Macedonian Journal of Chemistry and Chemical Engineering, Vol. **44**, No. 2, pp. xx–xx (2025)

MJCCA9 –
ISSN 1857-5552
e-ISSN 1857-5625

Received: September 14, 2025
Accepted: September 29, 2025
DOI: 10.20450/mjcce.2025.3273
Education

FROM THEORY TO SIMULATION: OPEN INTERACTIVE MATHCAD SIMULATION PROTOCOLS FOR EXPLORING COMMON ELECTRODE MECHANISMS IN CYCLIC VOLTAMMETRY

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Cyclic voltammetry is considered one of the most important techniques in electrochemistry, widely applied to investigate not only mechanistic aspects, but also kinetics and thermodynamics of various redox processes. Many biochemical transformations in living systems involve electron transfer steps coupled with preceding, subsequent, or regenerative chemical reactions, commonly referred to in electrochemistry CE, EC, and EC’ mechanisms, respectively. Accurately simulating such processes is essential for understanding their behaviour and for interpreting experimental voltammetric data. Despite the extensive theoretical work available in the literature, freely accessible computational tools for simulating these mechanisms remain scarce, limiting their use in both teaching and research contexts. This work introduces a set of ready-to-use simulation files developed using the software package Mathcad, designed to model cyclic staircase voltammograms for diffusional CE, EC, and EC' mechanisms under the Butler–Volmer kinetic formalism. The provided protocols define and explain all relevant physical constants, potential waveform parameters, and dimensionless kinetic and thermodynamic variables required to define recurrent formulae for current calculations. The approach also highlights the diagnostic value of analyzing relevant features of cyclic voltammograms to identify specific mechanisms from simulated voltammetric patterns. By making these simulation files freely available, the platform offers students and electrochemists an interactive and intuitive learning tool, while providing experienced scientists with a valuable theoretical resource for their experiments. This primarily educational work brings theoretical electrochemistry closer to all electrochemists, enabling a deeper mechanistic understanding of some of the most important electrode processes.

Keywords: cyclic voltammetry; Mathcad simulation platform; electrochemical mechanisms; educational electrochemistry

ОД ТЕОРИЈА ДО СИМУЛАЦИЈА: ОТВОРЕНИ ИНТЕРАКТИВНИ MATHCAD ПРОТОКОЛИ НАМЕНЕТИ ЗА СИМУЛАЦИИ НА НАЈВАЖНИ ЕЛЕКТРОДНИ МЕХАНИЗМИ ВО УСЛОВИ НА ЦИКЛИЧНА ВОЛТАМЕТРИЈА

Цикличната волтаметрија е една од најважните техники во електрохемијата, што е широко применета за студирање не само на механистичките аспекти туку и за определување на кинетиката и термодинамиката на различни електрохемиски процеси. Многу биохемиски трансформации во живите системи вклучуваат чекори на трансфер на електрони што се најчесто поврзани со претходни, последователни или регенеративни хемиски реакции, кои во електрохемијата вообичаено се означуваат како механизми CE, EC и EC′, соодветно. Теоретското студирање на овие процеси е од суштинско значење за разбирање на нивното електрохемиско однесување, но и за соодветна интерпретација на експерименталните волтаметриски податоци. И покрај големиот број на теоретски трудови достапни во литературата, слободно достапни компјутерски алатки за симулација на овие механизми во услови на циклична волтаметрија сè уште се ретки, а тоа ја ограничува нивната употреба како во истражувањето така и во наставата по електрохемија.

Во овој труд се дадени симулациски датотеки што се целосно подготвени за симулирање во циклична скалеста волтаметрија, а се развиени со помош на софтверскиот пакет Mathcad. Датотеките се наменети за симулирање на циклични волтамограми за дифузиските механизми CE, EC и EC′, добиени преку математичко моделирање на овие механизми во рамките на кинетичкиот формализам на Батлер–Волмер. Претставените протоколи во овој труд ги дефинираат и објаснуваат сите релевантни физички константи, параметрите на потенцијалниот сигнал, како и бездимензионалните кинетички и термодинамички параметри што се неопходни за дефинирање на рекурентни равенки за пресметка на струјата во циклична волтаметрија. Во протоколите се претставени и дијагностички критериуми за анализа на карактеристиките на цикличните волтамограми, што се неопходни да се изврши идентификација на специфични механизми преку симулираните волтаметриски одговори.

