CONCENTRATION FIELD IMAGING IN MICROFLUIDIC FUEL CELLS BASED ON OPERANDO VISIBLE SPECTROSCOPY

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ABSTRACT

Microfluidic fuel cells (MFCs) are microfluidic electrochemical conversion devices that are used to power small pieces of electrical equipment. Their performance relies on the improvement of the mass transfer of the reactants at the electrode interface. In this work, a novel operando imaging technique to measure the chemical concentration fields in an MFC is reported. An MFC specifically developed for imaging studies was built and operated using formic acid and permanganate potassium as fuel and oxidant, respectively. The imaging technique is based on visible spectroscopy, which links the light intensity passing through the MFC to its local reactant concentration. The two-dimensional transient concentration field of permanganate in the channel is imaged and compared to a numerical model to validate the method and to quantify the MFC mass transfer through the Damköhler and Peclet numbers. This work paves the way toward advanced imaging techniques for operando mass and charge transport characterisations in microfluidics.

Keywords Fuel cells · Imaging · Spectroscopy · Mass transfer · Microfluidic · Concentration fields
1 Introduction

Microfluidic fuel cells (MFCs) are particular microfluidic devices used to convert the chemical energy contained in fuels directly into electricity [1, 2]. Such devices are composed of a microfluidic channel that ensures rather good control of the hydrodynamic condition. Two electrodes are also embedded where the electrochemical reaction takes place: anode (where oxidation takes place) and cathode (where reduction occurs). Such an MFC can be used both in galvanostatic and electrolysis modes, which makes this technology a promising candidate for energy conversion and storage. There exists a wide variety of MFCs in the literature, and more details about them can be found in the following comprehensive reviews [3, 4, 5]. The present study focuses on a coflow membraneless MFC [6] using formic acid (HCOOH) and potassium permanganate (KMnO₄) as this system is relatively robust, requires classical soft photolithography micro fabrication techniques, uses nonhazardous chemicals and is relatively easy to operate [7, 8].

Three main phenomena govern the MFC performance. One can cite first the mass transfer based both on the diffusion, advection and reaction of the species in the microchannel. The second phenomenon is linked to charge transfer in the electrolyte and the electrodes. Several authors reported a thorough description of such [9, 10]. The last phenomenon is the entropy generated during the energy conversion, which is transformed into heat and impacts the rate of mass diffusion and electrochemical kinetics. Thus, the optimal MFC performance relies on accurate control and knowledge of these transfers. Such a need is a claim for developing a new operando and contactless imaging method for MFC multiphysic characterisation.

Several studies in the literature showed great interest in using imaging methods to characterise mass transport [11, 12, 13, 14]. For example, Sun et al. [12] used an optical microscope to study permanganate diffusion into formic acid. Their work was mainly qualitative to illustrate the hydrodynamic flow in the MFC. Lu et al. [15] used optical and fluorescence imaging techniques to validate their MFC model and to measure the concentration distribution profile at one position in the channel, but an entire image of the concentration field in the microchannel has not yet been reported. More advanced imaging techniques based on infrared [16, 17, 18, 19] or X-ray [20] can also be used to characterise the MFC structures, concentration fields or two-phase flow distribution. Among them, visible or ultraviolet (UV) spectroscopy has been identified as an efficient way to measure the chemical concentration of compounds in an aqueous solution, as these light wavelengths are not strongly absorbed by water [21]. However, although many imaging techniques exist for concentration measurement, to date, they have not been used for a thorough operando characterisation of the mass transfer simultaneously with the current produced by an MFC. Such a study would require designing an MFC specifically for imaging studies, an in-house imaging setup and an operating station to control the electrochemical conditions of the MFC. Although these challenges appear to be quite ambitious, the resulting operando images would be of prime interest for both MFC designers and/or advanced numerical models, as they would enable the measurement of the main parameters gov-
erning the cell performance such as the mass diffusivity, electrochemical kinetics and reactant concentration distribution.

The main goal of the present work is to report the use of imaging visible spectroscopy to measure the MFC mass transfer in operando. Such a technique has already been used for various concentration measurements in microfluidic reactors [22] but rarely to image a concentration field, although it would be well adapted for MFC transient concentration field characterisation. Thus, the use of an MFC model based on the hydrodynamics, mass transfer and electrochemical reaction lead to the estimation of the MFC physical properties and performance. In the first section, a description of the MFC design developed for visible spectroscopy, and the associated imaging setup is described. This is followed by a description of the MFC model. In the results section, the experimental concentration fields are presented and compared to the model. A thorough analysis of the technique is performed, and its limitations are discussed at the end of the article.

