Simulations of the ECEC Mechanism Using Scilab Software: Application in Optimization Studies

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ABSTRACT

Using Scilab 2024.0.0 software, an algorithm was implemented and tested to simulate the current response of electrochemical reactions in cyclic voltammetry (CV) and square wave voltammetry (SWV). Convergence was achieved with an error of less than 0.3% when compared to exact solutions from the literature. The inclusion of a chemical step, following the electrochemical step in the mechanism, was investigated by analyzing its effects on optimization simulations through altering SWV parameter values.

Keywords: Scilab, simulation, ECEC mechanism, finite differences.

Introduction

Simulation is an effective research tool for understanding experimental results and supporting decisions regarding analysis conditions. By representing a system and its processes, it highlights the relationships between the model's variables (1-2). Thus, simulations aim to predict the behavior of a system in terms of the parameters of the mathematical equations that represent it. In the case of electroanalysis, simulation results generate information that helps explain the observed behavior in optimization studies. Such behavior is dependent on the reaction mechanisms (1-2). Various commercial software packages, such as applications or programs, allow the implementation of simulations. However, high prices can become an obstacle for many researchers and students seeking this alternative. Furthermore, these software are maintained under the control of their developers, making it impossible to access and modify the simulation code. Using software without understanding the underlying algorithms poses a challenge for the advancement of science. It's recommended that software used in scientific research be open-source, allowing for its review (3). For example, Scilab is open source and offers a wide range of tools for developing and simulating models of various types, appearing as an alternative to paid software (4-6). Therefore, this work aimed to write an algorithm in Scilab to simulate the mechanism with the electrochemical-chemical-electrochemical-chemical (ECEC) steps and apply it in optimization studies.

Experimental

Methodology

The following mechanism was considered in developing the algorithm:

$A \rightleftharpoons B + e^-$; $B \rightarrow W$; $W \rightleftharpoons Y + e^-$; $Y \rightarrow Z$.

If mass transport occurs by diffusion and according to the previous mechanism, it is possible to write:

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}; \qquad \frac{\partial C_B}{\partial t} = D_B \frac{\partial^2 C_B}{\partial x^2} - k_1 C_B;$$

$$\frac{\partial C_W}{\partial t} = D_W \frac{\partial^2 C_W}{\partial x^2} + k_1 C_B; \qquad \frac{\partial C_Y}{\partial t} = D_Y \frac{\partial^2 C_Y}{\partial x^2} - k_2 C_Y;$$

$$\frac{\partial C_Z}{\partial t} = D_Z \frac{\partial^2 C_Z}{\partial x^2} + k_2 C_Y;$$ where C is the concentration of each species, t is time, x is space, D is the diffusion coefficient, k_1 is the rate constant of the first chemical step, and k_2 is the rate constant of the second chemical step.

The initial and boundary conditions were:

$t = 0$, $x \geq 0$ or $t > 0$, $x \rightarrow \infty \Rightarrow C_i = C_i^*$, where C_i^* represents the initial concentrations and i = A, B, W, Y or Z.

if $t > 0$, x = 0 (surface conditions)

$$D_A\left(\frac{\partial C_A}{\partial x}\right)_{x=0} = k_{f1} C_A(0,t) - k_{b1} C_B(0,t);$$

$$D_A\left(\frac{\partial C_A}{\partial x}\right)_{x=0} = - D_B\left(\frac{\partial C_B}{\partial x}\right)_{x=0};$$

$$D_W\left(\frac{\partial C_W}{\partial x}\right)_{x=0} = k_{f2}C_W(0,t) - k_{b2}C_Y(0,t);$$

$$D_Y\left(\frac{\partial C_Y}{\partial x}\right)_{x=0} = -D_W\left(\frac{\partial C_W}{\partial x}\right)_{x=0};$$

$$D_Z\left(\frac{\partial C_Z}{\partial x}\right)_{x=0} = 0;$$ where k_{f1} is the rate constant of the first forward electrochemical reaction, k_{b1} the rate constant of the first reverse electrochemical reaction, k_{f2} the rate constant of the second forward electrochemical reaction and k_{b2} the rate constant of the second reverse electrochemical reaction.

