

Bio-Fuel Cells – Energy Harvesting Nano Particles

by

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Bio-Fuel Cells – Energy Harvesting Nano Particles

Preliminary design document

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The document proposes to model the structure and properties of a producible Nano energy harvesting biofuel cell (BFC).

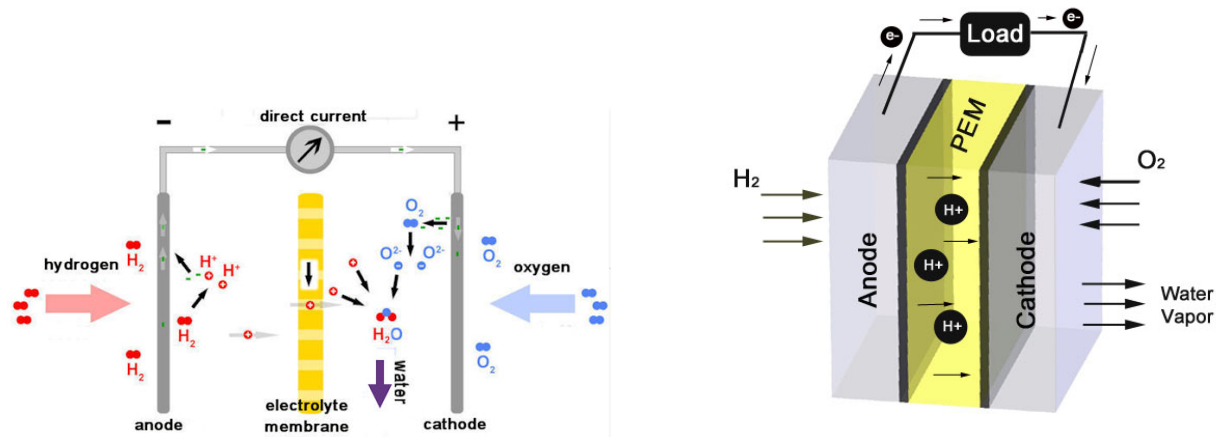


Fig 1: Fuel cell. PEM → Proton Exchange Membrane

Problem Statement:

Figure 1 provides a pictorial representation of a traditional PEM BFC. BFCs are defined as systems capable of converting chemical to electrical energy by biochemical pathways. Maintaining a net potential difference between the anode and the cathode of a BFC requires separation of the oxidation and reduction half-reactions, each to only one of the fuel cell electrodes respectively. Failing to do so results in lower/near-to-zero net potential between the electrodes. The fuel source for BFCs (hydrogen and oxygen) are twined into blood or other physiological fluids in the form of glucose. On the contrary, traditional fuel cells are designed to separate the fuel through compartments, permitting the delivery of fuel to the anode (for oxidation, liberating electrons as a result) and oxidant to the cathode (for reduction, using the electrons to form water as a by-product) via two different/separate processes. This prevents electro-chemical short circuits in the cell. BFCs face the problem of separating the fuel from a single source.

References [1, 2] have proposed designs where the above-mentioned problem is solved. In general, all the references suggest a laminar structure with (i): Electrodes and (ii) an ion-selective permeable membrane. The membrane's sole job is to separate the constituents of blood (combined fuel, in our case) to the desired fuel for the anode and cathode. There is a need for a mechanism where two pathways exist for the H^+ and e^- ions to permeate through the cell, thus inducing in a current.

According to definition, a fuel cell is biological if in at least one electrode: the reactant is found in biological fluids, or the reaction catalyst is biological. As we see from the figure, the inlet of hydrogen and oxygen, the two needed fuels for a bio-fuel cell (BFC) are provided in separate compartments. This reduces the fouling of electrodes. Moreover, in a BFC, Platinum (Pt) has the best ability to catalyze glucose but provides carbon monoxide as a by-product (hazardous). To avoid this, in most cases, oxygen depleted glucose is provided to platinum electrodes for catalysis and subsequent electron transfer.

