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

In this study, we perform experimental studies as well as simulations for cyclic voltammetry (CV) of the redox couple FeIII(CN)63-/FeII(CN)64- 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 μL) 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 μL), 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.
Hydrodynamics studies of cyclic voltammetry for electrochemical micro biosensors
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.
Numerical Modeling of Microelectrochemical Systems

The PhD dissertation is concerned with mathematical modeling and simulation of electrochemical systems. The first three chapters of the thesis consist of the introductory part, the model development chapter and the chapter on the summary of the main results. The remaining three chapters report three independent papers and manuscripts.

As a preliminary to the study, we describe a general model for electrochemical systems and study their underlying mechanisms through electroanalytical techniques. We then extend the model to a more realistic model for microelectrochemical systems which incorporates the finite size of ionic species in the transport equation. The model presents a more appropriate boundary conditions which describe the modified Butler-Volmer reaction kinetics and account for the surface capacitance of the thin electric double layer. We also have found analytical solution for the reactants in the bulk electrolyte that are traveling waves.

The first paper presents the mathematical model which describes an electrochemical system and simulates an electroanalytical technique called cyclic voltammetry. The model is governed by a system of advection–diffusion equations with a nonlinear reaction term at the boundary. We investigate the effect of flow rates, scan rates, and concentration on the cyclic voltammetry. We establish that high flow rates lead to the reduced hysteresis in the cyclic voltammetry curves and increasing scan rates lead to more pronounced current peaks. The final part of the paper shows that the response current in a cyclic voltammetry increases proportionally to the electrolyte concentration.

In the second paper we present an experiment of an electrochemical system in a microfluidic system and compare the result to the numerical solutions. We investigate how the position of the electrodes in the system affects the recorded cyclic voltammetry. We establish that at high scan rates and modest flow rates, peak currents are recorded. Finally, the results show that the position of the electrodes is critical when performing cyclic voltammetry under the flow condition. The numerical results show promising agreement with experimental findings which could be critical in designing highly sensitive electrochemical systems.

The last paper explores the numerical solution which describes the non-linear transient responses to a large applied potential at the electrode in a microelectrochemical system. In our analysis, we account for the finite size properties of ions in the mass and the charge transport of ionic species in an electrochemical system. This term characterizes the saturation of the ionic species close to the electrode surface. We then analyse the responses of the system on the charging of the electric double layer. We consider an arbitrary electrolyte solution that is sandwiched between electrodes and allow for electrochemical reactions at the electrode/electrolyte interface. One of the electrodes is biased with a potential which triggers the reaction and the dynamics of the system. We establish that there is a quick build up of boundary layers in the double layer, but the finite size constraint on the ionic species prevents overcrowding of the ionic species. The result also shows that reactants which undergo charge transfer at the electrode/electrolyte interface crowded the electric double layer and the dynamics of the electric double layer is controlled by the charge transfer.

General information
State: Published
Organisations: Department of Applied Mathematics and Computer Science, Dynamical Systems, Scientific Computing
Authors: Adesokan, B. J. (Intern), Evgrafov, A. (Intern), Sørensen, M. P. (Intern)
Number of pages: 116
Publication date: 2015

Publication information
Place of publication: Kgs. Lyngby
Publisher: Technical University of Denmark (DTU)
Original language: English
Simulating cyclic voltammetry under advection for electrochemical cantilevers
We present a mathematical model describing an electrochemical system involving electrode–electrolyte interaction. The model is governed by a system of advection–diffusion equations with a nonlinear reaction term at the boundary. Our calculations based on such model demonstrate the dynamics of ionic currents in the electrolyte. The model allows us to predict the effect of varying flow rates, scan rates, and electrolyte concentration of the electrochemical system.

General information
State: Published
Organisations: Department of Applied Mathematics and Computer Science, Dynamical Systems, Center for Intelligent Drug Delivery and Sensing Using Microcontainers and Nanomechanics
Authors: Adesokan, B. J. (Intern), Evgrafov, A. (Intern), Sørensen, M. P. (Intern)
Pages: 3384-3391
Publication date: 2015
Main Research Area: Technical/natural sciences

Publication Information
Journal: Mathematical Methods in the Applied Sciences
Volume: 38
Issue number: 16
ISSN (Print): 0170-4214
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): SJR 0.669 SNIP 0.748 CiteScore 0.92
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.755 SNIP 0.837 CiteScore 0.92
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 0.73 SNIP 0.896 CiteScore 0.85
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 0.871 SNIP 0.914 CiteScore 0.95
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 0.876 SNIP 0.851 CiteScore 0.82
ISI indexed (2012): ISI indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 0.88 SNIP 0.874 CiteScore 0.85
ISI indexed (2011): ISI indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.83 SNIP 1
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 1.017 SNIP 1.035
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 0.795 SNIP 0.96
Scopus rating (2007): SJR 0.736 SNIP 0.834
Scopus rating (2006): SJR 0.525 SNIP 0.721
Scopus rating (2005): SJR 0.779 SNIP 0.925
Scopus rating (2004): SJR 0.752 SNIP 1.043
Scopus rating (2003): SJR 0.805 SNIP 1.064
Scopus rating (2002): SJR 1.058 SNIP 0.949
Scopus rating (2001): SJR 0.685 SNIP 0.852
Scopus rating (2000): SJR 0.67 SNIP 1.011
Scopus rating (1999): SJR 0.956 SNIP 0.969
Original language: English
Cyclic voltammetry, Butler-Volmer, Advection, Cantilever sensors
DOIs:
10.1002/mma.3336
Source: PublicationPreSubmission
Source-ID: 105128032
Publication: Research - peer-review › Journal article – Annual report year: 2015

Projects:

Quantity of Interest Tomography
Department of Applied Mathematics and Computer Science
Period: 01/01/2017 → 31/12/2019
Number of participants: 4
Phd Student:
Jensen, Bjørn Christian Skov (Intern)
Supervisor:
Adesokan, Bolaji James (Intern)
Andersen, Martin Skovgaard (Intern)
Main Supervisor:
Knudsen, Kim (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)
Project: PhD

Mathematical Modelling and Optimization of Nano Mechanical Devices
Department of Applied Mathematics and Computer Science
Period: 15/12/2011 → 28/04/2015
Number of participants: 6
Phd Student:
Adesokan, Bolaji James (Intern)
Supervisor:
Sørensen, Mads Peter (Intern)
Main Supervisor:
Evgrafov, Anton (Intern)
Examiner:
Hjorth, Poul G. (Intern)
Berg, Peter (Ekstern)
Fuhrmann, Jürgen (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Eksternt finansieret virksomhed
Project: PhD