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IMAGING CONCENTRATION FIELDS IN MICROFLUIDIC FUEL CELLS AS A MASS TRANSFER CHARACTERIZATION PLATFORM

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ABSTRACT

1 Microfluidic fuel cells (MFCs) are microfluidic electrochemical conversion devices that are used to
2 power small pieces of electrical equipment. Their performance relies on the improvement of the mass
3 transfer of the reactants at the electrode interface. In this work, a MFC is developed to implement
4 a novel imaging technique that allows the measurement of reactant concentration fields, featuring
5 formic acid as the fuel and potassium permanganate as the oxidant. The concentration fields were
6 imaged based on transmitted visible spectroscopy, which links the light intensity passing through
7 the MFC to its local reactant concentration. An analytical model was developed to estimate the
8 mass diffusivity and kinetic reaction rate coefficient. For the first time, mass transport and transfer
9 coefficient were simultaneously measured during operation. These parameters estimated using the
10 proposed technique can be implemented in a numerical model to predict the MFC performance and
11 concentration distribution. This work paves the way toward advanced imaging tools for operando mass
12 transfer characterizations in microfluidics and Tafel kinetic characterization in many electrochemical
13 devices.

14 **Keywords** Fuel cells · Imaging · Spectroscopy · Mass transfer · Microfluidic · Concentration fields

15 **1 Introduction**

16 Microfluidic fuel cells (MFCs) are microscale systems used to convert the chemical energy contained in fuels directly
17 into electricity [1-2], making these devices promising energy sources. Such devices are composed of a microfluidic
18 channel that ensures rather good control of the hydrodynamic conditions. In the channel, two electrodes are embedded
19 to enable a oxidation reaction at the anode and a reduction reaction at the cathode. Such an MFC can be used both
20 as fuel cell or electrolyzers, which makes this technology a promising candidate for energy conversion and storage.
21 A wide variety of MFCs are present in the literature, and more details about them can be found in the following
22 comprehensive reviews [3-5]. The present study focuses on a coflow membraneless MFC [6] using formic acid 23
(HCOOH) and potassium permanganate (KMnO_4), as this system is relatively robust, is compatible with classical soft 24
photolithography micro fabrication techniques, uses nonhazardous chemicals and is easy to operate [7-8].

25

26 Three main phenomena govern MFC performance. First, the mass transfer is based on the diffusion, advection and
27 reaction of the chemical species in the microchannel. The second phenomenon is linked to charge transfer in the
28 electrolyte and the electrodes, several authors have reported a thorough description of such [9-10]. The last phenomenon
29 is the entropy generated during the energy conversion, which is transformed into heat and impacts the rate of mass
30 diffusion and the electrochemical kinetics. Thus, optimal MFC performance relies on accurate control and knowledge
31 of these phenomena which have the potential to be characterize through operando contactless imaging technique.

32

33 Over the last few decades, a large number of MFC numerical models were developed to predict their performance
34 [11-15]. Among them, Gervais & Jensen [16] describe several mass transport and electrochemical reaction 35
modelling methods. These models rely on the knowledge of the mass diffusivity and kinetic reaction rate coefficients. 36
Multiphysical modelling is also often used, such as in the work of Wang et al. [17]. Such models need many important 37
parameters, which are difficult to find in the literature or to measure ex situ. In the literature, numerical studies 38
are mainly compared to experimental results using the polarization curves. The comparison can be improved by 39
studying the mass transfer that occurs in an operating cell. Using imaging techniques, in-situ characterization of the 40
mass transport enables the derivation of the mass diffusivity coefficient and the kinetic reaction rate, allowing the 41
development of more accurate models.

42

43 Several studies in the literature have shown great interest in characterizing mass transport using imaging methods
44 [18-21]. For example, Sun et al. [19] used an optical microscope to study permanganate diffusion into formic acid.
45 Their work was mainly qualitative to illustrate the hydrodynamic flow in their MFC. Lu et al. [22] used optical and
46 fluorescence imaging techniques to validate their MFC model and to measure the concentration distribution profile
47 at one position in the channel. However, imaging the concentration field in the microchannel has yet to be been
48 reported. More advanced imaging techniques based on infrared techniques [23-26] or X-ray [27] can also be used to

49 characterize the MFC structures, concentration fields or two-phase flow distribution. Among them, visible or ultraviolet
50 (UV) spectroscopy are particularly efficient for measuring the chemical concentration of compounds in aqueous
51 solutions, as light in these wavelengths are not strongly absorbed by water [28]. However, although many imaging
52 techniques are used for concentration measurements, thorough operando characterization of the mass transfer and the
53 simultaneous acquisition of the electrochemical performance has yet to be implemented. Such a study would require
54 designing a MFC, a specifically tailored imaging setup and a potentiostat to control the electrochemical conditions
55 of the MFC. Although these challenges appear to be ambitious, the results that the operando images would yield
56 are of prime interest for all MFC research. In fact, they would enable the measurement of the main parameters
governing the cell performance such as the mass diffusivity, electrochemical kinetics and reactant concentration
distribution.

58

59 The main goal of the present work is to report the use of imaging visible spectroscopy to measure the operando MFC
60 mass transfer, specifically the mass diffusivity and kinetic reaction rate coefficient. Such a technique has already been
61 used for various global concentration measurements in microfluidic reactors [29], but rarely to image a concentration
62 field, despite it could be adapted for MFC transient concentration field characterization. The physical properties and
63 performance of a MFC can be estimated from a model of the hydrodynamic, mass transfer and electrochemical reaction.
64 In the first section, a description of the MFC design for visible spectroscopy, and the associated imaging setup is
65 presented. This is followed by a description of the analytical model for concentration diffusion in the channel used to
66 perform the parameter estimation. In the results section, the experimental polarization curve and concentration fields
67 are presented and compared to the model. A thorough analysis of the technique is performed, and its limitations are
68 discussed.

