Electrochemistry modeling of a smartphone based electrochemiluminescence sensor

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INTRODUCTION: 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 emmission 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).

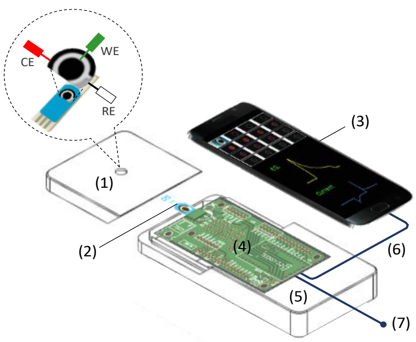

Figure 1. ECL sensor platform with the mobile phone

Figure 2. ECL sensor signal measured from a cell phone.

COMPUTATIONAL METHODS:

Geometry and mesh:1D geometry was used to describe the solution where the reaction. Finer mesh was assigned near the electrode surface.

Computational model: COMSOL electroanalysis module was used to describe the diffusion and reaction in the electrolyte solution.

ECL mechanism taking place in the smartphone-based ECL sensor

$$\mathrm{Ru(bpy)_3^{2+}} - e^- \xrightarrow{k_1} \mathrm{Ru(bpy)_3^{3+}}$$

$$\mathrm{TPrA} - e^- \xrightarrow{k_2} \mathrm{TPrA^{\bullet+}}$$

$$\mathrm{TPrA^{\bullet+}} - \mathrm{H^+} \xrightarrow{k_3} \mathrm{TPrA^{\bullet}}$$

$$\mathrm{Ru(bpy)_3^{2+}} + \mathrm{TPrA^{\bullet}} \xrightarrow{k_4} \mathrm{Ru(bpy)_3^{+}} + \mathrm{Im^+}$$

$$\mathrm{Ru(bpy)_3^{+}} + \mathrm{Ru(bpy)_3^{3+}} \xrightarrow{k_5} \mathrm{Ru(bpy)_3^{2+*}} + \mathrm{Ru(bpy)_3^{2+}}$$

$$\mathrm{Ru(bpy)_3^{2+*}} \xrightarrow{k_6} \mathrm{Ru(bpy)_3^{2+}} + h\nu$$

RESULTS:

Genetic algorithm was used to simultaneously determine parameters in the reaction rates using a simplified model (Rivera et al., 2020) to reach convergence. Using these values, the ECL and electric current was computed using the COMSOL.

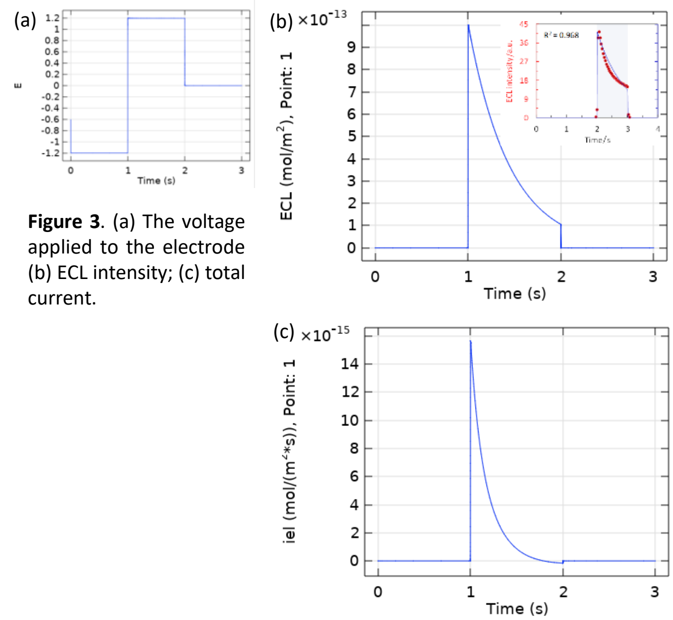

Figure 3. (a) The voltage applied to the electrode (b) ECL intensity; (c) total current.

The simulated ECL and current were in a good agreement with the experiments (R^2=0. 968).

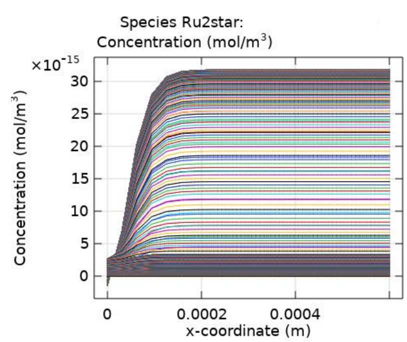

Figure 4.Spatial distribution of $\mathrm{Ru(bpy)_3^{2+*}}$ as time progresses. $\mathrm{Ru(bpy)_3^{2+*}}$ is directly related to ECL intensity.

CONCLUSIONS: The modeling approach developed (including a prior estimation of model parameters) was suitable for the mathematical description of reaction rates leading to the ECL generation in a smartphone-based sensor. COMSOL Multiphysics® provided full access to the equations and permitted flexible, user-controlled physical configurations for the detailed analysis of the kinetics of the ECL mechanism.

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REFERENCES:

1. Rivera, et al., Electrochemiluminescence Mechanisms Investigated with Smartphone-Based Sensor Data Modeling, Parameter Estimation and Sensitivity Analysis, *ChemistryOpen*, v. 9, 854-863, 2020.