Activated chitosan microspheres as air cathode catalyst for high power production in microbial fuel cells

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Abstract
This study aimed to modify chitosan microspheres to have large specific surface area as cathode catalysts in microbial fuel cell. Nitrogen-rich chitosan microspheres were first prepared and were used as precursors to prepare the activated carbon materials. The activation effects of KOH and activation temperature on the graphitization degree, specific surface area and electrochemical performance were investigated. The materials were characterised through various microscopic analyses and the electrochemical properties of the materials as cathode catalyst were also investigated. Before and after the activation, the materials remained in microspheric morphology, shown by SEM measurement, while the specific surface area of the activated material increased significantly and reached 1562 m\(^2\)g\(^{-1}\) measured by BET. The graphitization degree of the material showed synchronized increase with calcination temperature, which was detected by Raman spectroscopy. The materials activated were rich in nitrogen, revealed by XPS for elemental analysis. When activated at the temperature of 850 °C, the material demonstrated lower internal resistance (0.6 Ω cm\(^{-2}\)), higher alternating current density (24.27 × 10\(^{-4}\) A·cm\(^{-2}\)) and the highest power density (1531 ± 51 mW·m\(^{-2}\)) which was 1.4 times that of the original carbon felt. It was illustrated by the electrochemical tests that the material prepared from the precursor chitosan microspheres as cathode catalyst has the high activity of oxygen reduction reaction in MFCs.

1. Introduction
Microbial fuel cells (MFCs) have received extensive attention from researchers as a new alternative energy source that can simultaneously degrade pollutants and generate electricity [1]. One of the key reactions in energy conversion is the oxidation-reduction reaction in MFCs [2]. However, due to the slow oxygen reduction reaction (ORR), the output power of MFCs is ultra low, so new materials for high-efficiency and low-cost electro-catalysts are required [3]. It has been proved that platinum-based catalysts have higher ORR performance. But their wide application is hindered by high cost and poor durability. At present, various ORR catalysts that can replace platinum-based catalysts have been developed, including transition metal composites [4, 5], non-noble metal oxides [6] and heteroatom-doped carbon-based composites [7, 8]. In summary, carbon-based materials are considered to be very probable catalysts. Different raw materials, such as black fungus, chicken feathers, sucrose and other biomass materials from a wide range of sources can be used as carbon precursors to prepare carbon-based materials in physical and chemical activation methods [9–12]. For example, carbon spheres synthesized from natural biopolymer (alginate) by heat treatment at 400°C–800°C under inert gas had a specific surface area 765 m\(^2\)g\(^{-1}\), which was conducive to the oxidation-reduction reaction [13]. Watermelon rind was used as a precursor to prepare nitrogen-containing multi-stage porous carbon. And the prepared carbon material was severed as the cathode catalyst in microbial fuel cells, generating the peak current 0.19 mA cm\(^{-2}\) [14]. Furthermore, carbon materials co-doped with multiple elements also have excellent properties. The CoO/MgO@NC composite was prepared by Bolong Liang et al as the air cathode catalyst in MFCs and the improved ORR performance was considered to be the multiple doping that reduces the electron...
magnetically until the solution became clear and transparent. Added 50 ml liquid paraffin phase, and glutaraldehyde as the crosslinking agent. Added 1 g of chitosan to the acetic acid solution and stirred evenly, then added 25 ml chitosan solution, stirred for 30 min, then stirred for 4 h after adding 0.7 ml glutaraldehyde solution, adjusted the pH to 10 with 1 mol sodium hydroxide and reacted for 2 h, and then dried in an oven to obtain chitosan microspheres. The dried chitosan microspheres were placed in a tube furnace full of inert gas and carbonized for 3 h. The carbonized chitosan microspheres were mixed with KOH solution at mass ratio 2:1 of KOH to the material and the most active sites for ORR, in this study, chitosan microspheres were prepared by a one-step high-temperature roasting method. Studies have shown that using nitrogen-doped active materials could increase the electron transmission speed and thereby increase electrochemical performance.

