Measurements of mass transfer in a microfluidic membraneless fuel cell using microscale infrared spectroscopy

By M.Garcia, A. Sommier, J-C. Batsale and S Chevalier

*Arts et Metiers Institute of Technology, I2M UMR CNRS 5295, University of Bordeaux, CNRS, Esplanade des Arts et Métiers, 33405 Talence Cédex, France, marine.garcia@u-bordeaux.fr

Abstract

Microfluidic fuel cells (MFC) are micro-scale energy conversion systems where electrochemical reactions take place on two electrodes separated by an electrolyte. The mass diffusion of the reactants plays a crucial role in these reactions since it governs both the electrochemical and fuel utilization efficiency of the MFC. In this work, we measured the multi-spectral infrared absorbance in the mid infrared range (2 – 5 μm) and derived the mass diffusion coefficients for several reactants and electrolyte compounds at different temperatures. Finally, the diffusion coefficients were used to optimize operating conditions and to predict the performances of the MFC.

1. Introduction

Microfluidic fuel cells (MFC) are systems composed of two metallic electrodes integrated in a microfluidic chip [1]. They convert the chemical energy of two reactant fluids into electricity. The main advantage of MFCs are that they do not use physical barriers to separate the fluid at the anode and the cathode, making these systems easy to design and lowering the costs. Therefore, the reactant flows need to be carefully controlled to ensure optimal mass transport. It is a key parameter that controls the power density and the fuel utilization in MFCs, thus its effect on inter-diffusion needs to be accurately measured to predict and enhance MFC performance. However, a recent survey in the literature have shown that the mass transfer measurements of commonly used MFC reactants (e.g. formic acid, sulfuric acid, methanol) have not been performed in the operating condition range of the MFC.

Several imaging techniques exist to measure the mass diffusion coefficient in microfluidic chip. Among them, methods such as spectroscopic techniques are accurate for investigating mass transfer. For example, Salmon et al [2] used Raman spectroscopy to measure the molar fraction of species in a solution and to estimate the diffusion coefficient. However, Raman spectroscopy is a point by point measurement technique and suffers from long acquisition times. With integration times ranging from milliseconds to minutes [3], experimental measurements can take one hour [2]. An alternative technique with shorter acquisition times is infrared (IR) spectroscopy. This technique relies on the Beer-Lambert law to measure the molar concentration of each chemical species in the channel. One of the main advantages of IR spectroscopy is that a multispectral acquisition can be completed less than 15 s.

In this study, we propose an imaging method based on IR spectroscopy to measure mass transfer in a microfluidic channel. Mass transfer is modelled using the analytical inverse method based on Fick's equation. Experimentally, mass transfer is visualised using Fourier transform infrared (FTIR) spectroscopy coupled with a mid IR range camera. Model and experimental results are then used to determine the diffusion coefficient D for typical species at different temperatures in an in operando MFC.

2. Experimental setup

Experiments are conducted with an in-house T-shaped channel microfluidic cell (channel dimensions of 500 μm width x 2.5 cm length x 40 μm height). The cell consists of a stack with a sapphire wafer for the base, a 40 μm-thick PDMS sheet and a glass wafer for the top. The reactant flow is controlled with a syringe pump for precise control of the flow rate. The microfluidic cell is placed on a stage and integrated to the experimental setup presented Figure 1. A FTIR spectrometer is used as a mid IR source. The IR beam is collimated inside the spectrometer and directed through the cell. The camera placed above the sample measures the transmitted IR beam in the spectral range of 2 - 5 μm.
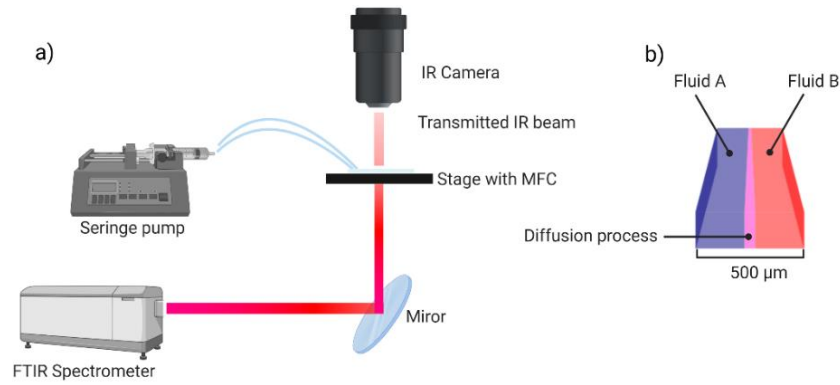
Figure 1 a) Experimental setup used for visualization of the multispectral absorbance fields in the microchannel. b) Schematic view of the interdiffusion process occurring in the microfluidic channel

