Short Communication

Enhancement of power production with tartaric acid doped polyaniline nanowire network modified anode in microbial fuel cells

Zhi-Hong Liao 1, Jian-Zhong Sun 1, De-Zhen Sun, Rong-Wei Si, Yang-Chun Yong*

Biofuels Institute, School of the Environment, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, Jiangsu Province, China

HIGHLIGHTS

• A tartaric acid doped polyaniline network was applied for MFC anode modification.
• Significant improvement on MFC performance was obtained with this modification method.
• This organic acid doped polyaniline was superior to that doped with inorganic acids.

ARTICLE INFO

Article history:
Received 27 April 2015
Received in revised form 26 May 2015
Accepted 27 May 2015
Available online 10 June 2015

Keywords:
Microbial fuel cell
Shewanella
Extracellular electron transfer
Polyaniline
Organic acid

ABSTRACT

The feasibility to use tartaric acid doped PANI for MFC anode modification was determined. Uniform PANI nanowires doped with tartaric acid were synthesized and formed mesoporous networks on the carbon cloth surface. By using this tartaric acid doped PANI modified carbon cloth (PANI-TA) as the anode, the voltage output (435 ± 15 mV) and power output (490 ± 12 mW/m²) of MFC were enhanced by 1.6 times and 4.1 times compared to that of MFC with plain carbon cloth anode, respectively. Strikingly, the performance of PANI-TA MFC was superior to that of the MFCs with inorganic acids doped PANI modified anode. These results substantiated that tartaric acid is a promising PANI dopant for MFC anode modification, and provided new opportunity for MFC performance improvement.

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1. Introduction

Microbial fuel cells (MFC) are devices that directly converting chemical energy in organic matters/wastes/pollutants into electricity with the catalysis of microorganisms (Logan, 2009). It was considered as green energy source and energy-saving environment treatment process due to the integration of environmental bioremediation with energy generation (Li et al., 2014; Logan and Rabaey, 2012). The microorganisms for MFC are responsible for electron releasing from the organic matters and subsequently electron transportation to the solid electrode with different extracellular electron transfer (EET) pathways, e.g., nanoscale outer-membrane redox protein or pili (conductive nanowire) mediated contact-based direct electron transfer and molecular scale redox chemical (electron shuttle) mediated indirect electron transfer (Logan, 2009; Lovley, 2006; Yong et al., 2014). Thus, nanoscale interaction between cells and the electrode is vital to achieve efficient EET (Qiao et al., 2008, 2007; Yong et al., 2012; Zhao et al., 2015). However, lack of nanoscale interaction between cells and the electrode is the common drawback of conventional electrodes, which usually results in low power output and becomes the major bottleneck of the MFC.

In order to meet the requirement of the MFC performance improvement, various nanostructured materials have been developed for anode surface modification (Qiao et al., 2008, 2007; Yong et al., 2012). Among them, polyaniline is of great interest due to its low cost, simple synthesis process, excellent electrochemical activity and biocompatibility (Lai et al., 2011; Li et al., 2011; Yuan et al., 2013). The morphology and chemical properties of polyaniline can be easily tuned by varying the polymerization parameters (Chiou et al., 2007; Guo et al., 2011). In particularly, the electrochemical activity, nanostructure, and biocompatibility of PANI are largely varied when using different acids as the dopants (Li et al., 2011; Rajasekharan et al., 2013). H₂SO₄ and HCl are commonly used as the inorganic acids for PANI doping, and were successfully applied for MFC anode modification, which significantly improved MFC performance (Lai et al., 2011; Li et al., 2011). It was also reported that PANI doped with organic acids...
showed some unique advantages such as more uniform nanoscale structure and higher conductivity compared to inorganic acid doped PANI (Rajasekharan et al., 2013). But, organic acid doped PANI was seldom applied in MFC, and whether this type of PANI could promote power generation in MFC or not is still unclear.

In this work, tartaric acid, a typical organic acid dopant of PANI, was selected as the model acid to investigate the feasibility to use organic acid doped PANI as MFC anode modifier. In a dual chamber MFC, the power output obtained by this tartaric acid doped PANI modified carbon cloth anode (PANI-TA) was dramatically improved in comparison with the plain carbon cloth anode. More strikingly, it was also superior to inorganic acid doped PANIs. The results suggested that organic acid doped PANI is promising to be used as practical anode surface modifier for high performance MFC.