Over the years, the electrochemical performance of chitosan has been widely studied. It has been found that chitosan is a potential carbon precursor material since it can easily be prepared and has high nitrogen content and good biological compatibility. It was used as a nitrogen-doped catalyst with high-performance [4]. Studies have shown that the catalytic activity of ORR and reusability of carbon catalysts were greatly improved by nitrogen-doping [18, 19]. For example, a low-cost Fe–N–C catalyst was synthesized by using iron trichloride and chitosan as precursors and carbonized by direct pyrolysis and its maximum power density of the air cathode in MFC increased 33% compared with the pure AC catalyst [20]. Using chitosan and chitosan oligosaccharides as high-grade carbon sources, a new type of nitrogen-doped carbon-coated Li2ZnTi3O8 anode active material were prepared by one-step high-temperature roasting method. Studies have shown that using nitrogen-doped active materials could increase the electron transmission speed and thereby increase electrochemical performance.

The carbon material made by chitosan doped with N and P had a larger power density, which was five times that of no doped material [22]. Feng Yi Zheng developed catalysts doped with N and P using shrimp shells as carbon precursors, which had activity stronger active sites for promoting ORR and higher electro-catalytic activity [23]. In addition, directly using chitosan as a carbon precursor was another optional method for preparing activated carbon, by which chitosan was dissolved in diluted acid and then hydrothermally carbonized at suitable temperatures [24]. Yi Liu investigated the influence of KOH content and calcination temperature on the activation of ORR and obtained a carbon catalyst of non-microsphere chitosan precursor with high surface area [25]. However, modification and application of chitosan microspheres as air cathode catalysts have been rarely reported. Since the morphology of microspheres has its specialty which provides the largest specific surface area and the most active sites for ORR, in this study, chitosan microspheres were prepared firstly, as carbon precursors carbonized by the reverse suspension crosslinking method and activated with KOH at calcination temperatures. Its structure and morphology was characterised with various microscopic analyses, including SEM, BET, Raman spectroscopy, XPS. Using three-electrode system, the effects of activation temperature of the material on electrochemical performance of an air cathode catalyst, such as internal resistance, alternating current density and power density, were investigated by LSV, Tafel and EIS measurement. Finally, the prepared electrodes were applied to MFCs to investigate its electrical performance.

2. Materials and method

2.1. Construction and start-up of microbial fuel cell

In this study, a dual-chamber MFC was composed of two rectangular parallelepipeds with a built-in 100 ml cylinder. The two chambers were separated by proton exchange membrane, and the distance between two electrodes was about 4 cm, connected by 0.5 mm titanium wire, generating external resistance of 1000 Ω. The anode was made of carbon felt. The anaerobic sludge in the anode chamber came from the anode effluent of MFCs whose voltage has been stable for more than one year. After the voltage kept stable, the nutrient solution was directly replaced and no anaerobic sludge was injected. When the voltage was less than 50 mV, replace with fresh nutrient solution. In order to stabilize the electrochemical activity of microorganisms, it was cultured in a thermostat at 30 °C for 3 months. The anode adopted a sequential batch operation mode, and an aeration pump was utilized to inject air into the cathode chamber to maintain aerobic conditions in the cathode chamber. Saturated Ag/AgCl electrode was used to measure the anode and cathode potentials when the MFC was open.

2.2. Catalyst synthesis and cathode preparation

Using chitosan as a raw material, a carbon catalyst was prepared by means of inverse suspension cross-linking. Firstly chitosan microspheres were prepared by using liquid paraffin as oil phase, chitosan solution as water phase, and glutaraldehyde as the crosslinking agent. Added 1 g of chitosan to the acetic acid solution and stirred magnetically until the solution became clear and transparent. Added 50 ml liquid paraffin and 5 ml span-80 in a three-necked flask, and stirred evenly, then added 25 ml chitosan solution, stirred for 30 min, then stirred for 4 h after adding 0.7 ml glutaraldehyde solution, adjusted the pH to 10 with 1 mol sodium hydroxide and reacted for 2 h, and then dried in an oven to obtain chitosan microspheres. The dried chitosan microspheres were placed in a tube furnace full of inert gas and carbonized for 3 h. The carbonized chitosan microspheres were mixed with KOH solution at mass ratio 2:1 of KOH to the material [25]. Finally, the material was calcined at different high temperatures to obtain the activated material. The material calcined at 350 °C but not activated with KOH was marked as CS-350 °C, while the materials prepared at different activation temperatures were denoted as AC-X,
where X means the temperature. The cathode was made by coating method. Dispersed the material uniformly in ethanol and mixed with polytetrafluoroethylene dispersion solution, and then coated it on the carbon felt, finally dried in an oven for 12 h to make an electrode.

