Optimizing mass transport of wall-tube electrode for studying metalloezymes by protein film electrochimistry

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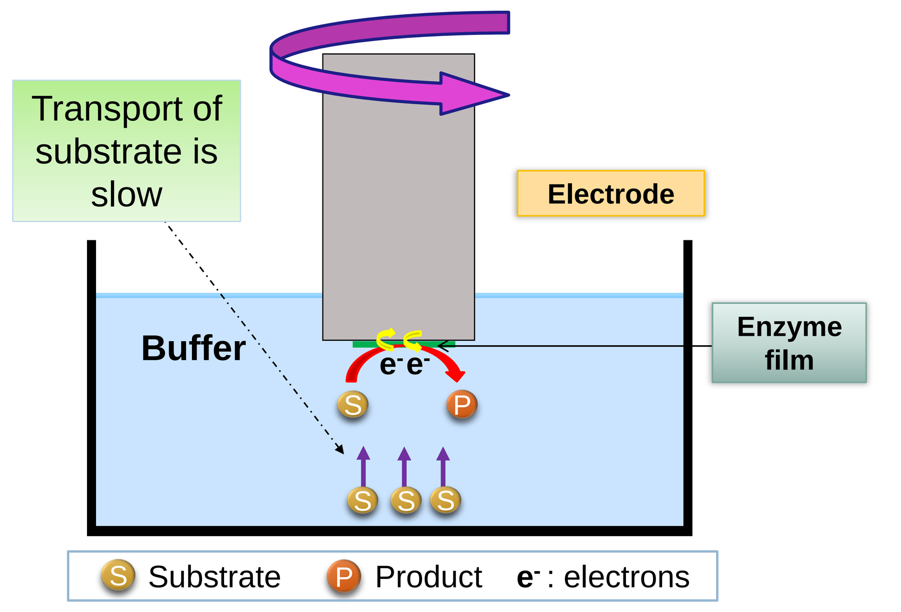
Context

Protein Film Electrochemistry (PFE) is a technique in which an enzyme is immobilized in an electrode and its catalytic turnover rate is measured under the form of an electrical current. This technique has proved very useful for the study of metalloenzymes [(1)], but it requires fast transport of the enzymatic substrate towards the electrode.
In a previous study [(2)], by means of computational fluid dynamics (CFD), our team designed and built a new electrochemical cell based on wall tube electrode configuration which provides better transport than RDE, However, this wasn't enough for our application. Therefore, the design must be optimized.
In this work, we explore using CFD the effect of the various parameters of the cell and propose semi-empirical formulas suitable to predict the mass-transport coefficient and the wall shear stress on the electrode. We use a 3D-printed cell to validate experimentally our predictions.



Material and methods

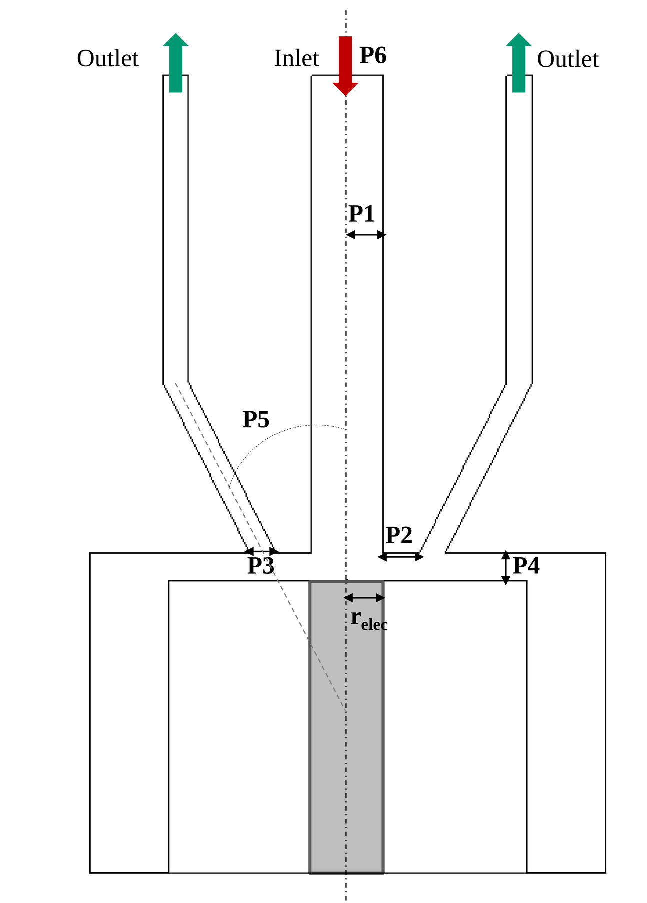
CFD simulations

CFD simulations were utilized in two steps:

