NANOPOROUS SILICA AS MEMBRANE FOR IMPLANTABLE ULTRA-THIN BIOFUEL CELLS

Tushar Sharma[1*], Tony Hu[2], Ashwini Gopal[1], Meryl Stoller[3], Kevin Lin[1], Rodney S. Ruoff[3], Mauro Ferrari[2] and Xiaojing Zhang[1]
[1]Biomedical Engineering, The University of Texas at Austin, Austin, USA
[2]Biomedical Engineering, The University of Texas Health Science Center at Houston, Houston, USA
[3]Mechanical Engineering, The University of Texas at Austin, USA

Abstract: In this paper, we report the design, fabrication and characterization of an inorganic catalyst based glucose Biofuel cell using nanoporous silica coating as a functional membrane. Blood vessel implantable biofuel cells are subjected to higher glucose concentrations and blood flow rates. However, reduction in the implant thickness is critical for the intra-vascular implantable Biofuel cells. Platinum thin-film (thickness: 15 nm) deposited on Silicon (500 μm) served as the anode while Graphene (65 μm) was used as the cathode. Control experiments involved the use of polypropylene based porous membrane (50 μm) and activated Carbon (198 μm) electrodes. We report that nanoporous silica thin film (270 nm) is capable of replacing the conventional polymer based membranes with improved performance.

Keywords: Implantable biofuel cell, Platinum, Graphene, Nanoporous Silica, MEMS

INTRODUCTION

Cardiovascular disease is the number one killer in the US and worldwide. Consequently, there is an upsurge in the various novel devices to diagnose, monitor, and treat cardiovascular disease. Recently, the spotlight has shifted towards the development of compact, efficient and low-power consuming implants. With the emergence of micro-electro mechanical systems (MEMS) based implantable devices [1, 2] along with reduction in power source capacity, alternative, safe and self-sustainable energy sources are being sought.
Biofuel Cells (BFCs) are capable of oxidizing sugars to generate electricity [3].Ideally, the only byproducts of the electrochemical reactions would be water and gluconic acid or carbon dioxide:

Anode: $C_6H_{12}O_6 + 2\ OH^- \rightarrow C_6H_{12}O_7 + H_20 + 2\ e^-$
Cathode: $0.5\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Overall reaction: $C_6H_{12}O_6 + 0.5\ O_2 \rightarrow C_6H_{12}O_7$

$\Delta G^\circ = -2.51 \times 10^5\ J/mol;\ V^\circ = 1.30\ V$ [4]

Various types of BFCs capable of generating electricity from carbohydrates can be broadly categorized into the following three categories: (1) Microbial fuel cell, (2) Enzymatic fuel cell, and (3) non-inorganic catalyst biofuel cells. Whereas implantable enzymatic glucose fuel cells are currently under development, the limited stability of enzymes renders their application in a long-term implantable fuel cell power supply difficult[5]. Abiotically catalyzed fuel cells employ mainly noble metal catalysts which are considered to be advantageous regarding their sterilizability, long-term stability, and biocompatibility [6] suitable for medical implant applications.

BIOFUEL CELL DESIGN

A common problem with implantable BFCs is the concomitant presence of glucose and oxygen and the lack of glucose selective inorganic catalyst. For this purpose there has been significant effort on development of electrodes materials [7, 8] and designs [4] to circumvent the oxygen interference on the anode. Thus the most popular design so far has been the sandwich type assembly of electrodes (Figure 1).