Фактот што овие симулациски датотеки се понудени во слободна форма ја прави симулациската платформа претставена во овој труд корисна алатка што на студентите и електрохемичарите може да им служи како интерактивно образовно помагало, додека за поискусните научници е вреден теоретски ресурс што е неопходен за разбирање и објаснување на електрохемиските експерименти. Овој едукативен труд ја доближува теоретската електрохемија до сите електрохемичари, овозможувајќи притоа подлабоко механистичко разбирање на некои од најважните електродни процеси во услови на циклична волтаметрија.

Клучни зборови: циклична волтаметрија; симулациска платформа Mathcad; електрохемиски механизми; едукативна електрохемија

1. INTRODUCTION

Cyclic voltammetry (CV) is a highly versatile electroanalytical technique, routinely employed across diverse disciplines including chemistry, physics, biology, and physiology.[1–5] Its capacity to probe redox processes with high resolution has established it as an indispensable method for elucidating the kinetics and thermodynamics of numerous electron transfer reactions.[1–3] Beyond its analytical capabilities, CV plays a fundamental role in identifying and characterizing various electrochemical mechanisms relevant to biochemical and chemical redox processes.[1,3,4] This step is crucial for interpreting reaction pathways and tailoring electrode processes to meet specific analytical or technological requirements.

In the redox transformations of many important classes of compounds, their electron transfer steps are almost inevitably coupled with preceding, subsequent, or regenerative chemical reactions. These coupled chemical reactions influence the characteristics of voltammetric responses, making theoretical modelling an essential component of every experimental investigation.[3–8] Understanding such complex electrochemical processes is particularly important in the study of redox-active biomolecules – including vitamins, redox enzymes, quinones, and hormones – as well as in the analysis of industrial and environmental redox systems.[1–5] Theoretical modelling of most common mechanisms in CV, CE (electrochemical reaction coupled with preceding chemical reaction), EC (electrochemical reaction coupled with a subsequent chemical reaction), and EC' (electrochemical reaction coupled with a regenerative chemical reaction), is regarded as a cornerstone, providing deep insight into how reaction kinetics, mass transport, and electron transfer rates interact to produce specific voltammetric patterns.[3,6–10]

Although a substantial body of literature exists on the theoretical treatment of various electrode mechanisms in cyclic voltammetry,[1–3,11] a notable gap remains: there are virtually no freely accessible computational platforms[8,10] that serve both educational and scientific purposes for modelling such processes. This limitation can hinder both newcomers – who require intuitive and interactive learning tools – and experienced experimentalists, who benefit from rapid and accurate simulation frameworks for designing and interpreting their experiments.

The aim of this work is to address this gap by providing open-access, ready-to-use Mathcad simulation files for CE, EC, and EC' mechanisms in cyclic voltammetry, freely available to the entire scientific community. By making these resources accessible, we aim to support the training of students and early-career researchers, enabling them to visualize and explore the complex dependencies of cyclic voltammetric responses on kinetic and thermodynamic parameters. For experienced experimentalists, such a platform will offer a rapid and reliable means of validating hypotheses, optimising experimental conditions and advancing the mechanistic understanding of electrochemical systems.

2. REACTION MECHANISMS CONSIDERED IN THE MATHCAD PROTOCOLS

The Mathcad simulation files provided in this work elaborate on three well-known electrode mechanisms[1,3,6–9] of a dissolved redox couple, which are considered under the Butler–Volmer kinetic formalism and assume semi-infinite diffusion to a stationary planar electrode. The underlying theoretical background required to derive the final solutions for simulating the voltammetric response is complex and beyond the scope of this communication. Briefly, it is based on rigorous mathematical solutions of differential equations that describe mass transfer phenomena at a planar electrode (i.e. linear diffusion model), incorporating the kinetic effects of the coupled chemical reactions in combination with the Butler–Volmer equation, which describes kinetic constraints at the electrode surface. The mathematical tools used, which go beyond conventional chemical education, include Laplace transforms, which provide rigorous mathematical solutions in the form of integral equations.[12] These equations are subsequently transformed into ready-to-use recurrent formulae for simulations by means of the numerical step-function method,[13,14] which is adopted for cyclic staircase voltammetry. These formulae form the core equations of the provided Mathcad files. Details of the mathematical modelling of the following electrode mechanisms are available in reference.[15]

