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. The result shows that convection influences the charge transfer dynamics on the electrode surface and hence the cyclic voltammetry recorded. In terms of relative high flow to scan rates, the current response is dominated by the convection due to the fresh supply of reactants towards the electrode surface and quick removal of the products. We also 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.

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