**Supplementary Material:Derivation of mathematical model based on Tafel equation explains microbial fuel cell performance**

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**Supplementary Material, Appendix A: Discussion of former models**

Regarding the effect of anodic materials, there has been much research on the use of graphite anodes in *MFC* [1-12, among others]. However, less has been published on the effect of the specific surface area of graphite anodes on *MFC* characteristics and performance in terms of the volumetric power. On the other hand, to the best of our knowledge there is little information on modelling the effect of the anodic specific surface area on performance of *MFC* [13-17] in terms of volumetric power, and could use the same influent (leachate) as the main experiment [18,19]*.* Indeed, the volumetric power is the variable to consider for a fair comparison of different processes. For instance, Hsu *et al.* [13] fitted the current intensity *i* to the anode surface area. This model gave an inverse relationship between the variables.

R2 not reported (A1)

where *i* is the current density, *Eanode* is the anodic potential, *Aanode* is the surface area of the anode, m and b are fitting coefficients. Incidentally, Hsu *et al.* [13] experimentally observed, but did not model, the decrease of the surface power densities *PAn* when the anode surface area was increased. They reported the values of *PAn* but they neither modelled the effect of the anodic surface area (or the specific surface area) on that variable nor the volumetric power of the cell. To some extent, the decrease of *PAn* with increase of anode area should be expected whenever the increase of *PMFC*is less than proportional to such an area. Furthermore, the model of Hsu *et al.* [13] was strictly empirical since it was not based upon electrochemical theoretical considerations. The authors did not report statistical parameters of the model, and consequently, it is very difficult to ascertain the goodness-of-fit of the proposed equation.

Dewan *et al.,* [14] worked with several anodic areas (graphite plates) in a two-chamber *MFC*. They modelled the *PAn* versus the logarithm of the total surface area of the anode. They found a linear, decreasing relationship (Eq. A2, R2 = 0.95). It can be seen that the coefficient of the term ln (surface area) is negative, which was consistent with the experimental results of Hsu *et al.,* [13]. As we commented above, it is debatable to use *PAn* as a variable for comparison of process intensity. In this regard, volumetric power *PV* is the dependent variable of choice. On the other hand, *PAn* is an adequate variable to assess anode performance. The model fitted by Dewan *et al.,* [14] was strictly empirical since it was not based upon electrochemical theoretical considerations. No statistical parameters of goodness-of-fit were reported, other than *R*2.

R2=0.95 (A2)

Di Lorenzo *et al.*, [15] presented a “Current distribution model” that found a relationship between a variable *ν* (the so-called ‘utilization of the electrode area’, (Siemens 0.5/sec) with a set of independent variables of electrode geometry (‘*L*’, thickness of the anode; ‘*a*’, specific area of the anode), the slope of the polarization curve ‘*s*’, and the conductivity of the influent *κ*

(A3)

They departed from theoretical grounds (Butler-Volmer kinetics in the anode) and several simplifying assumptions. They also defined a new variable efficiency *η* related to *ν*  by Eq. A4.

(A4)

(A5)

As a working example of their model, the authors calculated the current density peak *i2* during batch operation of a *MFC* based on a known current density peak *i1*, the corresponding values of L (L1 and L2), and the corresponding values of *η*, with an equation (not given by the authors and recreated by us).

(A6)

They showed that their model could give reasonable results compared to experimental values of current density peaks in a couple of their experimental cases. However, in their work, (*i*) they did not develop any general fitting of Eq. A3 to A5. Furthermore, they did not report any statistical measure of good fitness (no determination coefficients, no ANOVA of the model equations and predictions, etc.); (*ii*) they did not fit any model with volumetric power or internal resistance as dependent variable and the specific surface area of the anode as independent variable, i.e., their model was used just to approximately predict current density peaks but not powers (neither *PV* nor *PAn*); and (*iii*) the physical meaning of the variable *ν* given by the authors is vague. Furthermore, in spite of considerable work load to develop an expression for*ν*, this variable is only used as a ‘transition’ one in order to calculate the corresponding value of *η*.

In the end, Di Lorenzo *et al.* [15] concluded that, in spite of several recognized simplifying assumptions, the model could be useful as a starting point in selecting electrode geometries based on basic data of the influent and electrode conductivity.

Interestingly, the use of either *i* or *PAn* in the above mentioned models is very debatable as a means to express the *MFC* performance when the purpose is to compare the process intensity (unit power delivery) of a given *MFC* to the intensity of other competing processes such as other *MFC* configurations, anaerobic digestion, biohydrogen generation, etc., which could use the same influent as the main experiment*.* Indeed, the volumetric power is the variable to consider for a fair comparison of different processes [18,19].