1. **Sensitivity study:** we used DoE approach (full factorial design of **6** parameters with **2** levels) to identify the most influencing parameters on mass transport coefficient.
2. **In-depth study:** we used simulations with a greater number of values for each one of the most influencing parameters to explore more systematically the parameter space. We used these data to propose semi-empirical formula for both the mass-transport coefficient and the shear stress in the cell.

The studied parameters:

P1 inlet radius
P2 distance inlet-outlet
P3 outlet thickness
P4 distance nozzle- electrode
P5 inlet-outlet angle
P6 inlet velocity

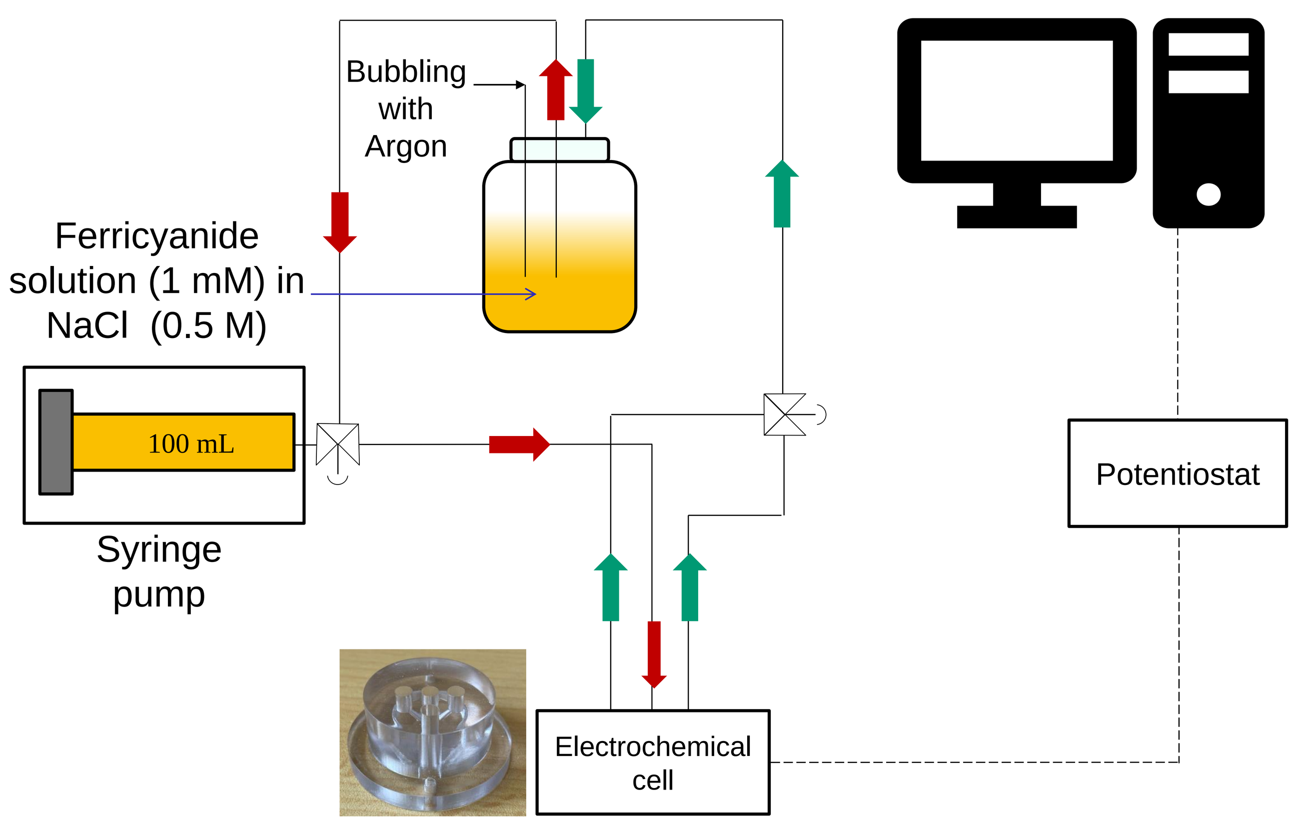


Schematic representation of the cell with the studied parameters

Experimental setup and conditions

In order to validate our approach, we recorded **cyclic voltammograms** of ferricyanide reduction in a cell that was selected from the in-depth simulations then was built by 3D printing (setup is shown bellow).

