



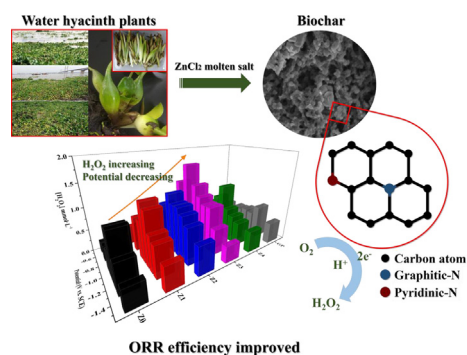
High oxygen reduction reaction performance nitrogen-doped biochar cathode: A strategy for comprehensive utilizing nitrogen and carbon in water hyacinth



Jiaxiang Liang, Diyong Tang, Li Huang, Yifei Chen, Wei Ren, Jie Sun*

Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission & Ministry of Education, Hubei Province, College of Resource and Environmental Science, South-Central University for Nationalities, Wuhan 430074, PR China

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a novel nitrogen-doped biochar oxygen reduction reaction cathode-water hyacinth carbon, was prepared by ZnCl₂ molten salt carbonization without additional nitrogen source, which displayed a high performance in electro-Fenton (E-Fenton) process. The BET result shows that water hyacinth carbon achieved a much larger specific surface area (829 m²·g⁻¹) than non-melt salt carbonized one (323 m²·g⁻¹) and graphite powder (28 m²·g⁻¹). Furthermore, characterization by XPS and EIS shows that both pyridinic-N (43.24%) and graphitic-N (56.75%) existed in water hyacinth carbon and Warburg constant was only 0.051. Because of a high H₂O₂ producing yield 1.7 mmol·L⁻¹ and corresponding current efficiency 81.2 ± 2.5% in molten salt carbonized water hyacinth biochar, a high kinetic constant 0.318 min⁻¹ in DMP degradation was achieved, which was 4 times higher than graphite powder (0.076 min⁻¹). The TOC removal achieved 86.8% in 30 min and the corresponding energy consumption reached a low level 60.15 kWh·kgTOC⁻¹.

1. Introduction

Nowadays four-electron oxygen reduction reaction (4e⁻ ORR) is one of the most essential parts in electrochemistry process, which is

applied in every corner of the energy field involving fuel cells designed, metal-air batteries fabrication and electrolytic industry (Xia et al., 2016). Also, the 2e⁻ ORR is equally important for water pollution treatment technology (Gao et al., 2017). E-Fenton technology is a kind

* Corresponding author.

E-mail address: jetsun@mail.scuec.edu.cn (J. Sun).

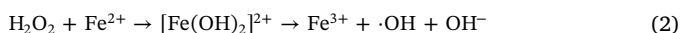
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of advance oxidation process developed from traditional Fenton technology, which has been reported as a very effective remediation technology in contaminants degradation (Sires et al., 2014). The *in situ* production of H₂O₂ during cathodic 2e⁻ ORR (Eq. (1)) is under the catalysis of Fe²⁺, causing the generation of a very powerful oxidizing agent hydroxyl radical ($\cdot\text{OH}$) (Eq. (2)). This radical has a high standard reduction potential ($E^0 = 2.80 \text{ V/SHE}$) so that it can mineralize most organics. Compared with the classical Fenton, the *in situ* generation of H₂O₂ can avoid the risks of its transport and storage. In this process, the generation of H₂O₂ by 2e⁻ ORR dominates the E-Fenton effect. Thus, improving the efficiency of 2e⁻ ORR is one of the key issues in the study of E-Fenton technology (Gao et al., 2016; Yang et al., 2018).



In the past years, carbon materials were widely used in the H₂O₂ producing process because of their high potential for hydrogen evolution, low catalytic activity in H₂O₂ decomposition, good conductivity and stability (Gao et al., 2015). The reported cathode materials with good performance in 2e⁻ ORR include graphite (Zhang et al., 2018b), carbon sponges (Özcan et al., 2008), activated carbon fiber materials (Zhang et al., 2018a), ordered mesoporous carbon (Peng et al., 2014). These days, a large bunch of N-doped carbon materials arise and exhibit high electrocatalytic activity (Yan et al., 2018). Nitrogen species has been proved to be active sites for ORR. Under acidic conditions, the lone-pair electrons from N dopants activates carbon π electrons. The O₂ is firstly adsorbed at the carbon atom next to the pyridinic-N and then the protonation is occurred, leading the reduction of O₂ molecules (Guo et al., 2016; Xia et al., 2016). Though nitrogen species is confirmed to be the active sites for ORR. The role of different types of N in ORR is still disputed. In general, the graphitic-N improves the electron transfer efficiency of carbon materials. So the content of graphitic-N has a direct effect on the onset potential of ORR. At the same time, the ORR current density is affected by the total content of graphitic and pyridinic-N (Ding et al., 2013; Zhang et al., 2013). However, due to the addition of various precursors, such as extra nitrogen sources and organic template, the preparation of these materials is complicated and high costs (Liu et al., 2015a). The scale applications of these material into tough wastewater treatment seems to be unsubstantial and also a waste of resources.