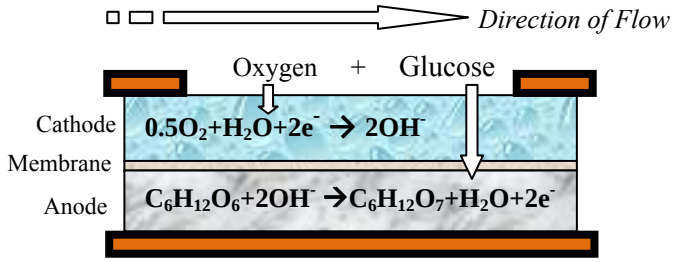

Figure 1: *Principle of Biofuel Cell.*

In order to further increase the power output from an implantable biofuel cell, the implant site can be shifted from the physiological tissue to an intra-vascular biofuel cell implant.
The intra-vascular designs were highly successful when tested in-vitro [9], but faced practical challenges during intra-vascular implantation due

to the bulky nature of the biofuel cells. Here we present the use of advanced nanomaterials for the development of ultra-thin biofuel cells.

EXPERIMENTAL SECTION

Electrode Fabrication

Anode was made of Platinum thin-film (thickness:15 nm), e-beam evaporated on a commercial silicon wafer (500 um, resistivity < 0.05 Ω-cm). The silicon wafers were then diced to 5cm x 5cm electrodes.

The cathode was constructed of chemically reduced graphene oxide as reported elsewhere [10]. Graphite oxide obtained using modified Hummers method was reduced and filtered. The agglomerates of graphene sheets were assembled into electrodes by mixing with 3% polytetrafluoroethylene (PTFE) binder and rolled into 65 µm thick sheets. Activated carbon (Norit) was used as the control for comparison with graphene based electrodes. PTFE was used as the binder for activated carbon electrodes as well. The thickness of the activated carbon electrodes was 198 µm.

The electrodes were soaked in phosphate buffered saline (PBS, pH 7.4) solution prior to use in biofuel cell assemblies. When not in use, the electrodes were stored in vacuum.

Nanoporous Silica Fabrication

The following steps were undertaken in order to produce a mesoporous silica thin film atop the platinum-coated silicon wafers. The precursor solution was prepared by combining the amphiphilic surfactant (pluronic L64), which serves as a structure-directing polymer, with hydrolyzed TEOS (tetraethyl orthosilicate) in ethanol solvent under acidic condition. The thin film itself was produced by spreading coating solution on the wafers followed by evaporation-induced self assembly in which preferential solvent evaporation pushes the formation of a uniform silica nanostructure. A process flow diagram for the procedure is shown in detail in the Figure 2 (a). The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show the morphology of the thin film silica (Figure 2 (b)).

Fuel Cell Assembly

Figure 3 shows the schematic of the BFCs assembled. For the polymer membrane based BFC, a polypropylene based membrane (Celgard 3501) was placed between the electrodes. The porous membrane acted as the insulator while simultaneously providing glucose diffusion across the membrane.

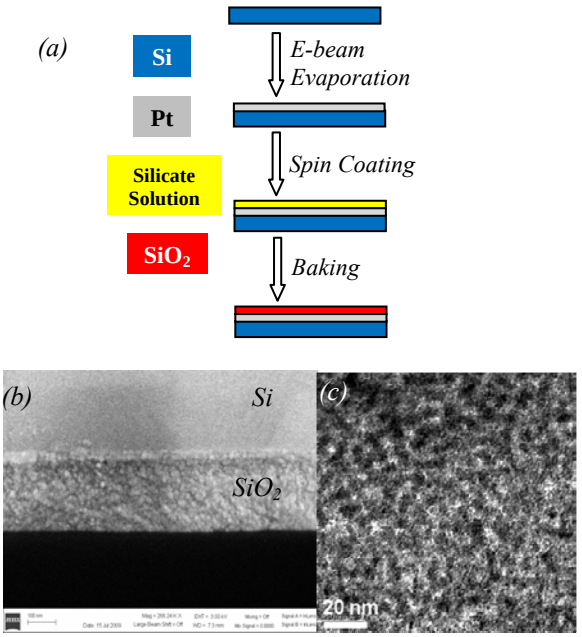

Figure 2: (a) *Fabrication Procedure for preparation of Nanoporous Silica, (b) SEM and (c) TEM images of fabricated Nanoporous Silica.*

