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Review

Experimentation and numerical modeling of cyclic voltammetry for electrochemical micro-sized sensors under the influence of electrolyte flow

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ABSTRACT

In this study, we perform experimental studies as well as simulations for cyclic voltammetry(CV) of the redox couple $\mathrm{Fe^{III}(CN)_6^{3-}/Fe^{II}(CN)_6^{4-}}$ on a gold plated ECC biosensor encapsulated by a microfluidic system. We examine the effect of flow rate, scan rate, varying supporting electrolyte, exchange current density and the position of electrode on the CV measurements. The results show that at a relatively high flow (250 μ/L) and low scan rates (50 - 200 mV/s), the current response is limited by the convection due to quick supply of fresh ions at the electrode surface which leads to fading hysteresis of the recorded CV. However, at high scan rates (250 mV/s) and slow flow rates (50 - 200 μ/L), peak currents are recorded which means that mass transport is dominated by the diffusion mechanism and a quasi-steady state of CV is recorded. In the case of insufficient supporting electrolyte, the excess charges generated during scan will lead to ohmic distortion of the electrolyte solution and consequently result into a ramping effect of the recorded CV. However, for sufficient amount of supporting electrolyte (200 mM), the simulation results show good agreement with the experimental data. In addition, the results also show that a decrease in exchange current density leads to a shift in the peak current of the recorded CV. Finally, the results also demonstrate that the working electrode at the center of the fluidic cell records accurate measurement than placing the electrode at the bottom of the cell. The numerical results and the experimental data show both qualitative good agreement and quantitative good agreement.

Contents

1. Introduction

The last decade has seen rapid progress in the use of microfabricated sensors in electrochemically charged environments for applications such as food safety, environmental monitoring, and medical and health

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applications [1–6]. These devices respond to changes in their physical, chemical and biological environments. In electrochemical systems, microfabricated sensors provide information of the chemical properties of a substance and translate them into electrical signals. This is done by coupling the devices with electroanalytical techniques. One of the most powerful analytical techniques employed for such a task is cyclic voltammetry (CV) [7–9].

Cyclic voltammetry is widely utilized as the main mode of operation for biochemical sensing devices [1,10–13] and is also useful for probing electroactive surfaces in electrical energy storage and conversion devices [14–16]. Typically CV measurements are carried out in an electrochemical system where electrodes are located in a still electrolyte solution. However, over the years rapid developments in electrochemical based sensing have inspired hydrodynamic voltammetric techniques where electrodes are placed in a fluidic cell [1,17–27], and electrolyte solution is pumped in and out of the system. There are several advantages one can derive from such a system. For a well defined flow, the mass transport rate can be controlled quantitatively by varying the electrolyte flow rates. In addition, the introduction of convection naturally increases the rate of mass transport and this can notably allow one to investigate both heterogeneous and homogeneous processes as well as studying faster reaction kinetics.

The fundamental understanding of the physics involved in cyclic voltammetry necessitates the development of mathematical models that can relate system parameters such as flow rates and scan rates used in an electrochemical system [28,29]. However, electrode kinetics is usually non-linear and CV is a transient technique implying that analytical solutions are not always available except in some limiting cases. Hence, numerical simulation is necessary. Furthermore, numerical solutions along with experimental methods allow for the effective study of parameters that characterize the output of a cyclic voltammetry measurement in more details.

Numerical solutions of the CV were first introduced by Feldberg [30,31]. Since then several other authors have numerically studied CV with diffusion as the only mode of mass transfer, see for example [32–34]. Furthermore, there is an extensive list of authors that have numerically simulated CV curves in a flowing stream, in particular the Compton's group [20,35–38]. These authors among others have employed numerical methods such as the alternating direction implicit method (ADI), strongly implicit procedure (SIP), the backwards implicit method (BI) and the hopscotch algorithm [39–41] with regular meshes. Recently, the group of Unwin have studied CV recorded in nanoscale electrodes in a walled carbon channel experimentally [42]. They have also numerically studied systems that are dominated by diffusion [43,44] using finite element solver which eliminates the problem posed by irregular geometries. In addition, the study in their paper [45] has introduced flow into an electrochemical system for the study of linear sweep voltammetry (LSV). In this present study, we focus on simulating cyclic voltammetry coupled with electrolyte flow and examine the mechanisms involved in a microelectrochemical system.

