Bridge between research in modern physics
and entrepreneurship in nanotechnology

Quantum Physics

The physics of the very small with great applications

Part 2

QUANTUM PROPERTIES & TECHNOLOGY

Learning Station XII:

Microbial Fuel Cell

Lifelong Learning Programme

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LEARNING STATION XII: MICROBIAL FUEL CELL

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Introduction

This learning station aims at introducing the basics of different disciplines necessary for understanding the functioning of microbial fuel cells (MFC); this knowledge also makes it possible to build a simple microbial fuel cell at home. In addition to the so-called book knowledge, the latest scientific achievements in the relevant disciplines are discussed in this learning station. From a broader perspective, these learning materials could get young people interested in STEM subjects, the functioning of things and hands-on activities, as an actual device will be built here based on the knowledge gained of phenomena which would otherwise perhaps remain distant and uninteresting for students. As the microbial fuel cell is based on phenomena related to many disciplines, this learning station is also composed of several interconnected yet independent sections.

First, we introduce the general operating principle of the microbial fuel cell and then have a look at what influences its efficiency. For this, we need to study the basics of different disciplines. The first background knowledge section is dedicated to cellular processes, focussing on cellular respiration and metabolism. Next, we will have a look at energy density in organic materials and how energy is derived from them. We will be introduced to electrochemical processes, including those occurring in the Biota. Finally, we will see which materials are suitable for building a microbial fuel cell and get a glimpse of the latest scientific achievements in the field.

1. Microbial fuel cell – operating principle and applications

In broad terms, the operating principle of the microbial fuel cell (MFC) is the following: electrons produced by microorganisms are captured in the device, thus generating (electrical) energy from the fuel cell. Microorganisms receive energy by perfoming various oxidation and reduction processes, in the course of which chemical energy is (partially) converted to electrical energy. When oxidizing organic matter, microorganisms release electrons. In nature, the released electrons are consumed in other processes, whereas the idea behind MFCs is that these electrons are captured by the electrode (anode), from which they move to an external circuit, making it possible for their energy to be used to drive an electrical apparatus. Then, the electrons move to the opposite electrode (cathode), where a reduction process (typically, reduction of oxygen) takes place. In addition to electrons, protons produced in oxidation and used up in reduction must move from one electrode to the other, as well. Typically, protons are transferred to the opposite electrode through a proton exchange membrane.

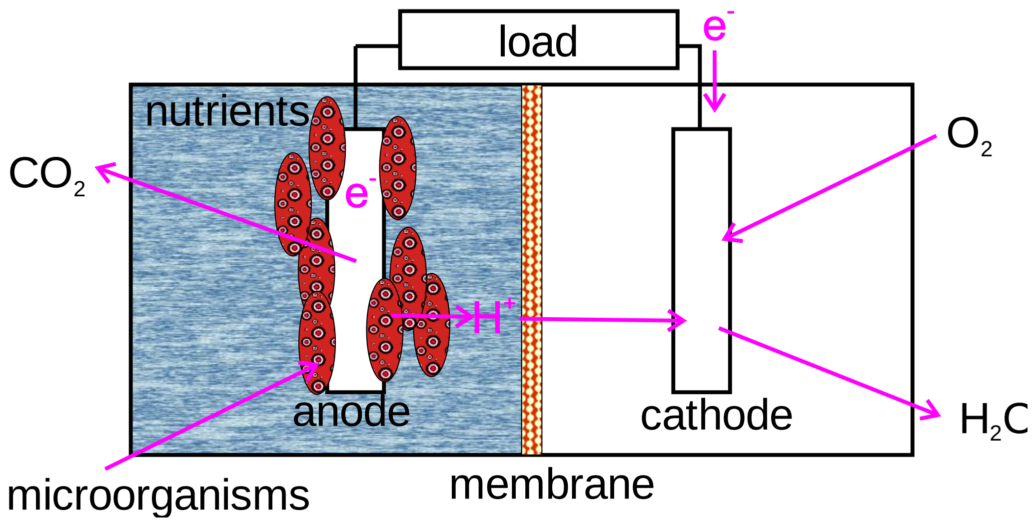

Figure 1. Operating principle of the MFC

Similarly to many other phenomena that are of interest to modern science, microorganisms' ability to generate electricity was discovered some time ago – already in 1911, M. Potter succeeded in making *E. Coli* produce electricity. However, decades passed until the principle behind MFCs was truly understood and scientists started to investigate it more closely. The work of H. P. Bennetto in the early 1980s helped considerably to turn MFCs from a curious object of investigation to a device of actual practical interest.

1.a Potential applications of the MFC

MFCs are often referred to as an important alternative energy source of the future. However, there is still a long way to go before this can be achieved. So far, only different niche applications have been developed. Some of the more realistic fields of application are listed below.

1. Wastewater treatment. Microorganisms have the advantage of having a double function: in addition to generating energy, they can also purify water. They are expected to be particularly beneficial in purifying wastewater from agriculture or food industry, which is high in organic matter. Here, the main function of MFCs would be to balance the energy-consuming wastewater treatment.