Cyclic voltammetry is an electrochemical technique for measuring the current response of a redox active solution to a linearly cycled potential sweep between two or more set values.



Cell parameters:

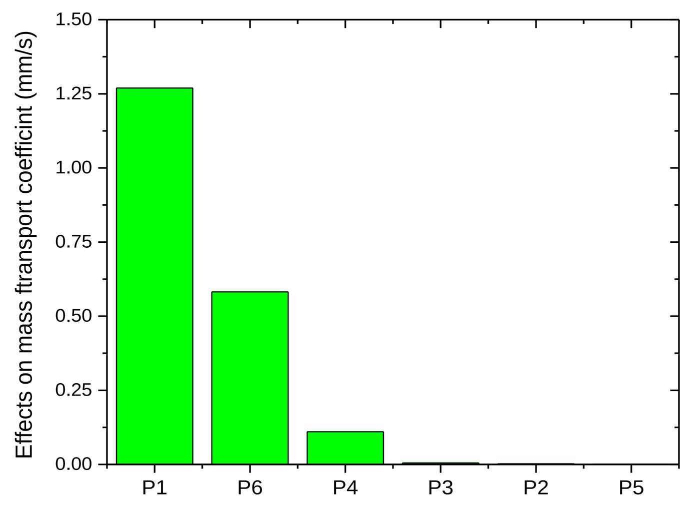
r_{inlet} = 0.3 mm
$r_{electrode}$ = 0.05 mm
h = 0.35 mm

Exp parameters:

- C $_{ferricyanide}$ = 1 mM (in 0.5 M NaCl)
- Scan rate = 100 mV/s

Results

The most influencing parameters



The single effects of the parameters on the average mass transport coefficient for r_{elect}=1e−4 mm

Only three parameters are significantly influencing mass transport in the cell:

- (**P1**) inlet diameter;
- (**P6**) flow rate;
- (**P4**) distance nozzle-electrode.

Now, we try to propose semi-empirical formulas to predict the values of the mass-transport coefficient and the wall shear-stress from the three main parameters.

Theoretical background

The steady-state convective diffusion equation:

$$D\frac{d^2c}{dz^2} - v\frac{dc}{dz} = 0$$

Mass transport coefficient expression:

$$m = \frac{D \times \frac{dc}{dz}}{c_\infty - c_0}$$

Axial and radial velocities in the uniform diffusion layer [(3)]

$$v = -2\sqrt{a\nu}\phi(\eta)$$

$$u = ar\phi'(\eta)$$

Newton's law of viscosity:

$$\tau_w = \rho\nu \times \left.\frac{du}{dz}\right|_{z=0}$$

Mass transport

$$\boxed{m = \beta D^{2/3}\nu^{-1/6}a^{1/2}}$$

With [(4)]

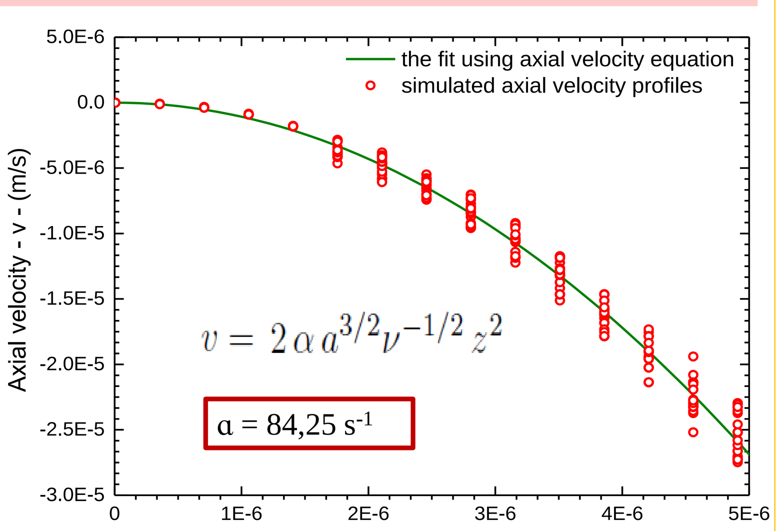
$$\phi(\eta) = \alpha\eta^2$$

Shear stress at the electrode

$$\boxed{\tau_w = 2\alpha\rho\nu^{1/2}a^{3/2}r}$$

Only "ɑ" depends on the three parameters → extract values of "ɑ" to find correlation that relates it to the parameters

