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Original Research Article

Dynamic polarisation reveals differential steady-state stabilisation and capacitive-like behaviour in microbial fuel cells

Pablo Ledezma [a,*], Nicolas Degrenne [b], Pascal Bevilacqua [c], François Buret [b], Bruno Allard [c], John Greenman [d], Ioannis Ieropoulos [a]

[a] Bristol Robotics Laboratory, Universities of Bristol and of the West of England, Frenchay Campus, Bristol BS34 8QZ, UK
[b] Laboratoire Ampère, Ecole centrale de Lyon, Université de Lyon, Ecully 69134, France
[c] Laboratoire Ampère, INSA de Lyon, Université de Lyon, Villeurbanne 69100, France
[d] Department of Applied Sciences, University of the West of England, Bristol BS16 1QY, UK

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ABSTRACT

In this paper we present several preliminary results produced with a purposely-designed external-resistor (R_{ext}) sweeping tool for microbial fuel cells (MFCs). Fast sampling rates show that MFCs exhibit differential steady-state stabilisation behaviours depending on R_{ext}, with consequences for time constant (t_c) selection. At high R_{ext} (35 kΩ), it is demonstrated that a $t_c \geqslant 10$ min avoids underestimation not overestimation, whilst at low R_{ext} (100 Ω) 5 min are sufficient, suggesting that sweeps with variable t_c are possible. However, within the maximum power transfer range (2.5 kΩ), steady-states are only observed at 20 min t_c but with a smaller confidence interval, questioning whether the polarisation technique is suitable to estimate maximum power transfer. Finally, a strategy towards the exploitation of a capacitive-like behaviour in MFCs is proposed, tapping into $\geqslant$10 min periods with up to 50% higher current and energy transfer that could prove important for MFC-powered applications.

Introduction

Microbial fuel cells (MFCs) are an exciting technology with a growing scientific interest and research dynamism due to the potential of sustainable electricity production from organic waste and, notably, wastewater. The latter is either released untreated into the environment – with severe environmental consequences – or treated through expensive and energy intensive processes. MFCs offer the possibility of transforming such wastewater treatment plants into energy- and carbon-neutral systems or even the longer-term potential of net energy production, similar to novel anaerobic digestion plants but operating at higher efficiencies and requiring less investment [1].

One of the most commonly used tools for characterising the behaviour of MFC systems is known as the polarisation technique. It is a process whereby the fuel cell is subjected to a set number of external loads (R_{ext} of known resistance in Ω) over a constant period of time (time constant, t_c), resulting in the production of an electric current (in A) at a corresponding cell voltage (in V). The graphical representation of the obtained results or *Polarisation curve* (voltage *vs* current) provides considerable information about the tested systems, particularly about the associated activation, ohmic and mass transfer losses [2]. Moreover, from the derivation of Joule's law, the electrical power (in W) can be calculated at the different exhibited current levels and plotted as a *Power curve* (power *vs* current), which again reveals information about the behaviour and stability of the system predominantly in comparison with a mathematical model. According to Jacobi's law, an *ideal* fuel cell produces a parabolic Power curve whereby the maximum power transfer (MPT) point occurs at the mid points of current and voltage [3]. This protocol has become almost ubiquitous for determining the maximum attainable power from MFCs.

A debate is currently ongoing with regards to this technique and in particular to the value (in Ω) and quantity of external resistors employed, as well as the time constant (t_c) in terms of accurately determining the real, sustainable MPT by MFCs. This investigation addresses these concerns, presenting a more accurate polarisation technique that aims to question the use of constant or long time intervals for the evaluation of MFC performance and whether the technique is suitable for the estimation of MPT.

Materials and methods

MFC assembly and operation

Eight 2-chamber MFCs (20 mL/side) made of four different materials [4] and of properties previously described [5] were

* Corresponding author. Tel.: +44 (0) 117 32 86350; fax: +44 (0) 117 32 83960.
E-mail address: pablo.ledezma@brl.ac.uk (P. Ledezma).

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inoculated with activated sewage sludge and then operated in continuous mode, under identical conditions, for at least 18 months. During this period, the MFCs were fed with acetate TYE (5 mM C2H3NaO2, 0.1% w/v Tryptone, 0.05% w/v Yeast Extract) at a low flow rate of 120 $\mu L\ min^{-1}$, with tap water (D.O. avg. 6.5 $mg\ L^{-1}$; Conductivity avg. 680 $\mu S\ cm^{-1}$) as the catholyte at a flow rate of 19.35 $mL\ min^{-1}$.

Our research focuses on the utilisation of MFC systems as power sources for practical applications e.g. robots [6]. For such purposes, we have already demonstrated that a suitable strategy to achieve the necessary voltages and currents is to construct MFC collectives (stacks) with combinations of series/parallel connections [6] and that we are able to maintain the operation of such stacks at MPT point with high efficiency [7], both necessary elements for the stable and predictable operation of applications. More recently, we have also shown that a stacking architecture that balances the internal resistances of embedded cells avoids cell voltage reversal even under fuel starvation [8] and that this strategy can be used for scaled-up reactors with up to 20 MFCs in series [9]. We have utilised the latter approach to energise applications previously considered impossible with MFCs e.g. a multi-channel peristaltic pump [9] and a mobile phone [10]. However, a significant amount of research is still needed into stacking at the fundamental levels – 2 to 4 MFCs in different configurations – in order to elucidate techniques that can enhance their collective electrical output without reversal. In concordance with these objectives, the experiments hereby presented involve four stacks of two MFCs connected in series (namely stacks A, B, C & D). Prior to stacking, all cells were individually verified for output under continuous load and polarisation conditions and no significant differences were found between MFCs fabricated in the same material (data not shown). The electrical output of each stack (voltage) was monitored/controlled in real-time with the tool described below.

