Brush-like polyaniline nanoarray modified anode for improvement of power output in microbial fuel cell

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\textbf{Highlights}

- A novel anode was fabricated by the pulsed voltage to form brush-like 3D structure.
- MFC was improved by using this brush-like PANI nanoarray modified material as anode.
- Structural factor was proved to be key for improvement of Brush-like PANI anode.

\textbf{Abstract}

Carbon cloth with brush-like polyaniline (BL-PANI) nanowire arrays generated on the surface was utilized as anode material in this study to improve the power output of MFCs. A novel pulsed voltage method was applied to fabricate BL-PANI with PANI nanowires of \textasciitilde 230 nm of length. By using BL-PANI modified carbon cloth as anode, the power output was improved by 58.1\% and 36.1\% compared to that of plain carbon cloth and PANI modified carbon cloth with ordinary structure, respectively. Electrochemical tests revealed that both electron transfer resistance and charge transfer resistance were decreased owing to high specific area for microbes’ growth and diffusion of charged species.

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\section{Introduction}

Microbial fuel cells (MFCs) process generating of clean energy by catalyzing oxidation of organic matters with assistance of microbes as a newly rising technology (Logan et al., 2006). Applications of MFCs involve such as denitrification, desalination, hydrogen production and biosensors (Cao et al., 2009; Clauwaert et al., 2007; Liu et al., 2005, 2004; Su et al., 2011). However, inefficient power production and high cost hinder MFCs from being more feasible and viable (Logan and Rabaey, 2012). Anode accounts for biofilm growth and current transfer between electricigens and external loads, which should be highly conductive and biocompatible with promising specific area (Reguera et al., 2005). In previous

http://dx.doi.org/10.1016/j.biortech.2017.02.124
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studies, chemical modification can significantly decrease anode impedance by decreasing ohmic resistance and promoting electron transfer based on highly conductive material and specific redox reaction. In which, metallic oxidation (Zhang et al., 2015) and graphene (Yong et al., 2012) have been widely applied. Besides, Structural factors significantly affect the specific area for the growth of biofilm to assure its high conductivity with appropriate thickness. Modifying anode with three-dimensional (3D) materials in nanoscale and microscale is also a feasible strategy to improve the surface participating in electron transfer and biofilm growth.

Carbon cloth is commonly used as anode material of MFCs, and its further treatment (Cheng and Logan, 2007) and chemical modification (Tsai et al., 2009) have been proved to dramatically improve the efficiency and power output of MFCs especially for carbon cloth modified with conductive polymers such as polyani-line (PANI) (Qiao et al., 2007) and polypyrrole (PPy) (Zou et al., 2008). PANI as a typical conducting polymer has been investigated for the improvement of MFCs due to its biocompatibility, conductivity and unique morphology with low cost for fabrication (Hou et al., 2013; Qiao et al., 2008). There are different forms of PANI with main chain containing benzenoid and quinonoid rings of variable ratio depending on the oxidation state in fabrication to obtain a suitable transfer potential to facilitate electron transfer from microbes to anode. Many quinone compounds are thought to be able to facilitate electron relay from microbes owing to prospered redox potential (von Canstein et al., 2008). Previous work has manifested PANI nanowire arrays viable as a solid-state mediator for extracellular electron transfer (Ding et al., 2012). Additionally, Morphology of PANI can be controlled in several nanostructures such as nanofibers (Wu et al., 2010), nanotubes (Wei et al., 2002) and nanosphere (Han et al., 2002) during fabrication which makes it accessible to design anode with higher specific area. Synthesis methods of PANI has been well investigated and reviewed, among which electropolymerization has been demonstrated to be more convenient and controllable (Cong et al., 2013).

In this work, a brush-like PANI (BL-PANI) nanoarray was generated by pulsed voltage method on carbon cloth and was used as anode material in dual chamber MFC to investigate the performance in comparison with that of PANI modified and unmodified carbon cloth anode. The performance of as-prepared anode was investigated in dual chamber MFCs comparing with PANI modified and unmodified carbon cloth. The improvement of power output is the evidence that highly oriented PANI nanoarray can prominently advance MFCs’ properties. In addition, the results and analyses of electrochemical traits demonstrated morphology a crucial factor to facilitate the diffusion of active matters.

2. Materials and methods

2.1. Materials and apparatus

Carbon cloth (CC, HCP332, Hesen Electric Corporation, Shanghai) was used as the base-material for the anode with pretreatment boiling in acetone (95%) at 80 °C for 2 h to remove possible residual resin and other impurities followed by washing with DI water for several times and cutting into pieces with a size of 2 cm × 2 cm. Aniline (Beijing Chemical Works, Beijing) was distilled under vacuum before used. Morphologies of materials mentioned above were inspected via a scanning electron microscope (SEM: Quanta 600, FEI) and FT-IR (Avatar360, USA) were applied to verify the existence of PANI. The cell voltages were monitored under vacuum before use. Morphologies of materials mentioned above were inspected via a scanning electron microscope (SEM: Quanta 600, FEI) and FT-IR (Avatar360, USA) were applied.

