Reproducibility and Robustness of Microbial Fuel Cells Technology

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Abstract

This work focuses on the evaluation of the robustness and reproducibility of the behaviour of microbial fuel cells (MFCs). Up to 112 MFCs were operated simultaneously under the same conditions, finding that the probability of high performance, maximum power, maximum current and internal resistance is 95%, 90%, 96% and 94% respectively. Reproducibility of stacks was also evaluated by testing different electrical connections, finding that when evaluating the performance of 7 stacks of 16 MFCs each connected in parallel and different combinations of series/parallel, the maximum power varies only between 1-2 mW. Results obtained also helps to demonstrate that the performance of the bioelectrochemical devices evaluated mainly depended on the internal resistance. All these information is of a great significance for future developments of the technology because it is a real first step in the characterization of the robustness of the bioelectrochemical technology.

Keywords

Microbial fuel cell; robustness; reproducibility; green energy.

1. Introduction

Microbial Fuel Cells (MFCs) are a promising green technology for a planet seriously affected by main problems related to traditional energy sources [1, 2]. This interest is reflected by the Web of Science database which index more than 7000 publications related to the keyword microbial fuel cell up to the end of 2018 [3]. However, MFCs are yet to be accepted by the market, being compulsory to demonstrate its robustness and reproducibility. Most of publications are scientific and not technical [4, 5], being focused on design parameters [6, 7], selection of materials [8] and of selection of suitable operational conditions in order to enhance the MFC performance [9-15]. A very low percentage of the publications are focused on the modelling of this technology [16-18], trying to shed light on the understanding of the processes that take place in the MFC and its dependence on the design and operation [19, 20]. However, despite the number and the variety of publications, from the authors' knowledge there is no article that points out the reproducibility of this technology with a high number of MFCs tested. Nowadays, most of the cases reported MFCs data from two or three replications. For example, Philamore et al. worked with two MFC replicates [21]; Chouler et al., Yi et al. and Beecroft et al. carried out their study by using three replicates of the same MFC [22-24]. while, Tremoulia et al. investigated a 12 MFC stacks and checked the reproducibility of the test by using two similar stacks [25]. These replications allow to confirm the reproducibility of the data obtained in the study but neither the reproducibility of the technology nor its robustness. In this sense, the study of the reproducibility as well as the robustness of the MFC technology is of great interest. The reproducibility can be defined as the degree of agreement between

the results of different experiments [26], while robustness is the ability to tolerate or overcome adverse conditions or rigorous testing [27]. In addition, the MFC technology is stagnated because of the limitations in the scale-up stage, which cannot lead to applicable devices, the variability of the performance reported in the large number of papers published and financial aspects [28]. With the aim to find its place in the market, authors consider that before carrying out economic estimations or real demonstrations it must be demonstrated the outstanding potential of this technology in terms of reproducibility and robustness. Thus, for MFCs, to find its place in the market, it is necessary to demonstrate also its robustness.

In the literature it has been described that higher yields should be obtained by the MFC in order to find real applications. Nowadays, the most convenient scale-up strategy is the connection of multiple small MFCs as a stack. This strategy has been suggested in several publications: in 2010, a robot provided with 48 mini MFCs connected as stack was able to store the energy that it generates by oxidising the food that it collected [29]. In 2017, 24 mini MFCs fed with real urine charged and power a smartphone Samsung Galaxy S I9000 [30]. Very recently, another work showed the continuous illumination of 220 LEDs with 112 mini stacked MFCs [31]. Because of that, real applications should be focused more on power technologies [30] [32] or sensors [33, 34] instead of the original concept of self-sufficient wastewater treatment plants [2] as small MFCs cannot face their typical high flow rates.

In this context, this work aims to evaluate the robustness and reproducibility of the MFC technology by comparing the steady state performance for 112 MFCs, operating in single mode and connected into several stacks by using different statistical parameters.

