



Carbon nanotube/enzyme biofuel cells

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ABSTRACT

Carbon nanotubes (CNTs) became a prominent material for its use in bioanalytical devices due to their biocompatibility, their particular structure, and their conductivity. CNTs have shown to be particularly appropriate to establish electronic communication with redox enzymes since the thin diameter can be approached closely to the redox active sites enabling therefore the regeneration of the biocatalysts either by direct electron transfer (DET) or with the help of so-called redox mediators which serve as intermediated for the electron transfer. The possibility to capture the enzymatic redox processes by obtaining catalytic currents, the use of such CNT-enzyme electrode for biological energy conversion represents the logic consequence. The development of CNT based enzyme biofuel cells (BFCs) is a still young but steadily growing research topic where original approaches to construct electron transfer based CNT-bioelectrodes and impressive biofuel cell performances are highlighted in this review. The evolution of reported biofuel cells consisting of CNTs and enzymes at the bioanode and the biocathode are summarized.

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1. Introduction

Fuel cells represent nowadays a promising alternative for energy production with many advantages compared to combustion of fossil energy or nuclear power. Fuel cells provide another mode of electric energy generation which is based on the transformation of chemical energy directly into electricity via redox reactions. This leads to higher efficiency by reducing the environmental impact. Fuel cells usually operate with two catalytic electrodes where the anode oxidizes the “fuel” (e.g. hydrogen or alcohols) and the cathode catalyses in most cases the reduction of oxygen.

A sub-class of fuel cells are biofuel cells (BFCs) where the involved redox processes are generally catalyzed by enzymes in their purified form or within an organism. The particularity of enzymatic biofuel cells is the high specificity towards the “fuel” (sugars, alcohols or hydrogen at the anode and the reduction of oxidants (O_2 , H_2O_2) at the cathode to generate electrical power (Fig. 1). Thanks to the energy conversion under mild conditions (20–40 °C at neutral pH) and the specificity to the substrates, such electrical power generators can be used in complex media found in living organisms or vegetables with no separation between the bioanode and the biocathode [1–5]. Furthermore, this type of fuel cells do not use any noble and transition metal catalyst such as platinum which are the main components in conventional fuel cells. These advantages made enzymatic biofuel cells promising power suppliers for portable electronic devices, biosensors, medical implants, or other

type of biorelated electrical devices. The possibility to generate electrical power via living organisms directed biofuel cell research towards glucose biofuel cells (GBFC) since the two required compounds (glucose and oxygen) are present in both, vegetal and body fluids. Furthermore, enzymes catalysing the oxidation of glucose and the reduction of oxygen, respectively, are generally easily available. In this vein, the first implantation of a biofuel cell in the rat abdomen [6] have paved the way for future applications of biofuel cells for continuous supply of implanted electronic devices such as pacemakers. Nevertheless, even when glucose biofuel cells are currently mainly focused, lots of efforts are also invested in hydrogen or alcohol-based biofuel cells, where the anode operates with hydrogenases or alcohol dehydrogenases, respectively.

Although the first example of a biofuel cell was described in 1964 [7], this research field remained almost unperceived for more than twenty years until a renewed interest arises in the late nineties [8]. This can be explained by important technological breakthroughs as the development of efficient immobilization strategies for biomolecule combined with enzyme wiring by molecular engineering using redox mediators. Indeed, the establishment of an efficient and lasting electrical communication between enzymes and electrode remains the most challenging issue. In this context, the availability of nanostructured conducting materials like carbon nanotubes (CNTs) contributed to important breakthroughs in the field of enzymatic biofuel cells. CNTs are nanowires constituted by one (called single-walled carbon nanotubes, SWCNTs) or more (called multi-walled carbon nanotubes, MWCNTs) seamlessly enrolled graphene layers with different diameters, length and chirality. CNTs exhibit high specific surface, excellent biocompatibility, antifouling properties, and high conductivity.

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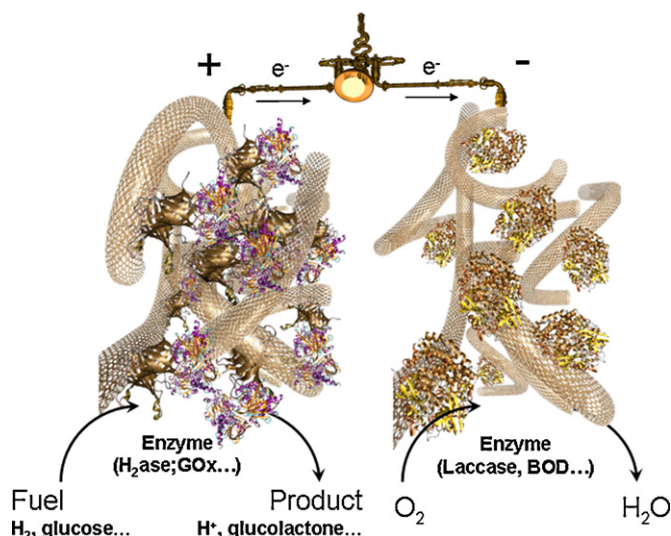


Fig. 1. Schematic representation of an enzymatic fuel cell based on CNTs.