2. Underwater or remote sensing power supply. Thanks to advances in electronics, modern devices require less and less energy. Various autonomous sensors which, for instance, monitor environmental conditions, are located in places that are difficult to access, which makes changing their batteries extremely inconvenient. The ability of MFCs to use local organic matter as fuel would be excellent for such applications, since the possibility of storing energy in accumulators or supercapacitors and using it as needed compensates for their low power. Some sensor systems based on MFCs have been in constant use for more than five years, which is a notable achievement compared to most of the alternatives.

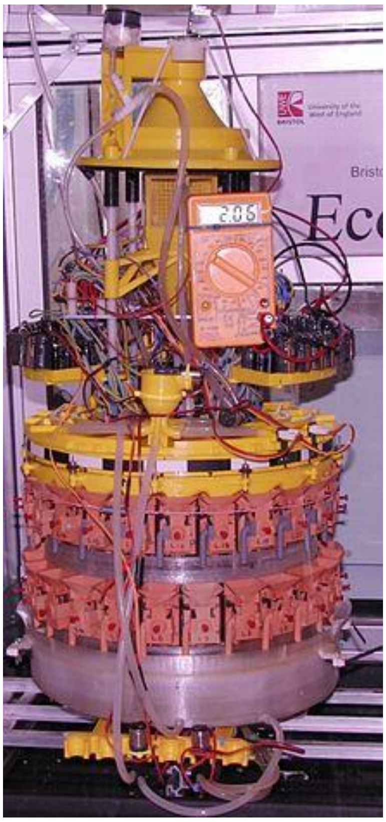

Figure 2. EcoBot III, MFC-based autonomous robot (source: Wikipedia)

3. Methane or hydrogen production. If the cathode compartment also has anaerobic conditions, then, at the cost of terminal voltage (which then slightly decreases), it is possible to produce either methane or hydrogen at the cathode, depending on the conditions; the methane or hydrogen can then be collected and used as fuel. This multifunctional system is also known as microbial reactor.

4. Autonomous robots. Using the MFC as a source of energy for autonomous robots has been investigated a lot. One of the most advanced systems developed here is the EcoBot series, the III generation of which (see Figure 2) was launched in 2010. The robot's power supply was taken care of by a battery composed of 48 MFCs. Among other things, the robot was able to find "food" by itself. At present, the IV generation is under development. You can find more detailed information about projects involving autonomous robots on the Bristol Robotics Laboratory website at *http://www.brl.ac.uk/researchthemes/bioenergyselfsustainable/ecobotprojectoverview.aspx*.

You can read more about scaling up MFCs in the following review: http://link.springer.com/article/10.1007/s00253-009-2378-9 (B.E. Logan. *Scaling up*

microbial fuel cells and other bioelectrochemical systems. Applied Microbiology and Biotechnology 85(6), 2009, 1665-71).

2. Cellular respiration

Just like other living organisms, microorganisms need energy for growing, developing, as well as for simply existing. To get energy, they also need – in addition to a suitable environment and nutrients – an electron acceptor which would accept the electrons released in the oxidation processes. Respiration in plants and animals is based on oxygen, which serves as the terminal (i.e. final) electron acceptor in the multi-stage electron transport chain. In other words, oxygen reduction is a process where the leftover electrons are finally used up. The energy system of bacteria is much more flexible than that: as electron acceptors, different bacteria can use sulphur and its various compounds, several nitrogen compounds and, in some cases, even metal compounds in higher oxidation states. Such adaptability allows bacteria to inhabit environments (including anaerobic environments) which are uninhabitable for higher organisms. Furthermore, many bacteria are also capable of adapting to unstable or changing conditions and using the most efficient processes for each occasion. Still, aerobic (i.e. oxygen-based) metabolism is much more effective than anaerobic metabolism, which is why bacteria also prefer aerobic processes for getting energy, whenever possible.

If an environment lacks any suitable electron acceptors, some bacteria (but also, e.g., yeasts) can use an even less effective alternative for getting energy – fermentation. In the case of fermentation, the terminal electron acceptor is found inside the cell. Lactic acid bacteria, for instance, receive energy through fermentation of lactose – a process which results in the production of lactic acid. In our everyday lives, we can see this phenomenon in soured milk (both intentionally soured and simply gone bad).

Cellular respiration is the interconnected set of metabolic reactions and processes in the cells of organisms. These processes result in converting biochemical energy from nutrients into energy stored in adenosine triphosphate (ATP) and then releasing waste products. In general, cellular respiration is exothermic, i.e. some of the energy is released as heat during the process. Anaerobic cellular respiration, where energy is received from sugar, is described by chemical equation (1).