2. Materials and methods

The experimental set-up used in this work consisted of 112 MFCs. Each MFC consisted of an anodic chamber of 0.695 cm^3 separated from the cathode by a Nafion N117[®] proton exchange membrane (DuPontTM). The anode was made of carbon felt (Sigracell[®] GF6EA) while the cathode, based on air breathing technology, was made of carbon paper (Freudenberg C2, Fuel Cell Products) modified by the addition of a catalytic layer of platinum. Both surface areas were 0.866 cm^2 . All these MFCs were identically constructed according to the standardized methodology previously described. This methodology was developed in previous studies in order to obtain an optimal performance of the MFC. The parameters and conditions evaluated were: anode material [35], cathode material [36], membrane [36], enrichment procedure [37], sludge age [38, 39], electron donor [40], electron acceptor [41] and configuration of stacks [31, 42]. The electrodes were placed as close as possible to the membrane to reduce the internal resistance. It is important to highlight that 0.5 mg Pt cm^{-2} was deposited on the cathode in order to avoid limitations in the MFCs and a Nafion proton exchange membrane was used to avoid short-circuiting the electrodes.

In order to evaluate also the robustness of the stacking process, the 112 MFCs were placed in 7 stacks of 16 MFCs each one. 4 horizontal lines of 4 MFCs were connected hydraulically in cascade. Each cascade was connected to an auxiliary tank of 115 mL. For the study of MFCs reproducibility, the electrodes of each MFC was connected externally by a load of $120\ \Omega$ leading to an individual electric connection per MFC. For the stacking process, the MFCs were electrical connection in series/parallel.

Each auxiliary tank was seed by using the effluent of an on-going MFCs and maintained under stirred conditions to avoid the settling of the sludge. This on-going MFCs was initially seed with conventional activated sludge taken from the aerobic reactor of a Wastewater Treatment Plant of Ciudad Real [43]. The solution of electrogenic bacteria was recirculated at a flow rate of 3 mL min^{-1} by the system during 24 hours. Then, the 50% of the solution was purged and fresh sludge was added. This procedure was carried out during the second and third day. The 4th day, a sludge age of 2.5 days was established by removing 46 mL of suspension that was replaced by fresh synthetic wastewater.

The synthetic wastewater used as feedstock was prepared in the laboratory. Its composition was based on a simple, and easy to be degraded by bacteria [35], carbon source and nutrients: 16.10 g L^{-1} of sodium acetate, 1.25 g L^{-1} of calcium chloride, 2.77 g L^{-1} of sodium carbonate, 0.92 g L^{-1} of hexahydrate magnesium chloride, 1.11 g L^{-1} of potassium dihydrogen phosphate, 1.85 g L^{-1} of ammonium sulphate and 0.07 g L^{-1} of ferric ammonium sulphate. In order to avoid its degradation, it was autoclaved at 105°C for 30 minutes [44].

For the electrochemical characterization, polarization curves were carried out at the steady state with a potentiostat/galvanostat AUTOLAB PGSTAT30 (Ecochemie, Netherlands) and GPES software, in potentiodynamic mode at a potential scanning from the OCV to 0.001 V , a scan rate of $1\text{-}0.5 \text{ mV s}^{-1}$, a pre-treatment stage of 4 minutes. 3 scans per polarization curve were performed to ensure accurate results.

3. Results and discussion

In this work, the reproducibility of 112 MFCs and the reproducibility of 7 stacks, composed of 16 individual MFCs, were evaluated. It was observed that the time required by the 112 MFCs to achieve the steady state was about 19 ± 2 d.

3.1. Study of reproducibility of MFCs

The reproducibility of MFC technology was evaluated by the operation of 112 MFCs and, once reached the steady state, the main operational parameters were determined: open circuit voltage (OCV), maximum power, maximum current and internal resistance. Figure 1 shows the relative frequency histograms of those parameters.