Availability of Glucose and Oxygen in Blood:

The power generated by a glucose fuel cell is given by

$$P = J_g * \eta * \Delta G_g$$

P is the generated power, η is the total coulombic efficiency of the BFC, ΔG_g is the heat enthalpy (combustion) of glucose and J_g is the minimum glucose flux required to power a BFC. From literature, a coulombic efficiency η_c exceeding 80% and a minimum efficiency of 8% was reported in [3]. The heat enthalpy ΔG_g is -2880 kJ/Mol . Assuming a power of 1 mW to be generated in a day, the minimum glucose flux is given by

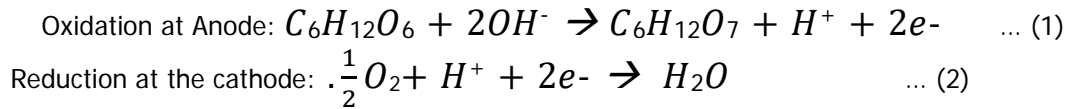
$$J_g = \frac{(1 \text{ mW}) * (86400 \text{ Sec / day})}{(0.80 \text{ to } 0.08) * (2880 \text{ kJ/Mol})}$$

Thus, **37.5 – 375 μMol of glucose per day (~6.75 mg)** is required to generate **1 mW of power** in a BFC. The amount of oxygen in blood is **~3ml per litre of blood**. This is calculated from the value of partial pressure of blood in the arteries. The cathode reaction $\frac{1}{2}\text{O}_2 + \text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$, requires 6 moles of oxygen per mole of glucose. The minimal oxygen flux is given by the equation

$$J_{\text{O}_2} = a_{g(\text{O}_2)} * J_g$$

The value of oxygen requirement is taken from this reference here []. Thus, it is calculated to be 225 – 2250 $\mu\text{Mol O}_2$ per day. This number is obviously very much lesser than the amount of oxygen present per litre of blood. **Thus, it is shown here that the amount of glucose and oxygen required for 1mW of power is more lesser than the amount generated and replenished by the blood.**

Please note: These calculations are irrespective of the device and structure of the BFC. It is only to show that the change in glucose and oxygen concentrations in blood is only fractional. Moreover, a supplement to enhance the concentrations in the blood, can be provided to the patient prior to the inducement of Nano robots.



The mean number of molecules transferred for a full oxidation of glucose is 24 electrons. This means that one molecule of glucose becomes completely oxidized. That is, the following reaction will be fulfilled.



But in the case of solid state catalysts, references suggest that the catalysts don't help in complete oxidation of glucose. Thus, the reaction in eq. 1 happens with the release of one electron pair.

The standard-state half-cell potential for the oxidation of glucose is -0.05 V . The anodic current generated by BFC varies according to the glucose concentration. The cathode consists of graphene sheet, where water evolution happens. The half-cell reaction at the cathode is in Eq 2. From references, the potential for the half-cell reaction is $+0.401 \text{ V}$. Thus, the total cell potential is $+0.45 \text{ V}$.

According to the Nernst equation, the non-standard cell potential is given by

$$E_{\text{Cell}} = E^{\circ}_{\text{Cell}} - \frac{RT}{zF} \ln Q_r$$

Where, E_{Cell} is the cell potential of our interest, E°_{Cell} is the standard cell potential, R is the universal gas constant: $R = 8.314472 \text{ J K}^{-1} \text{ Mol}^{-1}$, T is the temperature in kelvin, z is the number of moles of electrons transferred in the cell reaction or half-reaction, F is the Faraday constant, the number of coulombs per mole of electrons: $F = 9.64853399 \times 10^4 \text{ C Mol}^{-1}$, Q_r is the reaction quotient.

Model of Energy Harvesting in Blood:

1. Nafion:

Nafion, was developed by Dr. Walther Grot at DuPont in the late 1960's by modifying Teflon. Nafion was the first synthetic polymer ever developed with ionic properties, and is an ionomer.

- Extremely resistant to chemical attack. Nafion does not release fragments or degradation products into the surrounding medium.
- Relatively high working temperatures (some applications at temperatures up to 190° C).
- Highly ion-conductive. It functions as a cation exchange polymer. Functions as an extremely strong proton donor.
- Nafion is very selectively and highly permeable to water.