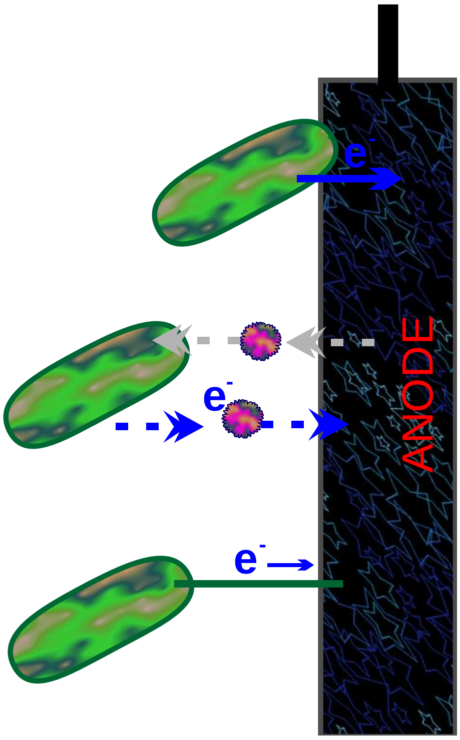

Figure 3. Different methods bacteria use for transporting electrons to the anode: direct (top), using a mediator (middle), and using a nanowire (bottom).

$$C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^- \qquad (1)$$

Equation (1) demonstrates that in addition to electrons, the reaction also results in a large amount of protons, i.e. hydrogen ions, which also need to be got rid of, since the environment in the organism would otherwise turn too acidic (i.e. the pH value would become too low).

To produce electrical energy through MFCs, bacteria are placed in conditions where the chances of finding suitable electron acceptors in the surrounding (solution) environment are extremely low. To still use respiration instead of the much less effective fermentation method for getting energy, bacteria use an extracellular electron acceptor – a solid electrode (anode). Protons, on the other hand, must end up at the cathode, where they will be neutralized. Using the electrode as an acceptor allows the bacteria to colonize the surroundings of the electrode (anode) and find the most suitable way of transporting electrons. Bacteria have developed various strategies for transporting electrons to the anode (see Figure 3).

One option is to use a mediator which will transport the electron through the cell membrane. A mediator is also added in order to use electrochemically inactive bacteria in MFCs. However, such artificially added mediators are expensive as well as toxic, which is why mediatorless MFCs, based on electrochemically active bacteria, are considered more promising. As one of the possible strategies for giving away electrons, some electrochemically active bacteria (e.g., the *Geobacter* and *Shewanella* genera, widely used in MFCs) are able to grow nanowires, through which the electrons will be transferred. Such bacterial nanowires (see Figure 4) can transport the electron directly to the electrode, but also to the neighbouring bacteria, who will then, in turn, pass the electron on. An even more exciting solution is the ability of some bacteria to produce or use existing molecules with specific properties as transport shuttles which "fly" the electrons to the acceptor.

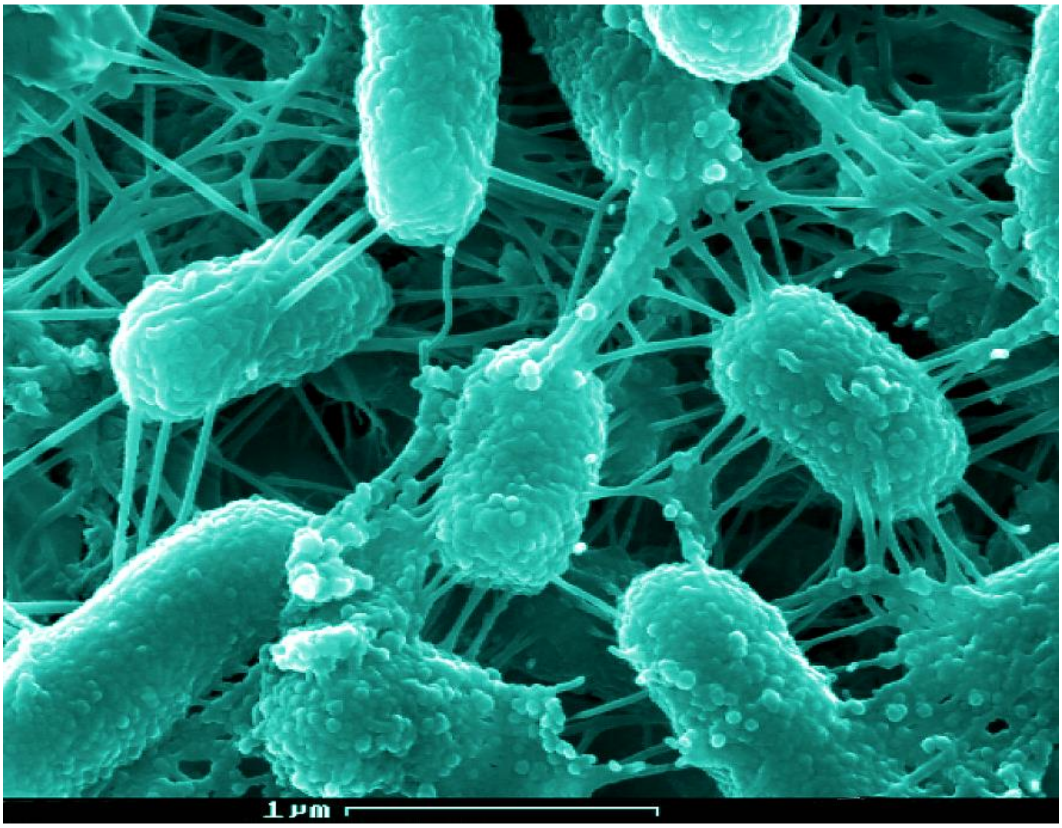

Figure 4. Nanowires connecting bacteria (adapted micrograph taken through a SEM, from BlueTechBlog – http://bluetechblog.com/2010/06/15/make-electricity-not-sludge/)