As it can be observed, the 74% of the MFCs achieved an OCV between 0.4 and 0.5 V and only a 3% performed really badly (0.2-0.3 V). In addition, around the 8% reached higher values of OCV than 0.5 V. Regarding to the maximum power, around the 75 % of the MFCs generated maximum power densities higher than 1 W m^{-2} , which indicates the superb performance of 74 MFCs. In addition, the 8 % could achieve values greater than 3 W m^{-2} and only the 5% of the MFCs performed at the undesired range ($<0.5 \text{ W m}^{-2}$). The highest maximum current densities ($>28 \text{ A m}^{-2}$) were achieved by the 4% of the MFCs while the 52% outperforms at the range of $8\text{-}16 \text{ A m}^{-2}$ and 26% at the range of $16\text{-}28 \text{ A m}^{-2}$. The 4% of the MFCs worked badly ($<5 \text{ A m}^{-2}$).

Figure 1. Relative frequency histograms of the OCV (a), maximum power (b), maximum current (c) and internal resistance (d).

At this point, it is important to compare the values obtained with reported data:

0.0073 A m⁻² [22], 0.48 A m⁻² [45], 0.8 A m⁻² [46], 2.2 A m⁻² [47], 9.0 A m⁻² [48]. The results reported in the literature point out the superb performance of the MFC operated in this work.

The internal resistance plays an important role in the performance of MFC. Higher internal resistances are related to bad performance. In Fig 1.d, only the 6% of the MFCs had an internal resistance higher than 1 kΩ and the 76% of these MFCs are

characterized by its lower internal resistance ($< 0.5 \text{ k}\Omega$). The low internal resistances obtained are due to the miniature size of the MFC. It reduces the spacing between electrodes and favours the mass transfer [22]. These results show a reproducible MFC performance because of rigorously following the construction and operation methodology previously described. Despite the efforts to avoid the effect of different COD concentrations along the MFC cascades, the bad performance can be due to influence of the position of the MFC in the cascade. This can lead to an unbalanced COD distribution because of COD excess in the influent [42], COD depletion [49, 50] or substrate fermentation processes [51]. In addition, despite of the superb enrichment procedure followed, the biofilm density and/or culture can be affected by the unbalanced COD distribution. Anyway, there is a low deviation percentage and attending to the performance of the MFCs, these results point out an efficient technology.

Figure 2 shows the ogives of the same parameters. An ogive represent the cumulative frequency for the different values of OCV, maximum power and current and internal resistance in order to determine the number of values that are below a particular value. In this study, these figures are very useful to define the number of MFCs that work poorly. For example, 4 MFCs shows an OCV lower than 0.3 V; 6 MFCs, a maximum power density lower than 0.5 W m^{-2} ; 5 MFCs, a maximum current density lower than 5 A m^{-2} . In the case of the internal resistance, it can be observed a high cumulative frequency at the lowest values of internal resistance and a constant trend at high values, indicating that only a small number of cells have high internal resistance.

Figure 2. Ogive of OCV (a), maximum power (b), maximum current (c) and internal resistance (d).

In probability terms, the probability of good performance, maximum power, maximum current and internal resistance is 95%, 90%, 96% and 94% respectively. As it can be observed, the probability of operated an MFC successfully is 90% regardless of the parameter studied. This high percentage after having operated 112 similar MFCs simultaneously at the same conditions indicates a superb robustness of the MFC technology. This demonstration can be very useful from the commercial point of view. MFC technology is stagnated due to scale-up limitations [3] and to the topic of performance variability. This study faced the variability problem of MFCs showing a promising future for MFCs.

More statistical information describing the behaviour of the MFC's are presented in

Table 1.

Table 1. Statistical analysis of the MFC.