2.2. MFC Construction and setup

The dual chamber MFCs (Plexiglas) used in this work was separated into two parts by cation exchange membrane (CM17000, Membrane International Inc., U.S.) with a volume of 28 ml as anode chamber and 21 ml as cathode chamber. Cathodes made of carbon paper (HCP135, Hesen Corporation, China) with 0.5 mg/cm² dispersed platinum and anodes were connected by pure titanium wires inserted with external loads. Inoculation of the MFCs was operated with bacteria-enriched effluent from well-started MFCs feed with acetate which has been operated for more than 4 months in laboratory. Anolyte was prepared with mineral (12.5 mL/L), vitamin solution (5 mL/L) (Jia et al., 2013) and phosphate buffer solution containing following constituents (in grams per liter of DI water): Na₂HPO₄·12H₂O, 10.311; NaH₂PO₄·2H₂O, 3.312; NH₄Cl, 0.34; MgSO₄·7H₂O, 0.492; CaCl₂, 0.0113; KCl, 0.1; sodium acetate, 1.0. Whereas, catholyte contains 50 mM PBS and oxygen supply in the cathodes was processed by aeration. The MFCs were operated in a batch mode at 30 °C with 1 kΩ external resistors as loads and the anolyte was inoculated after voltage of reactor dropped below 30 mV.

2.3. BL-PANI-CC preparation

Highly oriented BL-PANI was directly generated on carbon cloth by electropolymerization in a three-electrode system consisting of working electrode (carbon cloth), counter electrode (Pt) and reference electrode (Ag/AgCl, sat. KCl). The electrolyte was composed of 0.1 M aniline monomer and 1 M HClO₄. The process was operated under a repeated pulsed voltage for 30 min with three steps: −0.1 V for 1 s, 0.4 V for 2 s and 0.8 V for 0.1 s, to make sure that all PANI nanowires growing on the surface of carbon cloth were highly oriented and homogenized avoiding agglomeration. The fabrication schematic of BL-PANI modified carbon cloth (BL-PANI-CC) is presented in Fig. S1. PANI modified carbon cloth (PANI-CC) was also prepared in the same three-electrode system under 0.8 V of constant voltage for 5 min to form ordinary morphology (Cong et al., 2013). Then, all the three anode materials were thoroughly rinsed with DI water and dried at room temperature.

2.4. Electrochemical measurements

Polarization curves were obtained by varying external resistor from 10 kΩ to 100 Ω and there took 10 min to stabilize the MFCs for each measurement steps. Current densities (I) was calculated by I(A/m²) = V/(R₁A_{anode}) and Power densities were calculated by P(W/m²) = I²/R₁A_{anode}, where R₁ stands for external resistor and A_{anode} was the area of anodes. Cyclic Voltammetry before biofilm growth was obtained in a three-electrode system consisting of working electrode (BL-PANI-CC, PANI-CC, CC), counter electrode (Pt) and reference electrode (Ag/AgCl, sat.KCl) ranging from −0.2 to 0.4 V (vs. Ag/AgCl) according to the range of outer membrane electron transfer (Liu et al., 2010) in a solution of 0.2 mM PBS (pH = 7.2) at a scan rate of 20 mV/s (Mano et al., 2007). And CV curves after biofilm growth were also obtained in a three-electrode system using cathode as counter electrode instead of Pt and reference electrode was fixed in the cathode.
3. Results and discussion

3.1. Characterization of BL-PANI-CC

The SEM images of PANI-CC and BL-PANI-CC are shown as Fig. S2. As shown in the images, PANI generated by constant voltage was in a shape of clew-like network while brush-like PANI could be generated by pulsed voltage. In pulsed voltage methods, the process of PANI growth was divided into three steps including resting potential at $-0.1 \text{ V}$, diffusion-adsorption potential at $0.4 \text{ V}$ and oxidation potential at $0.8 \text{ V}$ to gain a highly oriented PANI nanowires array uniformly.