3. Electrochemistry and bioelectrochemistry

3.a Redox reactions

Before becoming acquainted with electrochemistry, let us take a look at oxidation and reduction reactions (i.e. **redox reactions**) in general – after all, electrochemical reactions are a subclass of redox reactions. Redox reactions are processes in which the electron moves from one particle (molecule or ion) to another (molecule or ion). Reduction and oxidation always go together: when one particle (reducer) loses an electron (oxidizes), another particle (oxidizer) must accept the electron (and thus be itself reduced). These transfers and related concepts are illustrated by Figure 5. Redox reactions are a very common type of reaction – each time an elementary substance turns into a compound substance or the other way around, we are witnessing a redox reaction. In the case of reactions occurring between compound substances, a redox reaction can be identified by a change in the oxidation state of some of the elements in the course of the reaction.

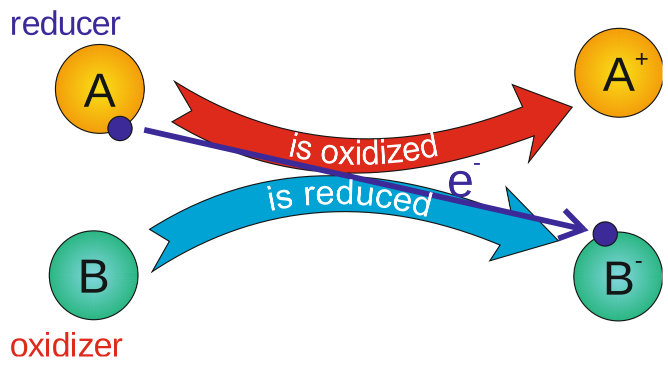

Figure 5. Terms describing redox reactions. Reducer is a substance that gives away electrons and is thus itself oxidized. Oxidizer is a substance that accepts the electrons and is thus itself reduced.

3.b Electrochemistry

Electrochemistry deals with **electrochemical reactions** – these are redox reactions which only occur when driven by an external electric current (electrolysis) or, the other way around, spontaneous reactions during which an electric current is produced (electrochemical element). Another characteristic of electrochemical reactions is that oxidation and reduction do not take place in the same location but are separated by an electrolyte (ionic conductor), whereas electrons move through an external electrical circuit. Electrochemical reactions generally occur on electrodes, which are usually made of metal or some semiconductor material.

When a piece of metal (e.g., an electrode) is submerged in a salt solution of the same metal, an electric potential difference occurs at the interface between the metal and the solution. The electrode acquires a certain potential compared with the solution – **electrode potential.** A less reactive metal (such as copper) obtains a positive potential, because some of the copper ions are attracted to the electrode. In the corresponding equation (2), the chemical equilibrium lies on the right-hand side (products of the reaction).

$$Cu^{2+} + 2e^{-} \rightleftharpoons Cu \qquad (2)$$

In the case of reactive metals (such as zinc), the situation is contrary: the piece of metal tends to be dissolved, and the electrode acquires a negative potential compared with the solution. In the corresponding equation (3), the equilibrium lies on the left-hand side (starting materials).

$$Zn^{2+} + 2e^{-} \rightleftharpoons Zn \qquad (3)$$

The size of the potential therefore depends on the nature of the metal as well as on the concentration and temperature of the solution. Neither process can go on very long on its own, because in the case of less reactive metals (Cu), the electrode will run out of electrons, whereas in the case of more reactive metals (Zn), there will be an excessive build-up of electrons. However, if we join these two pieces of metal in an electric circuit and establish ionic conductivity between the solutions (by using a salt bridge or membrane), we have built an electrochemical cell (see Figure 6). The electrons can move from one electrode (anode) to another (cathode), and the electrode processes can go on until there are enough reacting species.

