

FUEL 125

Systems biology and adaptive evolution approaches to understanding and increasing power output of microbial fuel cells

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Recent studies have demonstrated that the power output of *Geobacter*-based microbial fuel cells meets or exceeds that of undefined, mixed cultures. These fuel cells have the added advantage that they can be systematically investigated with genome-based technologies. Microarray analysis revealed significant upregulation in fuel cells of genes involved in the production of the electrically conductive pili, known as microbial nanowires, as well as several outer-membrane c-type cytochromes. Genetic studies demonstrated that nanowires and the outer-membrane cytochrome, *omcZ*, were absolutely required for high-density power production. *G. sulfurreducens* strains were adapted for faster extracellular electron transfer and to transfer electrons at significantly lower potentials than wild-type cells. Resequencing of the genomes of the adapted strains is providing insights into the mechanisms for this self-optimization for power production. These studies, coupled with genome-based *in silico* modeling, are aiding in optimizing microbial fuel cell output in a rational rather than an empirical manner.

FUEL 126

Isolation and Electrochemical activity evaluation of electricity generated bacteria

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Microbial fuel cells (MFCs) was designed as a two-chamber system with the bacteria enriched with the sediments of Songhua River in anode chamber and carbon paper with 10% Pt catalyst was chosen as cathode. PEM (Proton exchange membrane) was installed between the chambers. The anode solution was feed with sodium acetate of 800mg/L. The MFC was operated in batch cycles and then in the continuous flow. A maximum voltage of stable voltage of 450 mV, power density of 141.45 mW/m² and CE of 27% was achieved, while COD removal kept as 90%. To characterize bacterial population community structure, SEM was employed to detect the microbial micrograph and meanwhile, the anodic microorganism were enriched and analyzed with DGGE. Six bands were sequenced with 16rRNA gene library. Available enrichment process was constructed and microbial species were screened by Hungate method. The electricity activities of the isolations were evaluated with electrochemical method and MFC tests.

FUEL 127

Performance of different strains of the genus *Shewanella* in a microbial fuel cell

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A microbial fuel cell (MFC) utilizes the catalytic action of microorganisms to convert the chemical energy of fuel into electrical energy. MFC's can offer application flexibility because inherent microbial physiology allows many microbes and microbial communities to use several different chemical compounds as fuel. Additionally, microbes used as catalysts have the ability to self-repair and quickly adapt to varying operational conditions. This study compares the performance of different *Shewanella* strains as the biocatalyst in MFCs using lactate as fuel. Metabolic products, electrochemical activity, and biofilm formation were studied. The results show that different *Shewanella* strains yield different maximum power values and catalyze lactate oxidation at different rates. Additionally, each strain produces a different quantity and/or type of metabolic product(s) at any given time point during MFC operation.

FUEL 128

Enhancing initial bacterial adhesion to electrode materials in microbial fuel cell (MFC)

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The main problems for MFC are low electron transfer and low power density. Current studies have only focused on mono-layer cell adhesion to electrode surface. This study was to enhance cell adhesion by modifying electrode materials. The hypothesis was that the modification (topography and chemical) of electrode surfaces could increase the contact area between cells and electrodes, and enhance cell adhesion, and finally lead to higher electron transfer in MFC. The initial adhesion of *Geobacter sulfurreducens* to eight (8) electrode materials was extensively tested. Carbon paper, As-doped silicon, carbon cloth, and graphite have been micro-fabricated based on cell shape in order to maximize the contact area for electron transfer. Electrode surface roughness and chemical composition were also modified to enhance cell adhesion. In addition, SEM and AFM were used to visualize the *Geobacter* adhesion, especially the role of pili on cell adhesion and long-range electron transfer.

FUEL 129

Progress and challenges in scale up of electrogenic reactors such as microbial fuel cells

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Several new technologies are emerging based on the ability of certain bacteria, called exoelectrogens, to transfer electrons between respiratory enzymes inside the cell to exogenous surfaces such as an electrode. Two of the most promising technologies are microbial fuel cells, used for electricity generation, and bioelectrochemically assisted microbial reactors (BEAMRs), used for hydrogen production. Key attributes for scale up are anodes and cathodes that have high surface areas, cathodes that allow for oxygen reduction in a non-fouling manner, and the need for non-precious metal catalysts. Recent advancements have been made based on the development of new materials and configurations suitable for scale up of these electrodes. Thus, it is now possible to design and scale up reactors for generating electricity from dissolved organic matter.