2. Methods

2.1. Electrode preparation and characterization

Carbon cloth with the dimension of 2 cm × 1 cm served as the control anode and matrix for polymer modification. Tartaric acid doped polyaniline (PANI) polymers were synthesized on the carbon cloth by rapid-mixture polymerization of aniline monomers under acid condition with ammonium persulfate (APS) as the catalyst (Guo et al., 2011). Undoped PANI was synthesized with similar procedure by mixing APS with aniline monomer solution without tartaric acid. In brief, the carbon cloth was immersed into 10 ml aniline solution (tartaric acid, 0.1 M; aniline monomer, 0.4 M) was added into the above solution and stirred for 10 min at ice bath. Then 10 ml (NH4)2S2O8 (APS, 0.4 M) solution was pre-cooled and slowly added into the aniline solution. The mixture was stirred for 24 h at 4 °C for polymerization. After that, the modified carbon cloth was washed with a large amount of water and dried at room temperature. The surface morphology of the electrodes was observed by field emission scanning electron microscopy (FESEM) (JEOL, JSM-7001F, Japan). PANI doped with HCl (Li et al., 2011) or H2SO4 (Lai et al., 2011) were synthesized according to the procedure reported elsewhere and used for comparison.

2.2. Bacteria culture

Shewanella oneidensis MR-1 was grown in Luria–Bertani (LB) broth (peptone 10 g/L, yeast extract 5 g/L, NaCl 5 g/L, pH 7.2) with shaking (150 rpm) at 30 °C for 16 h. The cell pellets were harvested by centrifugation. Subsequently, the cell pellets were resuspended in 30 ml electrolyte (M9 mineral medium with 5% LB) with 18 mM lactate (Yong et al., 2014). The cell suspension (with an optical density at 600 nm (OD600) of ~1.5) was transferred into the anodic chamber. Finally, the anodic chamber was purged with nitrogen gas and tightly sealed to maintain the anaerobic condition during MFC operation.

2.3. MFC set-up and electrochemical measurement

A dual chamber MFC (6 cm × 4 cm × 5 cm) separated with proton exchange membrane (nafion 117) was used in this work. Carbon cloth or PANI modified carbon cloth was used as the anode (2 cm × 1 cm), while plain carbon cloth with larger surface area was used as the cathode electrode (2 cm × 3 cm). The cell suspension in electrolyte was added into the anodic chamber, while the cathodic chamber was filled with 50 mM K3[Fe(CN)6] and KCl solution. The power output and polarization curves were obtained by varying the external resistor when the current output reached steady state (Qiao et al., 2008). The voltage output (V) across the external loaded resistor was monitored by digital multimeter. For electrochemical measurement, a saturated calomel electrode (SCE) was used as the reference electrode and a platinum wire electrode was used as the counter electrode. All electrochemical measurements are performed with CHI 660E electrochemical work station (Chen Hua Instrument Co. Ltd., Shanghai, China).

3. Results and discussion

3.1. Preparation, structural characterization and electrochemical behavior of PANI modified anode

Carbon cloth (CC), the most commonly used anode for MFC, was used as the supporting matrix for PANI modification and control electrode. CC is woven carbon microfibers with smooth surface (Fig. S1). By in situ polymerization, the tartaric acid doped PANI (PANI-TA) was synthesized on the surface of the carbon cloth and nearly covered the whole surface of the microfibers (Fig. S2). The uniform PANI nanowires with an average diameter of about 100 nm formed mesoporous and interconnected networks (Fig. S2b and S2c), suggesting good substrate diffusion which might be suitable for bioelectrochemical application.

The electrochemical activity of the PANI is largely depending on its molecular structure. Thus, the molecular structure of the PANI-TA nanowires was characterized by FTIR. The FTIR spectrum of PANI-TA nanowires contained typical peaks corresponding to polyaniline (Guo et al., 2011), indicating the success of PANI growth on the carbon cloth surface. The strong adsorptions attributed to the stretching vibrations of B−NH+=Q, B−NH−N, N−B−N, C−N in N=Q=N (Q, quinoid ring; B, benzenoid ring) were clearly observed (Fig. S2d). The relative adsorption intensities of B−NH+=Q and C−N in N=Q=N is an indicative of the extent of oxidation and protonation, respectively (Dias et al., 2006). The FTIR result shown here proved that the PANI-TA nanowire synthesized was in the protonated intermediate oxidation state, which is the conductive emeraldine salt form of PANI.

