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Hydrodynamics studies of cyclic voltammetry for electrochemical micro biosensors

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Abstract

We investigate the effect of flow rate on the electrical current response to the applied voltage in a micro electrochemical system. To accomplish this, we considered an ion-transport model that is governed by the Nernst-Planck equation coupled to the Navier-Stokes equations for hydrodynamics. The Butler-Volmer relation provides the boundary conditions, which represent reaction kinetics at the electrode-electrolyte interface. The result shows that convection drastically affects the rate of surface kinetics. At a physically sufficient high flow rates and lower scan rates, the current response is limited by the convection due to fresh ions being brought to the electrode surface and immediately taken away before any surface reaction. However, at high flow and scan rates, the Faradaic current overrides current due to convection. The model also allows predicting the effect of varying electrolyte concentration and scan rates respectively.

I Introduction

Micro biosensors have been wide spread used in biomedical applications and as an analytical device for detection of biochemical substances [1, 2, 3]. It is essential that these devices recognise and translate biochemical properties of a substance into electrical signals. Therefore, the devices must be coupled with an electroanalytical technique to characterise such signals. One of the most powerful analytical techniques used for such a task is cyclic voltammetry (CV) [4, 5, 6]. CV is a widely used technique to probe the physics and chemistry at the electrode-electrolyte interface thereby used as the main mode of operation for sensing devices [7, 8]. This study focuses on simulating CV using the finite element method in a microfluidic cell under flow conditions. We investigate the effect of flow rates, the scan rates and the electrolyte concentration and compare to experimental measurements.

II Experiment: The electrode chip and the microfluidic cell

The electrode chip has dimension $12\text{mm} \times 11.3\text{mm}$ and was fabricated on a $375\mu\text{m}$ thick Si substrate. Four cantilevers were placed in the middle of the chip, each having



the dimensions $100\mu\text{m}$ (width) \times 550nm (thickness) \times $400\mu\text{m}$ (length). Each cantilever was capable of functioning as an independent working electrode (WE). The reference electrode with dimensions $100\mu\text{m} \times 200\mu\text{m}$ was placed on the right side of cantilevers and the counter electrode with dimensions $2700\mu\text{m} \times 400\mu\text{m}$ on the left side. All the electrodes were coated using e-beam evaporation with a 2nm chrome adhesion layer followed by 30nm of gold. The microfluidic chamber encapsulates the ECC biosensor with a volume of approximately $105\mu\text{L}$ and creates a flow path leading into the chip and through the channel past the cantilevers. The system was connected to a syringe pump (PHD 2000 Infuse/Withdraw syringe pump, Harvard Apparatus, USA) and set the flow rates of up to $600\mu\text{L}/\text{min}$. The electrolyte with active redox probes used in the CV measurements consists of 200mM KNO_3 solutions with 2mM of potassium ferricyanide(III) in Milli-Q water. CV was performed using a computer controlled CHI1030 Potentiostat.

III Mathematical Modeling

The conservation of mass for the ionic species j in the electrolyte bulk solution for a pure electrochemical reaction is governed by

$$\frac{\partial C_j}{\partial t} = \nabla \cdot (z_j u_j F C_j \nabla \phi + D_j \nabla C_j - C_j v), \quad (1)$$

where C_j , D_j , z_j and u_j are the ionic concentration, the diffusion constant, charge and the mobility of ionic species j . F , ϕ , v represent the Faraday's constant, the electrolyte potential and the convective velocity of the solution, respectively [5, 6].

The electrolyte solution is electrically neutral except at a very thin electric double layer close to the electrode so that ($\sum_j z_j C_j = 0$). The electric potential equation

$$\nabla \cdot (\kappa \nabla \phi) + F \sum_j z_j \nabla \cdot D_j \nabla C_j = 0, \quad (2)$$

can be easily derived from equation (1) by using the electro neutrality condition where $\kappa = F^2 \sum_j z_j^2 u_j C_j$ is the electrolyte conductivity. Finally, the velocity field v of the flowing electrolyte is solved by the Navier-Stokes equations for incompressible fluid flow

$$\nabla \cdot v = 0, \quad (3)$$

$$\rho \left(\frac{\partial v}{\partial t} + v \cdot \nabla v \right) = -\nabla p + \mu \nabla^2 v + s_f. \quad (4)$$

The fluid density is denoted ρ , p is the pressure, μ is the dynamic viscosity and finally s_f denotes an external force per unit volume [9]. We solved equations (1), (2), (3) and (4) with appropriate boundary conditions. Table 1 shows the prescribed boundary conditions. The applied potential as a function of scanning time can be modeled as follows,

$$\phi_{app}(t) = \begin{cases} \phi_{min} + vt & \text{if } 0 \leq t \leq \mathcal{T}, \\ \phi_{max} - vt & \text{if } \mathcal{T} \leq t \leq 2\mathcal{T}. \end{cases}$$

where v is the scan rate and $\mathcal{T} = \frac{\phi_{max} - \phi_{min}}{v}$ is the half cycle period.