	Average	Max.	Min.	Median	Fashion	Standard deviation	Variance
OCV (V)	0.450	0.550	0.207	0.457	0.452	0.053	0.003
P_{max} (W m⁻²)	1.730	4.018	0.098	1.667	2.09	0.773	0.051
J_{max} (A m⁻²)	14.124	40.282	0.948	12.755	10.739	6.748	45.090
R_{int} (kΩ)	0.536	4.727	0.137	0.412	0.302	0.565	316.285
	Kurtosis	Q1	Q2	Q3	Interquartile range	Semiinter- quartile range	Middle Quartile
OCV (V)	5.552	0.431	0.457	0.479	0.047	0.024	0.454
P_{max} (W m⁻²)	10.452	1.201	1.67	2.01	0.898	0.449	1.650
superbJ_{max} (A m⁻²)	2.351	9.963	12.755	17.046	7.0823	3.541	13.504
R_{int} (kΩ)	0.033	0.293	0.412	0.539	0.247	0.247	0.416

The average, the median and the fashion indicate the central values. The values of these parameters are very similar in all the cases, especially for the OCV and the maximum power. The error was calculated through the standard deviation (STDV), which reflects the deviation degree. When using the average as mean measure, The OCV is the parameter that showed the smallest STDV while the STDV of the internal resistance indicates that despite of the similar resistance in around 76% of the cases, the extreme values are very different. This fact can be observed in its maximum and minimum of 4.73 and 0.14 kΩ, respectively. It is important to remark that only the 6% worked under internal resistances similar to the maximum. The variance values reflect the same trend than the standard deviation, remarking also how different are the

extreme values of the internal resistance. It can be related to a bad assembly of the membrane-electrode or to a low electrogenic biofilm formation. This fact points out that the performance deviation can be due to a bad construction or enrichment process as a consequence of the human role instead of problems caused by the technology itself. The kurtosis indicates the amount of data that is close to the mean. The higher kurtosis, the higher data close to the average. The maximum power showed the higher kurtosis, followed by the OCV, the maximum current and finally, the internal resistance. Regarding to the quartiles (Q), Q2 is equal to the median. Q1 indicates that the 25% of the values are below Q1 value while Q3 indicates that the 75% of the values are below Q3 value and the difference between both is the interquartile range. This dispersion parameter is used when considering the median as main mean measurement.

Finally, standardized normal distribution curves were studied in Figure 3. It is a function with three differentiated parts: the middle zone, whose centre is value of the mean and it is concave; and the two ends, which are convex and tend to approximate the X axis. The most common elements are in the centre zone while the most unusual values at the extremes. Its shape is also related to the median, the fashion and the average. When fashion=average=median the curve is symmetrical. As these values are very similar in the case of the maximum power, its curve was practically symmetrical. In the case of the OCV, it was obtained a skewed curve to the left while for the maximum current and internal resistance, the curve was skewed to the right. The width of the curve indicates the data dispersion. The OCV curve is the narrowest one.

Figure 3. Standardized normal distribution curves of OCV (a), maximum power (b), maximum current (c) and internal resistance (d).

3.2. Study of reproducibility of 7 stacks

This section is focused on studying the reproducibility of the behaviour of 7 stacks.

Each stack has 16 MFCs. Therefore, the stack strategy followed the principle of the

“miniaturization and multiplication” due to the MFC size and the stack design [52]. The

stacks have been evaluated under different electrical connection in order to

demonstrate its robustness regardless the electrical connection of the MFCs. The

configurations tested were parallel and combinations of series/parallel 2/8 and 4/4.

The 2/8 configuration consists of 2 groups of 8 MFCs, the MFCs were connected in

parallel while the groups were connected in series. In the 4/4 configurations, 4 groups

were connected in series and each groups were formed by 4 MFCs connected in

parallel.

Figure 4 shows the OCV, maximum power and current and internal resistance (in logarithmic scale) for each stack and each connection.

Figure 4. Performance of the stacks under different electrical connections. (●) Parallel; (○) 2/8 combination; (◐) 4/4 combination.

As can be seen in Figure 4, results were reproducible in each configuration but the performance of stack 2 deviated from the trend and this deviation was more remarkable in configurations of series/parallel combination. This behaviour could be related to reversal voltage, which is a common phenomenon when working in series, due to unbalanced substrate distribution or different microbial communities [53-55]. In addition, maximum power values showed oscillations when increasing the series connection but it varied between 1-2 mW, which cannot be considered as a high

difference. The OCV and the internal resistance followed the same trend without remarkable oscillations: the OCV increased when increasing the groups in series [28, 56] and the internal resistance decreased with parallel connections. The decrease of the internal resistance when connecting MFC stack in parallel has been reported in the literature [52]. Furthermore, the maximum current increased also with the number of MFCs in parallel [28, 56]. The oscillations mentioned were confirmed by statistical parameters in Table 2.

