

Simulation of cyclic voltammetry of ferrocyanide/ferricyanide redox reaction in the EQCM Sensor

Hyun J. Kwon* and Ebenezer Akyiano

Department of engineering and computer science, Andrews University

*Corresponding author: HYH312, Berrien Springs, MI 49104, hkwon@andrews.edu

Abstract:

Electrochemical measurement of DNA in the EQCM setup provides quick detection of DNA hybridization or DNA damage. However, there is lacking understanding on relations on mass transport and electrochemical measurement in a given geometry. In this paper, the cyclic voltammetry behavior of Ferrocyanide /Ferricyanide, which is commonly used for electrochemical DNA detection experiment, was studied in the EQCM-D setup (commercial QEM from Q-sense) using the COMSOL multiphysics. The electrode reaction rate is governed by mass transport of the electro active species to the electrode surface. The mathematical model includes mass transport equation of electro active molecules in the QCM cell, electron transfer reaction on a working electrode and charge transfer kinetics. The model was established in a 3D geometry of QCM liquid cell. The simulation shows depletion of concentration of $\text{Fe}(\text{CN})_6^{4-}$ following applied electrode potential, which affects current through the liquid cell. Cyclic voltammogram (i vs. electrode potential E) of ferrocyanide /ferricyanide redox couple was plotted, showing peak potentials and peak current as expected. Effects of the electrode modification with DNAs were simulated to see how immobilization and hybridization of DNA would change the CV measurement. Additionally, effects of initial concentration of ferrocyanide and scan rate was also simulated. This model renders understanding of mechanisms in electrochemical measurement of QCM electrode cell and assists design of electrochemical measurement of DNAs in the EQCM setup.

Keywords: EQCM, Q-sense, cyclic voltammetry, DNA, ferrocyanide

1. Introduction

Cyclic voltammetry (CV) has become a commonly used electro-chemical analysis technique to characterize DNA, protein,

chemical binding [1]. CV allows monitoring of redox behavior of chemical species, such as ferrocyanide ($\text{Fe}(\text{CN})_6^{4-}$)/ferricyanide ($\text{Fe}(\text{CN})_6^{3-}$) within a wide potential range. The current at the working electrode flowing through a counter electrode is monitored as a triangular excitation potential is applied to the working electrode. The resulting voltammogram is plotted the current vs. applied electrode potential relative to reference electrode. The current intensity provides information on overall rate of many processes occurring at the working electrode surface. In this study, we are testing a basic electrolyte redox rate to understand CV behavior before actual molecule of interest is added into it.

The quartz crystal microbalance (QCM) comprises a thin quartz crystal sandwiched between two metal electrodes that establish an alternating electric field across the crystal, causing vibrational motion of the crystal at its resonant frequency. One side of electrode could be employed as working electrode and the electrochemical QCM (EQCM) system allows simultaneous measurement of electrochemical experiments and mass change. The system used for this study is a commercial EQCM system from Q-sense. For this study, only electrochemical experiments are considered in the EQCM cell.

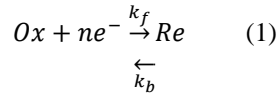
Ferrocyanide/Ferricyanide redox reaction couple is commonly used in electrochemistry [2] as a mediator shuttling electrons between electro active species dissolved in a solution and a working electrode. The working used for this study is gold and voltage is measured with respect to reference electrode, Ag/AgCl. The working electrode is often modified various way: ds-DNA probe to detect pollutants[3], Fc-PNA probe to detect DNA hybridization[4], ss-DNA immobilized gold nanoparticles to detect chemicals of interest[5], or protein probe to detect mismatched DNA, [2] etc. Understanding effects of surface modification is important to further characterize the binding of target molecules on the surface of modified electrode.

In this study, in the commercial EQCM setting was used to establish the cyclic voltammetry model. The mathematical model includes mass transport equation of electro active molecules in the QCM cell, electron transfer reaction on a working electrode that is governed by applied electrode potential, and charge transfer kinetics. The model was established in a 3D model of QCM liquid cell.

