



Short communication

Stainless steel mesh supported nitrogen-doped carbon nanofibers for binder-free cathode in microbial fuel cells

Shuiliang Chen^a, Yu Chen^a, Guanghua He^a, Shuijian He^a, Uwe Schröder^b, Haoqing Hou^{a,*}^a Department of Chemistry and Chemical Engineering, Jiangxi Normal University, 330022 Nanchang, China^b Institute of Environmental and Sustainable Chemistry, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany

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ABSTRACT

In this communication, we report a binder-free oxygen reduction cathode for microbial fuel cells. The binder-free cathode is prepared by growth of nitrogen-doped carbon nanofibers (NCNFs) on stainless steel mesh (SSM) via simple pyrolysis of pyridine. The interaction force between NCNFs and SSM surface is very strong which is able to tolerate water flush. The NCNFs/SSM cathode shows high and stable electrocatalytic activity for oxygen reduction reaction, which is comparable to that of Pt/SSM and ferricyanide cathode. This study proposes a promising low-cost binder-free cathode for microbial fuel cells.

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1. Introduction

Microbial fuel cell (MFC) is a green energy conversion technology that possesses double functions of combining waste treatment and energy recovery. Nowadays, many efforts are put on the study of the performance and cost of MFCs and aim for large scale application. Cathode is one of crucial factors on the cost and performance of MFCs. Though ferricyanide ions have been widely used as oxidant in the cathode in lab scale and generated 50–80% higher power than that obtained with dissolving oxygen with Pt as catalyst in MFCs (Oh et al., 2004), they are not sustainable and have to be replenished regularly (Rabaey et al., 2005). Oxygen reduction reaction (ORR) is believed to be the most important cathodic reaction in fuel cell technology for power generation, as well as in MFCs. The usually used ORR catalyst for cathode in MFCs is Pt which is embedded in a porous carbon electrode, but their large-scale application is precluded by the high cost of the requisite noble metals. In recent years most efforts have been focused on the development of new inexpensive, non-noble metal electrocatalysts to replace Pt. Phthalocyanines and porphyrins are firstly examined as alternatives to Pt in MFCs (Zhao et al., 2005). Thereafter, other metal complexes and metal dioxides have also been considered, such as Fe-EDTA (Aelterman et al., 2009), MnO₂ (Zhang et al., 2009) and PbO₂ (Morris et al., 2007). However, the

long-term instability of the phthalocyanines and transition metal macrocycles and the toxicity of metal dioxides block their wide application.

Recently, a series of non-precious metal catalysts based on hetero atom have been demonstrated to show high rate ORR electrocatalytic activities which are comparable to that of Pt (Jaouen et al., 2011; Morozan et al., 2011), including conducting polymers (Winther-Jensen et al., 2008), nitrogen-doped carbon (Gong et al., 2009; Liu et al., 2010; Xiong et al., 2010) and carbon-metal-nitrogen compounds (Lefevre et al., 2009; Wu et al., 2011, 2010; Yang et al., 2008). They are believed to be the most potential catalysts for ORR in the future due to their low-cost and good stability. Moreover, nitrogen-doped carbon nanotubes have been used as the cathodic catalysts for ORR in MFCs and show high electrocatalytic activity (Feng et al., 2011). However, most of these ORR catalysts used in the cathode of fuel cell are in the form of powder, and need to be bound onto current collector by using polymer binders, e.g. Nafion or polyfluorotetraethylene, which always involve in a complex post-treatment. Moreover, care should be taken in order for the catalysts to be uniformly distributed and properly adhered to the substrate surface.

Herein, we reported a binder-free oxygen reduction cathode for MFCs for the first time. The binder-free cathode was prepared by growth of nitrogen-doped carbon nanofibers (NCNFs) on stainless steel mesh (SSM) via simple pyrolysis of pyridine. The NCNFs/SSM electrode was directly used as cathode in MFCs without using any binders. The electrocatalytic activities of NCNFs/SSM were tested and compared with that of Pt/SSM and ferricyanide cathode.

* Corresponding author. Tel.: +86 791 8120536; fax: +86 791 8120536.
E-mail address: haoqing@jxnu.edu.cn (H. Hou).