Table 2. Statistical parameters for the stacks under different electrical connections.

Connection	OCV (V)	P _{max} (mW)	I _{max} mW	R _{int} (kΩ)	OCV (V)	P _{max} (mW)	I _{max} (mA)	R _{int} (kΩ)
	Average				Standard deviation			
Parallel	0.379	0.978	6.474	0.051	0.047	0.231	0.398	0.011
2/8	0.838	1.488	5.373	0.128	0.046	0.325	1.372	0.036
4/4	1.419	1.326	3.567	0.500	0.190	0.650	1.557	0.333
Connection	OCV (V)	P _{max} (mW)	I _{max} (mA)	R _{int} (kΩ)	OCV (V)	P _{max} (mW)	I _{max} (mA)	R _{int} (kΩ)
	Maximum				Minimum			
Parallel	0.454	1.270	6.930	0.706	0.326	0.653	5.689	0.041
2/8	0.933	1.877	6.311	1.967	0.796	0.192	2.426	0.096
4/4	1.597	2.232	5.300	1.204	1.054	1.010	0.849	0.240

For the OCV, Table 2 reports a low STDV regardless the kind of connection due to maximum and minimum values around the average value. Regarding to the maximum power and current, the STDV is especially low in parallel and 2/8 combination. The

STDV of the internal resistance in parallel and 2/8 configuration indicates reproducible data but the high value of internal resistance, which is an extreme value (maximum) in stack 2 with 4/4 configuration leads to a high STDV in this case. Anyway, in all the cases, the STDV increases when increasing the groups in series. However, the point is that, in general terms, attending to the same electrical connection, the values of STDV are acceptable. Because of that it can be stated that the data are reproducible as well as the technology is robust, not only for the operation of individual MFCs but also for the operation of MFC stacks. From the point of view of the scale-up, these results indicate that the miniaturization and multiplication strategy is viable because of the good performance and the reproducibility of the good performance in 7 stacks.

3.3. Relationship performance-internal resistance

As it was mentioned before, a low internal resistance can be linked with a good performance. For this reason, approach curves has been studied in this section considering the maximum power as the main parameter to represent the whole performance. In Fig. 5, it is shown the approach curve for individual MFCs.

Figure 5. Internal resistance vs maximum power of individual MFCs.

It can be observed that high internal resistances results in low maximum power and vice versa. High internal resistances decrease the electrons rate from the anode to the cathode and means a potential energy loss. The experimental data was fitted to a potential curve with a correlation coefficient of 0.78. This correlation coefficient increased up to 0.93 when attending to the fitting trends of the stacks for each electrical connection (Fig. 6). Fig. 6 demonstrates that regardless the number of MFCs and the way they are connected, the internal resistance and the performance are related by an exponential trend.

Figure 6. Internal resistance vs maximum power of the stacks under different electrical connections. (a) Parallel; (b) 2/8 combination; (c) 4/4 combination.

4. Conclusions

This work demonstrates the robustness of the MFC technology. After having operated 112 MFCs electrical connected individually, the statistical probability of good performance, maximum power, maximum current and internal resistance was 95%, 90%, 96% and 94% respectively. These figures indicates that the MFC is a robust technology. When evaluating the performance of the MFC stacks it was observed that low STDV were obtained regardless the kind of electrical connection. Being the best stack configuration the parallel and 2/8 combination where the 8 MFCs were connected in parallel while the 2 groups were connected in series. Finally, it was demonstrated that the performance of the MFCs and of the stacks mainly depends on the internal resistance. These figures indicates that the MFC technology is both a

reproducible and a robust technology, that could be used for real applications related to power technologies.

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