The following electrode mechanisms are considered:

1. **CE mechanism** (electrode reaction (**E**), preceded by a homogeneous chemical reaction (**C**)):

$$\mathrm{Y} \rightleftarrows \mathrm{Red} \qquad (k_\mathrm{f},\ k_\mathrm{b},\ K_\mathrm{eq})$$

$$\mathrm{Red} - \mathrm{e}^- \rightleftarrows \mathrm{Ox} \qquad (k_\mathrm{s},\ \alpha)$$

2. **EC mechanism** (electrode reaction (E) followed by a homogeneous chemical (C) step):

$$\mathrm{Red} - \mathrm{e}^- \rightleftarrows \mathrm{Ox} \qquad (k_\mathrm{s},\ \alpha)$$

$$\mathrm{Ox} \rightleftarrows \mathrm{C} \qquad (k_\mathrm{f},\ k_\mathrm{b},\ K_\mathrm{eq})$$

3. **EC' mechanism** (electrochemical catalytic (EC') mechanism, or electrochemical regenerative mechanism):

$$\mathrm{Red} - \mathrm{e}^- \rightleftarrows \mathrm{Ox} \qquad (k_\mathrm{s},\ \alpha)$$

$$\mathrm{Ox} + \mathrm{Y} \rightarrow \mathrm{Red} \qquad (k_\mathrm{c})$$

In the CE mechanism, the preceding homogeneous chemical reaction Y ⇌ Red generates the electroactive species (Red), which enters into an electrode reaction during the voltammetric experiment. Accordingly, in the EC mechanism, the electrochemically generated Ox species undergoes a chemically reversible follow-up transformation to yield the final, electrochemically inactive product C. In the EC' catalytic mechanism, the electrochemically generated Ox species reacts with Y in a homogeneous irreversible chemical reaction that regenerats the initial electrochemically active Red species.

3. SOME BASIC DEFINITIONS IN CYCLIC STAIRCASE VOLTAMMETRY

In modern electrochemical instrumentation, where the core station is known as a potentiostat, the technique is no longer considered classical cyclic voltammetry with a linear scan,[1] but rather a *cyclic staircase voltammetry* technique.[2,3] In cyclic staircase voltammetry, the applied potential signal consists of a series of small, discrete potential steps that approximate a linear scan in both forward and reverse directions (Fig. 1). The key parameters that define this potential waveform include the height of the *potential step* (dE, i.e. the potential increment), the *step duration* (τ), and the *initial* and *switching potentials* (E_start and E_switch, respectively), which determine the potential range of the experiment.