Variables	Insulating boundary $\partial\Omega_{ins}$	Electrode surface $\partial\Omega_e$	Inlet	Outlet
C_j	$\partial C/\partial n = 0$	$\kappa \frac{\partial \phi}{\partial n} + z_j D_j \frac{\partial C_j}{\partial n} = i_n(C_j, \phi, v; \phi_{app})$	C_{in}	$\partial C/\partial n = 0$
ϕ	$\kappa \frac{\partial \phi}{\partial n} = -z_j D_j \frac{\partial C_j}{\partial n}$	$\kappa \frac{\partial \phi}{\partial n} + z_j D_j \frac{\partial C_j}{\partial n} = i_n(C_j, \phi, v; \phi_{app})$		
v	0	0	v_{in}	
p				p_{out}

Table 1: Specified boundary conditions.

From Table 1, i_n is the local current density that implicitly models the electrode kinetics via the Butler-Volmer relation, see for example [4, 5, 6]. In a cyclic voltammetry curve, we compute the total current response to the applied potential on the electrode surface by integrating the current density across the surface of the electrode

$$i_{cv} = \int_{\partial\Omega_e} i_n dS. \quad (5)$$

IV Numerical method

We numerically solved our test problem using the finite element commercial software package, COMSOL multiphysics [10] on a Windows work station (Core i7 CPU, 4 cores, 2.40GHz, 16.0GB RAM). We employed a two step approach for solving the coupled fluid and ion-transport problems. First, we solve for the steady state solution to the incompressible Navier-Stokes equations and then substituted the solution of the velocity field into the ion transport problem. The fluid flow problem was solved by discretizing the computational domain using the linear Lagrange finite elements for the pressure field and quadratic elements for the velocity field. For the ion transport problem we employed the quadratic elements while linear Lagrange element was chosen for the potential field. For the time integration, we have used the implicit Euler method that is stable for the numerical computations.

V Results and Discussion

Figure 1 shows series of voltammograms with varying concentrations. Here, there is no flow in the system. The results show that the peak current varies linearly with the concentrations of bulk electrolyte as expected. The simulation was carried out at the scan rate of 50mV/s and electrolyte concentrations of 50 μ M – 2mM. There is a very good agreement between the simulated and the experimental results. In what follows, we introduce electrolyte flow into the system. Figure 2 shows the effect of flow rates on CV curves. At lower flow rates of about 50 μ L/min - 150 μ L/min peak currents are observed due to diffusion dominated mass transport. Hence, surface reaction is fast enough for electron transfer at the electrode surface. However, as the flow rate increases to about 250 μ L/min, voltammograms becomes thinner and the peak current diminishes. This is due to the rapid inflow of the reactants and fast removal of the products induced by the convection. The diffusion layer of ionic species disappears and mass transport is only by the convection. Finally, Figure 3 shows CV curves at different scan rates of 50mV/s - 250mV/s and at volumetric flow rate of 250 μ L/min. At high scan rate of 250mV/s, peak currents are observed despite the high flow rate. This is due to the fact that the electrode surface kinetics is fast enough for the electron exchange before the reactants are washed away from the electrode surface.

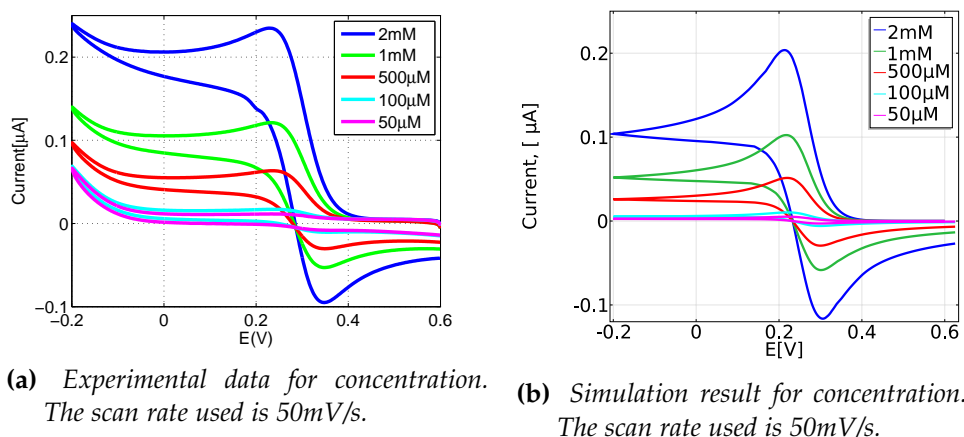


Figure 1: Cyclic voltammetry results as a function of concentration.

