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Application of surface-modified carbon powder in microbial fuel cells

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ABSTRACT

The catalytic activity of surface-modified carbon powder, Vulcan XC-72R (XC), for the oxygen reduction reaction (ORR) at an air cathode in a microbial fuel cell (MFC) has been investigated. The effects of treatment with different chemicals such as nitric acid and ammonia on the chemical characteristics of XC were studied. The catalysts were characterized by Fourier transform infrared spectroscopy (FTIR), Boehm titration, and X-ray photoelectron spectroscopy. FTIR analysis showed that the functional groups of the materials were changed by chemical treatment, with nitric acid causing the introduction of oxygen-containing groups, and ammonia leading to the introduction of nitrogen-containing groups. Electrochemical measurements of MFCs containing various modified carbon materials as ORR catalysts were performed, and the results showed that chemically modified carbon materials are promising catalysts in MFCs.

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1. Introduction

In recent years, microbial fuel cells (MFCs) have attracted much attention as devices that can convert the chemical energy stored in organic or inorganic substrates to electrical energy [1–3]. MFCs could potentially be used in biomass-based energy production. However, the high cost of the materials used in MFCs, particularly the cathode catalyst, has hindered their commercial application. To date, platinum (Pt)-based catalysts have been widely used as cathode catalysts in laboratory-scale MFCs because of their high catalytic activity in the oxygen reduction reaction (ORR). However, Pt-based catalysts are rare

and expensive [4]; therefore, development of alternative materials with high catalytic activity in the ORR and sufficient chemical stability is of high priority. Much effort has focused on the development of inexpensive, non-noble metal electrocatalysts to replace Pt-based catalysts. For example, phthalocyanines and porphyrins have been examined as alternatives to Pt in MFCs [5]. Subsequently, metal oxides such as MnO₂ [6] and PbO₂ [7] and heterocyclic complexes such as iron (Fe) and cobalt (Co) heterocycles [8,9] have been reported to possess good catalytic activity for the ORR. In addition, manganese phthalocyanine [10], carbon-supported cobalt hydroxide [11], manganese oxides and polypyrrole[12,13] composites prepared by

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electropolymerization have been investigated as potential ORR catalysts. However, these catalysts are unsuitable for practical applications because of the poor electrocatalytic stability of phthalocyanines and transition metal macrocycles, as well as the toxicity of metal dioxides.

Carbon powder has been widely used in fuel cells [14] and could be an inexpensive alternative to noble metal catalysts. The presence of different heteroatoms (O, H, S, and N) bonded at the active sites of carbon particles accounts for the surface activity of carbon powder [15]. Recently, Yuan et al. [16] used a polypyrrole/carbon black (Ppy/C) composite as a catalyst for the ORR in an air-cathode MFC. They assumed that the carbon atoms in the N-heterocyclic (pyrrole) ring provided active sites for chemical adsorption of oxygen, which decreased the oxygen activation energy. Their results demonstrated that although the power output with the Ppy/C cathode was lower than that with a commercial Pt cathode, the power per unit cost of the Ppy/C cathode was about 15 times greater than that of the Pt cathode.

Recent studies have shown that surface modification is a useful way to improve catalytic activity. Duteanu et al. [17] found that the electrocatalytic activity of carbon powder treated with nitric acid for the ORR was considerably higher than that of the untreated powder. Moreover, the current density was higher than that of an untreated carbon-supported Pt cathode. Cheng et al. [18] found that treatment of a carbon cloth anode with ammonia gas substantially increased its surface charge (from 0.38 to 3.99 meq/m²), and the combined effects of ammonia treatment of the anode and phosphate treatment of the solution enhanced the power production by 48% compared with their previous results using an air-cathode MFC. In addition, the start-up time was reduced by 50%. Wang and coworkers [19] investigated the electrocatalytic activity of ammonia-treated ordered mesoporous carbon in the ORR, finding that their modified catalyst exhibited high electrocatalytic performance.

In this study, to further improve the power output and reduce the cost of MFCs, carbon-based Vulcan XC-72R (XC) catalysts were modified by treatment with nitric acid and ammonia. Treatment introduced both oxygen- and nitrogen-containing groups into the XC catalysts. The obtained catalysts were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Boehm titration. The electrocatalytic performance of the XC catalysts for the ORR in MFCs was also tested.