2. Experimental

2.1. Growth of CNFs and NCNFs on SSM

304 stainless steel mesh (SSM) (200 mesh) was treated in 1 M H_2SO_4 for 4 h, then was washed with distilled water and dried up. The growth of NCNFs onto SSM was conducted in a furnace with a quartz tube. SSM was heated to 850 °C for 30 min under N_2 atmosphere, then let the furnace cool down to about 750 °C and ejected pyridine into the tube with feeding rate of 0.1 ml min⁻¹ for 10 min by a solution pump, at last, let the furnace cool down to room temperature naturally. The flow of nitrogen was 100 cm³ min⁻¹. Similarly, the growth of nitrogen-free CNFs onto SSM was performed under the same condition by pyrolysis of toluene at 750 °C. The Pt/SSM electrode was prepared by electrochemically platinising SSM in a 4 mM H_2PtCl_6 solution by CV with scan range from -0.2 V to 0.4 V and scan rate of 100 mV s⁻¹.

2.2. Characterization

The morphology of samples was observed by a TESCAN VEGA-3 scanning electron microscope (SEM) and a Tecnai G² 20 transmission electron microscope (TEM). The Raman spectra were obtained from HORIBA JOBIN VON and the X-ray photoelectron spectrum was measured by PHI Quantera.

2.3. Electrochemical cell tests

All the NCNFs/SSM and Pt/SSM samples with size of 1 cm × 1 cm were connected with stainless steel wires and directly served as working electrodes. The projected area of SSM ($S_{\text{projected}}$) electrodes were calculated by subtracting the area of holes (S_{holes}) from the covered area (S_{covered}) of SSM,

$$S_{\text{projected}} = S_{\text{covered}} - S_{\text{holes}}$$

The S_{holes} and S_{covered} were calculated according to the SEM images of SSM. According to the SEM image of SSM, the diameter of stainless steel wire in mesh was 135 μm, the size of holes in SSM was about 255 μm × 300 μm. Thus, the projected area of SSM with size of 1 cm × 1 cm was about 0.55 cm².

All electrochemical experiments were carried out on a potentiostat (CHI660D) with three-electrode arrangement, consisting of a working electrode, a Pt foil counter electrode and an Ag/AgCl reference electrode (sat. KCl, 0.195 V vs. SHE). The stability testing of cathode towards ORR was performed by applying a potential of -0.35 V (vs. Ag/AgCl) on NCNFs/SSM and run more than 6 h under oxygen purge. All the electrochemical experiments were performed in 0.05 M sodium phosphate buffer solution (pH 7.0).

2.4. MFC tests

All fuel-cell experiments were carried out in batch mode using two-chamber cubic MFCs, each chamber had volume of 120 mL. The two chambers were separated by a CMI-7000 cation exchange membrane. The anode was graphite plate with size of 2 cm × 2.5 cm and two sides were available to solution. Secondary artificial wastewater with 10 mM sodium acetate as substrate served as medium in the anode chamber, which was similar as our previous report (Chen et al., 2011). The size of cathodes was 1 cm × 1 cm and both sides were available to contact with media. For testing the NCNFs/SSM and Pt/SSM cathodes, 0.05 M PBS buffer solution (pH 7.0) were used as catholyte under air and oxygen purge. For ferricyanide ion cathode, plain SSM was used as electrode and 0.1 M ferricyanide ions in 0.05 M PBS buffer solution (pH 7.0) was used as

media. All electrochemical and full-cell measurements were conducted at temperature of 25 ± 0.5 °C.

3. Results and discussion

3.1. Preparation and characteristics

Commercial SSM showed advantages of low-cost, environmental stability, high conductivity and easy to be connected. It had been proved to be an ideal catalyst support or current collector in the cathode of MFCs (Dumas et al., 2008; You et al., 2011; Zhang et al., 2010). The growth of carbon nanotubes (CNTs) (Karwa et al., 2006; Masarapu et al., 2009; Masarapu and Wei, 2007; Xuan Hoa et al., 2010) or carbon nanofibers (CNFs) (Nerushev et al., 2008) on SSM in the presence of external catalysts had been present in many reports. However, these CNTs or CNFs grown on SSM were not well fixed and easy to be removed. Because they were grown from foreign catalysts, CNTs or CNFs were floated onto surface of SSM. In the present case, SSM served both as catalyst and support for the growth of NCNFs via simple pyrolysis of pyridine. Fig. 1A shows a digital photo of SSMs with and without NCNFs. After growth of a layer of NCNFs, the SSM displayed a brown color. SEM images of NCNFs/SSM with different magnifications are shown in Fig. 1B and C. A layer of NCNFs was covered on the surface of SSM. High resolution image in Fig. 1C revealed that NCNFs displayed a very rough surface. The TEM image (Fig. 1D) confirmed that the NCNFs on SSM were solid but not hollow. The TEM image also revealed that the NCNFs were in semi-amorphous state part-ordered graphitic layer, and contained plenty of tiny particles. The Raman spectrum (Fig. S1) also showed that the amorphous carbon (1317 cm⁻¹) was the predominant element in NCNFs. The reasons for the formation of the amorphous state NCNFs with high rough surface needed to be further investigated.

