Preparation and Performance of PEDOT-based Modified Composite as Anode for Anaerobic Fluidized Bed Microbial Fuel Cell

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Abstract. Poly(3,4-ethylenedioxythiophene)/multi-walled carbon nanotubes (PEDOT/MWCNTs) synthesis was manufactured by modifying graphite rod via cyclic voltammetry, and the electrocatalytic performance of the obtained PEDOT/MWCNTs was used as the anode in anaerobic fluidized bed microbial fuel cell (AFBMFC). The electrochemical behaviors of the modified anodes were investigated through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The obtained anode display superior electrocatalytic representation with an output power density of 217 mW·m⁻², which was 30% superior than modified anode by PEDOT. Due to the good mass transfer effect of the fluidized bed, COD removal rate of wastewater in the AFBMFC with PEDOT/MWCNTs as anode reached more than 90% after operating for six-day.

Keyword: Anode, Poly(3,4-Ethylenedioxythiophene)/Multi-Walled Carbon Nanotubes, Anaerobic Fluidized Bed Microbial Fuel Cell

1. Introduction
A microbial fuel cell (MFC) is an electrochemical device that be able to straightly exchange the chemical energy into electricity by means of microorganisms act as biocatalysts[1]. Currently, MFC is regarded as a foregrounding bio-electrochemical power source toward straightly retrieving electric power from carbohydrates and organic in wastewater[2]. Nevertheless, the MFC has the lower power, which impede its realistic application.

The anode is a critical component of MFC, which has significant impact on the MFC’s performance. The microstructure of the anode material have straightly influence on bacteria adherence, electron transfer and substrate oxidation. Therefore, there is a great need to modify the structure of anode materials and exploit an excellent style of anode material for MFCs.

Conductive polymers (CPs) have exhibited very promising application prospects because of their excellent performance in the electronic, energy, biological fields [3]. Recently, CPs/CNTs composite have geted major interest due to the combination of CNTs in conducting polymers can cause novel
compound materials occupying the characteristics of every element through a synergistic effect. The study about the application of conductive polymer composites modified anode in improving MFC electricity generation performance has made some achievements. Roh, et al. also studied the same compositeto modify carbon cloth anode for MFC, receiving the battery maximum output power of 480mW·m\(^{-2}\). Therefore, it can be seen that conductive polymer/CNTs composites can enhance the electrochemical activity of electrode and improve the electrons transfer betweenmicro-organism and anode, leading to an increase in the electric power produce performance of MFC, so it is of significance to develop conductive composites materials for the MFC[4].

In this study, modified graphite rod anodes with PEDOT/MWCNTs composite was prepared by cyclic voltammetry (CV), which was a more simple technology of modifying electrode than other physical or chemical methods. During preparing modified anode, this method avoided using any catalysts and toxic reagents, thus the modified anodes were more suitable for microorganism attachment and growth. The modified anodes could efficiently enhance the electrons transfer betweenmicro-organism and anode, and improved electricity generation performance of MFC. We succeeded in realizing the running of multi-electrode fluidized bed MFC, and found that the obtained anode could improve the stability of electricity generation. On condition that mass transfer reinforcement relying on liquid-solid fluidized bed, high sewage treatment capacity and short sewage treatment cycle were achieved on this obtained anodes.

2. Materials and Methods

2.1 Composite Anode Synthesis

The composite anode was prepared via cyclic voltammetry (CV), which was implemented in a conventional three-electrode system linked to CS310 electrochemical workstation (Corrtest Instruments Co., Wuhan, China). In the three-electrode system, a saturated calomel reference electrode (SCE) was used to a reference electrode, a platinum wire as a counter electrode, and as-prepared as a working electrode. for the working electrode, the graphite rod electrode was carefully polished, rinsed with 0.5 mol·L\(^{-1}\) H\(_2\)SO\(_4\) solutions as well as ethanol and water in the condition of ultrasonication. Then it was activated in the 0.5 mol·L\(^{-1}\) H\(_2\)SO\(_4\) solvent through CV scanning. PEDOT/MWCNTs composites-modified graphite rod electrode was manufactured via cyclic voltammetry from -0.8 V to 1.3 V by the scan ratio 0.05 V/s for twenty-four circles in a solvent containing 0.01 M EDOT monomer, wt.% purified MWCNTs and 0.1M K\(_2\)SO\(_4\) supporting electrolyte. The obtained electrode was cleaned through distilled water to get rid of any non-adsorbed species and then placed in a vacuum oven to be dried. For the sake of comparison, a PEDOT modified electrode was prepared under the same conditions.

