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Review

# Energy harvesting by implantable abiotically catalyzed glucose fuel cells

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ABSTRACT

Implantable glucose fuel cells are a promising approach to realize an autonomous energy supply for medical implants that solely relies on the electrochemical reaction of oxygen and glucose. Key advantage over conventional batteries is the abundant availability of both reactants in body fluids, rendering the need for regular replacement or external recharging mechanisms obsolete. Implantable glucose fuel cells, based on abiotic catalysts such as noble metals and activated carbon, have already been developed as power supply for cardiac pacemakers in the late-1960s. Whereas, *in vitro* and preliminary *in vivo* studies demonstrated their long-term stability, the performance of these fuel cells is limited to the μW-range. Consequently, no further developments have been reported since high-capacity lithium iodine batteries for cardiac pacemakers became available in the mid-1970s. In recent years research has been focused on enzymatically catalyzed glucose fuel cells. They offer higher power densities than their abiotically catalyzed counterparts, but the limited enzyme stability impedes long-term application. In this context, the trend towards increasingly energy-efficient low power MEMS (micro-electro-mechanical systems) implants has revived the interest in abiotic catalysts as a long-term stable alternative. This review covers the state-of-the-art in implantable abiotically catalyzed glucose fuel cells and their development since the 1960s. Different embodiment concepts are presented and the historical achievements of academic and industrial research groups are critically reviewed. Special regard is given to the applicability of the concept as sustainable micro-power generator for implantable devices.



## Contents



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## 1. Introduction

Although today batteries are considered to be the first choice in supplying power to electronic medical implants, there are numerous efforts to develop alternative power-supply systems that are capable of operating independently over prolonged periods of time, without the need of external recharging or refueling [1–4]. Among them are implantable fuel cell systems, which convert endogenous substances and oxygen into electricity by means of a spatially separated electrochemical reaction. Unlike batteries, these systems are constantly replenished with fresh reactants from the body fluids, and are therefore theoretically capable of operating indefinitely, as long as there is a constant supply of reactants. Its ubiquitous availability in body fluids makes glucose the most considered fuel for implantable fuel cell systems.

In general, glucose-consuming fuel cells can be divided into three main types according to the type of catalyst that is used to enable the electrode reactions: enzymatic, microbial, and abiotic glucose fuel cells. *Enzymatic fuel cells* employ enzymes such as glucose oxidase and laccase in their isolated forms, whereas in *microbial fuel cells* the enzymatic system of a whole, electroactive micro-organism is used. In contrast, *abiotically catalyzed fuel cells* make use of non-biological, abiotic catalysts, e.g., noble metals or activated carbon.

Over the last four decades there has been ample research activity both in the development of enzymatic and microbial fuel cells [5–7]. The recent developments in the field have been reviewed extensively [8–13]. Whereas implantable *enzymatic glucose fuel cells* are currently under development [14,15], the limited stability of enzymes renders their application in a long-term implantable fuel cell power supply difficult. Power-supply systems based on microbial fuel cells are not seriously considered for implantation, due to the infective nature of most known micro-organisms and the associated risks therewith.

In past reviews, only minor attention has been given to abiotically catalyzed glucose fuel cells, although these systems were already developed as implant power supplies in the late-1960s, and their feasibility to power cardiac pacemakers has been demonstrated *in vitro* as well as in animal trials. Abiotically catalyzed fuel cells employ mainly noble metal catalysts and are therefore considered to be advantageous regarding their sterilizability, long-term stability, and biocompatibility. However, following the introduction of the lithium iodine battery in 1972 [16–18] and the subsequent improvement of pacemaker battery lifetime no further development of abiotically catalyzed glucose fuel cells has been reported. Instead the research has been refocused towards the application of the concept for glucose sensor technology [19,20].

The current interest in autonomous, self-sufficient MEMS (micro-electro-mechanical systems) implants has revived the research in long-term stable, implantable glucose fuel cells based on abiotic catalysts [21]. This work reviews the development of abiotically catalyzed glucose fuel cells for implantable devices since the early beginnings in the 1960s. Not considered are non-medical applications of abiotically catalyzed glucose fuel cells [22,23], for instance as sensor power supply running on tree sap [24], since their operation conditions differ greatly from physiological environments and the design is not constricted by the vigorous demands on implantable systems in terms of patient safety and system size.

### 1.1. Operation principle of abiotically catalyzed glucose fuel cells

In a fuel cell electrical energy is generated by the electrochemical reaction of fuel and oxidant at two spatially separated electrodes. Electrons, released upon the electro-oxidation of the fuel, flow from the anode through an external load circuit to the cathode, where the terminal electron acceptor, usually oxygen, is reduced (Fig. 1). The driving force of the electron flow is the difference in electrochemical potential of the anode and cathode redox pairs.

An overview about the tentative oxidation pathways and intermediate reaction products of glucose oxidation is given in Fig. 2 [26]. Theoretically, glucose can be completely oxidized to carbon dioxide and water, releasing 24 electrons per molecule glucose [25]. The corresponding fuel cell reaction and the theoretical cell voltage $U^0$ would then be given as

$$\text{Anode}: \quad C_6H_{12}O_6 + 24\,OH^- \rightarrow 6\,CO_2 + 18\,H_2O + 24\,e^-$$

$$\text{Cathode}: \quad 6\,O_2 + 12\,H_2O + 24\,e^- \rightarrow 24\,OH^-$$

$$\text{Overall}: \quad C_6H_{12}O_6 + 6\,O_2 \rightarrow 6\,CO_2 + 18\,H_2O$$

$$\Delta G^\circ = -2.870 \times 10^6\,\text{J mol}^{-1}; U^0 = 1.24\,\text{V [25]}$$

In practice, the transfer of 24 electrons per molecule glucose has not yet been achieved. In their early study on glucose electro-oxidation in neutral media (0.5 mol $L^{-1}$ glucose in 1 mol $L^{-1}$ phosphate buffer at pH 7.4, 0.5 mol $L^{-1}$ NaCl) employing platinized platinum electrodes, Rao and Drake reported gluconic acid to be the only reaction product that could be identified by thin layer chromatography [27]. In a later mass spectroscopic study of glucose oxidation products (0.1 mol $L^{-1}$ glucose, in chloride free $NaHCO_3$ buffer at pH 7.4). Ernst et al. identified glucono lactone as the product of glucose oxidation in the potential range of 300–400 mV vs. RHE (reversible hydrogen electrode), which itself undergoes hydrolysis to form gluconic acid [28], a non-toxic metabolite [29]. The oxidation of glucose to gluconic acid only yields two electrons per molecule glucose and the corresponding electrode reactions are thus given as

$$\text{Anode}: \quad C_6H_{12}O_6 + 2\,OH^- \rightarrow C_6H_{12}O_7 + H_2O + 2\,e^-$$

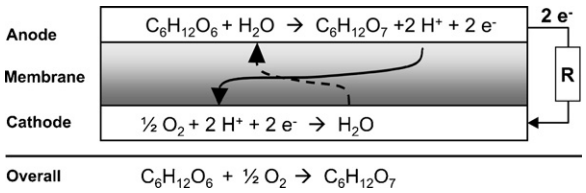


**Fig. 1.** General electrode reactions of an abiotically catalyzed glucose–oxygen fuel cell, assuming a hydroxyl ion conducting membrane and gluconic acid as the reaction product. According to Ref. [25].