The absorbance is calculated for each wavelength using the Beer-Lambert law described in Eq(1).

$$A(x, y, \lambda) = -\log\left(\frac{I(x,y,\lambda)}{I_0(x,y,\lambda)}\right) = \sum_i \mu_i(\lambda) c_i(x, y) \tag{1}$$

where A is the multispectral absorbance, I_0 is the transmitted signal recorded of the cell without flowing the solution of interest, I is the recorded signal with the cell flowing the solution of interest, μ_i is the absorptivity coefficient and c_i is the concentration field for each species i. Figure 2 shows absorbance fields of formic acid in sulfuric acid. The absorbance was obtained using Beer-Lambert law.
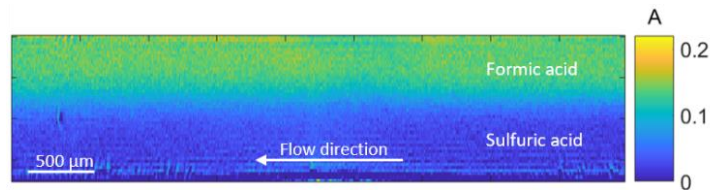

Figure 2 Fields of the absorbance of a formic acid in sulfuric acid solution with a flow rate of 20 µl/min.

From the obtained absorbance field, the diffusion coefficient D in mm²/s is calculated using the analytical solution of the diffusion equation presented Eq(2).

$$C(x, y) = \frac{1}{2}\left(1 + \mathrm{erf}\left(\frac{y}{2\sqrt{\frac{D\,x}{v}}}\right)\right) \text{ with } \mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-v^2)\, dv \tag{2}$$

3. Results and discussion

The rate of diffusion for formic acid in sulphuric acid at room temperature was studied and a diffusion coefficient value of 2×10^{-3} mm²/s was obtained. This order of magnitude of this first result appears to be consistence with respect to the literature [4]. In this communication, using the Fick model, the experimental data and an analytical inverse method, the diffusion coefficient measurements for several reactant species will be presented. Additionally, the impact of temperature on the mass transfer will be evaluated in order to gain a complete physical understanding of the masse transfer in the MFC operating condition range. Moreover, the insight gained from mass transfer visualization coupled with the modelling work will enable the optimization of experimental conditions (temperature, flow rate) and channel geometry for similar reactors.

REFERENCES

[1] M. Tanveer, E. S. Lim, and K. Kim, "Effects of channel geometry and electrode architecture on reactant transportation in membraneless microfluidic fuel cells : A review," *Fuel*, vol. 298, no. April, p. 120818, 2021, doi: 10.1016/j.fuel.2021.120818.

[2] J. B. Salmon, A. Ajdań, P. Tabeling, L. Servant, D. Talaga, and M. Joanicot, "In situ Raman imaging of interdiffusion in a microchannel," *Appl. Phys. Lett.*, vol. 86, no. 9, pp. 1–3, 2005, doi: 10.1063/1.1873050.

[3] A. F. Chrimes, K. Khoshmanesh, P. R. Stoddart, A. Mitchell, and K. Kalantar-Zadeh, "Microfluidics and raman microscopy: Current applications and future challenges," *Chem. Soc. Rev.*, vol. 42, no. 13, pp. 5880–5906, 2013, doi: 10.1039/c3cs35515b.

[4] L. A. Dunn and R. H. Stokes, "The diffusion of monocarboxylic acids in aqueous solution at 25°," *Aust. J. Chem.*, vol. 18, no. 3, pp. 285–296, 1965, doi: 10.1071/CH9650285.