The purpose of the work by Merkey & Chopp [16] was to examine the competition for space and nutrients of conductive and mediator-using bacteria in a *MFC*, assuming a bioﬁlm populated by both types of species. The model considered 41 parameters and 9 variables. The specific area of the anode is considered to have a fixed value in this work. Unfortunately, they neither considered the specific area of the anode as a variable itself nor evaluated its effect on the output of the model. The emphasis of the model was on microbiological features. Incidentally, the microbiological predictions from simulation runs using their model were not validated.

In another paper, Merkey & Chopp [17] sought to examine the dependence of *MFC* power output on electrode geometry and other operational parameters when electron transfer occurs through a conductive bioﬁlm. The authors warned that their model intended to elucidate the trends that one would expect to see in a *MFC*, and was not meant to make precise predictions regarding the power output. Furthermore, the predictions based on the simulation runs were not validated. Their model considered 21 parameters and 7 variables. Neither the anodic area nor the specific area of the anode was considered in the parameter set or the variable set of this work.

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**Supplementary Material, Appendix B: Relative error of the approximate expression when** *β*  **varies from 0 to 0.30**

We recall that

(B1)

Figure B1 represents the relative error of the approximate expression Eq. B1 when *β* varies from 0 to 0.30 [1]. Table B1 clearly shows and confirms that when

*β*  ≤ 0.30, the error of this formula does not exceed 9%, and when

*β*  ≤ 0.10, the error of this formula does not exceed 1%



**Fig. B1.** Relative error of the approximate expression 1/(1+*β*  ) = 1-*β*  . Horizontal axis = *β*; Vertical axis = relative error, in %

**Table B1.** Relative error of the approximation 1/(1+*β*  ) = 1-*β*



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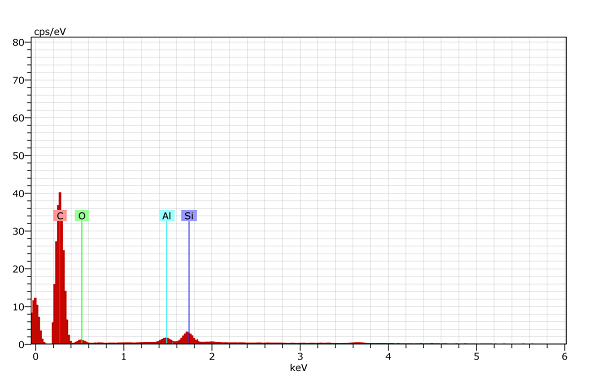
**Supplementary Material, Appendix C: Elementary analyses of the anodic materials**

The specification sheet of the supplier QR Minerales S.A. de C.V. who sold the *GF* only included the moisture and size distribution of the material *GF*, please see below Table C1.

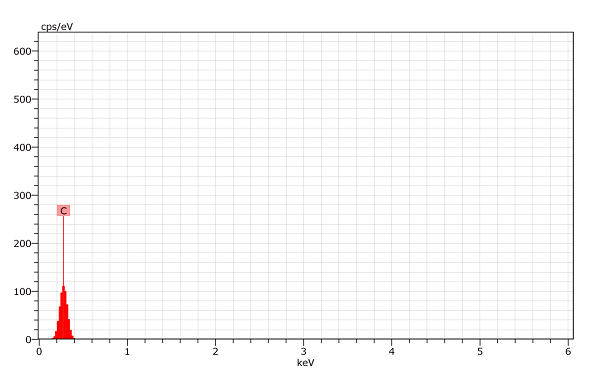
Results of the chemical composition of *GT* and *GF* by x-ray diffraction (XRD) are shown in Figs. C1 & C2, and Table C2. The composition of the *GR* was close to that of *GT* (data not shown).

**Table C1.** Moisture and size distribution of the material *GF.*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Mesh** | **Principio del formulario**  **Granulometry (%) Final del formulario** | | **Moisture (%)** | **Conductance (S)** | **Color** | **Bulk density (g/cm3)** |
| 1/2 | 0.64 | <20 | 1.84-2.5 | 0.13 ± 0.04 | Principio del formulario  shiny black Final del formulario | 1.024 |
| 1/4 | 72.72 | >45 |
| 1/4 | 26.64 | <35 |



**Fig. C1.** X-ray diffraction spectrum of graphite flakes.



**Fig. C2.** X-ray diffraction spectrum of graphite triangles.

**Table C2.** Summary of the chemical composition of the anodic materials used in our work.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Anodic material** | **Element (% by wt)** | | | | | |
| **Carbon** | **Oxygen** | **Aluminium** | **Silicon** | **Calcium** | **Others** |
| ***GT***a | 99.00+ | < LDc | < LD | < LD | < LD | < 1 |
| ***GF***b | 89.43 | 7.47 | 0.85 | 2.26 | < LD | < 1 |

