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Dynamic evolution of anodic biofilm when maturing under different external resistive loads in microbial fuel cells. Electrochemical perspective

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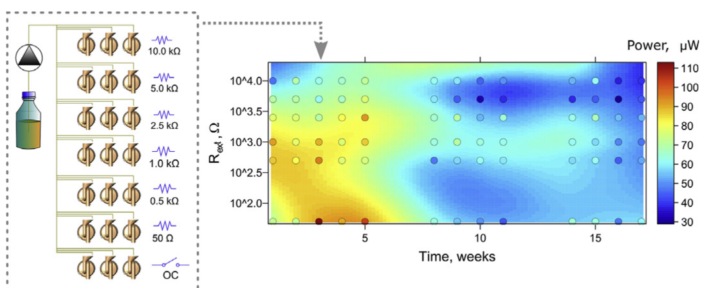
HIGHLIGHTS

- Dynamic changes of biofilm matured under different external loads are investigated.
- Most dynamic changes are observed in the first 3 weeks of operation.
- External resistance lower than internal resistance improves maturing of the biofilm.
- Internal resistance is dependent on external resistance applied in maturing phase.
- External resistance irreversibly affects the biofilm properties and performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Appropriate inoculation and maturation may be crucial for shortening the startup time and maximising power output of Microbial Fuel Cells (MFCs), whilst ensuring stable operation. In this study we explore the relationship between electrochemical parameters of MFCs matured under different external resistance (R_{ext}) values (50 Ω - 10 kΩ) using non-synthetic fuel (human urine). Maturing the biofilm under the lower selected R_{ext} results in improved power performance and lowest internal resistance (R_{int}), whereas using higher R_{ext} results in increased ohmic losses and inferior performance. When the optimal load is applied to the MFCs following maturity, dependence of microbial activity on original R_{ext} values does not change, suggesting an irreversible effect on the biofilm, within the timeframe of the reported experiments. Biofilm microarchitecture is affected by R_{ext} and plays an important role in MFC efficiency. Presence of water channels, EPS and precipitated salts is distinctive for higher R_{ext} and open circuit MFCs. Correlation analysis reveals that the biofilm changes most dynamically in the first 5 weeks of operation and that fixed R_{ext} lefts an electrochemical effect on biofilm performance. Therefore, the initial conditions of the biofilm development can affect its long-term structure, properties and activity.

1. Introduction

Microbial Fuel Cell (MFC) technology uses electroactive bacteria to produce electricity through oxidation of organic matter. The technology has received increased attention over past decades [1]. The bioelectrochemical reactions take place in anodic and cathodic components of

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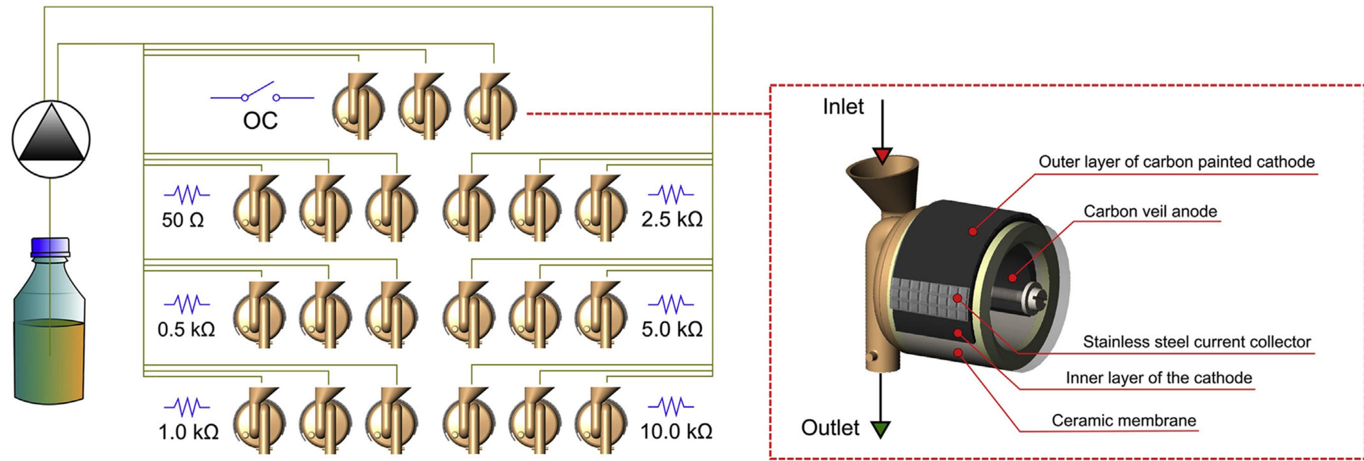

Fig. 1. Schematic representation of experimental design and MFC design. The experimental setup consisted of predefined external loads only in the first stage (weeks 1–5) of the experiment. In the second stage (weeks 6–17) external load was changed dynamically to the optimal value determined for each individual MFC. Individual graphical elements of this image were derived from our previous works [30,31].

the MFC have found many potential applications in the fields of wastewater treatment, electricity generation, biogas production, biosensors and bioelectrochemical synthesis [2–10]. Among various carbon sources that have been demonstrated as a fuel in MFCs human urine has proved to be a good substrate due to its high conductivity [11]. The ongoing development of the MFCs focuses on developing electrode materials, catalysts, membranes separating anodic and cathodic chambers, design and scale-up of the MFC-based systems [2,12–17].