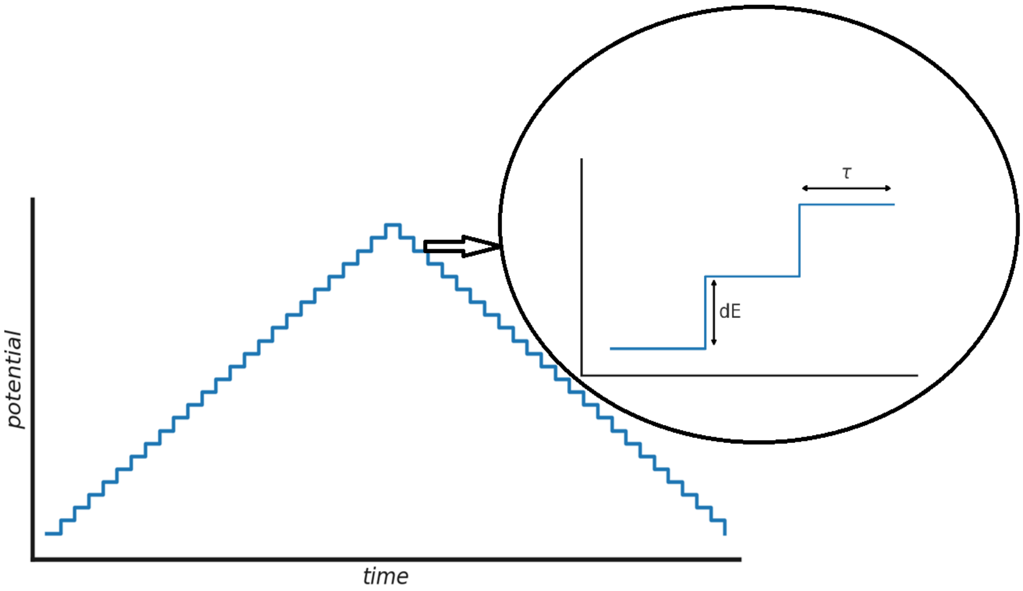

Fig. 1. Applied potential waveform in cyclic staircase voltammetry, with the insert showing the major parameters that define the potential ramp, i.e., the *potential step* (dE), and the *step duration* (τ)

The scan rate (v) is regarded as the most important parameter in cyclic staircase voltammetry, being defined as the ratio of the potential step height to the pulse duration (v = dE/τ), thus representing the average rate of potential change over time. The current in cyclic staircase voltammetry is measured within a specific time frame at the end of each potential step, in order to minimise the contribution of the charging and overall background current. The primary instrumental output of this technique is known as a *cyclic voltammogram*.

A cyclic voltammogram is typically displayed as a plot of current (I) versus applied potential (E) over a complete forward–reverse scan cycle. Commonly, the cyclic voltammogram exhibits a pair of well-defined peaks (Fig. 2) – an *oxidation peak* and *reduction peak* associated with positive current and negative current, respectively. In cyclic voltammetry, the primary descriptors derived from each voltammogram are the peak current, peak potential, peak-to-peak separation, and the mid-peak potential. The peak current (I_p) is defined as the maximum current (in absolute values) observed in each scan direction (measured relative to the baseline of the corresponding voltammetric curve) and is directly related to the concentration of the redox species, the scan rate, the electrode area, the diffusion coefficients, and the stoichiometric number of electrons involved in the electrode reaction.[1,3] The *peak potential* (E_p) is the magnitude of the applied potential at which the maximal current (in absolute value) is observed on a given peak of the cyclic voltammogram. The *peak-to-peak separation* (ΔE_p) is defined as the difference between the oxidation (anodic, $E_{p,ox}$) and reduction (cathodic, $E_{p,red}$) peak potentials:

$$\Delta E_p = E_{p,ox} - E_{p,red} \qquad (1)$$

In a Nernstian (thermodynamically reversible), one-electron, diffusional system (at 25 °C), ΔE_p is approximately 59 mV.[1–3]

The *mid-peak potential* ($E_{1/2}$) is regarded as a crucial thermodynamic descriptor of any electrode reaction in cyclic voltammetry, commonly defined as:

$$E_{1/2} = (E_{p,ox} + E_{p,red})/2 \qquad (2)$$

In thermodynamically reversible systems, $E_{1/2}$ closely approximates the formal potential ($E^{\ominus\prime}$) of the redox couple. Additional features such as the symmetry of the peak shapes, the ratio of oxidation to reduction peak currents $I_{p,ox}/I_{p,red}$ (note that $I_{p,ox}/I_{p,red}$ = 1 for all applied scan rates in Nernstian redox systems), together with the features of the baseline, provide further diagnostic information that can be derived from cyclic voltammograms. Deviations from the ideal values of ΔE_p, and $I_{p,ox}/I_{p,red} \neq 1$ indicate kinetic constraints, coupled chemical reactions, the presence of adsorption phenomena, or uncompensated resistance effects, and thus serve as important indicators for mechanistic and kinetic analysis.[1–3]