Notes: a Graphite triangles;b Graphite flakes;cLevel of detection

It can be seen that the *GF* material contained more impurities than *GT*, particularly oxygen and silicon. One may speculate whether the presence of oxygen would lead to some polarity niches in the graphite surface that could improve bacterial contact and posterior adhesion. On the other hand, the presence of other oxygen as well as other components could have a negative impact on the conductivity of the *GF*. However, this hypothesis was not valid. Indeed, in Table 1 of our article, the conductances of the materials are 0.61 and 0.13 S for *GT* and *GF*, respectively. Taking the average thickness as 0.5 and 0.1 cm for *GT* and *GF*, respectively, the corresponding conductivities are 1.22 and 1.30 S/cm. These values are quite close, in spite of the different chemical composition of materials.

**Supplementary Material, Appendix D: Physico-mathematical procedure of the specific surface area of the anode *A´s***

First, the calculation method based on mass and size data is a typical and accepted way to estimate specific surface area of particulate materials in process engineering [1].

Second, the value 0.43 as shape factor for *GF* based on literature data, i.e., Table 5-22 of Perry [2].

Third, when we chose to estimate the number of particles of the anode, because of space constraints, we only showed the final equation in our article Eq. 37, Eq. D1 in this Appendix.

(D1)

However, this equation is the outcome of a complete mathematical procedure. Below please find the derivation of Eq. D1.

We start focusing our attention on Fig. D1 and the definitions of the geometric variables ([2]; pp. 5.50 & ff)

**Dp**

Graphite flake sphere equivalent

**Fig. D1.** Actual graphite flake and its equivalent sphere.

Vp, volume of the particle

Ap, actual surface area of the particle

Lp, characteristic length of the particle,

: Average particle diameter, defined as the diameter of a sphere of the same volume as the particle

: Shape factor of the particle (also called sphericity factor), defined as the quotient of the area of a sphere equivalent to the volume of the particle Vp divided by the actual surface of the particle Ap.

We state the area of an equivalent sphere of diameter in Eq. D2, is still unknown

(D2)

The volume of the particle is given by Eq. D3

(D3)

We find the equivalent diameter of the particle with Eq. D4

(D4)

By definition, the sphericity factor is

(D5)

For beds of porosity, the equivalent particle diameter could be calculated as follows ( is also known as void space: fractional free volume)

(D6)

where

S: specific surface or area of particle surface per unit volume of bed = S0 (1 - ε)

S0: area of particle surface per unit volume of solids, see line above

M: total mass of particles in a given sample

mp: mass of particle

ρ: actual density of the material

in test tube (measuring cylinder) (D7)

where ρapp is the apparent density, as opposed to the actual density of the material.

If N denotes the total number of particles in a given sample weighing M kg, then

(D8)

Now, we start the process of estimating *A´s*

(D9)

where

V: volume geometric or net volume. We used the net volume

I do not know Ap. I know Asph.eq, why?

Because

(D10)

where ρ is the density of the solid material

then

(D11)

Moreover, (D12)

Algebraic manipulation of Eq. D12 leads to

(D13)

(D14)

(D15)

where (D16)

Regarding the value of the sphericity factor chosen for our calculation of the specific surface area of the *GF*, please refer to Table D1 and the text below.

**Table D1.** Sphericity factors of selected materials. Excerpt from table 5.22 of Perry [2].

|  |  |
| --- | --- |
| Material |  |
| ………………. | …….. |
| Coal dust pulverized | 0.73 |
| Crushed glass | 0.65 |
| mica flakes | 0.28 |
| Flint sand (jagged flakes) | 0.43 |

Please note that mica flakes are extremely flat, whereas the *GF* are more robust and similar to flint sand (jagged flakes) of Table D1. Because of this, we chose the value 0.43 for our estimations.

Fourth, an experimental method for determining specific surface areas of particulate materials require instrumental analysis, namely by adsorption or gas permeability. The specific surface area can be measured by adsorption using the BET isotherm. BET stands for Brunauer, Emmett, and Teller who developed the expression for a more general form of isotherm compared to the simple models of Freundlich and Langmuir [3]. This method has the advantage of measuring the surface of fine structures and deep texture on the particles. However, the results can differ markedly depending on the substance adsorbed.

Gas permeability method can also be used.This depends upon a relationship between the specific surface area and the resistance to gas-flow of a porous bed of powder (head loss). The method is simple and quick, and yields a result that often correlates well with the chemical reactivity of a powder. However, it fails to measure much of the deep surface texture.

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