Despite the broad interest in many engineering aspects of the MFCs, the most crucial role is played by the electroactive bacteria, which form the biofilm on the electrode's surface and generate electrical power from their population-level metabolism. The biofilm is a complex matrix of microorganisms and extracellular compounds which is considered to be very stable, albeit possessing physiological adaptive mechanisms [18] many of which are expressed during the initial biofilm formation period.

Several research groups have previously reported on power performance and start up times when the electroactive community has been matured under different poised anode potentials. For example the anodic biofilm formed by *Geobacter sulfurreducens* gives highest power performance and lowest MFC start-up time, when matured under a potential range between 0 and 400 mV vs SHE (standard hydrogen electrode). This optimal potential range promoted the biofilm growth and corresponding power density of the MFCs [19]. The study reported by Aelterman et al. showed, that optimal biofilm growth and activity was obtained when the anode was poised at −200 mV vs Ag/AgCl electrode, although the original source of the bacterial inoculum was not mentioned [20]. More recently, Zhu et al. reported, that acclimating the biofilm with positive potentials may lead to the decay of the power overshoot phenomenon which leads to improved power performance [21].

Easier ways of controlling the potential of MFC electrodes is by applying an external load (R_{ext}), which does not require any specialist equipment that could be limiting in particular for field applications. Comprehensive investigation on the effect of R_{ext} on biofilm formation and activity has been reported by Zhang et al. [22]. The authors investigated the ohmic range of 10–1000 Ω and indicated that optimal R_{ext} for their MFC setup was found to be 50Ω, although biofilm matured under 10 Ω produced the highest current. The study also showed that R_{ext} had an impact on the presence of extracellular polymeric substances (EPS) of the biofilm, and a more recent study showed that EPS plays a role in biofilm performance and in turn, power generation [23]. The influence of three different R_{ext} values on biofilm activity (after the maturing phase) was also studied by Jung and Regan [24]. The authors focused on methane production and the inhibition of methanogenesis was found to occur in parallel with the highest power efficiency for MFCs fed with acetate and operating under lowest (150 Ω) R_{ext}. Earlier studies also demonstrated the relationship of R_{ext} applied during operation (after maturing phase) with performance of the MFCs in relation to the fuel supply and the best results were obtained when MFCs were operated under R_{ext} closer to internal resistance (R_{int}) [25]. External resistance was also found to be a factor influencing diversity of the bacterial community [24,26,27].

Although significant work has been done to understand the interactions of R_{ext} with the biofilm, very limited knowledge is available on dynamic evolution of biofilm subjected to various external loads. Since the biofilm forms both stable and adaptive structure, such knowledge is indispensable to develop appropriate strategies for inoculation and operation of MFCs. It is therefore important to determine, whether the conditions applied to the biofilm in the initial stage of development may leave a structural and electrochemical profile and irreversibly affect its performance thereafter.

The aim of this study was to determine the temporal and long-term effects of fixed and dynamically-changed external resistance on changes of biofilm parameters and resulting MFC performance in time. The results revealed the irreversible effects that the initial R_{ext} causes to the biofilm, which may subsequently either induce or inhibit the power performance of the MFCs in long-term perspective. This is the first of two papers in series, where we have focused on analysis of electrochemical parameters. The second part of this study will focus on biological parameters of the biofilm.

2. Experimental

2.1. MFC construction and operation

The single chamber MFCs were built as described in detail in our previous work [28]. In brief, earthenware ceramic material was used both as the separator and housing for the anodic chamber (Fig. 1). The external side of the ceramic cylinder was supplied with carbon-painted cathode (carbon loading of 14.08 mgC cm^{-2}) and stainless steel wire mesh, acting as a current collector. The volume of an empty MFC anodic chamber was 11.4 mL. Carbon fiber veil (20 g m^{-2}, PRF Composite Materials, Dorset, UK) was used as the anodes with total surface area of 252 cm^2. A 3D-printed Nanocure® RCP30-resin lid with inlet and outlet tubes was used as a front panel of the vertically positioned MFCs.

All of the MFCs were manufactured manually in the same manner and used to build an array of 21 electrically and fluidically isolated