The figure shows how we extracted the values of "ɑ" from the in-depth simulations by fitting the simulated axial velocity profiles to the axial velocity expression for each simulation.



Semi-empirical expressions of mass transport and shear stress

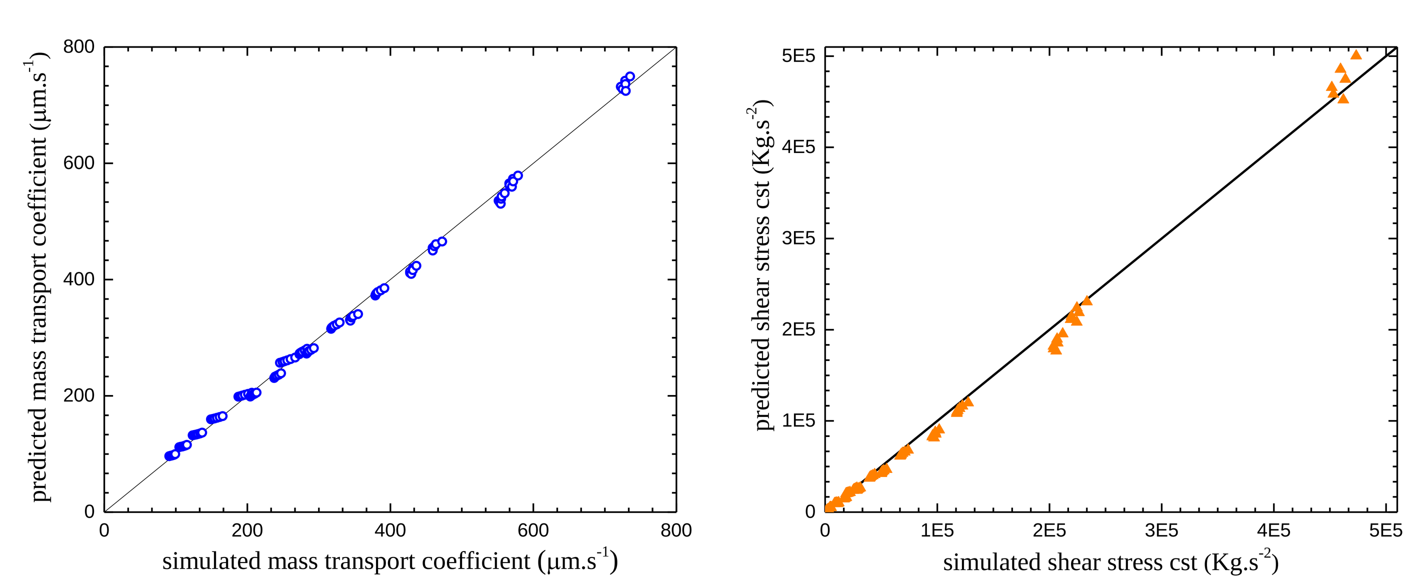
The correlation between "ɑ" and the parameters was found to be:

$$a = 0.97082\,\frac{Q_v}{r_{inlet}^3}\left(\frac{r_{inlet}}{h}\right)^{0,1685}\left(\frac{Q_v}{\nu h}\right)^{-0,0995}$$

$$\boxed{m = 0.83753\,D^{2/3}\,\nu^{-0.11692}\,Q_v^{0.45025}\,h^{-0.0345}\,r_{inlet}^{-1.41575}}$$

$$\boxed{\tau_w = 1.255\rho\,\nu^{0.64925}\,Q_v^{1.35075}\,h^{-0.1035}\,r_{inlet}^{-4.24725}\,r}$$

Q_v inlet's flow rate (m³.s)
h the distance between the nozzle and the electrode (m)
r_{inlet} inlet's radius (m)