FUEL 130

Enhanced power generation of air cathode microbial fuel cells with cloth electrode assembly

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Single chamber air-cathode microbial fuel cells (MFCs) hold a great promise for practical application due to their low operational cost, low maintenance requirements and relative high power density. Increasing the power density is one of the greatest challenges for their practical applications. In this study, a new cell configuration was designed by applying a cloth layer to a membrane-free single chamber MFC and tested using mixed bacterial culture with acetate as substrate. A volumetric power density of 627 W/m³ has been achieved, which is more than 10 times higher than those in the cloth-free MFCs using similar electrode materials. This study indicates that the power density of air cathode MFCs can be significantly improved without using expensive membranes, which greatly increases the feasibility for the practical applications of MFCs.

FUEL 131

Scalable tubular membrane cathodes for microbial fuel cell applications

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One of the greatest challenges for using microbial fuel cells (MFCs) for wastewater treatment is creating a scalable architecture that provides large surface areas for

oxygen reduction at the cathode and for bacterial growth on the anode. We demonstrate here a scalable cathode concept by showing that two tubular hydrophilic or hydrophobic filtration membranes with conductive graphite coatings and a non-precious metal catalyst (CoTMPP) can be used to produce power in an MFC. Using a high surface area graphite brush anode with two hydrophilic ultrafiltration tubular membrane cathodes placed inside the reactor ($A_{cat,s} = 93 \text{ m}^2/\text{m}^3$), the MFC produced $18 \text{ W}/\text{m}^3$ with a high Coulombic Efficiency (CE) of 70-74 %. Further increases in power output will require the development of membrane cathodes with lower internal resistances.

FUEL 132

Single chamber stackable microbial fuel cell with air cathode

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A single chamber stackable microbial fuel cell with consisting of four MFC units was constructed for organic matter biodegradation and electricity production. When the reactor was maintained in batch mode with sodium acetate (600mg/L) as carbon source, all MFC units had similar polarization curve and produced maximum power around 0.87 mW/unit. Cathode charge transfer was found to be the more important limiting factor than anode charge transfer. Parallel connection of all units produced maximum power of 3.12 mW/reactor (7.61 W/m³); however, series connection caused energy losses and could only produce maximum power density of 2.20 mW/reactor (5.36 W/m³). When the reactor was maintained in continues mode (0.7mL/min, 128 mg/L COD in influent), the overall COD removal rate was 73.4%. Under this condition, both voltage output of MFC units and COD decreased along the flow path, indicating heterogeneous distribution of organic matters.

FUEL 133

Direct electron transfer in microbial fuel cells via carbon nanotube network

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A microbial fuel cell converts chemical energy, available in a bio-convertible substrate, directly into electricity. It works through the action of bacteria, which can pass electrons to an anode of a fuel cell. The electrons flow from the anode through a wire to the cathode, producing an electric current. In the process, the bacteria consume organic matter in the surrounding liquid medium. The limiting step for the entire process is the electron transfer from bacteria surface to the electrode material. Introduction of carbon nanotubes into microbial culture creates a 3-D conductive network that allows avoiding transport limitations. Presented experimental data with corresponding theoretical model indicate significant increase of energy yield.

FUEL 151

Bio-Anode kinetics modelling: Effect of anode potential and substrate concentration

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The most important component of a microbial fuel cell is the bio-anode. A kinetic model has been developed that describes the current density of a bio-anode as a function of the substrate concentration and the anode potential. The model is based on two well known models; a modified Monod model for biochemical conversion kinetics and the Butler-Volmer model for electron transfer kinetics. These two models are merged to a full steady state model. The model has been tested using data on the effect of anode potential on current density. The current density varies almost linear with anode potential in the range of -0.4V to -0.1 V.(vs. Ag/AgCl) This feature could be well described using the developed model. It showed that with increasing anode potential, the micro-organisms can not extract all of the energy available. The model should be further tested both experimentally and theoretically.