CNTs with diameters between 1 nm (SWCNTs) and 10 nm (MWCNTs) have the ability to get placed in close proximity of the active site of redox enzymes, playing therefore an important role for interfacing enzymes with electronic circuitry. In particular, randomly-deposited or vertically-aligned CNTs constitute a versatile tool for the development of conductive three-dimensional biomaterials dedicated to improve the performance of the bioelectrodes in terms of electroactive surface, porosity and electron transfer rate. As a consequence, electrodes modified with CNTs have aroused widespread attention in the design of biofuel cells.

Besides their ability to access the embedded active site of the enzyme in order to achieve direct electron transfer, one major aspect has motivated scientists to use CNTs in BFCs: their high 3D electroactive area that increases the surface concentration of enzymes and others redox partners. Indeed the exceptional properties of CNTs in terms of conductivity and porosity have made them a very promising material for immobilizing biomolecules leading to many applications in biosensors and biofuel cells.

Since CNTs gain a steady increasing importance in enzymatic biofuel cell research, the accomplished milestones are reviewed in this article. Indeed, the possibility to use CNT-based bioelectrodes with electronic communication between a redox enzyme and the CNTs for biofuel cell applications led to an almost exponential increase of publication in this topic (Fig. 2).

2. Electrical enzyme wiring and mass transport of biofuels

For the development of high performance biofuel cells, two main bottlenecks have to be overcome: efficient electron transfer between the enzyme active site and the efficient supply of the enzymes with the combustible and oxygen within the electrode configuration of the biofuel setup.

In its natural environment, the electron transfer within enzymes is achieved by enzymatic cofactors such as nicotinamide adenine dinucleotide (NAD), pyrroloquinoline quinone (PQQ), or flavine adenine dinucleotide (FAD) for glucose oxidation, or iron-sulfur clusters in hydrogenases. When enzymes are immobilized onto the surface of electrodes, two main strategies are employed for the electric wiring of the active site to the electrode:

- Mediated electron transfer (MET), mediators are small redox active molecules with excellent electron transfer kinetics which serve as intermittent electron donor/acceptor between the enzyme and the electrode surface. The redox potential of such

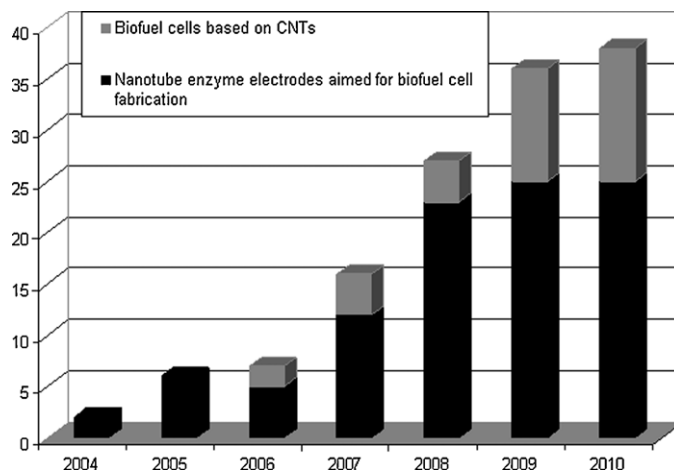


Fig. 2. Evolution of the number of published articles related to CNT based biofuel cells (until 2010). The black bars represent developed CNT-bioelectrodes, whereas the grey bars display the number of articles describing a working biofuel cell by using at least one CNT based bioelectrode.

mediators has to be as close as possible to the redox potential of the active center of the enzyme to ensure efficient electron relay between the enzyme and the electroactive surface;

- Direct electron transfer (DET), the active site of the enzyme is in direct electronic communication with the electrode surface where the redox center of the enzyme can be regenerated by the electrode. Therefore, the possibility to obtain DET is strongly related to the location of the active site inside the protein, the conformational morphology of the protein, and the ability of the electrode to access the redox center. A main advantage of this strategy is the absence of redox mediators which generally represent a limiting factor in fuel cell stability and power output by decreasing the open circuit voltage (OCV). DET, indeed, has significant consequence on the performances of a biofuel cell: the cell voltage is directly determined by the difference between the redox potentials of the enzymes wired at the anode and the cathode.

Besides the wiring of enzymes that determines the cell voltage, the amount of wired enzymes is of primary importance as well, since the current density is directly correlated with. The current density and the cell voltage determine the power of the fuel cell. This is why the engineering of three-dimensional electrodes became one strategic subject of research in the biofuel cell community in order to maximize the amount of wired enzymes by volume unit. However, such 3D structures have to enable sufficient permeation of the substrates (fuel and oxygen) for the optimum functioning of the biofuel cell.

In this context, CNTs represent a privileged material towards the challenge of enzyme wiring. Firstly, CNTs provide a high three-dimensional surface area that enables a high density immobilization of both, the redox mediator (if needed) and the enzyme that finally maximizes the current densities at the bioanode and the biocathode. Secondly, the specific nanowire morphology of CNTs allows intimate interactions with the active sites of an enzyme that favor DET, thus representing powerful configurations without any use of redox mediators. In this case, the open-circuit voltage and current density is maximized per volume unit.

There are many efficient and original approaches to wire redox enzymes to CNTs and to form enzyme electrodes for the bio conversion of energy. Therefore, some particular interesting strategies for both, direct and indirect electron transfer, as well as fabrication processes of CNT-enzyme based bioelectrodes that led to remarkable biofuel cell performances, are discussed.

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