Quite recently, cheap biochar has gradually become a priority choice in cathode material precursor. The large specific surface area of biomass precursors provides adequate reaction space. At the same time, the derived nitrogen species can act as active sites to improve the electrocatalytic effect. A series of biomass such as the *Euonymus japonicus* leaves (Huang et al., 2018), *Medulla tetrapanacis* (Liu et al., 2018) and *Red dates* (Xu et al., 2018) were applied as catalysts in 4e⁻ ORR research, showing a good performance and stability during ORR. Good application prospects in the energy storage have been obviously shown. Rarely reported of 2e⁻ ORR research can be seen, *Magnolia* flowers (Chen et al., 2017) and *Long bean* (Gao et al., 2018) were used as precursors to fabricate into electrode. However, the contribution of derived nitrogen in biochar to 2e⁻ ORR activity is still unclear and the efficiency of ORR needs further improvement.

Water hyacinth (trivial name: *Eichhornia crassipes*) is a sort of aquatic plant which was imported into China in 20th century from south America for the solution of feed shortage. However, frequent phenomenon of eutrophication provides sufficient nutrition for the growth of water hyacinth plants which directly leads to river blocking and polluting. Because the high rates of survival and regeneration, it is

generally difficult to clear these plants on the water. These days, water hyacinth plants are considered as one of the world's ten largest malignant weeds (Barua et al., 2017; Qin et al., 2017). Distinguished from other biomass materials, water hyacinth is an invasive alien species. It's fast-growing and cheap. Significantly, water hyacinth usually grows in eutrophic water where abundant nitrogen can be absorbed by plants. We suppose that after a high temperature disposal, these original nitrogen species in the plants can be used to form ORR electrocatalytic active sites on the surface of cathode. Therefore, water hyacinth biochar as a cathode material applied in E-Fenton was carried out in this study. What's more, molten salt ZnCl₂ is motivated for further exploiting the electrocatalytic potential of the biochar. Molten salt ZnCl₂ carbonization can create porous polymers scaffolds to enlarge the specific surface area for a better nitrogen species exposure. H₂O₂ producing and DMP degradation efficiency were tested to study the performance of water hyacinth biochar cathode in E-Fenton and the corresponding results are compared with commercial graphite power.

2. Experimental

2.1. The preparation and the activation of water hyacinth carbon

The water hyacinth plants were firstly washed by distilled water and then sliced into pieces. At last dried in oven in 373 K for 48 h. After complete dehydration, each 3.0 g of water hyacinth powder was mixed up with the ratio of ZnCl₂ salt from blank (without ZnCl₂ addition), 1:1, 1:2, 1:3 to 1:4. The ratio of water hyacinth powder and ZnCl₂ salt from blank (no salt), 1:1, 1:2, 1:3 to 1:4 corresponding from sample Z0, Z1, Z2, Z3 to Z4, respectively. Carbonization was performed in a tube furnace under a N₂ gas flow at 1073 K for 1 h. The carbonization samples were washed with deionized water. Products were dried at 373 K for 24 h in a thermostatically controlled oven.

2.2. Fabrication of water hyacinth electrode

Electrodes were prepared by mixing 80 wt% water hyacinth carbon powder obtained from above experimental steps, 10 wt% acetylene black and 10 wt% PTFE. The mixture slurry was mixed with ethyl alcohol stirred for 4 h to ensure homogeneity and then suppressed evenly onto titanium mesh and then put in a vacuum oven at 333 K for 2 h. Besides, graphite powder (GP) was prepared by an identical method and used as a control group.

2.3. Material characterization

N₂ adsorption/desorption was determined by Brunauer-Emmett-Teller (BET) measurements (JWGB SCI.& TECH, JW-BK132F, China) and the pore size distribution analysed by the BJH method. The surface morphology of the as-prepared products were obtained by scanning electron microscopy (Hitachi, SU8010, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed on a MULTI-LAB2000* X-ray photoelectron spectrometer, and the spectra were fitted with the XPS PEAK41 software.

Electrochemical impedance spectroscopy (EIS) measurements were analysed by using an electrochemical workstation (CHI-650D, China). The initial potential was set as open circuit potential. The range of angular frequency was applied from 0.01 Hz to 100 kHz. Re (Z_w) in Nyquist has a well linear relationship with -1/2 power of the angular frequency in low frequency region, which has been shown in Eq. (6) (Ren et al., 2016).

$$\text{Re}(Z_w) = \sigma \omega^{-1/2} \quad (6)$$

where σ is Warburg coefficient and ω is the angular frequency. The numerical value of the ion diffusion coefficient in the cathode can be estimated from Eq. (7).

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