69 **2 Methods**

70 **2.1 Fabrication of MFC**

71 A chip featuring a T-shaped microfluidic channel was fabricated using standard photolithography. The microchannel
72 height is 25 μm , width is 3 mm, and length is 15 mm. This specific aspect ratio was used to facilitate light transmission
73 through the MFC and to reduce the transfers to 2D; see the model in the next section. A negative photoresist was spin
74 coated on a silicon wafer, covered with a photomask and exposed to UV light. It was then submerged in a propylene
75 glycol methyl ether acetate (PGMEA) solution for development. The obtained mold was placed in a Petri dish and
76 coated with 5 mm of polydimethylsiloxane (PDMS). After being cured, the PDMS was peeled off the mould and
77 hole-punched to create two inlets and one outlet.

78

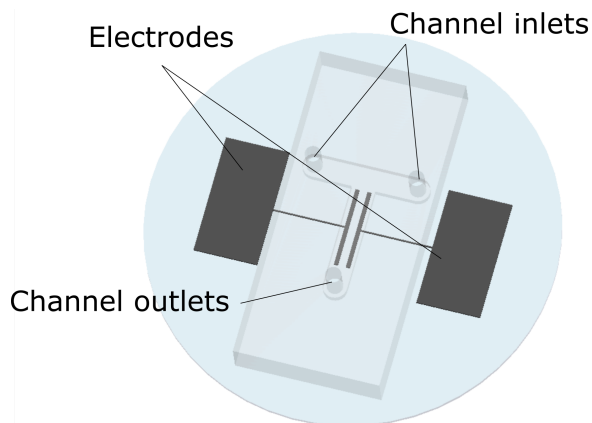


Figure 1: Three-dimensional view of MFC.

79 For the electrodes, an inverse pattern was created on a glass wafer using the same photolithography process as for
80 the PDMS stamp. The deposition was achieved by sputtering ~ 60 nm of titanium as an adhesion layer, and then
81 subsequently ~ 300 nm of platinum for the catalyst material. The remaining photoresist was removed by submerging
82 the wafer in a chemical etching solution (MicropositT - MF-319) to obtain only the platinum pattern directly on the
83 glass substrate. The PDMS stamp was plasma activated and bound to the glass substrate, resulting in the complete MFC
84 presented Figure 1. The electrodes dimensions are 500 ± 3.5 μm wide by 1 ± 0.0035 mm long, and are contained in
85 the main channel where the reactants flow. More details and schematics of the microfabrication process can be found in
86 the Supplementary Material.

87

88 2.2 Experimental setup

89 The concentration distribution and total current produced by the MFC were measured using the setup described in
90 Figure 2. It is made of a homemade inverse microscope. The primary light source is a white mounted LED (Thorlabs
91 - MWW4) assembled with collimation adapter (Thorlabs -SM2F32-A) and placed 12 cm above the cell. A narrow
92 bandpass filter ($\lambda = 540 \pm 5$ nm) is used to produce a monochromatic green light passing through the MFC. The
93 light is finally collected through a microscope objective and a lens to produce an image with x1 magnification on a
94 CMOS camera (Zelux 1.6 MP Colour CMOS Camera). Only the green channel of the camera was used in the image
95 postprocessing. The resulting spacial resolution is 3.45 $\mu\text{m}/\text{px}$ leading to observation field of approximately 5 by 4 mm.

96

97 The MFC is controlled using a potentiostat (Biologic SP-300) to measure the voltage and the current produced.
98 Electrical measurements are performed in a three electrodes configuration. An Ag/AgCl reference electrode is
99 immersed in a beaker filled with 0.5M of sulfuric acid. The chemicals from the outlet of the chip are spilled in the
100 beaker containing the reference electrode to ensure the electrical contact. In this configuration, anode and cathode

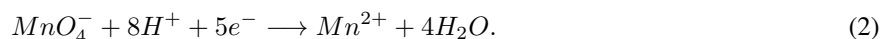
101 potentials are measured simultaneously in the same experiment allowing a full characterization. The reactant flow rate
102 is controlled using a syringe pump (Cetoni Nemesys) over a wide range from 0.5 to 100 $\mu\text{l}/\text{min}$.

103

104 The reactants (formic acid and potassium permanganate) were chosen for good performance [1]. In addition,
105 permanganate potassium has the advantage of a clear absorption signature in the visible range which allows the
106 investigation of mass transport at the cathode. However, mass transport at the anode can not be studied since formic
107 acid is transparent in the visible range. At the anode, the formic acid oxidation is



108 At the cathode, the permanganate reduction is



109 In equation 2, when a current is produced, the permanganate ions (MnO_4^-) are transformed into manganese ions Mn^{2+} .
110 Thus, the current applied through the MFC electrodes triggers a decrease in the permanganate concentration, which is
111 measured by visible spectroscopy. It is also assumed that Mn^{2+} ions do not absorb light at the chosen wavelength, and
112 that no CO_2 gas bubbles from the reaction appear during the experiment.