Furthermore, as-prepared BL-PANI-CC and PANI-CC were tested by FT-IR which proved the existence of PANI on carbon cloth containing quinoid ring (Q) and benzenoid ring (B). As shown in Fig. S3, several typical absorption at $1113 \text{ cm}^{-1}$ indicating the stretching vibrations of $\text{C}−\text{N}$ in $\text{B}−\text{NH}^{+}−\text{Q}$ (Mishra and Ramaprabhu, 2011) and $1165 \text{ cm}^{-1}$ corresponding to $\text{B}−\text{NH}−\text{B}$ (Cochet et al., 2000) presents. Besides the strong absorption at $1453 \text{ cm}^{-1}$ which proved the existence of $\text{C}−\text{N}$ in $\text{Q}−\text{N}−\text{Q}$, small peaks ranging from $1453 \text{ cm}^{-1}$ to $1259 \text{ cm}^{-1}$ were associated with linear deformation of $\text{C}−\text{N}^{+}$ and the absorption at $1060 \text{ cm}^{-1}$ was associated with doping process (Cochet et al., 2000). Absorptions of groups related to quinoid rings and benzenoid rings could be clearly observed at $1546 \text{ cm}^{-1}$ and $1631 \text{ cm}^{-1}$ which indicated that both BL-PANI and PANI were in conductive emeraldine salt form of structure (Dias et al., 2006).
Results of Cyclic voltammetry tests are shown as Fig. 1. A pair of redox peaks could be observed for BL-PANI-CC and PANI-CC except unmodified CC without biofilm growth in PBS buffer (pH 7.2) at scan rate of 20 mV/s, which was as a result of transition between PANI of oxidized form and reduced form. Comparing curves of BL-PANI and PANI, peak currents showed no obvious difference which indicated that the property of both materials as solid-state mediator was not account for remarkable enhancement. While the range of redox showed different capacitance of BL-PANI and PANI modified anode corresponding to higher specific area. Cyclic Voltammetry of whole cells was obtained to figure out dynamic electron transfer properties after biofilm growth. As shown in Fig. 1b, the curves demonstrate higher current at the same potential assisted by PANI compared with plain carbon cloth. Furthermore, BL-PANI shows transcendent property in charge transfer.

3.2. BL-PANI modified anode in MFCs

Modifications of PANI on anode of MFCs have been proved feasible for power output enhancement. Herein, a novel method for structure control of nanowire growth was practiced with its feasibility evaluated in MFCs as an application in bioelectrical system. Output of cell voltage with 1 kΩ external resistor for all MFCs has been improved by modifying BL-PANI on carbon cloth compared to ordinary PANI modified carbon cloth and plain carbon cloth (Fig. 2). In the start-up period, MFC with BL-PANI-CC anode used less cycles of operation to achieve stable output compared to PANI-CC and plain CC anode. In the first circle, output voltage of MFC with BL-PANI–CC anode remarkably increased as a result of BL-PANI with higher specific area in nanoscale for microbes’ growth and with proper redox potential to facilitate the metabolism of electricigen.

According to the polarization curves derived from stable MFCs (Fig. 2c), the maximum output of MFCs with BL-PANI modified anode is 567.2 mW/m² which is 36.1% and 58.1% higher than that of ordinary PANI-CC and unmodified CC. To estimate internal resistance resulted by charge transfer of charged species at working condition, the second section of polarization curves were linearly fitted. The dynamic internal resistance of BL-PANI modified MFC was about 317.3 Ω which was about 12.1% and 20.6% lower than that of PANI and plain carbon cloth. This could be explained as decrease of mass transfer resistance and facilitation of electron transfer.

3.3. Electrochemical impedance spectra studies

To figure out the constitution of inner resistance, EIS was obtained and an equivalent circuit (Fig. 3a) was used to fit the EIS data points. In the equivalent circuit, Rs stands for resistance of solution including anode solution, cathode solution and CEM. Rct and Ract stand for resistance of charge transfer at cathodes and anodes. Q stands for diffusion element and a constant-phase element (CPE) stands for electrical double layer resulting from accumulation of electrolyte near the surface of electrodes. Rs which stands for resistance of bulk solution and electrodes showed no obvious difference among MFCs in this work, while resistance of charge transfer part was drastically decreased for BL-PANI-CC compared to PANI-CC and plain CC according to the results from parameters fitting EIS data (Fig. 3b). The Ract of BL-PANI-CC was 17.4 Ω which is 58.8% and 70.1% lower than that of PANI-CC and unmodified CC which demonstrated that electron transfer between electricigen and electrode was faster at BL-PANI modified anode and charge diffusion was facilitated at the same time. The results of cathodes were quite in accordance with anodes which was due to the synergistic effect of charge transfer between anode and cathode chamber and indicated a limitation that specific area of PANI-CC and CC did not fit that of cathodes.

4. Conclusions

In this work, brush-like PANI modified anode has been studied and proved to be a promising strategy to improve power output of MFCs. High specific area and capacitive behavior caused by special morphology contributed to higher power output compared with ordinary PANI modified or plain carbon cloth. The maximum power density of MFC with BL-PANI modified anode reached 567.2 mW/m² which is 36.1% and 58.1% higher than that of ordinary PANI modified and unmodified carbon cloth. High specific area, charge transfer, good-enough redox potential are key factors. This might provide an example for further innovations for the bioanode fabrication of MFCs.

Acknowledgements

This work was supported by the International Science & Technology Cooperation Program from the Ministry of Science and Technology of China (2013DFR60250).
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.2017.02.124.

References