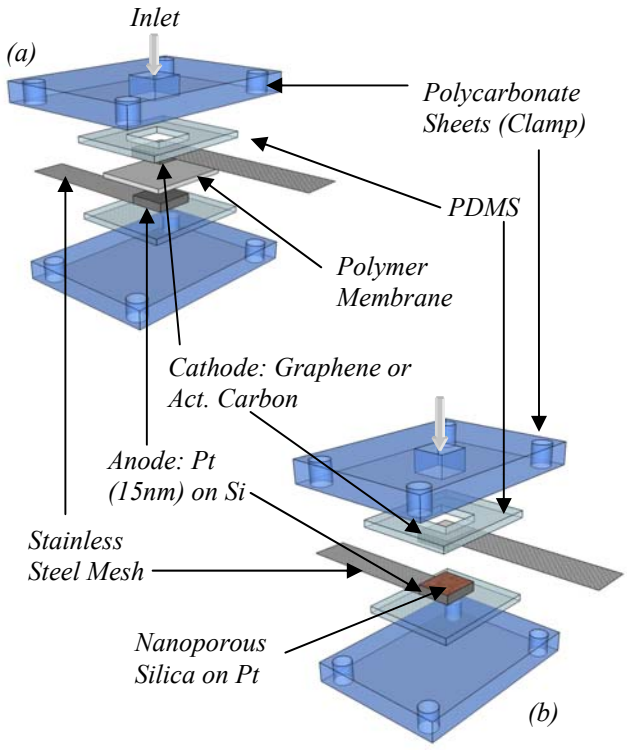

Figure 3: *Schematic for Biofuel Cell using (a) Polymer membrane, and (b) Nanoporous Silica.*

Stainless steel (316) was used as the current collector for the electrodes.

Since the anode is comprised of conductive silicon, which is non-catalytic in nature [11], the stainless

steel mesh (160 µm) was placed directly beneath the silicon wafer. For the cathode, chemically reduced graphene oxide or activated carbon was manually pressed onto stainless steel mesh. The final thickness of the cathode, including the contribution from the mesh itself, was 120 µm. The electrodes were stacked as shown in Figure 3(a). polydimethylsiloxane (PDMS) sheets with thickness (1-2 mm). PDMS sheets provided mechanical support to the silicon anodes while damping the pressure effects due to the clamp.

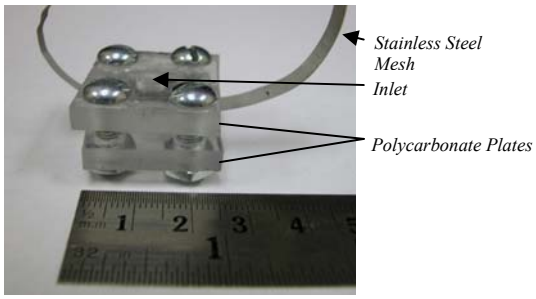

Figure 4: *Packaged Biofuel Cell (BFC).*

The packaged Biofuel Cell is shown in Figure 4. This biofuel cell was placed inside a glass beaker containing 0.42% glucose solution dissolved in phosphate-buffered saline solution (pH 7.4). Possible air trapped inside the BFCs was removed by placing the glass beaker under vacuum for 15 mins. The setup was then placed on a hot plate at 40 ˚C with continuous stirring to simulate physiological conditions. To measure the load characteristics of the assembled biofuel cell, the terminals were connected to a variable external resistance (0-12 kΩ), as shown in Figure 5.