113

114 The wavelength chosen in the imaging setup corresponds to the strongest light absorption of the MnO_4^- ions, whereas
115 formic acid is completely transparent. Thus, using the Beer-Lambert equation, one can link the variation in light
116 intensity to the variation in permanganate concentration as

$$\Delta c_{exp} = -\kappa^{-1} \ln \left(\frac{I_0 + \Delta I}{I_0} \right) \approx -\kappa^{-1} \left(\frac{\Delta I}{I_0} \right) , \quad (3)$$

117 where κ is the permanganate absorption coefficient (mM^{-1}), I_0 is the light intensity of the background and ΔI is
118 the light intensity variation induced by the current production. The linearisation of the Beer-Lambert was used as the
119 variation of light intensity is very small, i.e. less than 1.5%. The permanganate absorption coefficient was measured to
120 be $\kappa = 5,5 \times 10^{-3} \text{ mM}^{-1}$ at 540 nm (see the calibration curve in Figure S3 in the Supplementary Material).

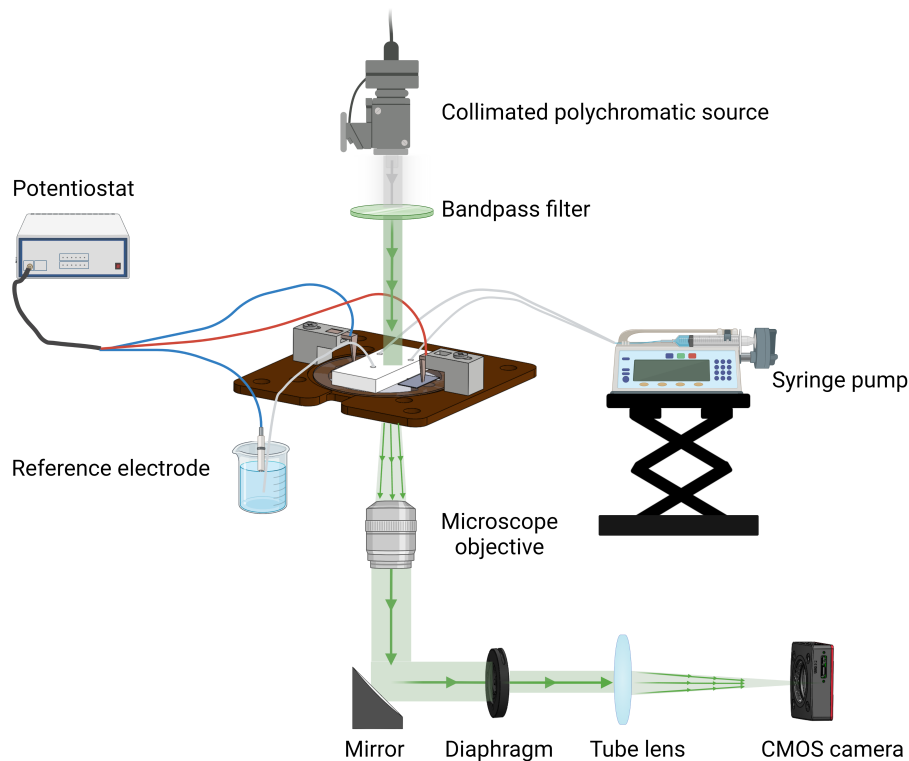


Figure 2: Schematic of visible spectroscopic imaging setup used to measure in operando concentration.

121 2.3 Permanganate diffusion in the depletion zone

122 In our MFC geometry, the chemicals flow at a given velocity v , diffuse with a mass diffusivity D and are consumed at
123 the electrode interface at a rate given by the kinetic reaction rate coefficient k_0 . The coefficient k_0 is linked to the
124 current produced by the cell (see the Tafel law defined in appendix). The resulting concentration decreases at the
125 electrode interface creating a depletion zone on each side of the electrodes where the concentration diffuses. Thus, the
126 magnitude and the spatial distribution of this depletion zone enable the mass diffusivity D and the kinetic reaction rate
127 coefficient k_0 to be measure in the operating MFC.

128 Between the two reactants, a diffusion zone is also formed due to the interdiffusion between the HCOOH and the
129 KMnO_4 . If the velocity of the fluid is large enough, the diffusion zone should not interact with the depletion zone
130 Figure 3.

131

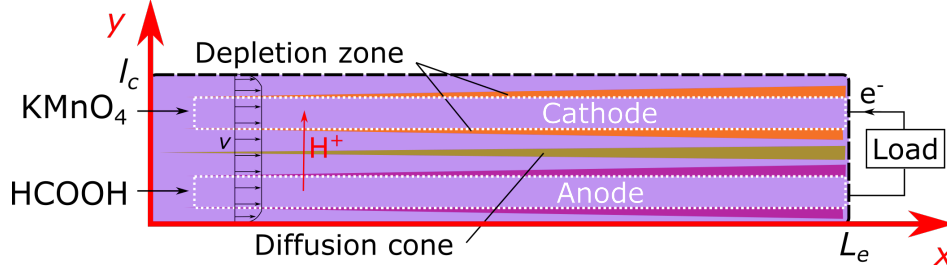


Figure 3: 2D schematic of channel with the electrodes placed at the bottom of the channel. The fluids flow from left to right. The main charge transport phenomena are indicated for sake of clarity, but are not modeled.

132 Given the specific aspect ratio of the channel, i.e. height to width ratio larger than 100, all the mass transfer can be
 133 considered in 2D. This assumption was checked numerically using COMSOL. The result presented in Section 3 of
 134 the supplementary material shows an excellent agreement between the concentration profiles computed analytically
 135 and numerically is found, see Figure S5. In addition, the velocity of the fluid can also be considered large enough to
 136 ensure a diffusion of the concentration using the semi-infinite assumption with no interaction with the diffusion zone.
 137 In this case, the diffusion of the permanganate in the depletion zone on each side of the electrodes can be analytically
 138 computed using a convolution product between the diffusive impulse response and the concentration at the electrode
 139 boundary, $y = e/2$, [30] as

$$c(x, y) = \int_0^x c_e(x - x_0) \sqrt{\frac{\delta(y)}{\pi x_0^3}} \exp\left(-\frac{\delta(y)}{x_0}\right) dx_0, \forall y > e/2, \quad (4)$$

140 where $\delta = vy^2/(4D)$, e is the electrode width (in the y -direction), and $c_e(x) = c(x, y = e/2)$, is the concentration at
 141 the channel/electrode interface. The concentration at the interface is mainly linked to the electrode dimension and the
 142 kinetic reaction rate constant, k_0 . The calculation of this function is detailed in the appendix.