## 2 Methods

### 2.1 Fabrication of MFC

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

![Figure 1: Three-dimensional view of MFC.](image-url)
For the electrodes, an inverse pattern was created on a glass wafer using the same photolithography process as for the PDMS stamp. The deposition was achieved through sputtering \(~ 60\) nm of titanium as an adhesion layer and subsequently \(~ 300\) nm of platinum for the catalyst material. The remaining photoresist was removed by submerging the wafer in a chemical etching solution to obtain only the platinum pattern directly on the glass substrate. The PDMS stamp was plasma activated and bound to the glass substrate, resulting in the complete MFC presented Figure 1. The electrode dimensions are \(500\ \mu m\) wide by \(1\ mm\) long. More details and schematics of the microfabrication process can be found in the Supplementary Material of this article.

### 2.2 Experimental setup

The concentration distribution and total current produced by the MFC were measured using the setup described in Figure 2. It is made of a homemade inverse microscope. White colimated light is used as the primary light source. A narrow bandpass filter (\(\lambda = 540 \pm 5\) nm) is used to produce a monochromatic green light passing through the MFC. The light is finally collected through a microscope objective and a lens to produce an image on a CMOS camera (Zelux 1.6 MP Colour CMOS Camera). Only the green channel of the camera was used in the image postprocessing.

The MFC is controlled using a potentiostat to measure the voltage and the current produced. An Ag/AgCl reference electrode was used to measure both anode and cathode potentials. The reactant flow rate is controlled using a syringe pump over a wide range from \(0.5\) to \(100\ \mu l/min\).

The reactants (acid formic and permanganate potassium) were chosen to have good MFC performance [1]. In addition, permanganate potassium has a great advantage in having a clear absorption signature in the visible range, whereas formic acid is transparent. At the anode, the formic acid oxidation is

\[
HCOOH \rightarrow CO_2 + 2H^+ + 2e^- , \quad (1)
\]

and the cathode, the permanganate reduction is

\[
MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O . \quad (2)
\]

In equation 2, one can notice that when a current is produced, the permanganate ions \((MnO_4^-)\) are transformed into manganese ions \(Mn^{2+}\). Thus, the current applied through the MFC electrodes triggers a decrease in the permanganate concentration, which is measured by visible spectroscopy.

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

$$\Delta c = -\kappa^{-1} \log_{10} \left( \frac{I_0 + \Delta I}{I_0} \right),$$

(3)

where $\kappa$ is the permanganate absorption coefficient (mM$^{-1}$), $I_0$ is the light intensity of the background and $\Delta I$ is the light intensity variation induced by the current production. The permanganate absorption coefficient was measured to be $\kappa = 5.5 \times 10^{-3}$ mM$^{-1}$ at 540 nm (see the calibration curve in Figure S3 in the Supplementary Material).

2.3 Three-dimensional mass transfer model

2.3.1 General equations

The 3D channel with a single electrode is presented in Figure 3. To simplify the model with only the most important phenomena, it was assumed that the velocity profile is considered laminar and established and modelled using a Poiseuille flow. The mass diffusivity is considered constant, the problem is solved in the steady state, the Fick law is used to model the mass diffusion in diluted solution, the ions and the reactants in the electrolyte and in the anolyte do not interact on the mass and charge transport at the cathode, and the electrochemical reaction is modelled by a Tafel law.
Figure 3: Three-dimensional schematic of channel with single electrode placed at $z = 0$ (in yellow). Boundary conditions are indicated.

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

$$
v_x(y, z) \left( \frac{\partial c}{\partial x} + \frac{\partial c}{\partial y} + \frac{\partial c}{\partial z} \right) = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right), \tag{4}
$$

$$
\left. \frac{\partial c}{\partial y} \right|_{y=0,l_c} = \left. \frac{\partial c}{\partial z} \right|_{z=h} = 0, \tag{5}
$$

$$
-D \left. \frac{\partial c}{\partial z} \right|_{z=0} = -\frac{j(x, y)}{n_e F}, \tag{6}
$$