2.3. Characteristics and morphology
The morphology of the materials was examined via scanning electron microscope (SEM). Before measurement, the material was polymerized in ethanol solution for 30 min to disperse, and dried at 45 °C in an oven. The element characteristics of the material surface were analyzed via x-ray photoelectron spectroscopy (XPS), and the binding energy ranged from 0 eV to 1350 eV. First, performed a quick scan, and simply identified the characteristic peaks with high energy and short residence time. High-resolution scanning was utilized to collect quantitative and chemical state information on the peaks with low energy and long residence time. The XPS PEAK software was used to perform the fitting analysis on the elements and peaks. Raman spectroscopy used 632.8 nm laser excitation in the spectral range of 100 to 4000 cm$^{-1}$. The specific surface area of the material was determined by the nitrogen adsorption-desorption isotherm (ASAP2460/Samsung 3000, Micronology). The total pore volume of the material was calculated from the amount of nitrogen adsorbed when the relative pressure $P/P_0$ was 0 to 0.99 [26].

2.4. Electrochemical characteristics
Injected fresh nutrient solution into MFC and kept it open for 6 h. All microbial cells were initially stabilized, and then the power density curve and the polarization curve of the MFC were measured. External resistance changed from 10000 Ω to 100 Ω, and the replacements of each resistance were retained for 15 to 20 min to ensure a stable voltage configuration. Plotted the voltage current density to get a polarization curve. Calculated the power density according to $P = UI/S$, and plotted the power density-current density to get the power density curve. In the experiment, the electrochemical performance of the prepared cathode catalyst was evaluated via a three-electrode system, using Ag/AgCl as the reference electrode. The platinum sheet was the counter electrode, and the prepared cathode was the working electrode. Before the test, nitrogen was fed into the catholyte for 20 min to remove oxygen. The scan rate of Linear Sweep Voltammetry (LSV) was 0.2 mV s$^{-1}$, and the range was from OCP to $-0.3$ V. The frequency range of the electrochemical impedance spectroscopy (EIS) of the air cathode was 100 kHz–0.1 Hz under open circuit conditions. The cyclic voltammetry curve ranged from $+0.4$ V to $-0.8$ V at a scan rate of 10 mV s$^{-1}$. The Tafel diagram was obtained by scanning the over potential from 0 mV to 100 mV at a scan rate 1 mV s$^{-1}$ [27]. All the cathodes were subject to the same conditions during the test.

3. Results and discussion
3.1. SEM characterizations
The chitosan microspheres prepared by inverse suspension crosslinking were carbonized at 350 °C, and then activated by KOH at higher calcination temperature. When the calcination temperature increased from 750 °C to 900 °C, the yield of the product decreased from 50% to 25%. The temperature was the key factor that determined the structural characteristics of the chitosan microspheres. SEM characterizations were performed to evaluate the morphology of the microspheres. Figure 1(a) showed the morphology of chitosan microspheres before carbonization and figure 1(b) after the activation by KOH at calcination temperature 850 °C. Shown in
figures 1 (a)–(b), the appearance of the microspheres before and after high temperature activation did not change significantly. The results of subsequent BET and Raman tests show that there are some changes in the interior structure of the microspheres. Compared with other microsphere materials such as CS/Fe₃O₄/Gelatin/GO particles, PSF/Fe₃O₄ particles, CI/Fe₃O₄/Gelatin/NT microspheres, the microspheres after activation in the experiment keep regular spherical shape and clear edges [28–30].
3.2. BET study