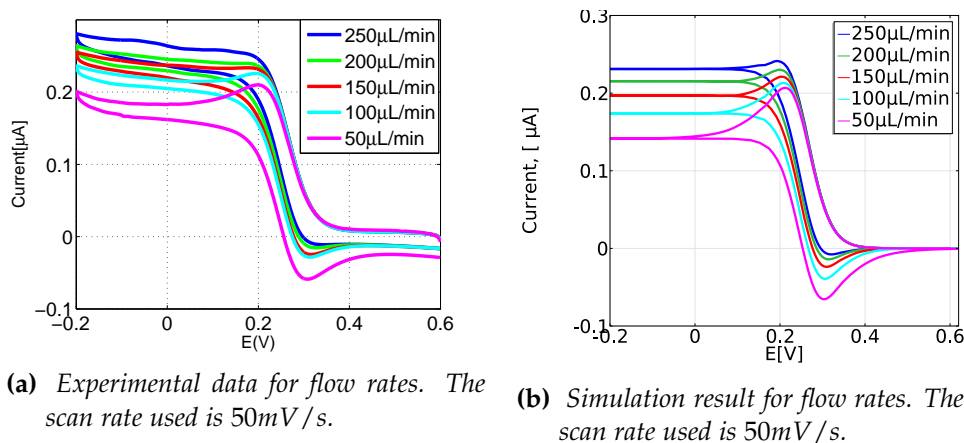


Figure 2: Effect of flow rates on cyclic voltammetry.

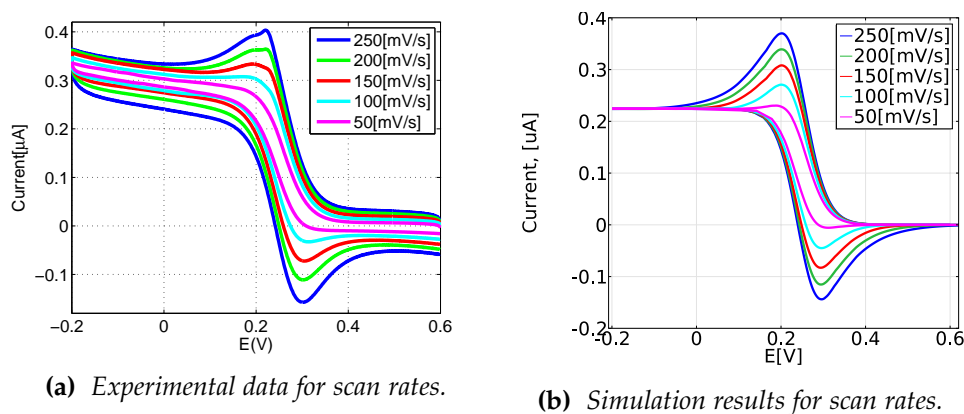


Figure 3: Effect of scan rates on cyclic voltammetry. Flow rate of 250µL/min.

However, at low scan rate of 50mV/s and at high flow rate of 250 μ L/min the CV curves reaches saturation and the width of the voltammogram becomes thinner. The reason is due to the fact that fresh reactants are brought very fast to the electrode surface while products are quickly flushed away from the electrode surface. In addition, because of the slow scan rate electrode kinetics is not fast enough for the electron exchange to record peak currents and hence the narrow and flattened voltammograms. Comparison between the experimental data and the simulation results show a very good agreement. See Figure 3a.

VI Conclusions

A two step numerical approach is used to simulate cyclic voltammetry measurement under hydrodynamic flow. We found that the flow rates has a great influence on the current response recorded during cyclic voltammetry. At fast flow rate, the peak current vanishes while at slow rate steady current response with peak current is recorded. We were able to identify characteristics of hydrodynamic effect on the dynamics of current response to applied voltage in cyclic voltammetry measurement. In addition, we predicted the effect of varying electrolyte concentration and scan rates, respectively.

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