$$
c(x = 0, y, z) = c_0(y), \tag{7}
$$

where $c$ is the reactant concentration (M); $D$ is the mass diffusivity ($\text{m}^2/\text{s}$); $x$, $y$ and $z$ are the spatial coordinates (m); $n_e$ is the number of electrons exchanged; $F$ is the Faraday constant ($\text{C/mol}$); and $j(x, y)$ is the current density distribution ($\text{A/m}^2$) on the electrode. It is zero outside it. Equation 6 is the Faraday law applied to the electrode interface. The current density in this equation is modelled using the Tafel law, which links the local reactant concentration to the fuel cell potential as:

$$
j(x, y) = i_0 \frac{c(x, y, z = 0)}{c_0} \exp(\eta/b), \tag{8}
$$

where $i_0$ is the electrode exchange current ($\text{A/m}^2$), $b$ is the Tafel slope (V) and $\eta$ is the overpotential (V) linked to the electrode potential. The velocity profile $v_x(y, z)$ can be written analytically under the assumption of a Poiseuille velocity profile in a rectangular channel as $10,23$

$$
v_x(y, z) = \frac{4h^2 \Delta p}{\pi^3 \mu L} \sum_{n,odd} \frac{1}{n^3} \left[ 1 - \frac{\cosh(n\pi \frac{2y-l_c}{2h})}{\cosh(n\pi \frac{2h}{2h})} \right] \sin \left( n\pi \frac{z}{h} \right), \tag{9}
$$

where $h$, $L$ and $l_c$ are the channel dimensions indicated in Figure 3 $\Delta p$ is the pressure difference (Pa) and $\mu$ is the viscosity (Pa.s).
2.3.2 Model solving

Given the geometry chosen for the MFC, the aspect ratio of the channel, \( \gamma = l_c/h \), is considered large enough to neglect diffusion in the \( z \)-direction compared to the others, leading to \( \partial^2 c/\partial z^2 \approx j(x, y)/(n_e FDh) \). The operating conditions of MFC allow us to consider the Peclet number in the \( x \)-direction large enough to neglect the diffusion in this direction, i.e. \( \text{Pe} \gg 1 \) and \( \partial^2 c/\partial x^2 \approx 0 \), and the velocity components in the \( y \)-direction can also be neglected. Therefore, the previous equations can be rewritten as

\[
f(\tilde{y}) \frac{\partial \tilde{c}}{\partial \tilde{x}} = \frac{\partial^2 \tilde{c}}{\partial \tilde{y}^2} - K(\tilde{x}, \tilde{y})\tilde{c}, \tag{10}
\]

\[
\frac{\partial \tilde{c}}{\partial \tilde{y}} \bigg|_{\tilde{y}=0,1} = 0, \tag{11}
\]

\[
\tilde{c}(x = 0, \tilde{y}) = \Theta(\tilde{y} - (l_c - l_{in})/l_c), \tag{12}
\]

where the dimensionless variables are used, such as \( \tilde{c} = c/c_0 \), \( \tilde{y} = y/l_c \), \( \tilde{x} = x/x_e \) with \( x_e = v\bar{l}_e^2/D \), which is the \( x \) scale length \([9]\), and \( \bar{v} = q_{tot}/(hl_c) \) is the average velocity of the reactants. The function \( f(\tilde{y}) \) is obtained from the integration of the velocity profile \([9]\) in the \( \tilde{x} \)-direction as

\[
f(\tilde{y}) = \frac{1}{1 - 0.63/\gamma} \left( 1 - \sum_{n,\text{odd}} \frac{96}{(n\pi)^4} \frac{\cosh(n\pi\gamma(2\tilde{y} - 1))}{\cosh(n\pi \frac{2}{\tilde{y}})} \right), \tag{13}
\]

where \( \Theta \) is the Heaviside function modelling the initial reactant concentration distribution. The function \( K(\tilde{x}, \tilde{y}) \) in Equation \([10]\) is a dimensionless Damkhöler number \([10]\) defined as

\[
K = \begin{cases} 
Da & \text{if } \tilde{x}, \tilde{y} \in \Omega_e \\
0 & \text{else} 
\end{cases} \tag{14}
\]

where \( \Omega_e \) is the electrode domain and \( Da = kl_e^2/(hD) \), where \( k = i_0/(n_e F c_0 e^{\eta/b}) \) is the electrochemical kinetics coefficient (m/s).