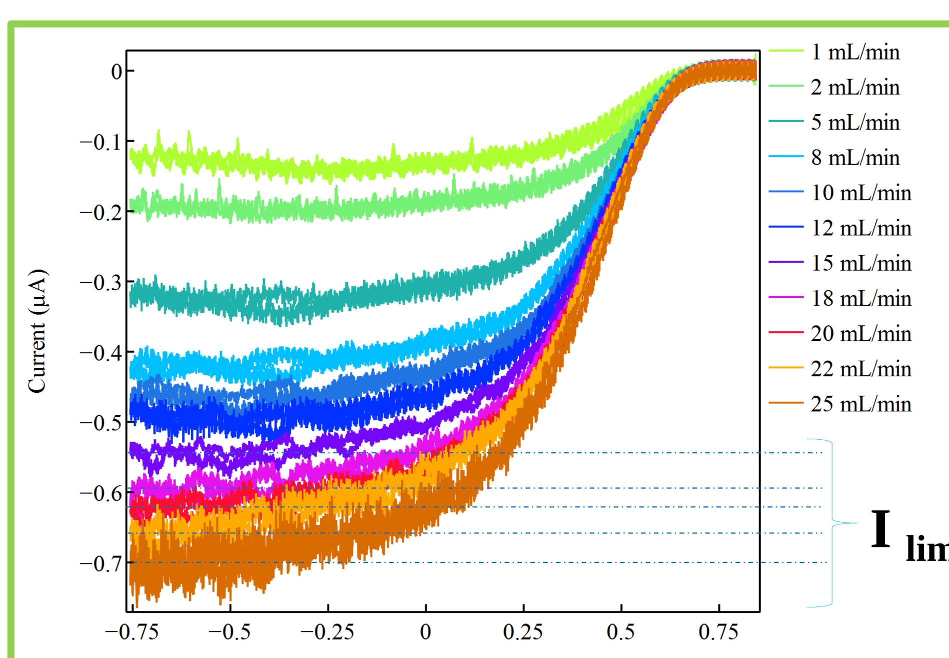
Results show that the proposed formulas give excellent predictions of the simulated mass transport coefficient and shear stress at the electrode.

Experimental validation

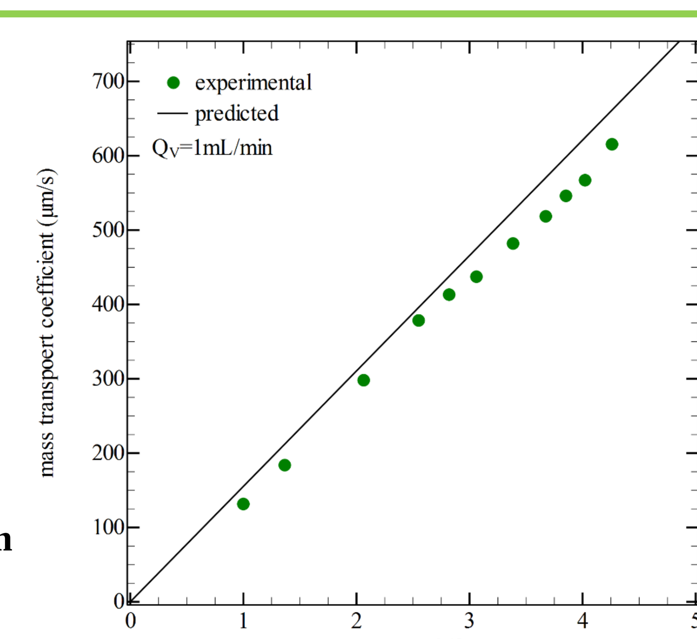
The limiting current values (I_{lim}) were extracted from the cyclic voltammograms in order to determine the experimental mass transport coefficients (**m**).

$$m = \frac{I_{lim}}{nFAC}$$

The values of the simulated mass transport coefficient (**in green**) were plotted with the predicted ones (black line) as a function of $Q_v^{0,45}$ (as in the proposed formula).



Cyclic voltammograms of ferricyanide reduction in the new cell at different flow rates



Simulated and experimental mass transport coef vs flow rate [0.45]

Good agreement between the predicted and the experimental mass transport coefficient which allows to validate the proposed mass transport formula

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