Motivated by the design and optimization of the electrode to ensure accurate CV measurement and for better characterization of the response signal in an electrochemical system, we seek a solution method that can handle complex geometry which also allows for high computational flexibility and maintain the stability properties of the method deployed. We do this by simulating CV using a flexible but powerful finite element method (FEM) solver, Comsol Multiphysics [46,47] under appropriate boundary conditions, electrode configurations in a microfluidic channel with suitable flow conditions.

This study focuses on in-depth analysis through simulation of systems parameters and variables involved in a CV measurement. In particular we investigate electrodes mounted in a microfluidic cell. We investigate the effect of flow rates, effect of scan rates, varying electrolyte concentration, changing the supporting electrolyte as well as rate constants of the reaction and compare simulations to experimental data recorded for CV measurements under different electrode configurations. We demonstrate that the location of electrodes in an electrochemical system plays a significant role while recording a CV measurement. This information will be utilized to understand the behavior of an electrochemical system needed in designing micro electrochemical sensors with improved performance.

2. Experimental setup of the electrochemical cantilever sensor

The electrochemical cantilever sensor (ECC) chip presented here was fabricated by standard microfabrication processes [17]. As shown in Fig. 1, the chip has dimension 12 mm × 11.3 mm and it was fabricated on a 375 μm thick Si substrate. Four cantilevers were placed in the middle of the chip, each having the dimensions 100 μm(width) × 550 nm (thickness) × 400 μm(length). Each cantilever was capable of functioning as an independent working electrode (WE). The reference electrode with dimensions 100 μm × 200 μm was placed on the right side of the cantilevers and the counter electrode with dimensions 2700 μm × 400 μm on the left side. All the electrodes were coated using e-beam evaporation with a 2 nm chrome adhesion layer followed by 30 nm of gold. The chips were cleaned before use. They were immersed in a piranha solution for 6min, and then rinsed thoroughly in MilliQ-water and ethanol [48]. Finally, the chips were blown dry with nitrogen gas and mounted in a microfluidic chamber. As shown in Fig. 1, the microfluidic chamber encapsulates the ECC biosensor with a volume of approximately 105μL and creates a flow path leading into the chip and through the channel past the cantilevers. The fluid enters from the side of the reference electrode and exits from the counter electrode side. There was an access to install a reference electrode in the microfluidic chamber as well. 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 μL/min.

The electrolyte with active redox probes used in the cyclic voltammetric measurements consists of 200 mM KNO_3 solutions with 2 mM of $K_3Fe(CN)_6$ in Milli-Q water. All the chemicals were used without further purification. A DriRef-2SH Ag/AgCl reference electrode (World Precision Instruments, Inc., Sarasota, FL, USA) filling with 3 M KCl solution was applied in the three electrode electrochemical cell. Cyclic voltammetry was performed using a computer controlled CHI1030 Potentiostat.

3. Mathematical modeling

The current response to the applied potential at the electrode surface is proportional to the rate of electron transfer across the electrolyte–electrode interface. Consider the following electrode reaction

$$\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_6^{3-} + e^- \rightleftharpoons \mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_6^{4-}, \tag{1}$$

where $\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_6^{3-}$ and $\mathrm{Fe}^{\mathrm{II}}(\mathrm{CN})_6^{4-}$ represent the oxidized and reduced species, respectively. When the potential is applied to the electrode, the electrolyte solution loses its equilibrium state due to the reaction at the electrode surface. The potential difference between the electrode and the adjacent electrolyte solution triggers the electrode-electron exchange in order for the system to relax to its original equilibrium state. Let N_j denote the ionic flux of species j in an electrolyte given by

$$N_j = -z_j u_j F C_j \nabla\phi - D_j \nabla C_j + C_j v, \tag{2}$$

where C_j,D_j,z_j and u_j are the ionic concentration, the diffusion constant, the charge and the mobility of the ionic species j. F, ϕ and v represent the Faraday's constant, the electrolyte potential and the convective velocity of the solution, respectively [7,8]. The first term in the right hand side of (2) describes the electromigration driven