2. Experimental

2.1. Preparation of catalysts

XC (Cabot, USA) was heated under reflux in 30% nitric acid for 6 h at 98 °C. Then, the treated XC was filtered, washed with deionized water, and dried at 60 °C in a vacuum oven for 12 h. The obtained catalyst is denoted XC-N.

The XC-N catalyst was heated under reflux in 25% ammonia for 6 h at 60 °C. The catalyst was then filtered, washed, and dried. The obtained catalyst is denoted XC-NA. Untreated XC is denoted XC-U.

A 20%-XC-supported Pt catalyst (E-TEK, USA) was used for comparison purposes. It is denoted Pt/XC.

2.2. MFC configuration

An MFC with a single chamber was constructed with 75 cm³ (5 cm × 5 cm × 3 cm) polymethyl methacrylate, polyacrylonitrile-carbon (6 cm × 8 cm × 0.5 cm) and graphite felt as the anode catalyst. 20% Pt or an XC carbon powder (0.5 mg/cm²) was used as the cathode catalyst. The carbon base layer and cathode catalysts were coated onto the cathode carbon cloth by alternately spraying slurries (2.5 mg/mL, $V_{\text{ethanol}}:V_{\text{nafion}}:V_{\text{polytetrafluoroethylene}} = 8:1:1$) and drying at room temperature. Titanium wire was used as the cathode and anode leads. To reduce expense, the proton exchange membrane was replaced by an ion-exchange film purchased from Zhejiang Qianqiu Company, China, and was used to separate the anode and cathode. The acrylic plates, electrodes, and membrane were assembled with a silicon gasket to prevent leakage. A resistor (1000 Ω) was routinely used as the load resistor.

2.3. Enrichment and operation

The enrichment and adaptation of the electrochemically active bacteria in the MFC were performed in batches; activated sludge was obtained from the Yudai River, Panyu District, Guangzhou (Guangdong, China) for this purpose. Reactors were inoculated with activated sludge (12.5 mL) and glucose (1 g/L, 62.5 mL) culture media solution. The culture media solution contained KH₂PO₄ (13.6 g/L), NaOH (2.32 g/L), NH₄Cl (0.31 g/L), NaCl (1.0 g/L), and a mineral stock solution (12.5 mL/L) [20].

The single-chamber MFCs were operated at ambient temperature. Each experiment was performed in duplicate.

2.4. Analysis and calculation

The external circuit voltages (E) of the MFCs were measured by a data acquisition card (model ZP1001) from Guangzhou NXP Ltd, China. The power density (P) was measured by varying the external resistance in the MFC circuit from 30 to 80000 Ω. Parameters of the MFC were calculated using the formulae: $j = E/RA$, $P = E^2/RV$ and $E = U - Ir$, where U is the electromotive force (V), r is the battery internal resistance (Ω), R is the external resistance (Ω), A is the apparent area of the anode catalyst (cm²), V is the volume of the anode chamber, and I is the current (A). FTIR spectra of the carbon supports were collected on an infrared spectrometer (Tensor 27, Brooke, Germany). For XPS measurements, a high-resolution Kratos AXIS Ultra (DLD) X-ray photoelectron spectrometer with an Al (K_{α}) radiation probe was used.

2.5. Electrochemical measurements

To investigate the ORR activity of the different catalysts, linear sweep voltammetry (LSV) was performed with a rotating disk electrode (RDE, Pine Instruments, USA). A Pt wire and

saturated calomel electrode were used as the counter and reference electrode, respectively. Catalyst-coated glassy carbon (5.0-mm diameter) electrodes were used as the working electrodes. All electrochemical measurements were conducted with 50 mmol/L phosphate buffered saline (PBS) as an electrolyte.

3. Results and discussion

3.1. Effects of surface modification of the materials

FTIR spectra of the cathode materials are shown in Fig. 1. The intensity of the bands at 1750–1680 and 3600–3300 cm^{-1} , corresponding to oxygen-containing groups [21], increased markedly after treatment with nitric acid (Fig. 1(2)). According to the literature [21,22], oxygen-containing groups exist mainly in the form of carboxyl groups. Nitric acid treatment made the surface of the carbon material rich in both weakly and strongly acidic groups [22]. Therefore, when the XC-N catalyst was further treated with ammonia, hydrogen bonds formed between the acid groups on the XC surface and ammonia. Peak splitting was found in the bands at 1750–1680 and 3600–3300 cm^{-1} following treatment with ammonia (Fig. 1(1)). This is mainly attributed to the stretching vibration of N–H [23].