The mechanical interaction between NCNFs and the surface of SSM was tested by flushing NCNFs/SSM with water. NCNFs were tightly fixed onto the surface of SSM without peeling or dissociating in water. SEM images of NCNFs/SSM after water flushing are shown in Fig. 1E. It confirmed that the NCNFs were still fixed on SSM. The tight fixation of NCNFs on SSM was probably because the NCNFs were grown from the internal catalysts in the SSM. The NCNFs were “planted” on the active sites of SSM and showed strong interaction between NCNFs and the substrate surface. The nitrogen element contained in NCNFs/SSM was confirmed by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 1F, and the ratio of nitrogen/carbon was about 7.66. Detailed investigation of N1s peak is shown in Fig. 1G. The N1s peak was fitted to two components of the binding energy (Fig. 1G), pyridine-like (398.6 eV) and pyrrolic-like (400.5 eV) which was consistent with Gong et al. (2009). The possible chemical structure of the N-doped carbon material is shown Fig. S2.

3.2. Electrochemical tests

The as-prepared NCNFs/SSM electrode was directly tested as cathode in MFCs without using any binders and additives. Electrodes of nitrogen-free CNFs/SSM prepared by pyrolysis of toluene (Fig. 1H) and Pt/SSM prepared by electrochemical deposition of Pt on SSM were also tested as cathodes for comparison. Fig. 2A describes linear scanning voltammetry (LSV) results of NCNFs/SSM, CNFs/SSM and Pt/SSM in neutral PBS under purging with oxygen and nitrogen. The LSV curves reveal that NCNFs/SSM display excellent electrocatalytic activity to ORR in neutral media, which is comparable to that of Pt/SSM. While the CNFs/SSM electrode which was free of nitrogen displays extremely low catalytic current under oxygen purging. It demonstrates that the nitrogen-atoms in NCNFs