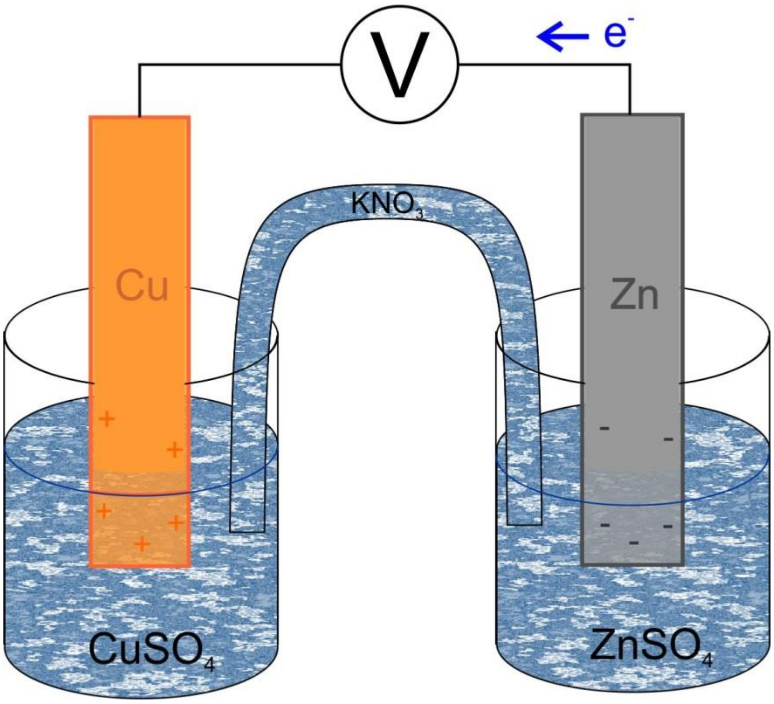

Figure 6. Electrochemical cell (Daniel cell), where the aggregate redox reaction Cu^{2+} + Zn = Cu + Zn^{2+} occurs on separate electrodes, and the electrons are moving through an external circuit from the anode (Zn) to the cathode (Cu).

3.c Bioelectrochemistry

Both electrochemistry and bioelectrochemistry originate from the experiments of the famous A. Volta and L. Galvani in the 18th century. **Bioelectrochemistry** is the study and application of biological electron transport processes. Today, bioelectrochemistry is more widely spread, having links to medicine and physiology as well as biochemical reactors, which also include MFCs. MFCs are not the only field where electrochemistry and (cell) biology come together. For instance, scientists are also investigating how biological materials could be used in electronics, data storage, construction of biosensors, bionics, and elsewhere. Another rapidly developing field is microbial electrosynthesis, which employs microorganisms to synthesize new substances.

To learn more about the possible applications of bioelectrochemistry, you can read the following article: http://www.sciencedirect.com/science/journal/13640321 (Deepak Pant, Anoop Singh, Gilbert Van Bogaert, Yolanda Alvarez Gallego, Ludo Diels, Karolien Vanbroekhoven. *An introduction to the life cycle assessment (LCA) of bioelectrochemical systems (BES) for sustainable energy and product generation: Relevance and key aspects*. Renewable and Sustainable Energy Reviews, 15 (2), 2011, 1305–1313.

4. Nanostructural materials for the MFC

4.a A short overview of nanostructural materials

For a long time, MFCs were considered unpromising owing to their low productivity and efficiency (especially compared to other fuel cells), whereas building them required rather expensive materials. Cathode material (usually platinum or some other oxygen reduction catalyst) accounts for more than half of the price of a typical MFC, and the price of the membrane material makes up most of the remaining half. However, the field has undergone some significant developments lately – introducing cheaper nanocomposite materials, often those based on nanostructural carbon (see Figure 7) for manufacturing electrodes has been one of the most important ones. Such electrodes have better conductivity, good durability, a large specific surface area, and they often also exhibit useful catalytic properties. This is a very important aspect in the design of MFCs, because electrode material plays the most important role in how efficient the MFC will be. Anode material regulates the attachment of bacteria and the speed of electron transport and nutrient oxidation, which, in turn, determine the power of the MFC. The specific surface area and catalytic properties for speeding up the oxygen reduction reaction are important for the cathode, as well.

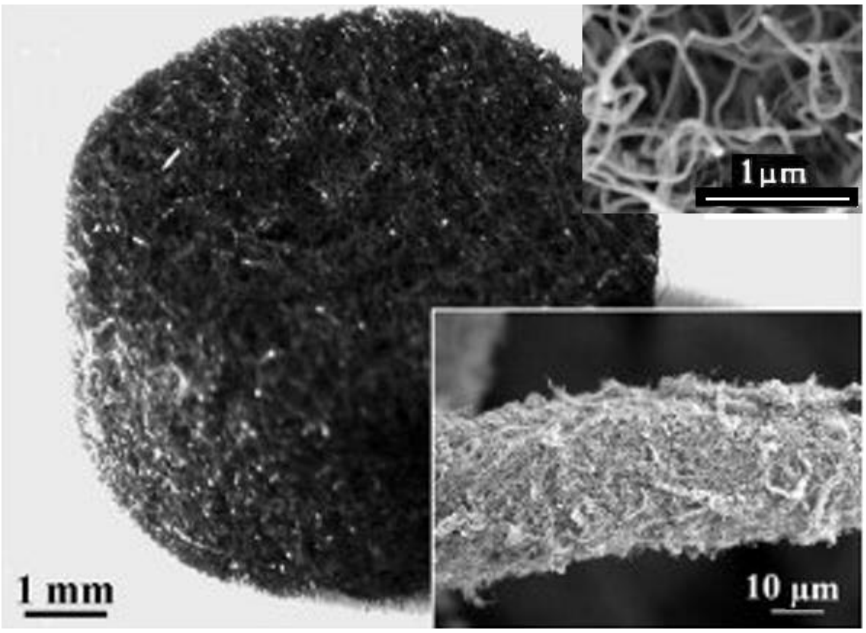

Figure 7. Carbon felt containing nanostructural carbon fibre, images in different scales (adapted images R. Vieira, http://dx.doi.org/10.5772/8145)

In recent years, nanotechnology has revolutionized many fields of science and technology, as specific properties resulting from the nanometre scale allow scientists to either significantly improve the performance of various materials or create surfaces and materials with new, previously unheard-of properties. The achievements of nanotechnology are exploited in a number of fields, including textile, glass, plastic and composite technology as well as production of power supplies, electronic, optical, medical and many other devices and objects. In addition to their extraordinary properties, nanotechnological materials tend to be relatively low-priced thanks to their high efficiency; also, manufacturing and using such materials produces less waste and environmental pollution. Nanotechnology is a term for technologies where using particles smaller than 100 nm leads to new properties (in a qualitative sense) compared with materials based on larger particles. A particularly large specific surface area, but also (partly resulting from the large specific surface area) higher activity and (chemical) selectivity are some of the most important properties of nanoparticles. Solar panels, supercapacitors and other modern technological achievements would not exist without nanotechnology. Nanoparticles also exhibit much higher biological activity, which, however, could also be a negative property in some cases, such as toxicity.