It is well known that oxygen-containing functional groups can enhance the ion-exchange capability of carbon. The total surface acidity and basicity of cathodic materials can be quantitatively measured by Boehm titration [24,25]. This classical method is the most popular approach for the chemical analysis (both qualitative and quantitative) of carbon surfaces. Figure 2 reveals that the nitric acid-treated carbon (XC-N) has the highest total surface acidity of the cathodes of 0.75 $\text{mmol L}^{-1} \text{g}^{-1}$; this sample also shows the lowest total surface basicity of $\sim 0.12 \text{ mmol L}^{-1} \text{g}^{-1}$. The total surface basicity of the XC-NA catalyst rose to 0.43 $\text{mmol L}^{-1} \text{g}^{-1}$, which is comparable to its surface acidity. This confirms that treatment with nitric acid can introduce oxygen-containing groups onto the surface of carbon, and that ammonia treatment can introduce nitrogen-containing groups [26]. This result is in accordance with those of FTIR analysis.

The carbon (C), nitrogen (N), and oxygen (O) contents of the different carbon materials used in this work were analyzed by XPS (Table 1). Combined treatment with nitric acid and ammonia increased the O and N contents from 1.05% and 0 to

Fig. 1. FTIR spectra of XC-NA (1), XC-N (2), and XC-U (3) catalysts.

Fig. 2. Total surface acidity and basicity of XCs determined by Boehm titration.

Table 1

Elemental composition of the XC-U, XC-N, and XC-NA catalysts obtained from XPS.

Sample	Element atomic fraction (%)		
	C	N	O
XC-U	98.95	0.0	1.05
XC-N	96.94	0.25	3.06
XC-NA	85.03	0.92	14.05

14.05% and 0.92%, respectively. This observation further confirms that treatment with nitric acid leads to the introduction of oxygen-containing function groups, and thus an increase of the oxygen (carboxylic acid group) content on the carbon surface. This increase in the superficial oxygen content is correlated with increased catalytic activity for the ORR [16,27].

Further differentiation between the types of all surface groups was obtained using XPS analysis, as shown in Fig. 3. The treatment method changed the number and kind of surface species. The XPS O 1s spectra of the XC-NA catalyst (Fig. 3(a)) contain peaks at around 531, 532–534, and 535 eV derived from C=O, quinone-type (O-1), and C–OH phenol groups and/or C–O–C ether groups (O-2) and chemisorbed oxygen COOH carboxylic groups) and/or water (O-3) [28]. Nitric acid treatment resulted in an increase of surface acidity because of an increase in the number of C=O species [29]. These are attributed to C=O of carboxylic groups, which are responsible for an increase in surface acidity, as demonstrated by wet titration data. Fig. 3(d) shows the N 1s spectra of the XC-NA catalyst, with binding energies located at 398.8 and 400 eV consistent with the pyridinic (N-6) and pyrrolic/pyridone (N-5) or nitrile groups, respectively. This further confirms that treatment with ammonia introduced nitrogen-containing groups onto the catalyst. It appears that ammonia treatment favored the formation of pyridinic (N-6) and pyrrolic/pyridone (N-5) groups [30]. No signal for N was detected from the XC-U catalyst, so the content of surface nitrogen in the catalyst was below the detection limit.

3.2. Performance of the MFCs with different cathodes

Figure 4 shows the relationship between voltage output and reaction time for the single-chamber MFCs equipped with XC-NA, XC-N, XC-U, and Pt/XC air-cathodes, respectively. The

Fig. 3. XPS O 1s spectra of XC-NA (a), XC-N (b), XC-U (c) and N 1s spectra of XC-NA (d).

Fig. 4. Relationship between voltage output and reaction time of different cathodes. (1) XC-NA; (2) XC-N; (3) XC-U; (4) Pt/XC.

stable voltage outputs of the MFCs with different cathodes were in the descending order Pt/XC > XC-NA > XC-N > XC-U. The fastest reaction time was demonstrated by the Pt/XC cathode (Fig. 4(4)). The catalyst treated with nitric acid and ammonia exhibited the second-best performance. The XC-U cathode had the lowest performance of the carbon cathodes. These results demonstrate that surface modification of XC improves not only the electrocatalytic activity but also the stability of the catalyst.