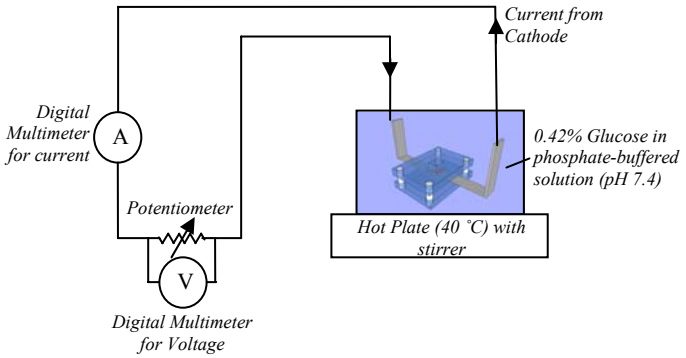

Figure 5: *Experimental Setup for Biofuel Cell load characterizations*

RESULTS AND DISCUSSIONS

Power density and polarization curves for the two BFCs have been plotted in Figure 6. From Figure 6a, it is clear that the replacement of activated carbon with graphene as the cathode can deliver high power densities (5 µW/cm^2). Hence graphene acts as a better cathode in place of activated carbon (3.24 µW/cm^2). Further, the open circuit potential (OCP) of graphene based BFC (0.261 V) was higher compared to the OCP of activated Carbon based BFC (0.234 V)

The power densities reported in the present study obtained from activated carbon (3.24 µW/cm^2) based BFC are higher than the values reported from similar studies (~2 µW/cm^2) [12]. This may be attributed to the higher glucose concentrations used to compensate for the presence of oxygen at atmospheric pressure conditions.

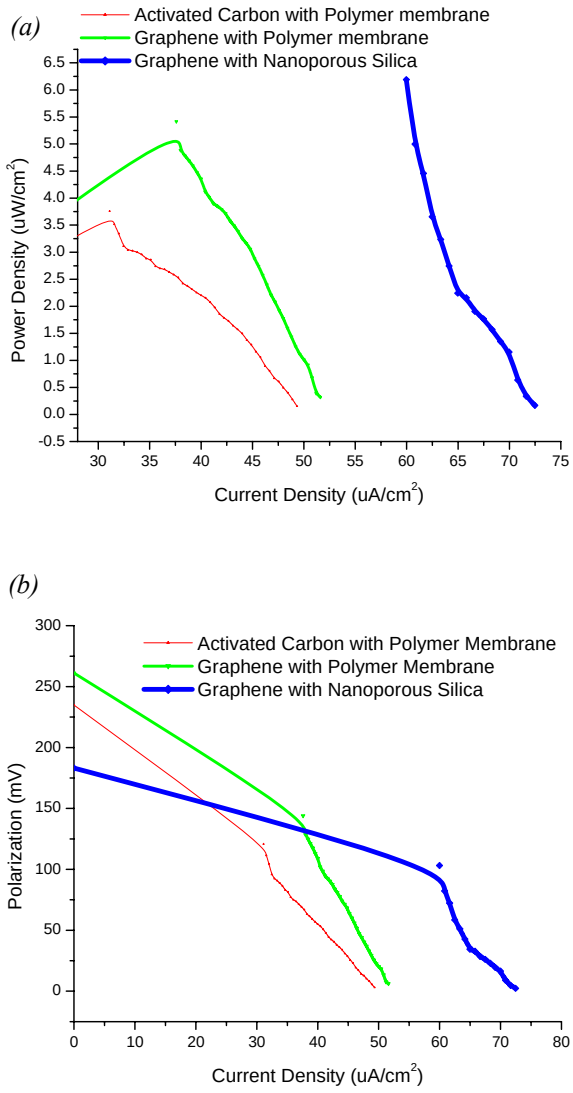

Figure 6: *Experimental results obtained with Polymer membrane vs. Nanoporous Silica based BFCs: (a) Power Density Curves, and (b) Polarization Curves*

Nanoporous silica based BFC is capable of delivering higher power densities (6.23 µW/cm^2) than the

polymer membrane based BFC (5 μW/cm^2, Figure 6a). The lower OCP obtained using Nanoporous silica based BFC (183.2 mV) indicates the presence of oxygen at the anode. The absolute values of polarization recorded are very low compared to the reported literature values [12]. This is an indication of the possible interference of oxygen at the anode which in turn, could be due to inadequate clamp pressure from the polycarbonate sheets as well as diffusion of oxygen through PDMS. Further, this could also possibly be due to the presence of residual air in graphene that was not removed during vacuuming. The polarization values were found to improve with time, however. Better BFC designs for the presented electrode system should avoid the observed low polarization values for the two BFCs.