Carbon nanotubes are, no doubt, some of the most talked-about recent nanostructural materials. The length-to-diameter ratio of the cylinder-shaped tubes can be millions to one, which, together with their strength and conductivity, is the main property that technology is trying to utilize. At the same time, several technical issues need to be solved when it comes to using nanotubes: for instance, unmodified nanotubes are insoluble, which makes producing thin even layers difficult. Using nanotubes in biological applications is complicated as well, because nanotubes tend to be cytotoxic, i.e. lethally toxic to cells. Therefore, carbon nanotubes cannot be used in MFCs or other microbial systems unless they go through a significant chemical modification to increase their solubility and decrease toxicity.

Nanocomposite materials, i.e. nanocomposites are multiphase compound materials where at least one of the components has at least one dimension of less than 100 nm (see Figure 8). Such materials can be of either organic or inorganic origin – both variants are increasingly used in science and technology. Special focus is on polymer nanocomposites, where the even distribution of nanoparticles in the polymer matrix gives the material significantly improved qualities at low material input.

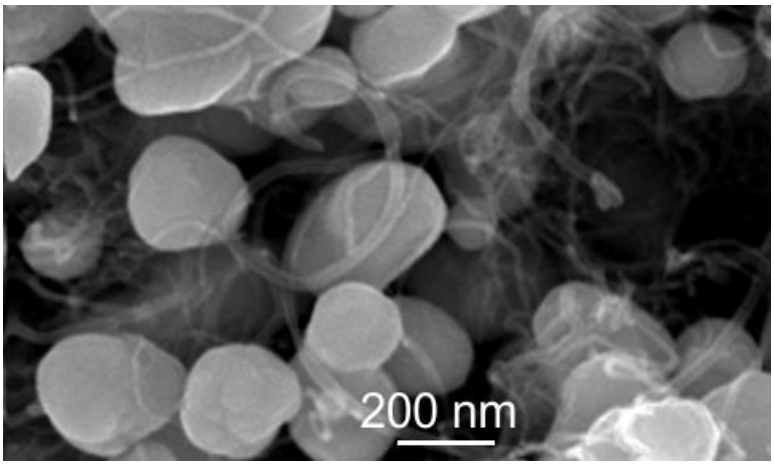

Figure 8. Nanocomposite made of carbon nanotubes and copper nanoparticles (adapted image Bioneer Corp. http://nanobio.bioneer.com)

You can read more about different nanostructural materials in Learning Station XI: From Quantum Mechanics to Nanoparticles and Their Applications.

4.b Nanocomposites for the MFC

Energy produced by the MFC directly depends on the area of its electrodes, but building devices with gigantic electrodes is obviously not practical. Therefore, electrodes should be built from materials with a large specific surface area, where the area of usable material per unit of mass or volume is as large as possible. Various carbon materials with large specific surface areas are currently used in the anodes of MFCs: carbon paper, carbon felt, carbon fibre, etc. The specific surface area of the microstructural main material is often increased and its qualities improved through nanostructural additives or modifications (see Figure 9). In addition to a large specific surface area, many carbon materials also have the good qualities of being stable in a biological environment and having a rather satisfactory electrical conductivity. As for cathodes, a traditional but rather high-cost approach involves covering large-surface-area (carbon) material with platinum, which is supposed to function as an oxygen reduction catalyst. Conducting polymers are also used in electrode manufacturing, whether as a catalyst in the cathode, for bonding some other catalyst or for bonding particles of carbon material in the anode or cathode. In addition to electrical conductivity, such polymers have several other good qualities: for instance, they are biocompatible, durable, and very easily and controllably synthesized. Controllability is certainly important in electrode manufacturing, as the efficiency of the MFC often depends on the micro- or nanostructure of the electrode. Lately, the focus has indeed shifted on the study of well-controlled polymer nanocomposites and their application as electrode materials.