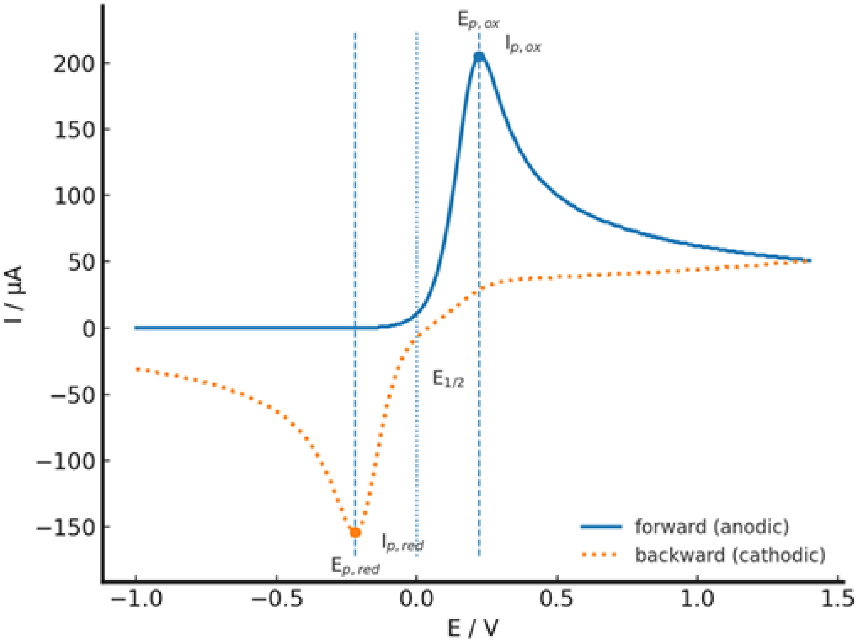

Fig. 2. Representative cyclic staircase voltammogram of a quasi-reversible electrode reaction

In systems that exhibit electrochemically reversible behaviour, the shape of the cyclic voltammogram is primarily governed by thermodynamic parameters such as the formal potential ($E^{\ominus\prime}$) of the redox couple, the stoichiometric number of electrons in the electrode reaction (n), and the mass transfer as reflected by the diffusion coefficients of the oxidized and reduced forms (D).[1] For systems described by the Butler–Volmer formalism (kinetically hindered heterogeneous electrode reaction, i.e. quasi-reversible electrode processes), the shape and form of the cyclic voltammograms additionally depend on electrode kinetic parameters such as the standard rate constant (k_s) and the electron transfer coefficient (α), as well as on mass transport parameters (D) and experimental parameters such as dE, τ, v, and temperature T.[2–4,6,10] These dependencies influence both the peak separation and the heights of the anodic and cathodic peaks, thus providing diagnostic criteria for mechanistic interpretation and kinetic analysis.

In the case of a CE mechanism studied under conditions of cyclic staircase voltammetry, the features of the voltammetric responses are predominantly governed by several key *dimensionless parameters*. The first is the *dimensionless electrode kinetic parameter* related to electron transfer, K, defined as $K = k_s\,(D)^{-0.5}\,(\tau)^{0.5}$, which unifies the influence of the heterogeneous electron transfer standard rate constant k_s and the common diffusion coefficient D, relative to the applied time window (τ) on each potential step. This parameter (K) reflects the interplay between charge-transfer kinetics and mass transport within the time frame of each applied potential step. The second controlling factor is the *dimensionless chemical kinetic parameter* K_{chem}, defined as $K_{chem} = (k_f + k_b)\,\tau$, where k_f and k_b are the forward and backward rate constants, respectively, of the homogeneous chemical reaction preceding the electron transfer. This kinetic parameter controls the rate of the chemical step relative to the time scale of each potential step. The thermodynamic aspect of this preceding chemical step is characterized by the third dimensionless parameter, i.e. the *equilibrium constant* defined as $K_{eq} = k_f / k_b$. The value of K_{eq} dictates the position of the chemical equilibrium and thus significantly affects the magnitude and position of the voltammetric peaks. Finally, the *electron transfer coefficient* α also plays a significant role, as it influences the symmetry and shape of the voltammetric profiles by modifying the activation barrier of the electron transfer step.

