Project title

BEC-ME—Microbial Electrochemical Cells with modified electrode based on ‘forest’ like carbon nanotube (CNTs) and CNT- conducting polymers nanocomposites

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Abstract

Microbial electrochemical cells (MECs) are an exciting new technology for renewable and sustainable hydrogen production from biowaste and efficient wastewater treatment. MECs are bio-electrochemical reactors in which the chemical energy stored in organic substrates is converted directly into electrical energy or hydrogen (or even other organic products) through immobilized microbial catalysts, usually termed electroactive biofilms (EAB). Improvements in electron transfer at the microorganisms/electrode interface and overall electroactivity of EABs are among the key scientific challenges to enable increased MEC output and to enable their cost-effective implementation in wastewater and other treatment plants. A possible solution is the development of biocompatible advanced materials for electrodes that will enable efficient “wiring” of EAB to the electrode.

A wide range of electrode materials and configurations have been tested and developed in recent years to improve MEC performance and lower material cost. The surface modifications of electrode materials were used to improve bacterial adhesion and electron transfer from bacteria to the electrode surface. The electrode structure can directly affect bacteria attachment, electron transfer and substrate oxidation. Thus, electrode material is the most important aspects in deciding the performance and cost of MEC. Carbon materials meet the general requirement as electrode for MECs because of their good biocompatibility, good chemical stability, high conductivity, and relatively low cost.

The project aim was focused on development of carbon based electrode materials with improved properties for implementation in MECs. The new electrodes will have high surface area and biocompatibility and support a fully active EAB, thereby increasing extracellular electron transfer and power (or hydrogen) output.

Carbon nanotubes exhibit excellent electron transfer characteristics with a high surface area to volume ratio and provide a viable support for biofilm growth. Bacterial sorption on CNTs is significantly larger than on microporous adsorbent media. The surface area and pore volume of CNTs, which are responsible for the large bacteria immobilization capacity, can be further enhanced by treating CNTs with chemical or thermal methods. The improvement in power generation with the acid and heat treated anode could result in the increase in specific area, higher ratio of protonated N to the total N gives more positive charge on electrode surface which facilitate bacteria adhesion on electrode and lower C–O composition on acid and heat treated anode surface may indicate less of contaminants that interfere with charge transfer from bacteria to anode surface. The increase of nitrogen content of the anode electrode, including ammonia, heat, or diazonium treatment, is a pathway to improved MFC performance through anode modifications.

In this work, the effect of chemical modification of carbon nanotubes through different chemical modifications has been studied. To modify the CNT surface, we treated CNTs with acidic (nitric acid, glacial acetic acid, Caro’s acid and citric acid) and basic (ammonium hydroxide/hydrogen peroxide) agents and diazonium salts (4-nitroaniline and 4-Nitrobenzenediazonium tetrafluoroborate). Carbon based material were modified with diazonium salt in order to increase nitrogen-containing functional groups. The addition of carbon radicals from diazonium salts to

CNTs has proved particularly successful in the covalent chemical modification of CNTs. Introduction of nitrogen-containing functional groups at the anode surface could be useful method to introduce more active site and to improve the electrical conductivity and catalytic activity. X-ray photoelectron spectroscopy (XPS), micro-Raman Spectroscopy and electrochemical measurements has been carried out in order to evaluate the changes induced by the modification of CNTs and carbon powder.

The polarization measurements show that the modification of CNTs with diazonium salts is improving the power generation of MFCs, but it needs a longer acclimatization time of anode MFCs. The improvement of power generation in MFCs is due to the nitrophenyl groups introduce on the surface of CNTs. The higher content of nitrogen on the surface of 14% at compared with 4.9% at increase the power generation of MFCs. Thus, the results show that the control of the nitrogen content is important for improving the MFCs performance and the modification of methods which increase the nitrogen content is an alternative to improve MFCs performance through anode modifications.

Recently, the preparation of conducting-polymer nanotubes has been systematically investigated only in recent years especially due to their conversion in nitrogen-containing carbon nanotube (NCNT). The carbonization of nitrogen containing conducting-polymer nanotubes (polyaniline and polypyrrole) seems to be simple ways for the preparation of NCNT which possess outstanding physicochemical properties when compared with ordinary CNTs. NCNTs were found to be important in the fabrication of new catalysts and fuel cells. The NCNT were successfully used to modify the anode in an MFC, and significantly improved the MFC performance compared with unmodified carbon cloth and CNTs anode. The electrochemical performance was correlated with its unique structures, higher surface area, and N-doping in NCNTs, which could provide more active sites for interface electrochemical reaction and better biocompatibility.

Template-free method was used in this work for the synthesis of conducting polymer nanotubes. The template free synthesis gives the advantage of omitting the hard template and post-treatment template removal, simplifying the synthesis process. The aims in this study are to investigate (i) different template free synthesis of conductive polymer materials based on PANI and their corresponding carbon containing nitrogen nanostructures and (ii) different morphology of polypyrrole their corresponding carbon containing nitrogen nanostructures.

Moreover, conjugated polymers, especially polyaniline (PANI) and polypyrrole (PPy), have been intensively studied in the fields of fundamental and applied researches, due to their potential use in areas such as electronics, biosensors and actuators, electrochemistry and electrocatalysis. Recently, the conducting polymers and their composite with carbon nanostructures, especially carbon nanotube (CNT), have earned more attention to improve MFC performance by modifying its anode.

In this study MFC performance using composite materials based on PPY/CNTs and PANI/CNTs as anode materials compared with MFC with commercial CNT as anode material was investigated.

The maximum power densities were obtained for MFC with PANI-CNT modified carbon cloth as electrode. The modification of carbon cloth with composite materials give a better performance of MFCs compared with CNTs modified carbon cloth, even after a short time of running (two weeks). Furthermore, the experiments with CNTs modified carbon cloth suggest that a longer acclimatization time of the electrode materials in the cell give better results in the term of maximum power density obtained with MFCs.