143 Equation 4 is used to compute the concentration of the reactant in the depletion zone. The convolution product is
 144 computed using a numerical Laplace transform algorithm [?]. The analytical and relatively simple mathematical
 145 writing of this equation enables to use an inverse method to estimate D and k_0 .

146 3 Results

147 3.1 Electrochemical performance of MFC

148 Before imaging the concentration field in the MFC, a polarization curve was measured. It was done using an aqueous
 149 solution with a 4M formic acid solution mixed with a 1M sulfuric acid solution in a ratio 1:1 at the anode. At the
 150 cathode, an aqueous solution containing 20mM of potassium permanganate mixed with 1M of sulfuric acid in a ratio
 151 1:1 is used. The flow rate was set to 5 $\mu\text{l}/\text{min}$ for both inlets. The current and electrodes potentials were recorded for a
 152 range of cell potential between OCV and 0.2 V. Each cell potential was held for 5 min, and the current measured over
 153 the last min was average in the reported points. The electrode potential were measured against an Ag/AgCl reference

154 electrode immersed in the MFC electrolyte.

155 The polarization curve obtained in Figure 4 shows that the MFC underperformed compared to the literature 21,32. This
 156 is attributed to the catalyst used at the anode. For sake of simplifying in the fabrication process, the same catalyst was
 157 used for both the anode and the cathode, i.e. platinum. However, using palladium as a catalyst could enhance the formic
 158 acid oxidation process as reported in the literature [33-35]. The poor performance of the anode can be observed through
 159 the value of the anode potential, which increases drastically compared to the cathode potential. However, the present
 160 MFC was developed for imaging purposes and despite poor performance, the current density produced by the cell was
 161 enough to create a decreasing concentration gradient of the permanganate.

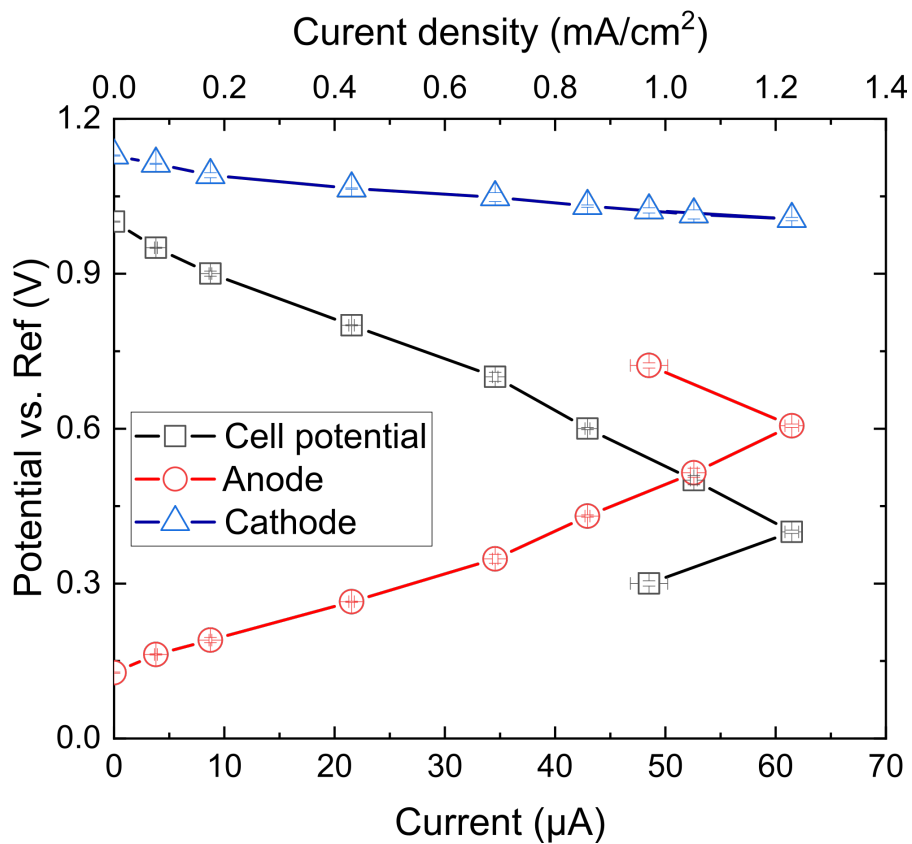


Figure 4: MFC polarization curve. Each point is an average of the recorded data for one minute.

162 3.2 Concentration field measurements

163 The concentration field was imaged during a cell operation at 20 μA and 40 μA. The images were acquired using
 164 the setup described in Figure 2. The camera frame rate was set to 5 fps. The cell was imaged first at rest for a 15 s
 165 before generating a current to obtain the background image I_0 . The anode and cathode flow rates were set to 1 μl/min,
 166 respectively. This flow rate ensures an average velocity of 0.42 mm/s and a residence time of 24 s which increase the
 167 width of the depletion zone on each side of the electrode. Consequently, the MFC can be considered as operating in
 168 steady state for any time longer than 24 s.