2. Mathematical models

2.1. Governing equations

To simulate the cyclic voltammetric response, a simple one-electron transfer reaction with Butler-Volmer kinetics is considered:



where n is the number of moles of electrons transferred per mole of electroactive species, $n=1$ for ferrocyanide/ferricyanide reaction. The forward and backward rate constants, k_f and k_b , are defined by

$$k_f = k^0 \exp(-\beta f(E - E^0)) \quad (2)$$

$$k_b = k^0 \exp((1 - \beta)f(E - E^0)) \quad (3)$$

where k^0 is the standard heterogeneous rate constant for the redox couple, β is the transfer coefficient ($\beta = 0.5$ is taken in this work), E^0 is the formal potential, E is the applied potential on the electrode/solution interface. The f is defined as F/RT where F , faraday constant 96490 C/mol, A is the area of the electrode surface.

The reaction occurs on the upper surface of QCM crystal gold electrode. For simplicity we assume pseudo first order reaction kinetics.

$$R = k_f c_{Ox} - k_b c_{Re}$$

This is under assumption that high concentration of supporting electrolyte (such as 0.1 M KCl) supplies electrons.

Bulk phase transport: Main analyte(s) transport method is bulk diffusion in the quiescent solution. The diffusion of two molecules are governed by transient diffusion equation:

$$\frac{\partial c_{Ox}}{\partial t} = D \nabla^2 c_{Ox} \quad (4)$$

$$\frac{\partial c_{Re}}{\partial t} = D \nabla^2 c_{Re} \quad (5)$$

Where c_{ox} , c_{Re} is the molar concentration of an Ox and Re in the solution (mol/m^3) and D is the diffusion coefficient of the ox molecules (m^2/s). When flow is applied, u was applied at a steady state flow at a predetermined flow rate.

Before the experiment starts, only the species Ox is present in the solution with initial bulk concentration of c_0 .

$$c_{ox} \text{ (at } t=0) = c_0 \quad (6)$$

$$c_{Re} \text{ (at } t=0) = 0 \quad (7)$$

Electron transfer equation: In electrochemical reactions, the current at any potential is a direct measure of the electron transfer. The cyclic voltammetry is the record of current through the electrodes vs. applied electrode potential. The current flowing in either the reductive or oxidative steps can be predicted using the following expressions

$$i = nFAR = nFA(k_f c_{Ox} - k_b c_{Re}) \quad (8)$$

The reductive current is negative and the oxidative positive because current flows in opposite directions across the interface[6].

2.2. Boundary conditions

No-slip boundary conditions are applied to all surfaces except at the inlet and outlet of the fluid chamber for the Navier Stokes model.

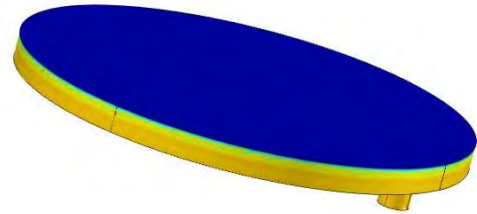


Figure 1. The geometry of QCM liquid 3D model. The top surface is working electrode (Au). The model consists of 85000 degrees of freedom.

Table 1. Values used in the simulation

parameters	Values	ref.
k^0 (cm/s)	2.5×10^{-4} (bare gold) , 4.6×10^{-7} (ds-DNA)	[7]
E^0 (vs. Ag/AgCl)	0.18 V	[6]
c^0 (M)	1×10^{-3}	
Scan rate (mV/s)	100	[7]
D (cm ² /s)	0.7×10^{-5}	[8]

The bottom of the chamber is impenetrable, and the flux of the species B through the surface is zero, i.e.

$$\mathbf{n} \cdot (-D\nabla c_{Ox} + c_{Ox}\mathbf{u}) = 0$$

On the active electrode surface, the boundary condition couples the rate of reaction at the surface with the flux of species B.

$$\mathbf{n} \cdot (-D\nabla c_{Ox} + c_{Ox}\mathbf{u}) = R$$

3. Use of COMSOL Multiphysics

The disk shaped 3D geometry was developed at the actual scale. Transport of dilute species model was employed to simulate mass transport of electro active $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ in bulk phase in transient time. On the surface of working electrode, excitation voltage is applied as a triangular shape. The applied electrode potential was implemented using the built-in wave functions: $\text{wv1}(t[1/s])$ with frequency $0.1 \cdot \pi$, a phase shift of $-0.5 \cdot \pi$, and amplitude 0.5 V. The applied excitation potential is shown in Figure 2. The scan rate is set as 0.1 V/s as default unless otherwise stated. For the CV data, average surface concentrations of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ were calculated in each time frame by integrating surface concentration over surface and divide by the electrode surface area. The current is then calculated by the equation (8) and plotted versus electrode potential.