Dynamic polarisation method with novel Resistorstat

The constructed stacks were connected to an 8-channel automated *Resistorstat* tool, whose development and architecture is described in detail by Degrenne et al. [7]. This system was programmed to perform sweeps of external resistor (R_{ext}) values, ranging decreasingly from 38.5 kΩ to 4 Ω (35 values with avg. 18.5% resistance reduction per step, so as to make the reduction rates constant), at different time constant (t_c) intervals (1, 5, 10 and 20 min). The cells were kept in open-circuit mode for 1 h prior to testing. Their voltage was recorded every 30 s in order to monitor the dynamic response of MFCs to changes in R_{ext} over the extent of each t_c step.

Calculations

The resulting voltage output readings were automatically processed by the *Resistorstat* system, calculating current (I) and power (P) output per MFC stack, as previously described [7]. For the sake of clarity, exemplars of the most representative results are shown, which illustrate responses that were consistently observed in the more than 25 polarisation sweeps performed per stack.

Results and discussion

Novel dynamic polarisation and power curves

The data produced with the technique hereby presented result in a new form of polarisation (Fig. 1A) and power curves (Fig. 1B), distinguished by the presence of *spikes*. These seem to indicate a *plateauing* tendency in the output or convergence for each R_{ext} tested.

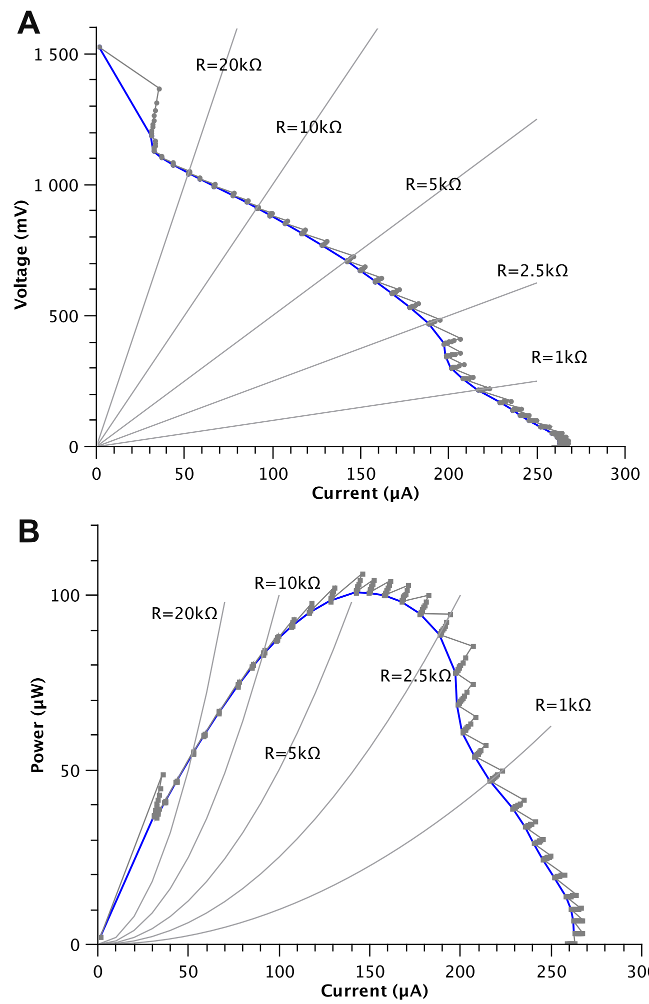

Fig. 1. (A) Polarisation curve of a 2-MFC stack connected in series with a 30 s sampling time resolution and a 5 min time constant. The modelling lines (in gray) highlight the fact that the *spikes* converge, in a linear manner, in concordance with the external resistor employed. (B) Power curve of the same 2-MFC stack. The modelling lines (in gray) exhibit the parabolic convergence behaviour of the *spikes*. In both cases, blue lines indicate the typical polarisation and power curves that would be obtained from examined systems, showing the difference with dynamic curves.

Although the variation observed can be considered low, both curves (see Fig. 1A and B) illustrate that the aforementioned behaviour is different between points tested in terms of the orientation/width of the *spikes* depending on the *zone* in the curves. Simple modelling revealed that the orientation of the *spikes* in the polarisation curve can be explained by a linear relationship depending on R_{ext}, each *spike* aligning with the Cartesian equation $V = R_{ext} \times I$ of Ohm's law (grey modelling lines, Fig. 1A). In a similar manner, the *spikes*' orientation in the power curve (see Fig. 1B) can be explained by the square function $P = R_{ext} \times I2$. The latter formula is commonly employed in electrical engineering to determine power losses in an electrical transmission, so the *spikes* could be considered as an indicator of the power that is lost (or in the power curves, initially *overestimated*) whilst the system stabilises into a new steady-state (stable electrical production over time).

Since it was observed that these *spikes* appeared substantially different throughout the curves (see Fig. 1), more detailed examinations of the converging behaviour at different sections of the polarisation range were undertaken and are presented in the next section.