169 In Figure 5(a), the electrochemical performance of the cell during the imaging experiment at 20 μA is presented. The
170 anode potential is quite steady, but a small decrease of the cathode potential is observed from 0.85 to 0.7 V. This
171 behaviour is attributed to the creation of solid MnO_2 [5,8] which sediments on the electrode surface, lowering the
172 cathode performance. Thus, the concentration field was imaged once the steady state is reached, i.e. after 25 s, for
173 10 seconds before an important solid MnO_2 layer covers the electrode. This period of time is indicated by the grey
174 rectangle in Figure 5(a).

175

176 During this period of time, a change in light intensity of approximately 10-15 camera counts out of 900, i.e. less than
177 1.5%, was detected on each side of the electrode. The signal-to-noise ratio (SNR) was estimated to be approximately
178 ~ 3 (noise is roughly 4/5 camera counts), which is very low. To reduce the signal to noise ratio, all images recorded
179 during 10 s (50 images in total) were averaged and converted to concentration fields using equation 3. Then, the
180 absolute concentration field is deduced as $c_{exp}(x, y) = c_0 - \Delta c_{exp}(x, y)$. This result is presented in Figure 5(b). No
181 signal can be recorded through the electrodes as they are fully opaque to visible light. Figure 5(b), a concentration
182 gradient appears and diffuses along the channel creating a depletion zone which is almost symmetrical on each
183 side the cathode. A slight change is visible at the bottom and can be explained by small flow instability in the
184 MFC. The magnitude and the width of the depletion zone is more pronounced towards the end of the channel than
185 at the inlet due to advection. Since the depletion zone are quite small, i.e. width of 300 μm at the maximum, a
186 spatial resolution at the microscale was chosen (i.e. 3.45 $\mu\text{m}/\text{px}$, see section 2.2). However, the field of view is
187 limited, i.e. 5 mm in the channel direction, so only the first half of the channel is imaged (red rectangle in the Figure 5(b)).

188

189 In the depletion zone, a maximum decrease of 2 mM is observed, which is a small variation in concentration. However,
190 the results presented here demonstrated that it was possible to measure it using the rather simple setup proposed. From
191 the data presented in Figure 5, a noise of ± 0.2 mM is estimated. These results highlight the sensitivity of the setup for
192 detecting small concentration variations in MFCs.

193

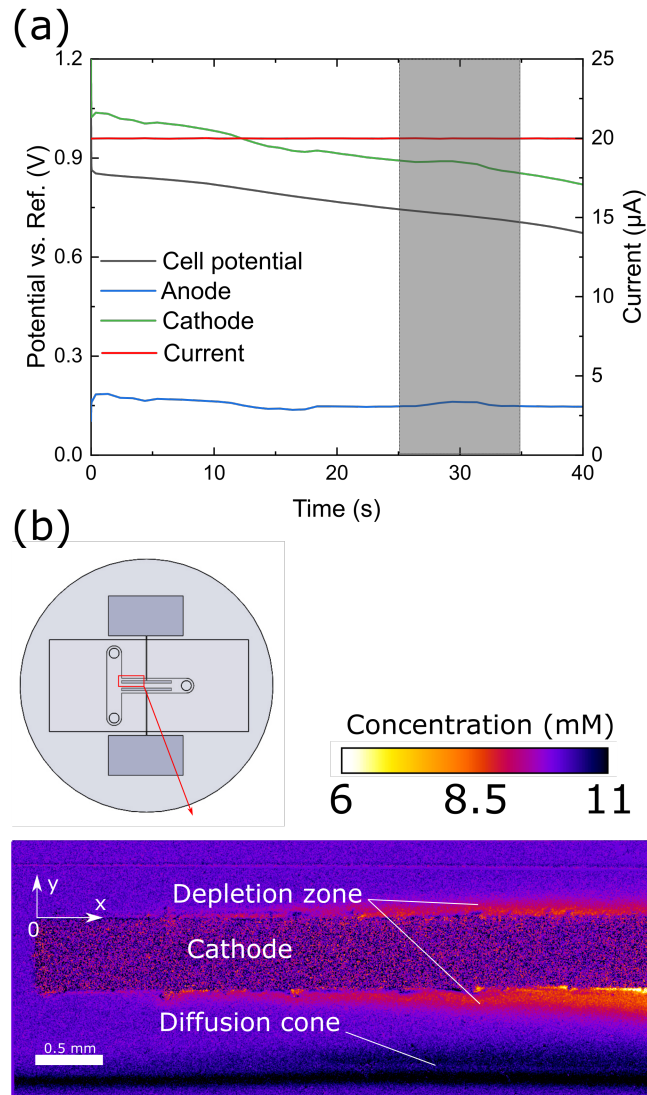


Figure 5: (a) MFC electrochemical parameter during the measurements of the concentration field at $20 \mu\text{A}$. The grey rectangle indicates the time used to average the imaging data. (b) The steady state concentration field imaged at the inlet of the cathode (see the red rectangle in the MFC insert).

194 3.3 Estimation of D and k_0

195 In this next step, the data of both depletion zones are used and averaged together. The estimation of the mass diffusivity
 196 and the kinetic reaction rate coefficient was performed with the concentration measurements in the depletion zone and
 197 the analytical model presented in section 2.3. The experimentally measured depletion zones and the analytical model's
 198 concentration distribution are presented in Figure 6. This model is only valid because of the choice in cell geometry:
 199 MFC with high aspect ratio ensuring a 2D diffusion of the concentration with an average velocity.