Since concentrations of electro active molecules are depleted/accumulated at the surface of working electrode where the reaction occurs, the finer mesh should be defined near the surface (non equidistant). The mesh used in the model yielded approximately 85000 degrees of freedom. The transient diffusion model was simulated for time progress of a full cycle of

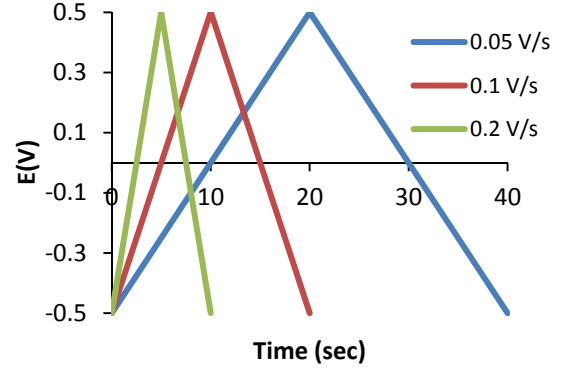


Figure 2. The excitation potential applied in working electrode at the scan rate of 0.05, 0.1 and 0.2 V/s. Scan rate of 0.1 V/s was used for most of simulation unless otherwise stated.

excitation voltage, (20 seconds for the scan rate of 0.1 V/s) at an interval of 0.1 second.

Parameters considered in this simulation study are scan rate (E), concentration of Ferrocyanide (c_0), surface modification (k^0) The rate constant k^0 changes when ss DNA or ds-DNA is immobilized on the gold electrode. The values for simulation study, shown in Table 1, are selected to represent values encountered in actual electrochemical experiments[7].

4. Results and Discussion

4.1. Surface concentration depletion

The redox reaction on an electrode is affected

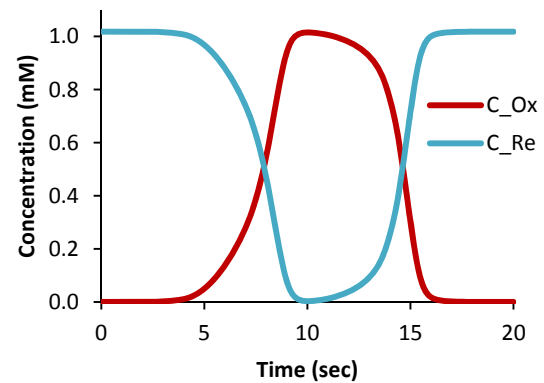


Figure 3. Concentration profile of Ox($\text{Fe}(\text{CN})_6^{4-}$) and Re ($\text{Fe}(\text{CN})_6^{3-}$) near the surface of the working electrode at the scan rate of 0.1 V/s.

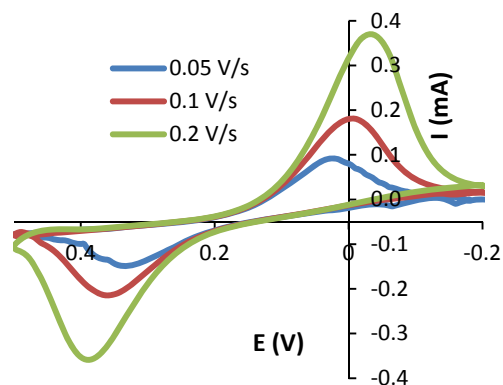


Figure 4. A simulated cyclic voltammogram of ferrocyanide/ferricyanide redox reaction in EQCM cell with gold working electrode, Ag/AgCl reference electrode, and scan rate of 0.05, 0.1, and 0.2 V/s.

by multiple factors. First, the surface concentration of the reactant and second, reaction constant (k^0). The former depends on mass transport of molecules to the electrode in a given geometry. Surface concentrations of oxidized and reduced reactants were simulated to examine how they change as the applied potential varies. As the excitation potential is applied, the concentration of the oxidized species is depleted at the surface and replenished as the potential is reversed. On the contrary, the concentration of reduced species develops opposite to the oxidized species. The surface concentration of the two redox couple over CV scanning time is shown in Figure 3.