FUEL 152

Electrochemical Impedance Spectroscopy Studies on Microbial Fuel Cells

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Recent design improvements helped increase the power densities of Microbial Fuel Cells (MFCs) by orders of magnitude by decreasing the internal ohmic resistance. With the ohmic resistance of the MFC systems no longer a dominant issue, identification of other intrinsic resistances is the need of the hour. Electrochemical Impedance Spectroscopy (EIS) is a useful tool to delineate the individual contributions from different resistances to the overall cell impedance. Preliminary EIS experiments were conducted with acetate fed two-chamber MFC inoculated with *Geobacter Sulfurreducens* and using a ferricyanide catholyte. Results showed that the anode played a dominant role in limiting the kinetics of the bio-electrochemical reaction, thereby contributing to the majority of the polarization loss. Based on the equivalent electrical circuit fitting of the EIS data, parameters such as charge transfer resistance, membrane resistance and exchange current density have been estimated for the first time for the case of MFCs.

FUEL 153

Continuous flow microbial fuel cells for sustainable energy from wastewater

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In the UK alone, there are 347000 km of feed a daily volume of 11 billion litres to about 9000 sewage treatment works resulting in a daily treatment cost of ≤ 9 million. Microbial fuel cell (MFC) is a biological processing strategy that could accomplish satisfactory treatment of waste water as energy source to produce alternative fuel at the same time. In essence, MFC generates both electricity and biogas, mainly hydrogen, from biodegradable such as carbohydrates and complex substrates which are present in domestic and industrial wastewater. Tests were carried out using a hexagonal (anode) MFC reactor containing a cylindrical air cathode. The system was operated a continuous flow of primary treated wastewater which was collected from local wastewater treatment plant where the COD ranged from 70-200mg/L. Without adding any assistant chemicals, maximum power density 2mW/m² at a hydraulic retention time (HRT) of 1h and hydrogen was co-generated, a COD removal up to 33% was achieved.

FUEL 154

High Hydrogen Yield from Renewable Resources Using an Improved Beamr System

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Biological processes are an environmentally friendly technology for producing hydrogen from renewable resources such as biomass. However, biological fermentation has low yield and low energy recovery for hydrogen production. To increase hydrogen production from biomass, we have recently developed a new method to produce hydrogen from organic matter based on a modified microbial fuel cell (MFC). We report here that by optimizing the reactor configurations and operation conditions the hydrogen yield increased to 3.9 mol H₂/mol acetate with an average of current efficiency of 99.6%. Hydrogen production rate was 1300 L H₂/d-m³-reactor volume with COD removals of 90-97%. This hydrogen production rate is ~ 70 times higher than that previously reported.

FUEL 155

Model of microbial fuel cells in which bacteria employ a direct electron transfer strategy

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Many experimental studies of microbial fuel cells (MFCs) have been performed. MFC modeling, however, has not been adequately explored. We are aware of only one publication, in which a relatively simple model was used to simulate current production by bacteria employing an exogenous electron-transfer mediator. In this research, a model was developed to simulate power production by bacteria employing a direct or wire-like electron transfer strategy. The model considers a thin layer of bacteria on the anode that consume substrate and transfer electrons to the anode via wire-like connections. The effects of resistance of these connections and of the external circuit on power production are addressed. To verify the model, simulated sustainable power curves were compared with experimental results. The model successfully reproduced experimental trends, suggesting that the key processes are captured in the model.

FUEL 156

Electrochemical and molecular-biological analyses of microbial fuel cells operated at different external resistances

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In this research, the effects of external resistance on the community structure and performance of mixed-culture microbial fuel cells (MFCs) were investigated. For the experiments, bench-scale flow-through MFCs were inoculated with anaerobic digester sludge and supplied with a mixture of acetate, propionate, butyrate, and lactate as electron donor. Potassium ferricyanide served as the electron acceptor in the cathodic chamber. After steady state was reached, non-destructive electrochemical analyses including cyclic voltammetry were conducted. At the end of the experiment, destructive analyses of the biofilm on the carbon cloth anode were performed including examination via scanning electron microscopy, measurement of protein content and DNA extraction for community analysis. The results suggest that the applied external resistance has a significant impact on the performance (i.e. power production), electrochemical characteristics, and community structure of MFCs.