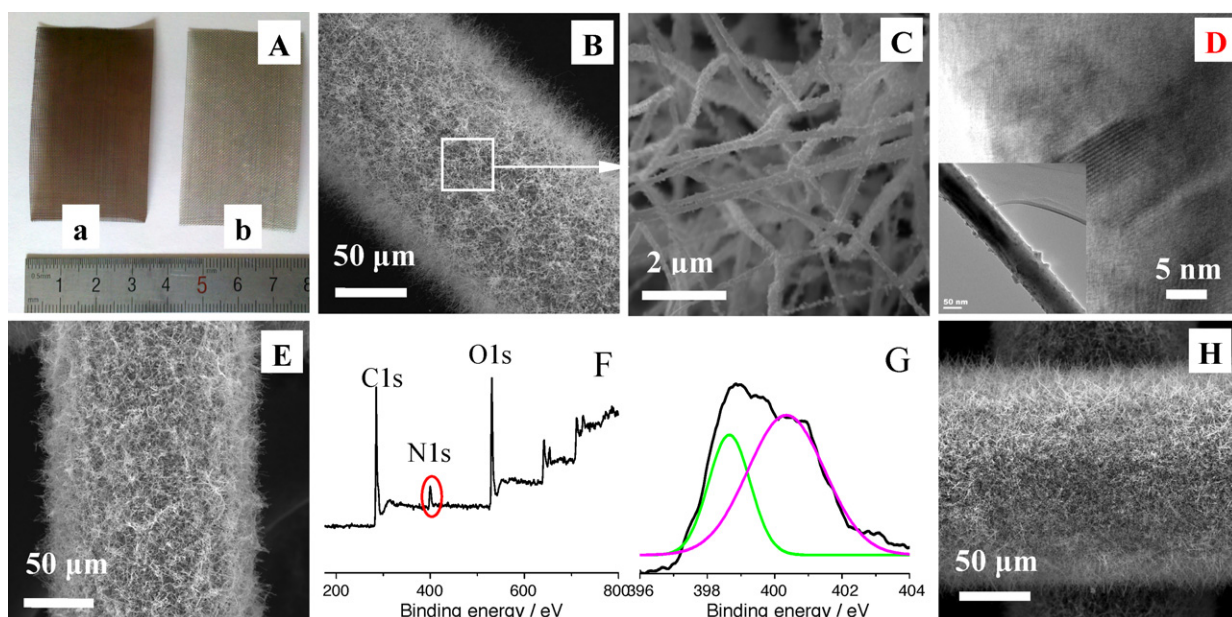


Fig. 1. (A) Digital photos of SSMs grown with (a) and without (b) NCNFs; (B and C) SEM images of NCNFs on SSM by pyrolysis of pyridine; (D) high resolution TEM image of NCNFs grown on SSM, inset was TEM image at low magnification; (E) SEM images of NCNFs on SSM after water flush; (F) XPS survey for NCNFs/SSM and (G) high-resolution N1s spectrum; (H) CNFs grown on SSM by pyrolysis of toluene.

play crucial for the high electrocatalytic activity of NCNFs/SSM to ORR. Moreover, it should be mentioned that the pyridine-N is a type of nitrogen that contributes to weaken the O–O bond and facilitate the reduction of oxygen (Feng et al., 2011). The percentage of pyridine-N in NCNFs is up to 34% according to the integral areas of peaks in Fig. 1G, is far higher than that in Feng et al. (2011). Higher percentage of pyridine-N leads to more active sites for facilitation of oxygen reduction, then result higher electrocatalytic activity towards oxygen reduction. Thus, the high electrocatalytic activity of NCNFs can be attributed to the high pyridine-N percentage.

It is well-known that the cathode durability plays crucial role in the development of MFCs. The stability of NCNFs/SSM towards ORR also was tested by chronoamperometry and shown in Fig. 2B. After about 6 h test, NCNFs/SSM still attained high electrocatalytic activity without any reduction. This result not only indicates the stable electrocatalytic activity of NCNFs but also confirms the strong inter-action between NCNFs and SSM.

3.3. MFC performance

The performances of NCNFs/SSM under air (NCNFs/SSM-air) and oxygen purge (NCNFs/SSM-O₂), were tested in a dual-chamber MFC and compared with the ferricyanide cathode by using SSM as electrode (SSM-Fe(CN)₆³⁻) and Pt/SSM purging with oxygen (Pt/SSM-O₂). The cell polarization curves and power density curves of different cathodes are shown in Fig. 3A and B. The maximum power generated from NCNFs/SSM cathode under the air purge was around 0.096 mW cm⁻². It was doubled under oxygen purging which was up to about 0.19 mW cm⁻² due to higher concentration of dissolving oxygen under oxygen purging than that under air purging. As shown in Fig. 3A, the NCNFs/SSM cathode had a low OCV of about 500 mV. The OCV depends on the nature of the ORR. Oxygen can be reduced to water (four electron reduction) or to hydrogen peroxide (2 electron reaction). The reduction potential to water was 1.229 V, to hydrogen peroxide was 0.695 V (against SHE) (Zhao et al., 2006). Thus, the lower OCV at NCNF might