2. Electrodes:

Solid state Raney-type Platinum electrode is chosen as the anode electrode. References here suggests methods to increase the surface area of the platinum electrode, thus increasing its catalytic capacity. The cathode is a semiconducting mesh graphene sheet.

The structure is shown and the details are explained below.

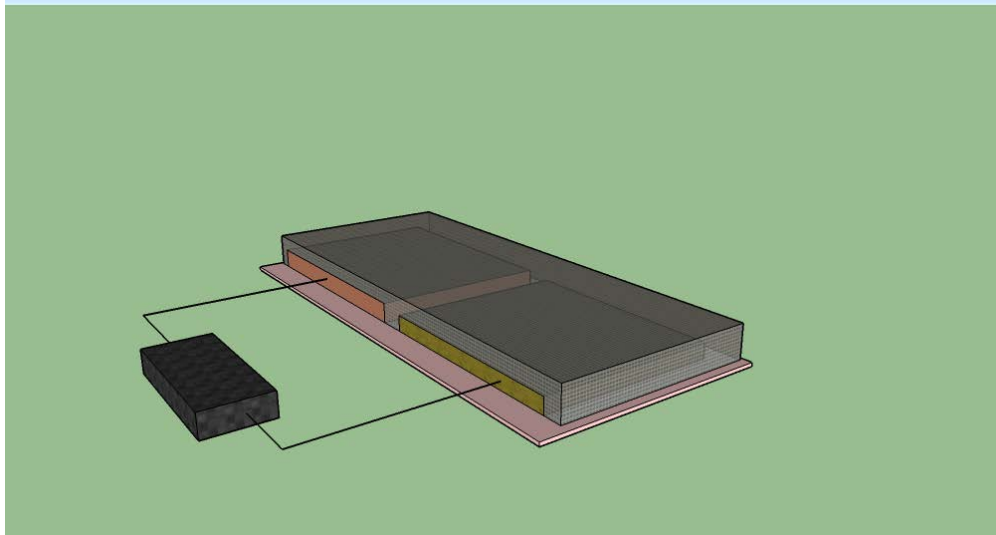


Fig 2: Cross Section of the Electrodes

A Raney-type platinum electrode anode (shown in brown) and a graphene nano sheet cathode (green) are covered under a Nafion-CNT composite membrane (a dielectric as well as a semi-permeable membrane). The purpose of this structure is to solve the problem of bio-fouling and to maintain a non-zero value in the net potential. The Nafion-CNT composite will act as a barrier, restricting negatively charged ions, smaller proteins and molecules to pass to the electrodes. But the composite is completely permeable to water vapor and glucose molecules. In the first process, glucose enters the Nafion membrane and platinum catalyst catalyses the glucose to gluconic acid, thus liberating two electrons (as shown in Eq 1). The figure shown above is a test structure.

As you see in Figure 3, the whole structure is covered by the Nafion-CNT composite. By the first process (Eq. 1), two electrons are liberated. Since the composite dielectric is non-permeable to negative charged ions, electrons cannot be transferred by the same way as protons do (H^+ ions can permeate through the Nafion membrane, it acts as a proton exchange membrane). So, in figure 3, a CNT channel is designed between the two electrodes to facilitate the transfer of electrons (black colored cylinder shapes between the electrodes, in Figure 3). Thus, it is possible to provide H^+ ions (through the membrane) and e^- (through the CNT) through separate channels, and the cathode then reduces oxygen to water.

Please note: The structure in figure 2 was designed in such a way to test it. Fig 3 is a completely enclosed version of Fig2, to be used in blood. These designs don't consider the provision to include the circuit and other elements to it. The only concern of this document is to provide a producible design of energy harvester.