FUEL 157

Towards the Naval Applications of Benthic Microbial Fuel Cells

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We are carrying out experiments on benthic microbial fuel cells in the Narragansett Bay to explore their practical value (Refs. 1-3). The recent progress will be presented. First, we will report the results of a comparison of stainless steel electrodes with graphite electrodes. Second, we will describe a voltage converter and power storage system that has proven reliable in trickle power harvesting continuously over months. The storage of electrons in a large capacitor will also be shown. Third, we will describe the characteristics of power storage and discharge for the intermittent powering of a small beacon for nearly two months and the in-water swimming of a 1 m long Biorobotic unmanned undersea vehicle that has shark-like low power characteristics, for several minutes. To our knowledge, the powering of the UUV in-water is a first.

FUEL 158

Importance of Cathode Size in Microbial Benthic Fuel Cells Equipped with Manganese Anode

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For a microbial benthic fuel cell (MBFC) in which the anode process is mass transfer controlled, limitations due to the cathode process remain important. We report here on the use of a sacrificial manganese anode, which offers the combined advantage of high power delivery in electrochemical applications and extremely slow chemical corrosion. Then, we examine in a systematic manner the effect of cathode size on the power output of a MBFC that harvests energy from marine or river sediment. MBFC consists of a manganese anode imbedded in marine sediment and a cathode in overlying seawater. This newly introduced manganese anode offers the combined advantage of extremely slow chemical corrosion, and high power delivery in electrochemical applications. Results of this study substantiate the usefulness of Tafel plots as a major technique for the investigation of the half cell of interest in any fuel cell.

FUEL 159

Power output assessment of cellulose-based microbial fuel cells operating under different external resistances

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The purpose of this study was to demonstrate the effect of external resistances on the power output of microbial fuel cells (MFCs). The MFCs were operated with rumen microbial consortia as biocatalysts and microcrystalline cellulose as the sole substrate. Graphite plates were used as the anode and cathode electrodes connected via 20, 249 and 1000 ohm resistances in separate MFCs. The anodic potential varied under the different loading resistances employed but the cathodic potentials were constant. Maximum power output of 66 mW/m² was obtained in MFCs with 20 ohm external resistance, whereas with higher external load the power output was substantially lower. Thus the initial external resistance of MFCs can affect the attainable power output as the result of the effect of external load on the anodic potential.

FUEL 160

Examining the efficiency and biogeochemistry of plankton-fed microbial fuel cells

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Decomposition products, power output, electrode potentials, microbial communities and Coulombic efficiency were investigated as a function of discharge potential in two-chamber, seawater-filled, microbial fuel cells (MFCs) fed with marine plankton. In the aquatic environment, particulate organic carbon derived from plankton is the most abundant "biofuel" available for MFCs, and hence could be used to power autonomous sensors, beacons and communication devices for ocean monitoring and navigation. In this study, increased plankton decomposition rates were observed in active MFC experiments compared to those in an open circuit control cell. These increased decomposition rates coincided with peak electricity generation and sulfide removal and are interpreted to be due to the catalysis of organic matter degradation by andophilic microorganisms. Coulombic efficiencies for the MFCs were between 9-12%, and ~20% of the planktonic carbon added remained after 56.7 days. Optimization of MFC designs specifically aimed at plankton degradation reactions has the potential to improve these recoveries.

FUEL 191

Biofuel cells based on reconstituted enzymes

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Effective electrical wiring of redox enzymes is an important condition for the enhanced power generation in enzyme-based biofuel cells. The present paper summarizes the present state-of-the-art in the area of the monolayer immobilization of redox enzymes using the reconstitution approach. This approach was successfully developed in several laboratories resulting in the efficient electron transfer between the aligned monolayer-immobilized enzymes and electrodes. The vectorial electron transfer was achieved in supra-molecular systems composed of enzymes, cofactors and mediators appropriately assembled on electrode surfaces. Various enzymes (FAD-, NAD+-, PQQ-, heme-, or cytochrome-dependent) were electrically wired through the reconstitution procedure on cofactor-modified electrode surfaces. A similar approach was applied to assemble a photobioelectrode based on reaction centers from photosynthetic bacteria reconstituted on a quinone-functionalized surface. Future developments based on the application of nanotechnological approaches will be discussed.

FUEL 192

Conversion of a plant chloroplast to a biological fuel cell

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We are working on a design for a biological fuel cell based on a plant chloroplast. One of the problems is to design an electrode to be inserted in the stroma, which will compete with FNR for electrons from reduced ferredoxin. On the theory side, calculations have been carried out of the electronic coupling matrix element H_{if} for electron transfer from reduced ferredoxin to FAD and to cluster models of the Au 111 surface. We conclude, based on H_{if}^2 , that a gold electrode is ~9 times less efficient as an electron acceptor than FAD. It is also likely that the gold surface is even less efficient when orientation effects are considered. By contrast a gold surface covered by a mercaptopropyl SAM is predicted to be efficient both in orienting the ferredoxin and in electron transfer with properties similar to the FAD moiety of FNR. We have confirmed these predictions by cyclic voltammetry studies.

