Electrochemistry Modeling Of A Smartphone Based Electrochemiluminescence Sensor

H. Kwon[1], E. C. Rivera[2]

[1]Andrews University, Berrien Springs, MI, USA
[2]Laboratório Nacional de Ciência e tecnologia do Bioetanol, Campinas, SP, Brazil

Abstract

An electrochemiluminescence (ECL) sensor was developed in a smartphone-based platform using a disposable disk-shaped carbon electrode. A time-varying square waveform potential was applied to the working electrode, and the current and ECL intensity data were measured. The applied potential triggered a series of reactions involving the ground state and intermediate species in the system.

The ECL sensor gives out two type of output, ECL light emission and chronoamperometric current measurement. The modeling for this system is challenging as ECL intensity is strongly dependent on the sensing conditions and thus any changes in these conditions can influence all the kinetic parameters. Thereby, it is necessary to estimate a set of optimal values of the kinetic parameters simultaneously for each sensing condition. In our previous study, using a simplified model without diffusion, we have successfully estimated the optimal values of the kinetic parameters simultaneously, achieving a high correlation between the model prediction and the measured ECL intensity (Rivera et al., 2020).

In the present study, the previously estimated values of the kinetic parameters were used in the development of a rigorous model in COMSOL Multiphysics® which integrally represents the charge, momentum and mass transfer of the ECL reactions under diffusion limited conditions. The disk-type electrochemical cell was simulated as 2D axisymmetric geometry. Electrochemistry module was used to simulate series of six reactions and a potential step (±1.2V) was applied at the electrode. The total and Cottrell current were obtained for different ruthenium concentrations. The depletion of reactants near the electrode surface were also obtained. The total current was compared to the experimentally obtained data.

A comprehensive mechanistic model was developed to describe multimodal-electrochemical measurement prediction for series of reactions using COMSOL Multiphysics®. The great challenge of this modeling work is related to the simultaneous determination of the values of the kinetic parameters to the conditions studied. As ECL intensity is strongly dependent on the sensing conditions, any changes in these conditions can influence all the parameters. Using the trial-and-error method to assign values to parameters can led to non-convergence during simulation. In this study the values of the kinetic parameters for the required experimental sensing conditions were obtained from a previous work in which we used a simplified model appropriate for parameter estimation purposes (due to its quick convergence). Thus, the reaction rates of the detailed model proposed in the present study incorporated these parameters. The charge, momentum and mass transfer of the ECL system were implemented in COMSOL Multiphysics®. The simulated data were compared with the experimental data to evaluate the prediction performance of the model. he model implemented in COMSOL Multiphysics® can be used to evaluate how sensing conditions affect simultaneous measurement of ECL emission and current, and thus aid in experimental design and optimization.

Reference

Rivera E.C., Summerscales R.L., Uppala P.P.T., Kwon H.J. Electrochemiluminescence mechanisms investigated with smartphone-based sensor data modeling, parameter estimation and sensitivity analysis. ChemistryOpen, 2020, doi.org/10.1002/open.202000165

Figures used in the abstract

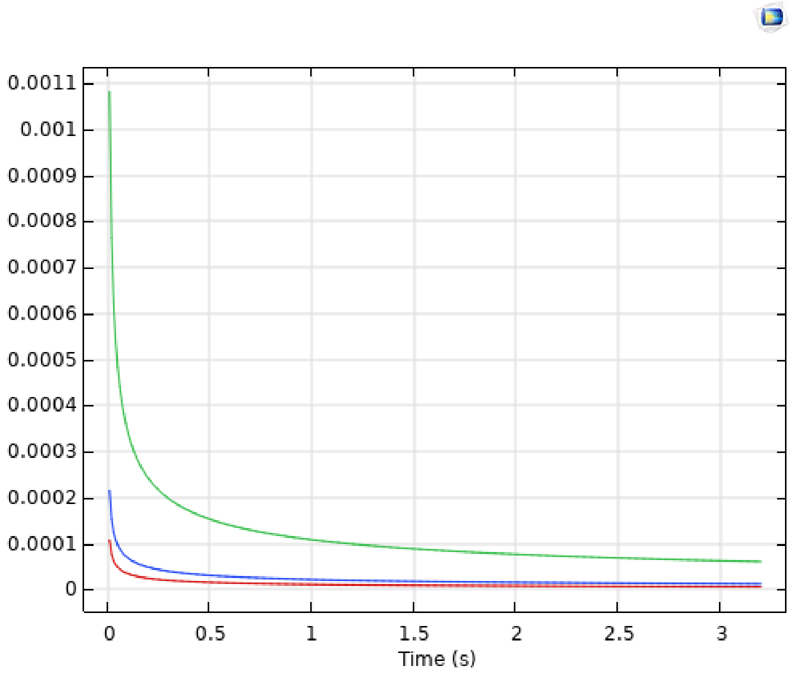

Figure 1 : Current calculated by the Cottrell equation for 5,1, 0.5 uM of Ru(bpy)3^2+ and 20 mM of TPrA.