrode has important influence for practical application, Therefore, the stability of modified ACF electrode material was tested in this study. The continuous operation of hydrogen peroxide production was investigated by using modified electrode in 6-times continuous runs. The modified electrode was used for the first time, the concentration of  $H_2O_2$  was1525.55 mg L<sup>-1</sup>, after 6 consecutive uses, the concentration of  $H_2O_2$ produced up to a balance in a high state (around 1500 mg L<sup>-1</sup>) and the EEC has been below 47.98 kWh kg<sup>-1</sup>, reveal that the cathode modified by NPC is comparatively stable and reusable in the production process of  $H_2O_2$ .

3.5 Degradation of tetracycline hydrochloride and diclofenac sodium by EF



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# Fig. 8 The degradation of tetracycline hydrochloride (a) and diclofenac sodium (b) and TOC removal rate (c). Conditions: 0.05 M Na<sub>2</sub>SO<sub>4</sub>, pH=3, tetracycline hydrochloride or diclofenac sodium 50 mg L<sup>-1</sup>, current density 20 mA⋅cm<sup>-2</sup>, Fe<sup>2+</sup> 0.4 mM.

The performance of tetracycline hydrochloride and diclofenac sodium degradation and mineralization efficiency on ACF-(1:7) was further compared with the unmodified electrode. Fig. 8a shows the degradation of diclofenac sodium and diclofenac sodium reach 100 % at 90 and 55 min on ACF (1:7), but unmodified ACF need more than 120 min. In different system, the fitting curves of pseudo-first order kinetic equation as Fig. 8a shows. The apparent rate constants of tetracycline hydrochloride treated with unmodified electrode and ACF (1:7) electrode were 0.0126 min<sup>-1</sup> and 0.0293 min<sup>-1</sup>, respectively. Meanwhile the apparent rate constants of diclofenac sodium treated with unmodified electrode and ACF (1:7) electrode were 0.0127 min<sup>-1</sup> and 0.0293 min<sup>-1</sup>, respectively. Meanwhile the apparent rate constants of diclofenac sodium treated with unmodified electrode and ACF (1:7) electrode were 0.0177 min<sup>-1</sup> and 0.0293 min<sup>-1</sup>, respectively. The differences of TOC removal rate as shown in Fig. 8b. The TOC removal rate of diclofenac sodium and diclofenac sodium were reached 10.8 % and 19.6 % on ACF but 69.2 % and 79.5% on ACF (1:7). The results show the modified cathode is more efficient than ACF. The main is the modified cathode greatly increases the production of H<sub>2</sub>O<sub>2</sub>. The insert of Fig. 8C proved the advantages of ACF (1:7) in EF. A typical two lines EPR spectrum of •OH further confirmed the possibility of above speculation, and two lines represents the raw ACF and ACF (1:7), respectively. As shown in Fig. 6c, the amounts of •OH on the raw electrode was far lower

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 than those on the modified electrode, suggesting the increased production of electro-generated we Article Online  $H_2O_2$  on the cathode with loading NPC was benefited to •OH production and the mineralization of tetracycline hydrochloride and diclofenac sodium.

# Conclusions

In this study, NPC and CNTs were used to modify the traditional ACFs electrode. The modified ACFs electrode showed stronger  $H_2O_2$  generation ability. ACF (1:7) obtained the maximum concentration of  $H_2O_2$  reached 1554.55 mg L<sup>-1</sup>, which was about 30 times higher than the unmodified electrode (59.96 mg L<sup>-1</sup>). The ACF (1:7) electrode showed stable degradation of tetracycline hydrochloride and diclofenac sodium, the degradation effect was more than 4-5 times that of the unmodified electrode, with high efficiency but low energy consumption. That the degradation rate of tetracycline hydrochloride and diclofenac sodium by the ACF (1:7) cathode reached 100 % within 50 and 90 min, and the removal rate of TOC reached 69.2% and 79.5% in 180 min. The excellent performance of the NPC is mainly attributed to the fact that the modification increases the surface area, contains higher content of sp3-c bond, improves the electrocatalytic activity of the electrode and accelerates the mass transport rate, thus promoting ORR. The method of modified electrode provides a new theoretical basis for the design of efficient carbon-based EF cathode materials.

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