To further demonstrate the electrocatalytic capability of these catalysts for the ORR, their power output was examined in terms of the maximum power density (Fig. 5) and open-circuit voltage (OCV) of the MFCs (Table 2). The maximum power density was obtained from the MFC with the XC-NA cathode (1788 mW/m³). This value is lower than that obtained with Pt/XC (2525 mW/m³) and higher than that from the MFCs with XC-N and XC-U cathodes (1560 and 501 mW/m³, respectively). The internal resistance of the MFCs with different cathode catalysts decreased in the order XC-U > XC-N > XC-NA > Pt/XC. This indicates that surface modification can decrease the internal resistance of the MFC although the resistance is still higher than that of the MFC with the Pt/C catalyst. It is well known that OCV is an important indicator for MFCs because it shows its capacity for electricity generation.

The OCV values of the MFCs with different cathodes exhibited the order Pt/XC > XC-NA > XC-N > XC-U (Table 2). The superior electrocatalytic performance observed for XC-NA compared with the other carbon cathodes can be attributed to the incorporation of both oxygen- and nitrogen-containing groups into the XC structure increasing the content of electrocatalytically active groups. This result strongly suggests that XC-NA contributes to the power increase because of its catalytic activity for the ORR. Notably, the electrocatalytic performance of the XC-NA catalyst was only slightly improved compared with that of the XC-N catalyst. Thus, C=O groups may contribute more to the activity of the catalysts in the ORR than the N groups.

3.3. Catalytic activity of the catalysts in the ORR

In catalytic chemistry, treatment of carbon catalysts can markedly influence their performance. We used an RDE to study the ORR activity of the catalysts treated by different

Fig. 5. Power density versus current density curves for different cathodes. (1) XC-NA; (2) XC-N; (3) XC-U; (4) Pt/XC.

Table 2
OCV of MFCs with different cathodes.

Sample	Processing method	OCV (V)
XC-U	Untreated	0.26
XC-N	Nitric acid	0.52
XC-NA	Nitric acid-ammonia	0.60
Pt/XC	Untreated	0.68

Fig. 6. LSVs of XC-NA (1), XC-N (2), XC-U (3) and Pt/XC (4) catalysts for the ORR at a scan rate of 10 mV/s in 50 mmol/L PBS.

methods. Figure 6 shows the LSVs of different catalysts for the ORR at a scan rate of 10 mV/s in 50 mmol/L PBS. The onset potentials of the ORR on different catalysts exhibited the order Pt/XC > XC-NA > XC-N > XC-U. The Pt/XC catalyst showed the highest catalytic activity in the ORR of the catalysts investigated. Notably, surface treatment improved the catalytic activity of XC in the ORR. This could be related to the introduction of oxygen and nitrogen radicals supplying more active sites for oxygen chemical adsorption, which could weaken the O–O bond and lower the activation energy for reduction. Even though the XC-NA catalyst is less active than the Pt/C catalyst, it is more cost effective, which is an important advantage.

4. Conclusions

The aim of this study was to reduce the cost of the cathode in MFCs and improve its performance. We found that chemical treatment with nitric acid and ammonia modifies the surface and improves the electrocatalytic performance of carbon powder. Electrochemical analysis revealed that the XC-NA cathode catalyst exhibited the highest catalytic performance in the ORR (1788 mW/m³) of the investigated catalysts, following the reference Pt/XC catalyst. Such a chemically modified carbon material can act as a cheaper alternative to the Pt-based catalysts currently used in MFC cathode construction.

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Graphical Abstract

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Application of surface-modified carbon powder in microbial fuel cells

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The introduction of nitrogen- and oxygen-containing surface functional groups onto carbon catalysts improved their catalytic activity toward the oxygen reduction reaction in microbial fuel cells.

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表面改性炭材料在微生物燃料电池中的应用

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摘要: 研究了在空气阴极微生物燃料电池中修饰方法如硝酸处理和硝酸-氨水酸碱等对XC-72R作为阴极氧还原催化剂催化活性的影响, 并且使用傅里叶变换红外光谱(FTIR)、Boehm滴定法和X射线光电子能谱(谱(XPS))等手段对催化剂进行了表征. FTIR测试证明硝酸处理可引入含氧基团氨水处理可引入含氮基团. 另外, 还测试了含有不同表面官能团的XC-72R对氧还原的活性, 并将其作为阴极催化剂用在MFC中, 测试了电池性能. 实验表明, 经酸碱修饰的XC-72R作为空气阴极MFC的催化剂具有很好的应用前景.

关键词: 微生物燃料电池; 氧还原反应; 碳粉; Vulcan XC-72R碳黑; 表面改性; 产电性能

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