CONCLUSIONS

We present the use of Nanoporous silica as a functional membrane and graphene as cathode for the fabrication of an ultra-thin implantable biofuel cells. Load characteristics are measured for the assembled BFCs and showed the potential of using Nanoporous silica as a replacement membrane for an implantable BFC. We also observed the higher current densities from the Nanoporous silica based BFC. Good understanding of the contribution from the various BFC components will help design better BFC. A better assembly of the various components that avoids the oxygen diffusion to the anode should result in higher polarization values. We have also presented the use of graphene and silicon based micro fabrication to design the biofuel cell. As Nanoporous silica and graphene processing are becoming semiconductor clean-room friendly, the future holds great promise for the development of mass-producible, high power-density, ultra-thin biofuel cells for biomedical implant applications.

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REFERENCES

[1]Chau, H.L. and K.D. Wise, *An Ultraminiature Solid-State Pressure Sensor for a Cardiovascular Catheter.* IEEE Transactions on Electron Devices, 1988. **35**(12): p. 2355-2362.

[2]Najafi, N. and A. Ludomirsky, *Initial animal studies of a wireless, batteryless, MEMS implant for cardiovascular applications.* Biomedical Microdevices, 2004. **6**(1): p. 61-65.

[3]Wolfson, S.K., Jr.; Gofberg, Sheldon L.; Prusiner, Paul; Nanis, Leonard *Bioautofuel cell: a device for pacemaker power from direct energy conversion consuming autogenous fuel.* Transactions - American Society for Artificial Internal Organs, 1968. **14**: p. 198-203.

[4]Kerzenmacher, S., et al., *Energy harvesting by implantable abiotically catalyzed glucose fuel cells.* Journal of Power Sources, 2008. **182**(1): p. 1-17.

[5]Boland, S., et al., *Biocatalytic fuel cells: A comparison of surface pre-treatments for anchoring biocatalytic redox films on electrode surfaces.* Journal of Electroanalytical Chemistry, 2009. **626**(1-2): p. 111-115.

[6]Rao, J.R., *Bioelectrochemistry. I. Biological Redox Reactions,*, M.B. G. Milazzo, Editor. 1983,, Plenum Press, New York. p. 283–335.

[7]Palmore, G.T.R., et al., *A methanol/dioxygen biofuel cell that uses NAD(+)-dependent dehydrogenases as catalysts: application of an electro-enzymatic method to regenerate nicotinamide adenine dinucleotide at low overpotentials.* Journal of Electroanalytical Chemistry, 1998. **443**(1): p. 155-161.

[8]Willner, I., G. Arad, and E. Katz, *A biofuel cell based on pyrroloquinoline quinone and microperoxidase-1 monolayer-functionalized electrodes.* Bioelectrochemistry and Bioenergetics, 1998. **44**(2): p. 209-214.

[9]Weidlich, E., et al., *Animal-Experiments with Bio-Galvanic and Bio-fuel Cells.* Biomaterials Medical Devices and Artificial Organs, 1976. **4**(3-4): p. 277-306.

[10]Stoller, M.D., et al., *Graphene-Based Ultracapacitors.* Nano Letters, 2008. **8**(10): p. 3498-3502.

[11]Choi, Y.K., et al., *A hybrid biofuel cell based on electrooxidation of glucose using ultra-small silicon nanoparticles.* Biosensors & Bioelectronics, 2009. **24**(10): p. 3103-3107.

[12]Kerzenmacher, S., et al., *An abiotically catalyzed glucose fuel cell for powering medical implants: Reconstructed manufacturing protocol and analysis of performance.* Journal of Power Sources, 2008. **182**(1): p. 66-75.