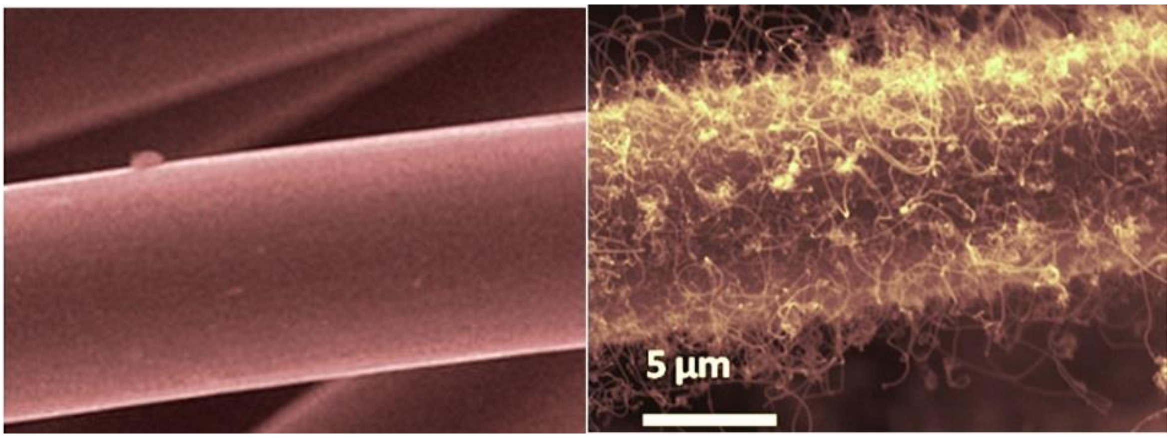

Figure 9. Fibres of unmodified graphite carbon felt (left) and those of graphite carbon felt modified with carbon nanofibres (right) (adapted micrograph taken through a SEM Shen *et. al.* http://dx.doi.org/10.1155/2014/130185)

5. Efficiency of the MFC

As usual in a current source, the available power (P) is determined by the potential difference (ΔE) and electric current (I), described by equation (4):

$$P = I \times \Delta E. \quad (4)$$

Electric current, potential difference and external resistance (R_{ext}) are interrelated, as described by Ohm's law – equation (5):

$$\Delta E = I \times R_{ext}. \quad (5)$$

If the external resistance were infinitely high and there were no electric current, the potential difference would be equal to the electromotive force (E, also known as open-circuit voltage) of the current source. And, the other way around – if there is no resistance (short circuit, $\Delta E = 0$), electric current is equal to short-circuit current (I_{lv}). The relationship between electric current (or, to be more precise, current density) and potential difference is well described by the polarization curve (see Figure 10), where you can easily see both the electromotive force and short-circuit current. Both the optimal current density (I_{opt}) and optimal potential difference (ΔE_{opt}) necessary for the functioning of the MFC can be derived from the maximum power (or, more precisely, power density).

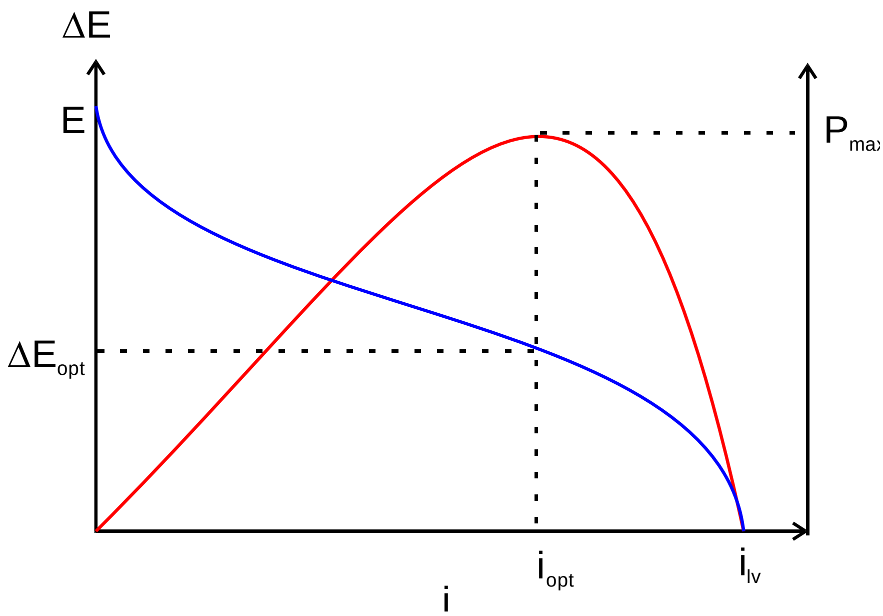

Figure 10. A typical polarization curve of the MFC (blue) and the corresponding power curve (red)

The ideal performance of the MFC depends on the nature of the electrochemical processes going on between the organic raw material and the terminal acceptor (typically oxygen). Approximately 50–90% of the energy produced through the oxidation of organic nutrients is converted into electricity by the MFC; the rest is spent on the growth of microorganisms.

The actual terminal voltage from the electrodes is lower than this ideal estimate, because MFCs always have at least three types of energy loss. The first of them – activation polarization – plays an important part in low current densities and is related to activation energy, which needs to be exceeded in order to have a reaction. This includes the adsorption of starting materials, desorption of products, and the energy barrier for electron transfer – all of this, in turn, depends on the area and properties of the surface of the electrode, but also on the organism used and other parameters. When greater loads are applied, ohmic resistance starts to play a part in the energy loss caused by limited electron and ionic conductivity in the different parts of the MFC (membrane, electrolyte, etc.). The design of the MFC has an important role in decreasing ohmic resistance: electrolytes and membranes with good conductivity should be preferred, and the distance between the electrodes should be kept to a minimum. In the highest charge densities, concentration polarization becomes the dominant factor in reducing efficiency, caused by a decrease in the available amount of nutrients owing to the general concentration of nutrients or complications in their distribution. Mixing – whether mechanical or using gas bubbles – as well as smart design of the MFC helps fight this type of loss.