2.2 Assembling and Operating MFC

The MFC device was an anaerobic fluidized bed microbial fuel cell (AFBMFC), which combined technology of fluidized bed with MFC. Such a design could strengthen mass transfer while increase the facial charge of the electrode (supplement of activated carbon in the anode chamber). This AFBMFC with the loftily ratio dealings with waste-water could be more easily scaled up than other single chamber MFC. In AFBMFC, the wastewater in the tank was pumped to the anode-chamber. After staying in the chamber for the moment, the wastewater flowed back to the wastewater tank again via an overflow tube. At anode-chamber, the bacteria grown on the anode and active carbon particles could oxide organic molecules and liberate electrons to the anode and protons to solvent. The two electrodes are linked through a wire with a resistor load; thus the electrons could transfer to the cathode from anode. At the same time, the protons diffuse to the cathode through solution, and oxygen in the air also reaches the cathode catalyst layer. In presence of cathode catalyst, oxygen is reduced by accepting electrons, then unites with proton to form water. The generated electricity was recorded by continuous data acquisition, and the change of voltage could also be monitored by the computer.
2.3 Incubating and Conditioning MFC
The MFC was hatched accompanied by anaerobic sludge acquired from anaerobic digester of Qingdao Wastewater Treatment Plant (China). The sucrose solution (1.0 g·L⁻¹) was used as fuel to imitate the wastewater and incubated in a phosphate buffer solution (K₂HPO₄ 1.3 g·L⁻¹, KH₂PO₄ 0.42 g·L⁻¹, NH₄Cl 0.23 g·L⁻¹, CaCl₂ 0.123 g·L⁻¹, KCl 0.33 g·L⁻¹, NaCl 0.31 g·L⁻¹, MgCl₂ 0.315 g·L⁻¹, yeast extract 1.0 g·L⁻¹). The imitated wastewater was acted as the fluidizing liquid driven via a peristaltic pump. During measurement, the provender solvent was replaced when the chemical oxygen demand (COD) of solution was less than 100 mg·L⁻¹, meaning one whole period of operation. AFBMFC tests were commonly implemented at 30 °C.

2.4 Analytical Measurements and Calculations
The electrochemical performance of revised anodes with or without MWCNTs was investigated by cyclic voltammetry (CV) in 0.001 mol·L⁻¹ ferroprussiate solution (0.1 mol·L⁻¹ KCl, PBS of pH=7.0). Field emission scanning electron microscopy (FESEM) was used to portray the appearance morphology and intersect part construction of PEDOT/MWCNTs composite anode. Electrochemical impedance spectroscopy (EIS) measurements for the PEDOT and PEDOT/MWCNTs composite electrodes were performed over a frequency range of 0.5Hz to 100KHz in 0.1M phosphate buffer solution (pH=7) at open-circuit potential and a perturbation signal of 10 mV.

Cell voltages were monitored by a data acquisition system (PDM1608FS, American measurement) connected to a personal computer. Current (I) was calculated according to I = U/Rex, where U is the voltage and Rex is the external resistance. Power density (P) was calculated according to P = U/I, where A is the surface area of the cathode. Polarization curves were generated by varying outside obstruction ranges from 30 to 90,000 Ω in a resistor case.

Chemical oxygen demand (COD) of sewage was measured using standard methods [6]. Chemical oxygen demand removal rate (ΔCOD) (percent) was calculated by the following equation:

\[ \Delta \text{COD} = \frac{\text{COD}_{\text{in}} - \text{COD}_{\text{out}}}{\text{COD}_{\text{in}}} \times 100\% \]

where \( \text{COD}_{\text{in}} \) and \( \text{COD}_{\text{out}} \) are the initial and final measured COD respectively.

3. Results and Discussion

3.1 Morphology Characterization
Field emission scanning electron microscopy (FESEM) was used as investigate appearance and transversal profile of PEDOT/MWCNTs compound (shown in Fig.1). Fig.1A shows that PEDOT/MWCNTs composite has mushroom-fungus-like morphology. Polymer is polymerized with MWCNTs as its "core" when MWCNTs is regarded as a doping agent. The microstructure of cross-section of composite electrode (Fig.1B) shows that film thickness is about 1.5µm. As shown in Fig.1B, some of MWCNTs were doped into the membrane, coating in the PEDOT polymer. Some of MWCNTs grew on the surface of the membrane. Therefore, PEDOT/MWCNTs composite anode prepared by cyclic voltammetry possesses good electrical conductivity and special surface structure, and the carbon nanotubes concerning appearance of membrane offer more energetic places for attaching of microorganism[5].
3.2 Cyclic Voltammogram Analysis

Cyclic voltammograms measurement was carried out to study the electrochemical performance of PEDOT/MWCNTs composite electrode, PEDOT modified electrode and plain electrode in the 0.001M [Fe(CN)6]3/4- solution (0.1 M KCl, PBS of pH=7.0) with the scan rate 0.05 V/s.