200

201 In order to increase the SNR, the concentration field in the depletion zone was averaged every 50 μm on each side of the
202 electrode in the y -direction (see the axes in Figure 5). In line with the experimental data, Equation 4 was integrated
203 between the same boundary, i.e. for the first zone : $\bar{c}_1(x) = \int_0^{l_1} c(x, y)/l_1 dy$. A minimization algorithm (simplex
204 algorithm from `fminsearch` function in Matlab) was then used to estimate parameters k_0 and D , minimizing the error
205 between the model and the experimental data. The use of an analytical model enables fast processing of the data
206 (almost real time ~ 3 s).

207

208 The identification of D and k_0 was performed for two currents 20 and 40 μA . In Figure 6(a), a good agreement between
209 the model and the measurements was obtained from the parametric estimation. The parameters were determined were
210 $D = (5.5 \pm 2.5) \times 10^{-3} \text{ mm}^2/\text{s}$ and $k_0 = (0.9 \pm 0.1) \times 10^{-3} \text{ mm/s}$. For a first time, an operando value of k_0 is
211 provided. However, the value of the diffusivity D is largely overestimated when compared to the literature. This is
212 mainly due to the poor sensitivity of this parameter in the model used (see supplementary materials). As the sensitivity
213 of the two parameters is quite similar, a large D could be compensated by a small k_0 and conversely. However, the
214 estimation procedure was still able to converge to a unique global minimum (see supplementary materials Figure S6)
215 and to give a correct value of k_0 (see next section).

216

217 A second identification of the parameters was performed at 40 μA (see Figure 6(b)). It leads to $D = (3.7 \pm 0.5) \times 10^{-3}$
218 mm^2/s and $k_0 = (2.4 \pm 0.1) \times 10^{-3} \text{ mm/s}$. The value of D is still not in the range expected by the literature, but, the
219 value of k_0 was increased as expected since the current density increased. Thus, the proposed method can be used to
220 identify these parameters in simple MFC geometry. However, the correlation between both parameters would first
221 require a precise estimation of the diffusivity, before the proposed method is used to estimate the kinetic coefficient rate.
222 Finally, Tafel parameters could also be estimated over a range of cathode potentials, but this is out of the scope of the
223 work, which demonstrates the use of imaging techniques to measure mass transfer parameters.

224

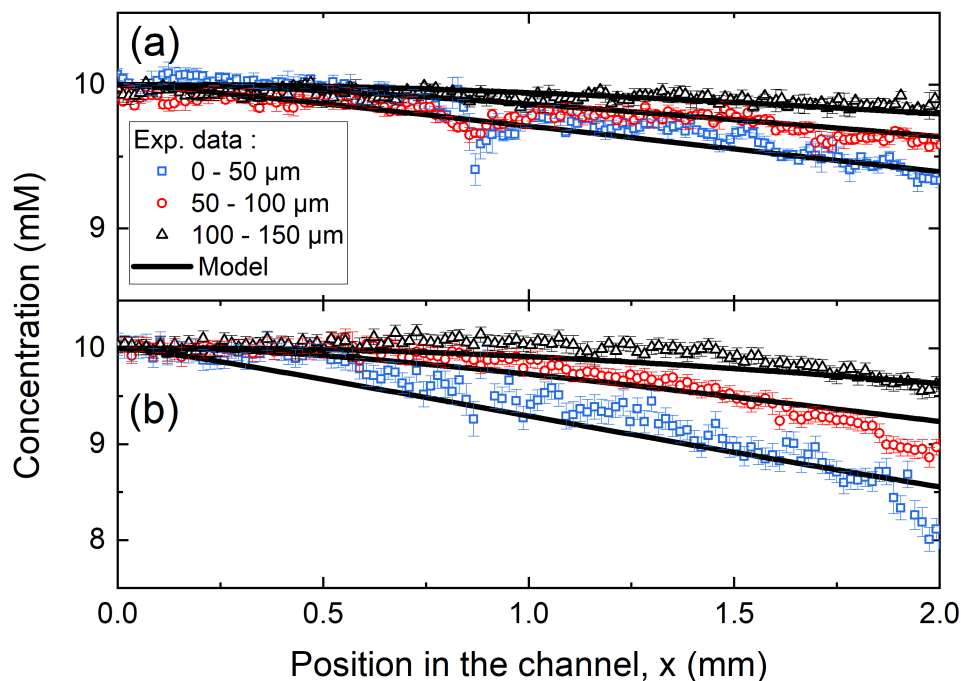


Figure 6: Comparison of the concentration distributions in the depletion zone for 3 y-positions to the analytical model once D and k_0 were estimated. Results obtained at (a) $20 \mu\text{A}$ and (b) $40 \mu\text{A}$. The errors bar were computed from the standard deviation of the measurements over 50 images.

225 3.4 Comparison with the model in steady state

226 In the last section, the concentration field computed using a numerical model (see appendix) is presented to validate
 227 the values of the estimated parameters. In the numerical model, all the operating conditions and cell geometry are
 228 representative of the experiments (e.g. flow rates, current density and MFC dimensions). The only unknown parameters
 229 that remain are the mass diffusivity of permanganate in the aqueous solution and the kinetic reaction rate coefficient.
 230 These parameters were taken from the previous estimation at $20 \mu\text{A}$. The resulting concentration field is presented in
 231 Figure 7.

232

233 Qualitatively, the concentration fields that were obtained with the numerical model are similar to the measurements
 234 presented in Figure 5, including depletion and diffusion zones. The magnitude is also similar, i.e. $\sim 2 \text{ mM}$ in decrease
 235 for the concentration over the first 5 mm of the channel length. Another interesting result is the total current predicted by
 236 the model, which can be computed using Faraday's law (see appendix). A total current of $18.5 \mu\text{A}$ was obtained using
 237 of the estimated value of k_0 which is very close to the $20 \mu\text{A}$ set in the experiment. If a value of $k_0 = 1,04 \times 10^{-3}$
 238 mm/s was used instead (which is in the uncertainty range of this parameter), then a total current of $20 \mu\text{A}$ was obtained.