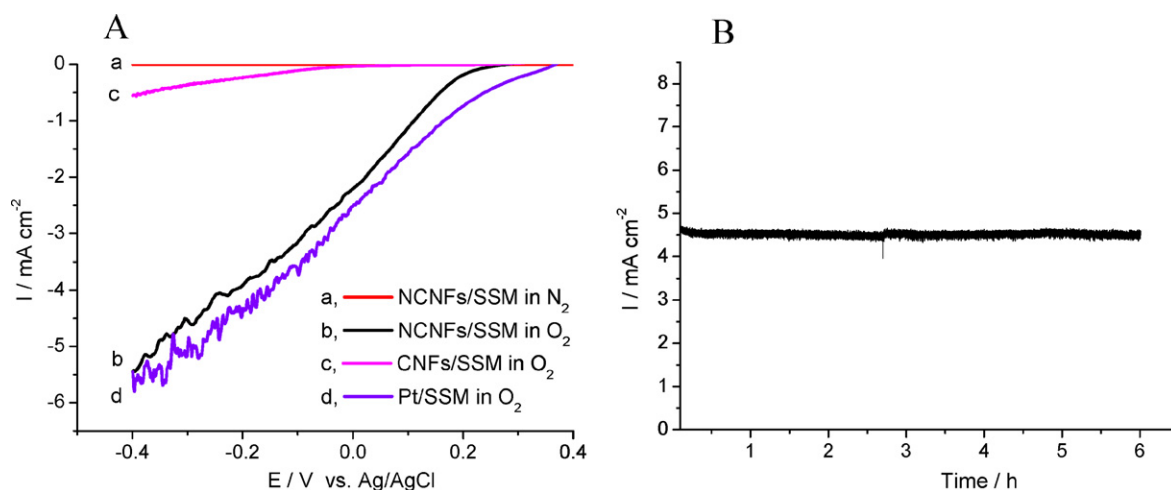


Fig. 2. (A) Linear sweep voltammetry of electrodes in phosphate buffer solution (pH 7.0) under oxygen purging. Scan rate: 10 mV s⁻¹, cell temperature: 25 °C. (B) Current–time (*I*–*T*) chronoamperometric response of SSM-P-750 at potential of –0.35 V (vs. Ag/AgCl) in O₂ saturated 0.05 M PBS (pH 7.0).

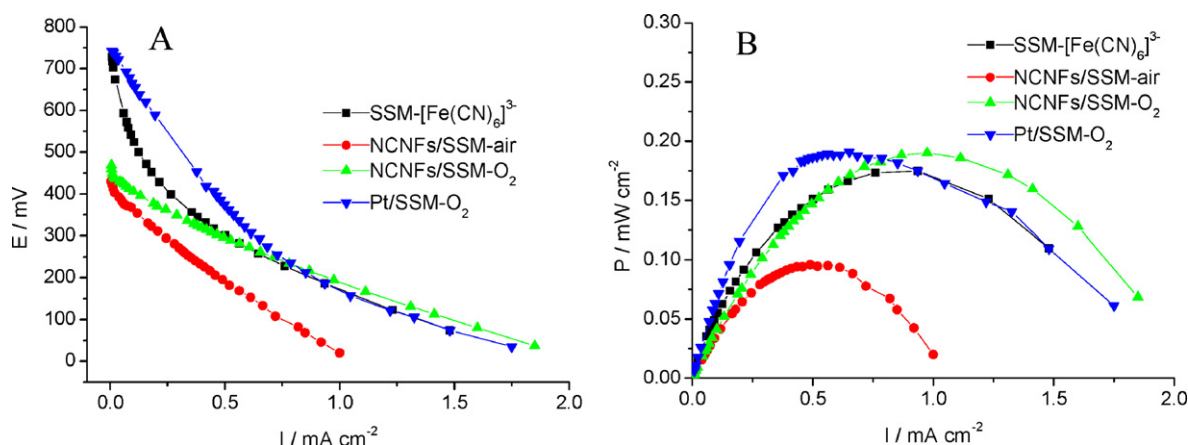


Fig. 3. (A) Polarization curves and (B) power density curves of MFCs using different cathodes.

indicate an oxygen reduction to hydrogen peroxide or led to a mixture of water and hydrogen peroxide. Another possibility would be the interaction with oxidizable material (Harnisch and Schroder, 2010; Harnisch et al., 2009), but this would require further investigation. Though the NCNFs/SSM cathode had a low OCV which was lower than that of ferricyanide and Pt/SSM cathode, it generated a high maximum power density, which was comparable to that generated by Pt/SSM cathode and even slightly higher than that by ferricyanide cathode. The possible reason might be due to the high surface area and high electrocatalytic activity of NCNFs on SSM, which generated high current density.

4. Conclusions

A binder-free cathode NCNFs/SSM was developed for MFCs and showed high electrocatalytic activity towards ORR. The NCNFs/SSM was prepared by growth of NCNFs onto SSM via simple pyrolysis of nitrogen-containing organic matters. The NCNFs/SSM cathode showed good properties of excellent conductivity, good flexibility and connectivity, high electrocatalytic activity. This study provided a promising method for preparation low-cost cathode for large-scale high performance MFCs. The mechanism for the growth of rough NCNFs on SSM and catalytic mechanism of NCNFs towards ORR require further investigation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2011.10.049.

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