Most experiments with MFCs have been conducted at the laboratory scale, using relatively miniature devices. The experiments have shown that simply constructing a larger MFC is not enough to increase its power: it will lead to a decrease in efficiency (primarily energy density). Better results have been achieved through connecting together several smaller MFCs – both in series and in parallel – in order to increase the terminal voltage and power, respectively.

6. Building a makeshift MFC

Everyone can build a MFC with available materials and relatively little effort. Of course, such a device is no top scientific achievement, but building it is certainly an educative and exciting experience. You can find various ready-made kits (e.g., http://www.mudwatt.com/products/mudwatt?variant=766869483) and instructions on the Web. The following is one of the ways to build your own MFC using handy materials.

To build your own MFC, you will need the things listed below.

- Mud – the easiest way to collect it is from the bottom of a water body. The mud should have as little exposure to air as possible to retain the anaerobic bacteria.
- A container – a regular round box with a consistent diameter will do.
- Electrodes – you can make electrodes with large specific surface areas from charred cloth. Put pieces of cotton cloth (denim is a good material) in a metal box with a small opening. Heat the box in a flame or on coal until no more smoke comes out of the box. Let it cool down. Take the pieces of charred cloth out of the box. If possible, measure the resistance of the burnt cloth with a multimeter – if the resistance is less than 200 ohms over a distance of 1 cm, the material is suitable. If the resistance is more than 200 ohms, the charring should be repeated. To build electrodes, wrap two pieces of charred cloth in a metallic net or spin some thin wire around them (preferably not a copper wire, which is toxic to many bacteria).
- A membrane – you can make a simple membrane from table salt, water and gelatine. Take 75 g of table salt and 5 g of gelatine for 200 ml of water. Mix them together and bring to a boil. Pour the mixture in a vessel with a smooth surface (ideally of the same shape and diameter as the one used for building the MFC). Let it cool down, preferably in the fridge.

To build the MFC, pour the mud in the container and immerse one of the electrodes (anode) in the mud so that one end of the surrounding wire sticks out of the container. Cover the mud with the membrane. Place the other electrode (cathode) on top of the membrane so that one end of the surrounding wire sticks out of the container. Pour some water on the membrane so that half of the cathode remains out of the water. And your MFC is ready (see Figure 11)! You can measure the terminal voltage generated by your MFC by connecting a voltmeter to the ends of the wires. Write the measure down. The voltage should increase in a couple of days or weeks, caused by bacterial growth and attachment to the anode. If possible, connect a resistor between the terminals of your MFC for the time of the bacterial growth, for instance, 100 Ω to 1 kΩ.

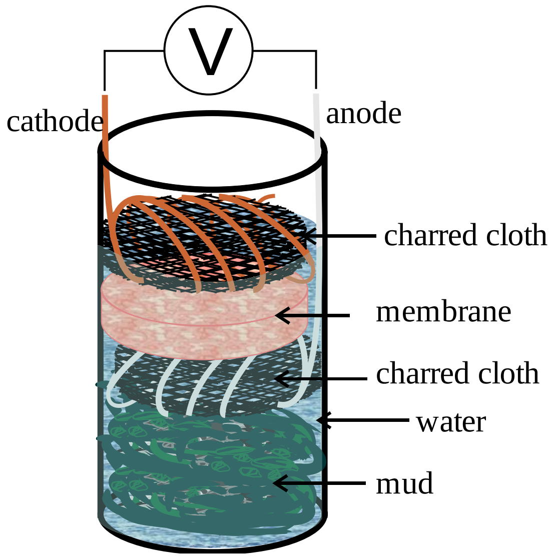

Figure 11. Homemade MFC

Concepts in Learning Station XII

Complete by adding the missing concepts

In this learning station we do not devide into classical and quantum concepts. The main concepts belong indeed not only to physics, but rather to various disciplines and they draw a link between quantum mechanics and other scientific areas, like biology and chemistry.

When oxidizing organic matter, microorganisms release .... that, in MFCs, are captured captured by the electrode (anode), from which they move to an external circuit, making it possible for their energy to be used to drive an electrical apparatus.

To get energy microorganisms need an .... which would accept the electrons released in the oxidation processes. As acceptor they can use several .... which allows bacteria to inhabit environments (including anaerobic environments) which are uninhabitable for higher organisms.

In the absence of enough electron acceptors, bacteria can also receive energy through ...., which is much leff effective than ....

In the MFC bacteria have extremely low chances of finding suitable .... To still use respiration for getting energy, bacteria use an extracellular electron acceptor – a .... Bacteria have developed various strategies for transporting electrons to the anode.

One possible strategy for giving away electrons, some electrochemically active bacteria grow ...., through which the electrons are transferred. Such bacterial nanowires can transport the electron directly to the electrode, but also to the ...., who will then pass the electron on.

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