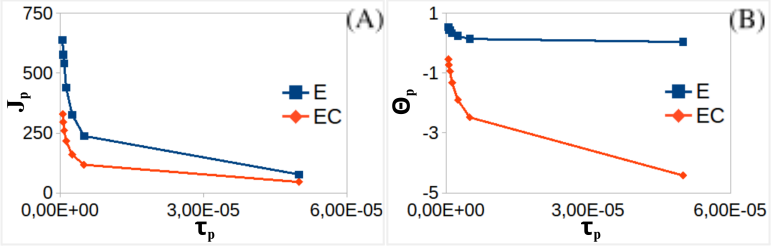
The Butler-Volmer model was used to include the dependence of the k_f and k_b constants on the potential difference. To solve the mathematical model, dimensionless variables defined in the literature and the Newton-Raphson method were used (1-2).

Scilab 2024.0.0 software was used to implement the algorithm and formulate the simulations. Initially, the obtained values were evaluated for convergence by comparing the numerical solution with the response of the exact solution described in the literature, for the reversible and irreversible cases in cyclic voltammetry (CV) and for the reversible case in square wave voltammetry (SWV). After confirmation, new simulations were performed with the inclusion of the irreversible chemical reaction, and the current behavior was analyzed when the SWV parameters were varied. The dimensionless parameters were calculated from real values observed in literature for the cleavage of methylcobalamin (7).

Results and Discussions

The accuracy tests produced satisfactory results. For CV, the relationship between simulated peak current and square root of the sweep rate was linear and had a slope equal to that described in the literature (considering 4 decimal places). For SWV, the numerical (simulated) solution showed adequate accuracy in terms of peak current when compared with the exact solution described in the literature (error < 0.3%).

After the inclusion of the irreversible process in the electrochemical system, peak currents (J_p) increased with frequency, amplitude, and step size. However, a comparative analysis between the electrochemical and electrochemical-chemical mechanisms (Figure 1) demonstrated a decrease in currents when the chemical reaction was included.



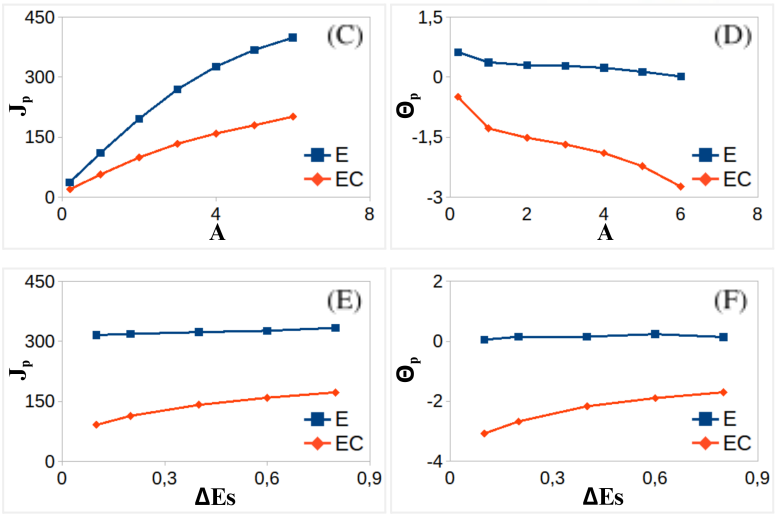


Figure 1. Peak current as a function of: (A) pulse time; (C) amplitude; (E) step. Peak potential as a function of: (B) pulse time; (D) amplitude; (F) step.

In addition to what was observed for peak current values, the relationship between peak potentials (Θ_p) and SWV parameters also was dependent on the mechanism considered. Peak potentials were more sensitive to pulse time, amplitude, and step size when the chemical step was considered. This behavior is essential to consider in optimization studies commonly conducted in the development of electrochemical sensors.

Conclusions

Using the free software Scilab 2024.0.0, it was possible to simulate the current response in CV and SWV for the EC mechanism. According to the simulations, the relationships between peak current and peak potential with respect to the SWV parameters are influenced by the mechanisms considered, E or EC. Therefore, the interpretation of the optimization studies must consider this effect. In future analyses, we intend to conduct studies considering the complete mechanism, that is, considering the electrochemical-chemical-electrochemical-chemical stages.

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