The surface characterizations of all materials were measured by the nitrogen adsorption-desorption isotherms at 77 K, since the number of active sites for ORR were directly related to specific surface area of the material. The nitrogen adsorption-desorption isotherms were shown in figure 2. All of the adsorption isotherms were Type IV, with H4 type hysteresis loop, which was formed from slit-shaped pores and had the characteristics of activated

| Materials                        | \( \text{S}_{\text{BET}} (\text{m}^2 \text{g}^{-1}) \) | References |
|----------------------------------|------------------------------------------------------|------------|
| Chitosan microsphere carbon      | 1561.85                                              | This work  |
| Alfalfa Leaf-Doped Carbon        | 883.67                                               | [35]       |
| Rapeseed meal- N and S-Doped     | 996.97                                               | [36]       |
| Silk gel-doped porous carbon     | 569.75                                               | [37]       |
| kapok fibres-Porous hollow carbon tube| 825.6                                               | [38]       |

| Materials | \( \frac{I_D}{I_G} \) value of the materials. |
|-----------|-----------------------------------------------|
| CS-350    | 0.72                                          |
| AC-750    | 0.98                                          |
| AC-800    | 0.96                                          |
| AC-850    | 0.92                                          |
| AC-900    | 0.75                                          |

![Figure 4. XPS survey scan of chitosan microspheres (a), C1s (b) and N1s (c) both activated at 850 °C.](image)

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literature, the oxygen functional group was an important factor in improving the performance of carbon [31]. Obviously, all materials, except AC-750 and AC-800, had hysteresis loops. The rapid increase in nitrogen absorption rate at lower relative pressure (P/P0 < 0.4) indicated the existence of micropores, while at higher relative pressure (P/P0 ≥ 0.4–1.0) the hysteresis loop indicated the existence of mesopores [32]. Therefore, AC-750 and AC-800 were typical microporous carbon materials. Table 1 showed the structural parameters of all materials obtained by the calculation of the adsorption isotherm data. It can also be seen that the specific surface area of the sample increased with the increase of the temperature but decreased at the temperature 900 °C. AC-850 had the highest specific surface area (1562 m²g⁻¹) and the largest volume of pores (0.70 cm³g⁻¹), indicating that KOH was an effective activator for the chitosan. The specific surface area (982.18 m²g⁻¹) of the nitrogen-phosphorus co-doped catalyst obtained by heat treatment and activation with phosphoric acid was lower than that of AC-850 [33]. The specific surface area of other materials used in electrodes was shown in table 2, being lower than that of this work. Although a high activation temperature was beneficial to the reaction between the material and KOH, the excessively high temperature lead to decrease specific surface area due to the evaporation [34]. Thus it was necessary to find a suitable temperature for preparing the material. In summary, the activation at a proper temperature was beneficial to the increase of specific surface area but on the contrary higher ones led to the reduction of the specific surface area.

3.3. Raman spectroscopy study
Raman spectroscopy was used to characterize the surface crystal structure of the materials, shown in figure 3 where two characteristic peaks located at 1350 cm⁻¹ (D band) and 1600 cm⁻¹ (G band) respectively for each spectrum. Generally, the intensity I_D of D band indicates the concentration of disordered carbon and the intensity I_G of G band the concentration of graphitized carbon [39, 40]. The ratio I_D/I_G can represent the degree of graphitization of the materials and estimate defects [41]. As showed in table 3, the ratio I_D/I_G of non-activated CS-350 was 0.72 which was the lowest among all the materials. After activation, it increased, indicating that the degree of graphitization of the material decreased. In contract, it decreased at the temperature 900 °C, indicating that the disorder of the material decreases, which was consistent with the results of others [42]. Electrochemical properties showed that activation decreased the graphitization degree, and increased some activation sites of carbon materials, improving the ORR properties [43].

3.4. XPS study
XPS analysis was performed to determine the elements presented in the materials and the oxidation state. A survey scan of the materials followed by the narrow scan of individual elements was conducted. Figure 4(a) represented the XPS survey scan, which indicated the presence of C, O and N. Table 4 listed the contents of C, O and N elements in all materials. Obviously, all materials contained still nitrogen due to the existence of –NH3 groups in the chitosan precursor. Meanwhile it can be seen from figure 4(a) and table 4 that the nitrogen content decreased with the increase of the activation temperature, which was consistent with the reports in the literature [44].
Furthermore, figure 4(a) showed that the characteristic peaks of C1s (285.0 eV) appeared strongly and those for N1s (400.0 eV) stepped down with the increase of the temperature, almost died away at 900 °C. This was because –NH2 gradually decomposed into elemental N and H during high temperature activation [42] and KOH activation attacked the edge nitrogen atoms between graphene layers in nitrogen-containing carbon materials [45].