239 This result demonstrates that with a few set of free parameters, predictive modelling for the MFC performances is
240 viable. Further MFC characterizations would help improve the precision of the model.

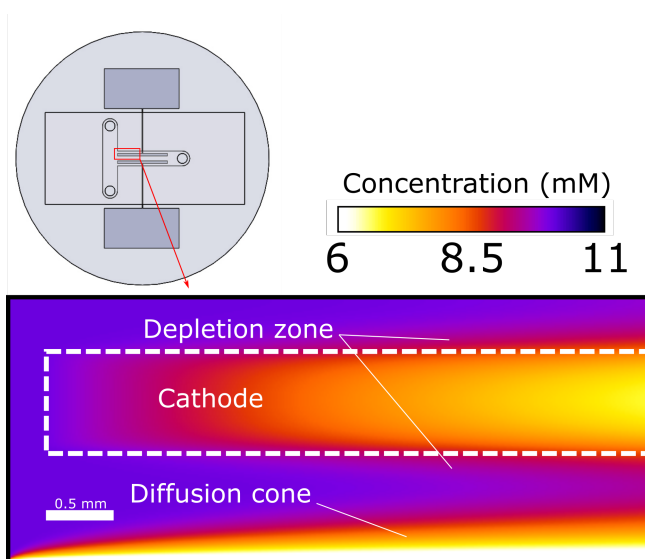


Figure 7: Result of the concentration field computed using the numerical model presented in appendix. Only the electrode onset at the MFC inlet is presented to match the imaging data. The red rectangle in the MFC insert indicate the position. The white rectangle represents the electrode position.

241 4 Conclusion

242 In this work, an operating MFC was imaged using an in-house visible spectroscopy setup. A specific imaging setup and
243 MFC design were specifically designed to achieve this goal. The concentration fields were measured based on the
244 Beer-Lambert law, enabling a measurement of reactant concentration variations as low as 0.2 mM when a current is
245 triggered. The obtained image was the first reported in the literature and shows the potential of advanced imaging
246 techniques for MFC characterization.

247

248 Along with the experimental data, an analytical model of the concentration diffusion in the depletion zone close to the
249 electrode is proposed. The comparison between this model and the experimentally measured concentration fields
250 enables operando measurements of the main mass transfer parameters, i.e. D and k_0 . Eventhough a large uncertainty in
251 the value of D was found, this values allow us to model the concentration distribution and current. Validity of the
252 model could be enhanced by determining the diffusivity D prior to the reaction rate k_0 .

253

254 Finally, this work demonstrates the feasibility of both imaging and modelling for transient concentration fields in an
255 MFC, and the viability of this platform for characterizing the mass transfer in MFCs. Given the importance of the
256 numerical models in the research community for predicting the MFC performance, such characterization platforms are

257 of prime importance for validation of this models. However, several improvements to the present work are necessary
 258 for estimating the Tafel parameters or the impact of the operating conditions on the mass transfer parameters. By
 259 elaborating upon the presented techniques, MFCs can be optimized as more powerful and efficient electrochemical
 260 energy conversion systems.

261 Acknowledgement

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 263 I2MPAC, Grant No. ANR-20-CE05-0018-01.

264 Appendix

265 General equations of the concentration diffusion and reaction

266 To simplify the model the velocity profile is assumed to be laminar, established, and modelled using a Poiseuille flow.
 267 The mass diffusivity is considered constant and the problem is solved in the steady state. Fick's law is used to model
 268 the mass diffusion in diluted solution, the ions and the reactants in the electrolyte and in the anolyte do not interact on
 269 the mass and charge transport at the cathode, and the electrochemical reaction is modelled by a Tafel law.

270 Under these conditions, the 3D problem of mass transport can be written as

$$\nabla \cdot (v_x c) = D \nabla^2 c \quad (5)$$

$$\left. \frac{\partial c}{\partial y} \right|_{y=0, l_c} = \left. \frac{\partial c}{\partial z} \right|_{z=h} = 0, \quad (6)$$

$$-D \left. \frac{\partial c}{\partial z} \right|_{z=0} = \frac{j(x, y)}{n_e F}, \quad (7)$$

$$c(x = 0, y, z) = c_0(y), \quad (8)$$

271 where c is the reactant concentration (M); D is the mass diffusivity (m²/s); x , y and z are the spatial coordinates (m) as
 272 defined in Figure 3, with z the vertical direction; n_e is the number of electrons exchanged; F is the Faraday constant
 273 (C/mol); and $j(x, y)$ is the current density distribution (A/m²) on the electrode. The current density is zero outside of
 274 the electrode. Equation 7 is Faraday's law applied to the electrode interface. The current density in this equation is
 275 modelled using the Tafel law, which links the local reactant concentration to the fuel cell potential as:

$$j(x, y) = i_0 \frac{c(x, y, z = 0)}{c_0} \exp(\eta/b), \quad (9)$$

276 where i_0 is the electrode exchange current (A/m²), b is the Tafel slope (V) and η is the overpotential (V). The velocity
 277 profile $v_x(y, z)$ can be written analytically under the assumption of a Poiseuille velocity profile in a rectangular channel

278 as [10,36]

$$v_x(y, z) = \frac{4h^2 \Delta p}{\pi^3 \mu L} \sum_{n, \text{odd}} \frac{1}{n^3} \left[1 - \frac{\cosh(n\pi \frac{2y-l_c}{2h})}{\cosh(n\pi \frac{l_c}{2h})} \right] \sin\left(n\pi \frac{z}{h}\right), \quad (10)$$

279 where h , L and l_c are the channel dimensions indicated in Figure 3, Δp is the pressure difference (Pa) and μ is the
280 viscosity (Pa.s).