FUEL 193

Enzymatic biofuel cells for micro-power source applications

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Enzymatic bio-fuel cells present a viable candidate for ultimate miniaturization because it is a class of energy conversion devices that employ molecular electrocatalysts –

enzymes and hierarchical surface architectures developed in the course of the advancement of bio-nano interface technology. Many of the fabrication technologies and 3D structural motifs can be achieved with today's MEMS fabrication tools. In general, enzymatic bio-fuel cells can be successfully employed in devices where "scavenging" for environmentally available fuel sources is feasible and diversity of fuels is desirable. We have developed the synthesis of a hierarchically porous conductive membranes derived from carbon papers with consecutively grown multi-walled carbon nanotubes (MWCNT). The enzyme electrode formation was then achieved by layer-by-layer deposition of the protein and polymers with opposite charges. The coverage was following the hierarchically structured material architecture. This paper will discuss devices that take advantage of these nanostructures for power generation.

FUEL 194

Biocatalysis of carbon nanotube-attached enzymes for biofuel cells

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Carbon nanotubes(CNTs)-attached glucose oxidase was examined for biofuel cell applications. The reaction kinetics of glucose oxidation reaction in the presence of a mediator, hydroquinone, was probed by using a Ping-Pong Bi-Bi model. It was observed that the value of K_m of the enzyme varied from 29 mM at free state to 38 mM upon immobilization onto suspended CNTs, while the values of V_{max} only showed a very mild change from 1.1×10^{-3} to 1.3×10^{-3} mM/s, indicating the immobilization only slightly changed the kinetics of the mediated reactions. The use of CNTs showed a 6-fold enhancement of current density as compared to biofuel cells applied the same amount of enzyme but without the use of CNTs. That was believed to be a result of the increased surface area and improved mass transfer property of the CNTs-containing electrodes. Studies also revealed that the maximum electrical current density of the fuel cells only matched less than 1% of the reactivity the enzyme mounted on the electrodes. This indicated that electron transfer and other electrical resistances within the fuel cells, instead of enzyme activity and availability, are the limiting factors of the power density of the biofuel cell systems examined in this work.

FUEL 195

Biofuel cells fundamentals: electron transfer mechanism in laccase from *Trametes versicolor*

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This paper describes electrochemical behavior of laccase from the fungi *Trametes versicolor* by using the protein film voltammetry. The issues related to discrimination of the redox potentials corresponding to copper centers T1 and T2/T3 in the active site and possible mechanism of intra-molecular electron transfer have been discussed. The electron-transfer rate constant for laccase immobilized on carbon electrode is 3.4 s⁻¹. The bio-electrocatalytic activity of enzyme was studied also in the presence of 1,4-hydroquinone (HQ). The kinetics of HQ oxidation is very fast (K_M = 3.8 μM). However, the catalytic activity of laccase in the presence of high concentration of HQ decreases drastically. It is suggested that the T2/T3 copper center is able to accept electrons directly from HQ molecules via intra-molecular channel. As result of that, the catalytic reduction of oxygen to water is partially or completely inhibited.

FUEL 196

A high-power glucose / oxygen Biofuel Cell

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We have developed a new high-power biofuel cell under natural diffusion of glucose and oxygen, which has the anode with improving reactivities within the immobilized membrane and the cathode having the reactive structure. We will discuss in detail on that day.

FUEL 197

Redox active molecular sieves as enzyme supports for biofuel cells

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The enabling technology for enzyme based biofuel cells is the ability to wire the enzyme to an electrode. We have prepared redox active mesoporous molecular sieves that respond to electrochemical and optical stimuli. Small enzymes and proteins have been encapsulated in the pores of these molecular sieves. Glucose oxidase (GOx) and Microperoxidase-11 (MP-11) have been supported in diazapyrene decorated periodic

mesoporous organosilica as well as mesoporous TiO₂. Preliminary results for electron transfer between molecular sieve host and guest biocatalyst will be presented.