Various atomic percentages were listed in table 5. The C1s XPS spectrum of AC-850 was decomposed into five kinds of carbon structures: sp² hybridized carbon (284.5 eV), sp³ hybridized carbon (285.0 eV), C–N band (286.2 eV), CO group (286.6 eV) and C=O group (288.1 eV) [44], shown in figure 4(b) and table 5. It can be seen that the sp²/sp³ ratio of CS-350 was the highest, indicating the highest degree of graphitization. After activation, the ratio continues to increase with the increase of the activation temperature, which was consistent with the results of the Raman examination. In the other hand, after KOH activation, the percentage of C–N decreases, but the percentage of oxygen-containing functional groups (C–O and C=O) increased significantly. According to reports in the literature, the oxygen functional group was an important factor in improving the performance of carbon.
the catalyst, which proved that the electrochemical activity of the carbon material can be improved by activation, consistent with the results of electrochemical tests [46].

The N1s XPS spectrum of AC-850 was shown in figure 4(c). N1s had four peaks: pyridine-N (N1) (398.3 ∼ 399.4 eV), pyrrole-N (N2) (400.2 ∼ 400.8 eV), graphite-N (N3) (401.1 ∼ 402.1 eV) and oxidation-N (N4) (403.3 ∼ 410.1 eV). A large number of studies have shown that pyridine-N (N1) and graphite-N (N3) help electron transfer to enhance catalytic activity [47, 48]. Nitrogen-doped carbon materials provide more active
sites and improve the catalytic activity of ORR. In this study, AC-850 had more pyridine-N (N1) and graphite-N (N3), and larger specific surface area and pore volume, leading to its better electrochemical performance.

3.5. Electrochemical studies

3.5.1. Linear sweep voltammetry (LSV)

The LSV curve was used to evaluate the influence of the temperature on the oxygen reduction performance, and shown in figure 5. In the key potential ranged from −0.1 V to 0.1 V, AC-850 sample had a wider potential window, the highest limiting current density of 3.3 mA cm$^{-2}$, and a higher starting potential. The higher the limiting current density, the faster the reduction rate of cathode oxygen [49]. When the scan was close to end, the maximum current density of AC-850 reached 1.1 mA cm$^{-2}$, which was higher than those of the materials activated at other temperatures. The results of LSV showed that proper activation temperature was of great significance for improving the electro-catalytic activity and AC-850 had the best electrochemical performance for ORR.

3.5.2. EIS

Electrochemical impedance spectroscopy (EIS) is an effective method to identify different resistances, by which the internal resistance of the electrode can be studied [50]. The Nyquist curves of the air cathode were illustrated in figure 6. The equivalent circuit is composed of external ohmic resistance ($R_{ohm}$), electrolyte diffusion resistance ($R_d$), and charge transfer resistance ($R_{ct}$) [51]. Since the same kind of MFCs was used, $R_{ohm}$ of all cathodes were almost the same. $R_{ct}$ could be obtained from the semicircle on the left side of the figure 6, which represents the charge transfer resistance at the electrode and electrolyte interface. Comparing $R_d$ shown in table 6 with BET data, it was found that $R_d$ decreased with the increase of the specific surface area. It can be seen from table 6 that the $R_d$ of the material activated by KOH at high temperature continuously decreases with the increase of temperature. A lower $R_d$ was conducive to the rapid transfer of electrons and made the ORR catalytic activity higher. In the chart, the total resistance ($R_t = R_{ohm} + R_d + R_{ct}$) of AC-850 was also the smallest (11.11 Ω), which was 5.19 Ω lower than AC. The $R_d$ of biochar using watermelon peel (49.18 Ω) as air cathode catalyst was much higher than that of AC-850 [14]. In short, activating carbon materials with KOH at high temperature can reduce the resistance of AC, thereby improving the performance of MFC.