Cyclic voltammetry (CV) and electrochemical impedance spectrum (EIS) were used to characterize the electrochemical activity of the PANI-TA. The CV profiles of plain carbon cloth and PANI-TA were shown in Fig. 1a. In the PBS solution, carbon cloth electrode showed no obvious redox waves. For PANI-TA and undoped PANI, a pair of uniform redox waves was observed (Fig. 1a). The redox peaks are characteristic redox waves for PANI, which derived from the redox transition between its leucoemeraldine form and emeraldine form through proton insertion and deinsertion (Wang et al., 2013; Yong et al., 2012). Compared with undoped PANI, PANI-TA showed higher CV peak current and smaller cathodic/anodic peak separation (Fig. 1a), indicating tartaric acid doping significantly increased the electrochemical activity of PANI. The presence of this characteristic redox peaks indicated the electrochemical active PANI was successfully modified on the surface of the carbon cloth. The EIS Nyquist plot illustrates a preceding well-defined semicircle and a following straight line (Qiao et al., 2008). The diameter of the semicircle indicates the charge-transfer resistance. As shown in Fig. 1b, the semicircle of PANI-TA is smaller than that of plain CC, suggesting lower interfacial charge-transfer resistance (Rct) for PANI-TA. As estimated from the EIS profiles, the Rct for PANI-TA was 21 Ω, while it was 65 Ω for plain carbon cloth. Smaller Rct indicates a faster electron transfer rate (Qiao et al., 2008). The results suggested that the PANI-TA nanowire networks could significantly enhance the charge transfer rate, suggesting PANI-TA modification holds great potential to improve MFC performance.
3.2. Enhanced MFC performance by PANI-TA nanowires network

Although bulk PANI-TA was synthesized and had been applied in different fields (Guo et al., 2011), it has not yet been used in bioelectrochemical systems. Here, the feasibility for bioelectrochemical application of PANI-TA was evaluated in MFC, and the performance was compared with other kinds of PANI doped with inorganic acid. In accordance with other reports (Lai et al., 2011; Li et al., 2011), PANI modification significantly improved the MFC performance as evidenced by increased cell voltage output for all MFCs equipped with PANI modified electrode compared to the that with plain carbon cloth (Fig. 2a). The maximum cell voltage of the MFCs across a 2 kΩ loading resistor for PANI-TA is 435 ± 15 mV, which is about 1.6 times higher than that for the plain carbon cloth. More impressively, it is even much higher than the cell voltages obtained from the MFCs equipped with inorganic acid doped PANI modified anode, i.e., 47% higher than PANI-H2SO4 and 40% higher than PANI-HCl (Fig. 2a).

To estimate the maximum power output of the MFCs, the power output and polarization curves were obtained by varying the exterior loading resistor (Yong et al., 2014). In good accordance with the voltage outputs results (Fig. 2a), all MFCs with PANI modified anode delivered much higher power density outputs compared to that of the plain carbon cloth MFC (Fig. 2b). The maximum power output for PANI-TA MFC is 490 ± 12 mW/m², which is 4.1, 0.9, and 0.8 times higher than that obtained from carbon cloth, PANI-H2SO4, and PANI-HCl MFC, respectively.

The charge-transfer resistance of the MFCs, which directly reflects the electron transfer efficiency of the anode, was estimated from the polarization curves (Shen et al., 2014). As illustrated in Fig. 2c, three linear parts with different slopes could be discriminated for each polarization curve, in which the slope of the second part represents the charge-transfer resistance. As estimated from the polarization curves, the charge-transfer resistance of PANI-TA MFC was about 1.2 kΩ, which is about 4.3 times lower than that of the carbon cloth MFC (~6.4 kΩ). In accordance with the MFC performance, the charge-transfer resistance of PANI-TA MFC was also significantly lower than that of the PANI-HCl MFC (~1.9 kΩ) or PANI-H2SO4 MFC (~1.8 kΩ). The results indicated that
PANI-TA anode had much faster electron transfer rate than carbon cloth anode or inorganic acids doped PANI anodes, which might contribute to the improvement of power production.

4. Conclusion

In summary, a mesoporous and electrochemical active PANI nanowire network doped with tartaric acid was grown on the surface of carbon cloth, and successfully employed as the anode of MFC. A 4.1 times enhancement on MFC power density output was obtained by using this tartaric acid doped PANI modified anode. More interestingly, it is also superior to other inorganic acids (HCl, H2SO4) modified anodes. This finding not only proved that organic acid doped PANI could be used for MFC anode modification, but also provided new opportunity for MFC performance improvement as well as PANI application.

Acknowledgements

The authors sincerely acknowledge the financial support from Specialized Research Fund for the Doctoral Program of Higher Education (Ministry of Education, China, 20133227120014), Natural Science Foundation of Jiangsu Province (BK20130492), ‘Six Talent Peaks’ program (2012-NY-029, Jiangsu Province, China), recruitment program of global experts sponsored by Jiangsu provincial government, and a project funded by the Priority Program Development of Jiangsu Higher Education Institutions.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2015.05.105.

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