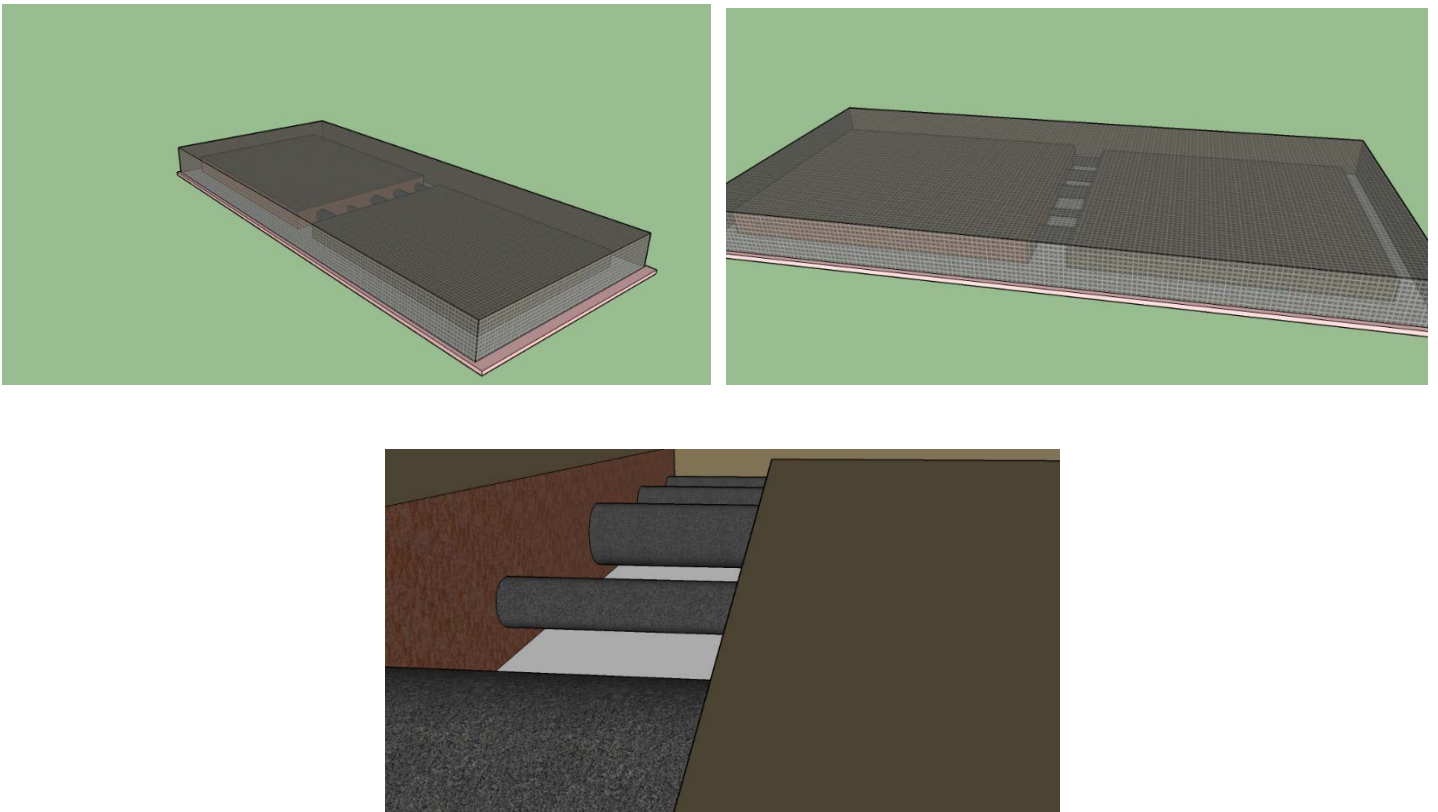


Fig 3: Fully enclosed structure, CNT channel between the electrodes

References:

- [1]. Rapoport BI, Kedzierski JT, Sarpeshkar R (2012) A Glucose Fuel Cell for Implantable Brain–Machine Interfaces. PLOS ONE 7(6): e38436. <https://doi.org/10.1371/journal.pone.0038436>
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- [3]. Kazuyo Kobayashi, Masahiro Nagao, Yuta Yamamoto, Pilwon Heo, and Takashi Hibino Rechargeable PEM Fuel-Cell Batteries Using Porous Carbon Modified with Carbonyl Groups as Anode Materials *Journal of the Electrochemical Society* 2015 162: F868-F877.