281

282 Equations of the numerical model used in Figure 7

283 Given the geometry of the MFC, the aspect ratio of the channel, $\gamma = l_c/h$, is considered large enough to neglect
284 diffusion in the z-direction, leading to $\partial^2 c / \partial z^2 \approx j(x, y) / (n_e F D h)$. The operating conditions of the MFC allows us
285 to consider the Peclet number in the x-direction to be large enough to neglect diffusion in this direction, i.e. $Pe \gg 1$
286 and $\partial^2 c / \partial x^2 \approx 0$. The velocity components in the y-direction can also be neglected.

287 Therefore, the previous equations can be rewritten as

$$\bar{v}_x(y) \frac{\partial \tilde{c}}{\partial x} = D \frac{\partial^2 \tilde{c}}{\partial y^2} - K(x, y) \tilde{c}, \quad (11)$$

$$\left. \frac{\partial \tilde{c}}{\partial y} \right|_{y=0,1} = 0, \quad (12)$$

$$\tilde{c}(x=0, y) = \Theta(y - (l_c - l_{in})/l_c), \quad (13)$$

288 where the dimensionless concentration is used, such as $\tilde{c} = c/c_0$, and Θ is the Heaviside function modelling the initial
289 reactant concentration distribution. $\bar{v} = q_{tot}/(hl_c)$ is the average velocity of the reactants. The function $\bar{v}_x(y)$ is
290 obtained from integrating of the velocity profile (10) in the z-direction as

$$\bar{v}_x(y) = \frac{\bar{v}}{1 - 0,63/\gamma} \left(1 - \sum_{n, \text{odd}} \frac{96}{(n\pi)^4} \frac{\cosh(n\pi\gamma(2y-1))}{\cosh(n\pi \frac{\gamma}{2})} \right). \quad (14)$$

291 The function $K(x, y)$ in Equation 11 is the kinetic rate [10] defined as

$$K = \begin{cases} k_0/h & \text{if } x, y \in \Omega_e; \\ 0 & \text{else,} \end{cases} \quad (15)$$

292 where Ω_e is the electrode domain, and $k_0 = i_c^0 / (n_e F c_0) e^{\eta/b}$ is the kinetics reaction rate constant (m/s).

293

294 The previous set of equations is solved using a numerical scheme based on Finite Difference to approximate the
295 Laplacian in the y-direction and a Runge-Kutta algorithm in the x-direction. This numerical model is solved using
296 MATLAB, and the subroutine *ode15s* was used for the Runge-Kutta integration scheme. A total of 150 elements in the

297 y-direction were used in the finite difference mesh, and this was considered enough to ensure mesh independence.

298

299 Once the concentration field is solved, the current density produced by the cell can be estimated as

$$I_{tot} = n_e F q_c c_0 \varepsilon, \quad (16)$$

300 where q_c is the permanganate solution flow rate, and ε is the cell efficiency defined as

$$\varepsilon = 1 - \frac{\int_0^1 \tilde{c}(y, x = L_e) dy}{\int_0^1 \tilde{c}(y, x = 0) dy}. \quad (17)$$

301 It is the ratio of the quantity of reactant consumed at the outlet to the initial quantity of reactant injected in the MFC at

302 the inlet; therefore, $\varepsilon \in [0; 1]$. A high MFC efficiency ($\varepsilon \approx 1$) is needed to improve this technology.

303 Analytical solution of the concentration at the channel/electrode interface

304 As mentioned in section 2.3, the concentration of the channel/electrode interface, $c_e(x) = c(y = e/2, x)$ is needed in

305 Equation 4. This function is obtained using a Laplace transform of Equation 11 for the electrode domain and for the

306 channel domain. Moreover, a constant average velocity \bar{v} also needs to be considered, which is justified in the middle of

307 the channel regarding the aspect ratio [9]. This leads to the following equations:

$$\frac{d\hat{c}_1}{dy} - \alpha_1^2 \hat{c}_1 = \frac{k_0}{hD}; \quad y \in [0; e/2] \quad (18)$$

$$\frac{d\hat{c}_2}{dy} - \alpha_2^2 \hat{c}_2 = 0; \quad y \in [e/2; \infty] \quad (19)$$

308 with

$$\hat{c}_i(p) = \int_0^\infty (\tilde{c} - 1) \exp(-px) dx, \quad (20)$$

309 and $\alpha_1 = \sqrt{\bar{v}p/D + k_0/(hD)}$, $\alpha_2 = \sqrt{\bar{v}p/D}$, p are the Laplace complex parameters, and h is the channel height.

310 These equations can be solved analytically using the adiabatic condition at $y = 0$, continuity conditions at $y = e/2$ and

311 the semi-infinity condition when $y \rightarrow \infty$. The following expression of $\hat{c}_e(p)$ in the Laplace domain is :

$$\hat{c}_e(p) = -\frac{k_0}{phD\alpha_2} \frac{e^{\alpha_1 e/2} \tanh(\alpha_2 e/2)}{\alpha_1 + \alpha_2 \tanh(\alpha_2 e/2)}. \quad (21)$$

312 Equation 21 is then used in the inverse Laplace transform algorithm [31] to get the concentration at the channel/electrode

313 interface for any x-position, i.e. $c_e(x) = \mathcal{L}^{-1}\{\hat{c}_e(p)\}$.

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