Design of C-MEMS Based Enzymatic Biofuel Cell

G. Bisht[1], S. Ehsan[1], Y. S. Parikh[2], J-H Yang[2], M. Gillespie[3], A. Demirel[3], X. Liu[3], E. Dikici[3], L.Kulinsky[1], M. Madou[1], C. Wang[2], S. Daunert[3], L. G. Bachas[3]

1 *University of California, Irvine*; 2 *Florida International University*; 3 *University of Kentucky*

Research Objective

In recent years, the quest for alternative sources that can autonomously power bioMEMS devices, especially those geared for *in vivo* applications, such as monitoring and drug delivery, has been the focus of research by scientists and engineers as new power sources will prove critical for the advancement of the field. Current batteries are still less than optimal and often present drawbacks related to safety, reliability and scalability. An ideal power source for implantable devices should take advantage of natural compounds present in the body of an individual and use them as fuel to produce power in a continuous and reproducible manner, as long as the patient's physiological functions remain steady. Biofuel cells, which are capable of converting biochemical energy into electrical energy, have been deemed as a potential solution to the drawbacks presented by conventional batteries, but the power density and operational lifetime requirements for implanted devices have not been met yet. To that end, we propose to integrate genetically engineered catalytic proteins and carbon-based 3 dimensional (3D) MEMS/NEMS structures to create new biofuel cells. The biofuel cell electrode surfaces, especially fractal electrode array, presents significantly increased surface area as compared to traditional architecture, increasing the biocatalyst loading capacity considerably for high power throughput. The genetically engineered enzymes inherently increase enzyme stability, consequently increasing biofeul cell lifetime. The Finite Element Analysis simulation helps to optimize the enzymatic biofuel cell (EBFC) design.

Reaction Mechanism

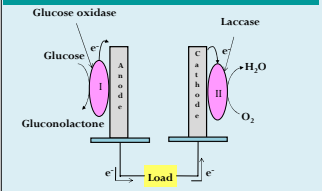


Fig. 1 Reaction Mechanism of EBFC

Anode: Glucose + O_2 $\xrightarrow{GOx}$ Gluconolactone acid + H_2O_2

$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^-$ (Oxidation)

Cathode: $O_2 + 4H^+ + 4e^- \xrightarrow{laccase} 2H_2O$ (Reduction)

Structure & Applications

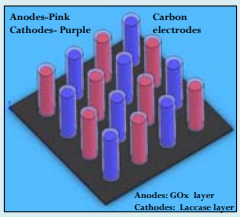


Fig. 2 Schematic diagram of EBFC chip

Highly dense 3-D micro-electrodes arrays gives more power density due to higher surface per footprint area compared to 2-D thin films electrodes.

Applications:

To supply power to the active implantable medical devices:

- Pacemakers,
- Cochlear implants,
- Neuron stimulators,
- Left ventricular assist device
- Defibrillators,
- Insulin pumps,
- Drug delivery pump,

Power requirement of these devices are in the range of 50 µW to 30 mW.

C-MEMS Fabrication Process

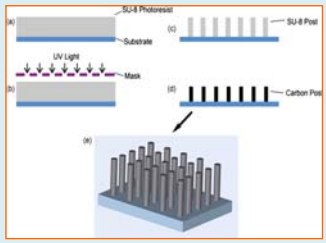


Fig. 3 Fabrication procedure of an EBFC electrodes

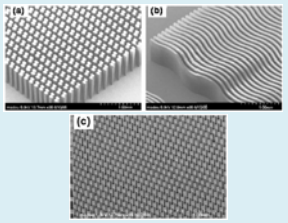


Fig. 4 Fabricated CMEMS electrodes: (a,b) – before pyrolysis, (c) – after pyrolysis

Enzymes: Lacasse

Laccase, from the bacterium *Thermus thermophilus HB27*, is of great interest for use in the biofuel cell because it allows for faster kinetics and higher working temperatures during catalysis of the reaction.

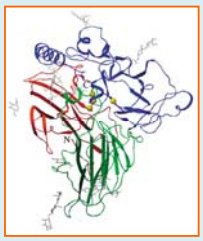


Fig. 5 A *Homologous Laccase* from *Melanocarpus albomyces*.

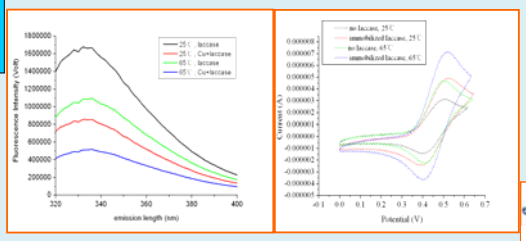


Fig. 6 Effect of temperature and copper on fluorescence of recombinant *Thermus thermophilus HB27* laccase.

Fig. 7 Cyclic Voltammograms for the electrochemical oxidation of 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) with laccase on a glassy-carbon electrode.

Enzymes: Glucose Oxidase

Glucose oxidase (GOX, from the fungus *Penicillium amagasakiense*) catalyzes the oxidation of ß-D-glucose to D-glucono-1,5-lactone, while laccase (Lac) catalyzes the reduction of O_2 to water. The use of the wild-type GOx is problematic due to the competition of oxygen for the electrons released during the oxidation of glucose. A H520A mutation has been introduced into wild-type GOx in order to prevent the loss of electrons to oxygen. This site is believed to be the oxygen binding site of the enzyme, therefore, the mutant GOx is being tested against wild-type GOx. It is believed that if oxygen binding to GOx is prevented, the electrons from oxidation will be carried to the electrode more efficiently.

