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Influence of the electrode size on microbial anode performance

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HIGHLIGHTS

- Microbial anodes were scaled-up from 9 to 50 cm^2 surface area.
- Kinetics curves showed significant performance loss.
- The distribution of the potential over the anode surface was modelled numerically.
- Ohmic drop was responsible for only a part of the performance loss.
- Heterogeneity in biofilm development matched with the potential distribution.

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ABSTRACT

The performance of microbial fuel cells and other related microbial electrochemical processes is seen to deteriorate severely when they are scaled up. This crucial problem is addressed here by comparing the kinetics of microbial anodes with projected surface areas of 9 and 50 cm^2 under well-controlled electrochemical conditions. The microbial anode kinetics were characterized by low scan rate voltammetry. The 9-cm^2 anodes showed Nernstian behaviour, while the 50-cm^2 anodes showed significantly lower performance. The distribution of the electrostatic potential in the experimental set-up was modelled numerically. The model predicted the general trend of the voltammetry curves recorded with the 50-cm^2 anodes well, showing that part of the performance deterioration was due to ohmic drop and to non-uniformity of the local potential over the anode surface. Furthermore, the biofilm presented slightly different electrochemical characteristics when grown on the 9-cm^2 or 50-cm^2 anodes, and the difference in local potential over the 50-cm^2 anodes induced spatial heterogeneity in biofilm development. The effect of local potential on biofilm characteristics was an additional cause of the lower performance obtained with the 50-cm^2 anodes. In the current state of the art, the soundest way to design large-sized microbial anodes is to adopt the dual main aim of minimizing the ohmic drop while keeping the most uniform possible potential over the electrode surface. Modelling potential distribution inside the reactor should make an essential contribution to this.

1. Introduction

For around 15 years, microbial biofilms developed on anode surfaces have revealed an amazing capacity to catalyse the electrochemical oxidation of a large variety of organic compounds [1,2]. Microbial anodes have shown very high performance in terms of current density produced [3–5] and have opened up avenues for a huge number of new electrochemical processes [6,7]. Interesting applications have been predicted in various application sectors. Microbial fuel cells (MFCs) have been the pioneering systems implementing microbial anodes for the local production of small amounts of electrical energy [8–12] and its storage [13,14]. In microbial electrolysis cells (MECs), microbial anodes reduce the energy cost of hydrogen production [15–17]. Microbial anodes have also been envisioned in the design of new wastewater treatment processes [18–20]. Extremely simplified processes, called electro-microbial snorkels, have been derived, based on short-circuiting a microbial anode with a cathode in order to maximize the organic matter consumption rate [21]. Such low-cost and low maintenance electrochemical systems may have promising futures in wastewater treatment [22] and environmental depollution [23,24].

These thrilling perspectives will only become reality when the difficulty of scaling-up laboratory devices to large-sized industrial equipment has been overcome [8]. Many attempts have been made, particularly with MFCs and MECs, but with only modest suc-

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cess [25–27]. In the case of MFCs equipped with air-breathing cathodes, which are the archetype of electro-microbial devices, the maximum power densities reported so far are 4.7 [28] and 6.4 $W.m^{-2}$ [29], but the maximum performance has been observed to fall to 2 $W.m^{-2}$ when the volume of the MFC is increased, even modestly, to 100 mL [30]. The problem is so tricky that some research teams think that the best way to develop MFC applications at reasonable scale should be to stack several small MFCs rather than increasing the size of a single cell [31]. Impressive results have been reported in this way, by stacking up to 400 individual small MFCs [32].

Nevertheless, the interest of the stacking approach should not discourage us from attempting scale-up. Little success has been reported so far in this domain, probably because scaling-up attempts have been carried out with whole reactors [8,33]. Considering microbial electrochemical reactors as a whole and trying to directly increase their size is a tough challenge because of the complex interactions that occur in these reactors. The performance decrease of the reactor can be due to the microbial anode itself, which may lose a part of its catalytic efficiency when its surface area increases, but it may also be caused by any other element of the reactor: cathode kinetics, ion transport through the electrolyte(s) [34] and any coupled effects such as the cross-over of substrates and metabolites between anode and cathode. Actually, scaling-up complex technological systems such as cars, planes or industrial chemical equipment is never carried out by considering the system as a whole and trying to increase its size from a small laboratory device to industrially-sized equipment. For example, planes are not constructed by increasing their size from a child's toy to a final long-haul aircraft, but by characterizing materials, hydrodynamics, motors, tyres, electric and hydraulic systems, etc. separately and then organizing all the information with numerical models in order to design the optimum prototype. Designing chemical equipment, e.g., catalytic hydrogenation columns or fuel cells, follows the same strategy: the reaction kinetics, the nature and the structure of the catalyst are firstly determined in analytical conditions according to well-defined analytical methods. In parallel, the hydrodynamics is characterized in so-called "cold prototype" by specific experiments performed in the absence of reaction. All these pieces of information are then used to design a numerical model that allows first prototype to be made. The deviations between the numerical predictions and the experimental data produced by the prototype are analysed in order to identify and quantify non-anticipated behaviours and non-anticipated interactions. Some gaps in fundamental knowledge may thus be pointed out, which must be overcome. It can consequently be decided to go back to some analytical investigations with specific experimental set-ups or to make another prototype to refine the model. When numerical predictions and experimental data are satisfactorily consistent, the size of the prototype can be increased. Finally, when the numerical model is assessed to be sound and accurate enough it is used to design the final industrial equipment.