4.2. Effects of scan rates

The scan rate was changed from 0.05 V/s to 0.2 V/s as shown in Figure 2 and the responding current was computed for each case. The current intensity as a function of excitation potential is simulated and plotted as shown in Figure 4. Overall, relatively large ($\sim 10^{-4}$ A compared to mA) magnitude of the current is observed due to the large surface area of the working electrode. At faster scan rate, the peak magnitudes appeared higher. Both oxidation and reduction peak was observed, however, the locations of two peaks are not identical and peak occurs at slightly different position at different scan rates. This indicates that the redox reaction is slightly irreversible in this setting. This is mainly due to mass transport limitation of the redox pairs. As seen in Figure 3, the surface concentration is slightly nonsymmetrical. This

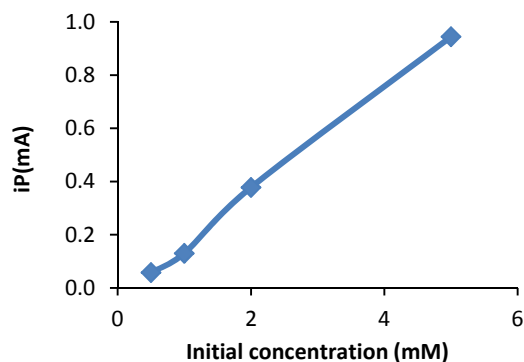


Figure 5. Effects of initial concentration of ferrocyanide dissolved in solution on the cathodic peak current. The scan rate is 0.1 V/s.

could be the cause of irreversibility of the redox reaction in the EQCM cell.

4.3. Effect of initial concentrations of ferrocyanide

To examine the effect of initial bulk concentration of $\text{Fe}(\text{CN})_6^{4-}$, the magnitude of cathodic current was plotted versus initial concentration of $\text{Fe}(\text{CN})_6^{4-}$ (Figure 5). The peak current was measured by extrapolating the baseline current. The result demonstrated linear increase in the magnitude of peak current within the concentration range while peak appeared at the same voltage. This indicates that the experiment could be designed anywhere at the given concentration range.

4.4. Effect of electrode modification

For electrochemical measurement of biomolecules or chemical pollutants, the gold working electrode is often modified with ss-DNA, ds-DNA, or other receptor chemicals. When the electrode property changes due to deposition of probes, k^0 changes as shown in Table 1. Effect of the electrode modification with ds-DNA was simulated. As shown in Figure 6, when the working electrode was deposited with ds-DNA, the cathodic peak was shifted to negative voltage and the anodic peak did not appear. The result indicated that irreversible reaction occurred after the surface is modified.

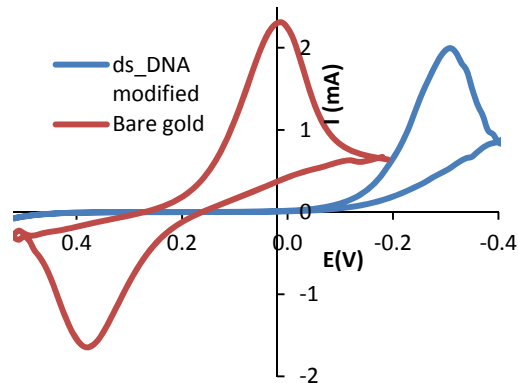


Figure 6. Effect of surface modification with ds-DNA on the CV gram compared to that of bare gold. The scan rate was 0.1 V/s.

The results indicate that the model could be used to understand effect of various surface modification method on reaction constants and CV data.

5. Conclusions

This model successfully demonstrated that multiphysics simulation of electrochemical reactions coupled with mass transport for a specific geometry of a electrochemical cell where mass transport and electrode conditions are unique. This simulation rendered understanding of underlying mechanisms in CV measurement of ferrocynide solution in a commercial EQCM-D setup. Fundamental understanding of interfacial electron transfer among electrolyte / DNA/ solid surface will facilitate the design for electrical detection of DNA molecules or chemicals. This model could be further developed to design and interpret experimental data when the working electrode is modified and binding occurs on the electrode surface.

6. References

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7. Acknowledgements

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