The previous system has no evident analytical solution. It is solved using a numerical scheme based on Finite Differences to approximate the Laplacian the \( \tilde{y} \)-direction and a Runge-Kutta algorithm in the \( \tilde{x} \)-direction. Such a numerical model is solved using MATLAB, and the subroutine \textit{ode15s} was used for the Runge-Kutta integration scheme. A total of 150 elements in the \( \tilde{y} \)-direction were used in the finite difference mesh, and this was considered enough to ensure mesh independence. Once the concentration field is solved, the current density produced by the cell can be estimated as

\[
I_{tot} = n_e F q_c c_0 \varepsilon, \tag{15}
\]
where \( q_c \) is the permanganate solution flow rate, and \( \varepsilon \) is the cell efficiency defined as

\[
\varepsilon = 1 - \frac{\int_0^1 \tilde{c}(\tilde{y}, \tilde{x} = L_e/x_e) d\tilde{y}}{\int_0^1 \tilde{c}(\tilde{y}, \tilde{x} = 0) d\tilde{y}}.
\]

(16)

It is the ratio of the quantity of reactant consumed at the outlet to the initial quantity of reactant injected in the MFC at the inlet; therefore, \( \varepsilon \in [0; 1] \). A high MFC efficiency \( \varepsilon \) close to 1 is expected to improve this technology.

3 Results

3.1 Image acquisition

The images were acquired using the setup described in Figure 2. The camera frame rate was set to 10 fps. The cell was imaged first at rest for a few seconds before generating a current. The anode and cathode flow rates were set to 1 and 0.5 µl/min, respectively, for 5 min before starting the experiment, which ensures that the flow is fully developed. This flow rate ensures an average velocity of 0.42 mm/s and a residence time of 24 s.

In Figure 3(a), a complete image of the MFC is presented, where the channel (in green) and the electrodes (in black) are visible. Only the concentration field around the electrodes can be imaged since they are opaque to visible light. At \( t = 0 \) s, a current of 20 µA was generated by the MFC for 25 s, and the images were kept recording for 1 min. This protocol ensured the measurement of the transient response of the concentration field before reaching the steady state and the measurement of the permanganate concentration relaxation after the current was switched off. A typical recorded greyscale image is presented in Figure 3(b). It is located at the cathode where the permanganate is consumed, as predicted in equation 2. The transient profiles of the current and of the light intensity are also presented in Figure 3(c).

In the results presented in Figure 3(c), it is observed that the current triggers a change in light intensity of approximately 10-15 camera counts, i.e., less than 1.5%. The signal-to-noise ratio (SNR) was estimated to be approximately 4, which is very low. It is therefore advised to average the images over 1 s using this technique.

Then, when the current is switched off, the light intensity slowly decreases back to its initial value. Such behaviour is explained as follows. When permanganate is consumed during current generation, less light is absorbed by the solution, and the medium becomes more transparent. When the current is switched off, the continuous flow rate slowly brings back the permanganate concentration at its initial state. Note that approximately 25 s is needed for the light intensity to return to its initial value corresponding roughly to the residence time of the solution in the MFC. Thus, the results presented in Figure 3 confirm the relevant use of visible spectroscopy to image the transient concentration variations in operating MFCs.
3.2 Concentration maps and profile

The greyscale images are converted to concentration fields using the Beer-Lambert law described in equation \( \Delta c(x, y, t) \). The background image is taken as the average of all images recorded before the current was switched on. Then, the Beer-Lamber law is applied to each pixel of the images to obtain a stack of concentration variation fields, i.e. \( \Delta c(x, y, t) \). Then, the absolute concentration field is deduced as \( c(x, y, t) = c_0 - \Delta c(x, y, t) \).

In Figure 5(a) to (e), the concentration field is presented for a range of times. As expected, before the current was triggered, the concentration field was uniform. Then, a gradient of concentration appears and diffuses [see Figure 5(b) to (d)]. It is more pronounced toward the end of the channel than at the inlet due to the effect of...
A maximum decrease of 2 mM is observed, which is a rather small quantity of concentration variation, but it was possible to measure it. From the data presented in Figure 5, a noise of ±0.2 mM is estimated. Such results highlight the somewhat quite good sensitivity of the setup to detect rather small concentration variations in MFCs.

Figure 5: From (a) to (e), concentration fields obtained by visible spectroscopy several times at \( t = -5, 0, 10, 20, 30 \) and 60 s, respectively. (f) Temporal evolution of concentration variation close to electrode for several positions. Mobile averages were added as eye guides. Black rectangle in (a) indicates x-position where temporal concentration profiles were taken.