| Materials | $R_{ohm}$ (Ω) | $R_d$ (Ω) | $R_{ct}$ (Ω) | $R_t$ (Ω) |
|-----------|---------------|----------|-------------|----------|
| AC        | 11.24         | 1.45     | 3.69        | 16.38    |
| AC-750    | 11.65         | 0.58     | 0.89        | 13.12    |
| AC-800    | 11.46         | 0.46     | 0.65        | 12.57    |
| AC-850    | 10.51         | 0.24     | 0.36        | 11.11    |
| AC-900    | 12.25         | 0.52     | 0.31        | 13.08    |

Figure 7. Tafel plots of Chitosan microspheres as air cathode catalysts at different activation temperatures.
3.5.3. Tafel

Figure 7 showed the Tafel diagrams obtained by fitting overpotentials from 80 mV to 100 mV for all materials and carbon felts. Exchange current density \((i_0)\) was a key parameter of ORR activity. Table 7 showed the \(i_0\) of all air cathodes. The \(i_0\) of AC-850 reached \(24.271 \times 10^{-4} \text{Ac m}^{-2}\), which was \(18.758 \times 10^{-4} \text{Ac m}^{-2}\) higher than carbon felt \(5.513 \times 10^{-4} \text{Ac m}^{-2}\). The higher the \(i_0\) value, the faster the transfer rate; the smaller the activation hindrance, the faster the reaction. Tafel analysis of all materials was consistent with the conclusions drawn from other electrochemical analyses. The material obtained by KOH high-temperature activation has higher ORR catalytic activity by using chitosan as the carbon precursor. Studies have found that the mesoporous structure facilitates ORR through the transport of oxygen, while the microporous structure provides active sites to promote the catalytic activity \([52]\). This was consistent with our research results.

![Figure 8. Power density and cell voltage curves (a) and polarization curve (b) of materials as air cathode catalysts.](image)

| Materials   | Fitting equation\(R^2\)  | \(i_0 \times 10^{-4} (\text{A cm}^{-2})\) |
|-------------|-------------------------|----------------------------------------|
| AC          | \(y = 2.0538x - 3.2586(0.991)\) | 5.513                                  |
| AC-750      | \(y = 0.6511x - 3.886(0.990)\) | 13.01                                  |
| AC-800      | \(y = 0.5714x - 3.7195(0.991)\) | 19.08                                  |
| AC-850      | \(y = 0.4628x - 2.6149(0.995)\) | 24.271                                 |
| AC-900      | \(y = 0.6068x - 2.7977(0.994)\) | 15.933                                 |

3.6. The performance of MFCs

In order to have a mature and stable potential, the polarization curve test was performed after the microbial fuel cell was stable for three cycles. Through the measurement of the polarization curve, the overall performance of the MFC cathode material was investigated and the carbon felt was used for comparative testing. Figure 8(a) showed the polarization curves and power density curve of MFC, and the polarization curves of all cathodes and anodes were shown in figure 8(b), where all anode curves showed the same trend, indicating that the anode resistance of MFCs was almost the same. The cathode curves had a certain deviation, indicating that the cathode was the main factor affecting the performance of MFCs. As the temperature increases, the power densities showed the same trend, but their values followed \(\text{AC-850} > \text{AC-800} > \text{AC-900} > \text{AC} > \text{AC-750}\). The voltage had the same reduction rate as the power density. It can be shown that an appropriate activation temperature could improve the electrochemical performance of AC. It can be seen from the figure 8(a) that the highest output power density of AC-850 electrode was \(1531 \pm 51 \text{mW m}^{-2}\), 140% higher than that of the carbon felt. Besides it
was higher than the maximum power density $892 \text{ mW m}^{-2}$ obtained by nitrogen and phosphorus co-doped carbon material [23] and $189 \text{ mW m}^{-2}$ by nanotube/chitosan composite cathode MFC [53]. The maximum power density of other materials was shown in Table 8, being lower than that of this work. This showed that the cathode materials prepared in this study has better electrochemical performance.

### 4. Conclusion

### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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