The large number of studies that have demonstrated the difficulty of scaling up microbial electrochemical reactors show that it is now time to consider such reactors as complex technological devices. Some microbial electrochemical reactors, e.g., MFCs, are easy to build and it is pretty simple to get the first interesting results. This apparent simplicity, which is an asset in some respects, should not mask the real complexity of microbial electrochemical reactors and the need to use a rigorous engineering approach if the objective is to scale them up.

The purpose of the present study is to contribute to the strategy for scaling up electro-microbial processes starting from the very first step. The study focuses on the microbial anode, just looking at how its performance drops when the electrode size is increased from 9 to 50 cm^2. The study was performed under well-controlled electrochemical conditions, i.e., using a three-electrode analytical set-up, to extract the microbial anode from the interactions occurring in complete microbial electrochemical reactors, such as MFCs or MECs. In a three-electrode set-up, the potential of the anode is controlled accurately with respect to a reference electrode so that the evolution of the cathode kinetics or of some other steps of the system does not impact the value of the anode potential. For the same reason, the temperature was controlled so that the bioanodes were characterized in conditions that were as reproducible as possible. Experimental and numerical approaches were combined to unravel the causes of the performance degradation. Finally, practical suggestions were drawn for the design of analytical set-ups and on how progress could be made in scaling up microbial anodes.

2. Materials and methods

2.1. Microbial anode formation

Microbial anodes were formed under constant polarization in 3-electrode set-ups. Flat carbon cloth (PaxiTech, Grenoble, France) connected to a platinum wire was used as the anode support (working electrode). The platinum wire was woven into the carbon cloth to form three stitches and the part outside the carbon structure was protected by an insulating heat shrink sleeve. Two electrode sizes were compared, with 9 cm^2 (3 cm × 3 cm) and 50 cm^2 (5 cm × 10 cm) projected surface area. Unless otherwise stated, current densities were calculated by using the total surface areas, which included both sides of the electrode and the edge area due to the electrode thickness of 1 mm [35]. The total surface areas used for all calculations were consequently 19.2 and 103 cm^2 for the 9- and 50-cm^2 anodes, respectively.

A platinum grid was used as the auxiliary electrode and a saturated calomel reference electrode as the reference (SCE, potential + 0.24 V/SHE). Microbial anodes were formed under constant polarization at −0.2 V/SCE using a VSP potentiostat (Bio-Logic SA, Claix, France) and current was recorded as a function of time. Reactors had a volume of 1.8 L and were kept in a heat chamber at 40 °C. The microbial anodes were firstly formed in garden compost leachate prepared by filtering a mix of 1.5 L of garden compost and 2.25 L of water containing 60 mM KCl through a loose-weave cloth [36]. This leachate served as both the culture medium and the inoculum for the first phase of microbial anode formation. Once the anodes were supplying constant current, the compost leachate was replaced by a synthetic medium. The synthetic medium contained bicarbonate buffer 50 mM, 10 $mL.L^{-1}$ macronutrients, 1 $mL.L^{-1}$ micronutrients, 1 $mL.L^{-1}$ vitamins, 4.5 $g.L^{-1}$ KCl and 2.4 $g.L^{-1}$ NaH_2PO_4. pH was adjusted to 7.0. Sodium acetate was used as the substrate in both media. Its initial concentration of 20 mM was maintained by supplementation according to the need revealed by periodic measurements (enzymatic kit K-ACETAK, Megazyme, Ireland).

Cyclic voltammetry (CV) curves were recorded from −0.2 V/SCE to +0.2 V/SCE and then back to −0.5 V/SCE at 1 $mV.s^{-1}$. Three successive cycles were achieved between the upper and lower potential limits. The first cycle was generally slightly different from the two others, which were perfectly matched. Only the second cycle is presented here. Faradaic yields (ϕ_e) were calculated as the amount of electrons collected by the electrochemical reaction with respect to the amount provided to the reactor by the successive additions of acetate:

$$\phi_e = \frac{\Delta C V n F}{\int i dt} \quad (1)$$

where ΔC ($mol.L^{-1}$) is the concentration of acetate consumed between two additions, V = 1.8 L is the reactor volume,