The results calculated from the CVs show the charge capacity through the composite electrode modified by PEDOT/MWCNTs is up to 0.182 C·cm⁻², that is 4.1 times superior than which of PEDOT modified electrodes (0.0443 C·cm⁻²), and 150.4 times higher than which of plain electrodes (0.00121 C·cm⁻²). The consequent indicates that the compound anode heightens the electrode conductivity. The electrons transfer from MWCNTs to PEDOT through this π-π system, which can prolong the effective conjugated chain of PEDOT and improve the conductivity of the composites. Therefore, the adding of MWCNTs improves the electrochemical activity and conductivity of the composite electrode to a certain extent.

3.3 Electrochemical Impedance Spectra Studies

The surface behavior of the electrode was characterized using electrochemical impedance spectroscopy (EIS). Impedance measurements were executed in 0.1M phosphate buffer solvent (pH=7) among a rate of recurrence range from 105 to 0.005 Hz with sinusoidal perturbation of 10mV vibration amplitude. Nyquist impedance spectroscopy as well as equivalent circuit used to fit the EIS were shown in Fig.3. The circuit contains of the solution resistance (Rsol), double layer capacitance of electrode solution interface(Cdl), charge-transfer resistance(Rct) and weber impedance through a barrier layer during charge-diffusion (W).
The measured EIS results show that the semicircle over high frequency is not obvious, followed by a straight line of 45 degrees in the low-frequency region. The results illustrated the electrode chemical reaction was restrained via the spreading process. About intersection on straight line and x-axis represents the sum of solution resistance ($R_{sol}$) and charge transfer resistance ($R_{ct}$), which is called Faraday resistance. The Faraday resistances of modified electrodes are $9.51 \, \Omega$ (PEDOT/MWCNTs) and $24.15 \, \Omega$ (PEDOT) respectively. Obviously, the insistence of composite anode is much lower than that of PEDOT anode. So the special surface effect of composite anode provides more accesses for charge transfer, and believe that MWCNTs have an visible melioration effect for a quicker charge transfer ratio than with PEDOT.

3.4 Power Production of MFC

The results of polarization and power density curves of MFC with different modified anodes are showed in Fig.4. The polarization curve demonstrates the cell voltage of PEDOT/MWCNTs MFC reaches 837.8mV, which is higher than PEDOT(754.0mV) and unmodified anodes(552.8mV). The map of power density versus current has a volcano shape. Highest-level power density of composite anode MFC is 217.0 mW·m$^{-2}$, which is 30% superior than that the revised anode by PEDOT. The PEDOT/MWCNTs anode has superior electrocatalytic activity, which contributes to improving the electricity generation performance of MFC.

3.5 Sewage Treatment efficiency of AFBMFC
Fig. 5. Change of COD and COD removal rate of MFC with PEDOT/MWCNTs electrodes in the operation cycle

The result of sewage treatment efficiency of AFBMFC with PEDOT/MWCNTs electrodes is shown in Fig. 5. By means of better mass transfer effect of the fluidized bed, COD value of sewage decreases with an increase in running time. COD removal rate reaches more than 90% on the seventh day when the nutrition matrix in the solution is almost used up. Thereafter, COD value decreases to a small degree because of the slower growth and metabolism of microbes. On the eleventh running day, the COD value drops below 100 mg·L⁻¹, completing a cycle of producing electricity and treating sewage[10].

4. Conclusions
In this paper, poly(3,4-ethylenedioxythiophene)/multi-walled carbon nanotubes (PEDOT/MWCNTs) compound anode was made via electrochemical method, which simplified the preparation technological process and avoided the use of catalysts and toxic reagent. Compared to the modified electrodes with PEDOT, the increasing of carbon nanotubes enhanced electrical conductivity of composite anode as well as improved situation of microbial adherence. Using the prepared composite anode for AFBMFC, the output power density reached 217 mW·m⁻², that was 30% higher than the anode altered by PEDOT. Combining good mass transfer effect of the fluidized bed and running for six days, COD removal rate of wastewater in the AFBMFC with PEDOT/MWCNTs electrodes reached more than 90%.

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