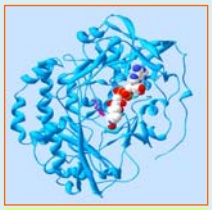


Fig. 9 Glucose Oxidase from *P. amagasakiense*.

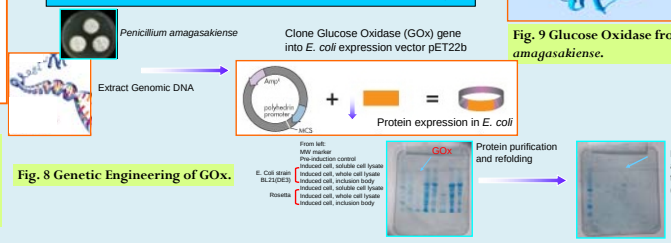


Fig. 8 Genetic Engineering of GOx.

CMEMS Functionalization

Direct Attachment

The enzyme was found to be functional without any adverse affects on its activity.
Further it was proven that CMEMS structures can be functionally modified with biomolecules.
However, no direct electron transfer was observed when tested in deoxygenated Glucose. Thus, mediator is required for the efficient EBFC.

Fig. 10 Cyclic Voltammetry of plasma-treated CMEMS with direct attachment of GOx.

GOx with Hydroquinone Mediator

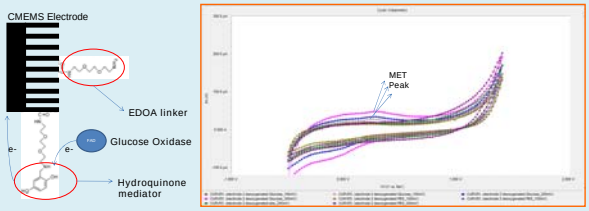
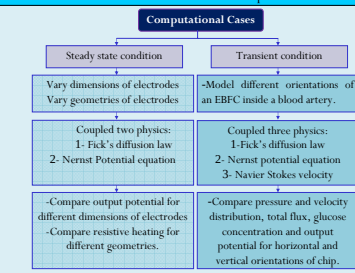


Fig. 11 Schematics of Hydroquinone mediator and GOx immobilization. Peaks on Cyclic Voltammogram indicate activity of GOx in the presence of mediator in deoxygenated solution.

Simulation Framework

Performance of a 3-D C-MEMS (Carbon MicroElectroMechanical System) based enzymatic biofuel cells (EBFC) is optimized by using the COMSOL 3.4 Multiphysics software. Various 2-D models of the EBFCs have been simulated in order to: 1) analyze diffusion phenomenon of glucose around micro-electrodes by considering the effect of velocity and pressure of glucose flow inside a blood artery due to heart pumping, 2) inspect potential and current density distribution throughout the depth of electrodes, 3) derive the design rule based on a relationship between dimensions of electrodes and output potential, 4) investigate the effect of current density, electric field and resistive heating at electrode surfaces for various electrode geometries, (5) study and compare horizontal and vertical orientation of the EBFC chips inside a blood artery.



Computational Results

Steady State Analysis

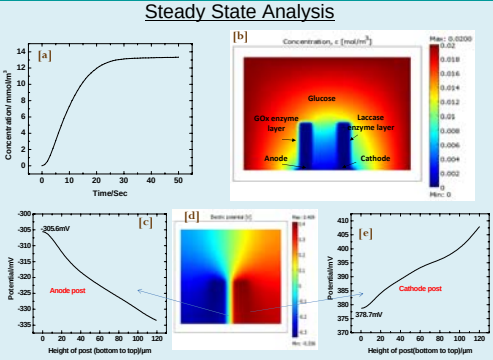


Fig. 12 (a) Concentration of glucose vs. time graph, (b) glucose concentration profile, (c) potential values for anode, (d) potential profile, (e) potential values for cathode

Transient State Analysis

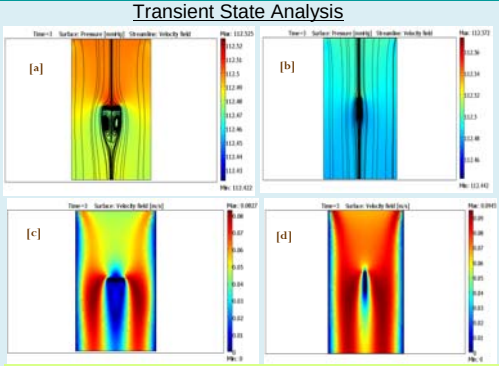


Fig. 13 Pressure simulation with velocity streamlines for(a) horizontal position (HP)and (b) vertical position (VP) and velocity profiles for (c) HP and (d) VP of an EBFC chip.

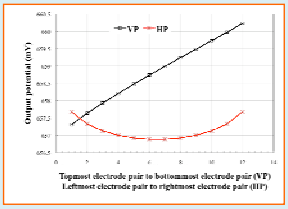


Fig. 14 Output potential for 12 pairs of electrodes in HP and VP of a chip

Conclusions and Future Work

Comprehensive design and optimization of enzymatic biofuel cell included employment of genetically-engineered enzymes, construction of carbon electrode arrays, and functionalization of enzymes and mediators on CMEMS electrodes. Finite Element Analysis was performed for steady state as well as for transient conditions to help guide the optimization of the EBFC design.

Future work will include implementation of the EBFC design suggested by the simulation and functionalization of robust genetically engineered enzymes.

Acknowledgements

National Science Foundation NIRT-0709085.