In Figure 5(f), several transient concentration profiles are presented for a range of vertical positions in the channel: from the border of the electrode (0 µm) to 200 µm from it. As expected, as soon as the current is triggered (at \( t = 0 \) s), the concentration starts to decrease at the electrode interface before slowly diffusing toward the channel. At 150 µm, the concentration profile starts to decrease 13 s after the current is triggered. After 200 µm, no additional concentration variation is visible in this region of the MFC. This diffusion length is governed by the Peclet number [24], \( \delta_D \sim \sqrt{Dx/v} \sim 150 \mu m \) (with \( D = 2 \times 10^{-3} \text{ mm}^2/\text{s} \) and \( x = 5 \text{ mm} \)).

In Figure 5(e) and 5(f) for the profile at 0 µm, an increase in the concentration is observed. Such behaviour is due to the formation of manganese oxide (MnO\(_2\)) from the reaction of the manganese ions and the water in the presence of low-solution pH. This byproduct is nonsoluble and trapped at the bottom of the channel. This was already observed in some previous studies [5]. It is known to decrease the MFC performance and degrade the electrode material. However, in our case, the MFC electrodes can be cleaned up using an isopropanol solution at the end of the experiment. Thus, the proposed imaging setup is also an interesting tool to study this side reaction and to help develop a future efficient
strategy to eliminate it in order to improve the MFC performance and lifetime.

3.3 Comparison with model in steady state

In the last section of this work, the numerical model and experimental data are compared to validate the study. In the numerical model, all the operating conditions are set identically (flow rates, current density and MFC dimensions) to the experiments. The only unknown parameter remains the effective diffusivity of permanganate in aqueous solution. This parameter was estimated to be $D = 2 \times 10^{-3}$ mm$^2$/s, which is on the order of magnitude for mass diffusion in aqueous solutions [10]. The corresponding Peclet number is 625. The other parameter, the kinetic coefficient $k$, was obtained using an iterative algorithm to satisfy a total current of 20 µA. It is found to be $1.54 \times 10^{-3}$ mm/s, leading to a Damköhler number of 348 and fuel cell efficiency of almost 50%. The resulting concentration field is presented in Figure 6(a). A black rectangle was added at the electrode position.

To match the steady-state assumption of the model, the experimental concentration field before the current was switched off was used (i.e., at $t = 25$ s) and averaged over 2 s. This time was long enough to ensure the steady state at the location between 0 and 5 mm in the x-direction. This concentration field is presented in Figure 6(b), and qualitatively, the same order of concentration variation can be observed in both the numerical and experimental data. It is important to note that no parameters were fitted to achieve such results in the model.

Moving forward, the concentration profiles at three channel positions were extracted for comparison with the model. Their positions are indicated in Figure 6(a). These profiles are in excellent quantitative agreement with the model. The concentration gradients increase with the channel position, as expected. Some small deviations are, however, observed toward the end of the channel (position 3), which may be due to some flow instability observed during the experiment or the presence of manganese oxide, as previously noticed. This ultimate result validates both the experimental setup and the MFC design to perform operando imaging of the concentration. The assumptions made in the numerical simulation to model the mass and electrochemical transfer in MFCs also appear to be well justified.
4 Conclusion

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

Figure 6: (a) Numerical simulation of concentration field for current of 20 µA. (b) Concentration field measured by visible spectroscopy at same current 25 s after current was triggered. Colour bar indicates concentration in mM. (c) Comparison of numerical and experimental concentration distributions for several positions in channel. Abscissa $y = 0$ in c) corresponds to MFC top wall.
Along with the experimental data, a numerical simulation of the 3D problem taking into account the velocity field, the mass diffusion and the electrochemical reaction at the electrode was developed. All parameters of this model were known or measured ex situ. In comparing the simulation to the experimental data, excellent agreement was found. In particular, the Peclet and Damköhler numbers were found to be 625 and 348, respectively, indicating that the electrochemical kinetics are quite fast and that diffusion is the limiting factor. Such a limiting diffusion configuration is expected to result in a high MFC efficiency (50% in the present work).

Finally, this work demonstrates the feasibility of both imaging and modelling the transient concentration fields in an MFC. These data were used to thoroughly analyse the mass transfer, which is of prime importance to improve the MFC performance and efficiency. With these techniques, one can improve the operating conditions and the MFC design toward more powerful and efficient electrochemical energy conversion systems.

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