All of the above dimensionless parameters govern the characteristics of the cyclic staircase voltammetric patterns for an EC *mechanism* as well. In this case, the dimensionless electrode kinetic parameter K, dimensionless chemical kinetic parameter K_{chem}, and the equilibrium constant K_{eq} retain the same mathematical definitions as for the CE mechanism. Clearly, in the EC mechanism, K_{chem} and K_{eq} refer to the kinetics and thermodynamics of the *homogeneous follow-up chemical reaction* that occurs after the electron transfer step.

In the third mechanism considered in this work, denoted as the EC' or *electrochemical catalytic mechanism*, the electrochemically generated species Ox undergoes a chemically irreversible reaction with the substrate Y (which was present in large excess compared to the bulk concentration of the electroactive reactant Red), resulting in the regeneration of the initial redox reactant Red. Within this model, the chemical parameter is expressed as $K_{\mathrm{chem}} = k_c\ \tau$, where k_c denotes the rate constant of the irreversible (regenerative) chemical step, while the dimensionless kinetic parameter associated with electron transfer (K) was defined in the same manner as in the previously described mechanisms. In the following sections of this work, we explain all relevant parameters and procedures required for establishing a successful protocol to simulate cyclic voltammograms in the Mathcad software package.

4. DEFINING CRUCIAL ENTRIES IN MATHCAD FILE TO SIMULATE CYCLIC VOLTAMMOGRAMS

Simulations in voltammetry are typically carried out in the so-called dimensionless domain.[15,16] Thus, all entries in the Mathcad file have no units. In other words, they refer to the numerical value of a particular physical quantity represented in its respective units, which are provided in the Mathcad files. The protocol in a Mathcad simulation file begins by defining the parameters of the potential staircase ramp. Starting and switching potentials are expressed relative to the formal potential of the electrode reaction:

Es : = –0.5 (starting potential in V, relative to the formal potential);

Ef : = 0.5 (switch potential in V, relative to the formal potential, at which the direction of the potential reverses);

ΔE : = Ef – Es (potential window of the experiment);

dE : = 0.005 (potential step increment in V).

The potential scan rate v is the most important parameter in any cyclic voltammetric experiment. As previously mentioned, in cyclic staircase voltammetry it is related to the potential increment dE and the time duration of a single potential step τ, with $v = \mathrm{d}E/\tau$, allowing τ to be determined based on the chosen scan rate value and potential step increment.

In addition, for the purpose of the numerical calculation method, the time increment parameter was defined as $\mathrm{d} = \tau/\mathrm{M}$. The value of d represents the subdivision of a single potential step with duration τ into M time fractions. Typically, M = 25, which was sufficient for the numerical model to calculate the current with acceptable precision.[15] M was optionally increased to allow for longer simulation time.

Following the incrementing of time, the value of potential at any time increment with a serial number m (Em) is defined using "if" and "ceil" functionalities of Mathcad:[17]

$$E_m := \mathrm{if}\left[m \le \frac{\Delta E}{dE}\cdot 25, Es + \left(\mathrm{ceil}\left(\frac{m}{25}\right)\cdot dE - dE\right), Ef - \left[\mathrm{ceil}\left[\frac{m - \left(\frac{\Delta E}{dE}\cdot 25\right)}{25}\right]\cdot dE - dE\right]\right] \tag{3}$$

In addition, the values of the following physical constants are specified:

F : = 96485 (numerical value of the Faraday constant in C mol^{-1});

R : = 8.314 (numerical value of the universal gas constant in J mol^{-1} K^{-1});

n : = 1 (stoichiometric number of electrons involved in the electrode reaction);

T : = 298.15 (thermodynamic temperature in K);

D : = 5 × 10^{-6} (common diffusion coefficient for both redox species in cm^2 s^{-1});

***k*s** – standard rate constant of electron transfer in cm/s. This parameter is adjustable within a large range of values, typically from 10^{-4} to 10.

Based on these constants, the dimensionless potential corresponding to each time increment Φ_m is defined as:

$$\Phi_m := n\cdot\frac{F}{R\cdot T}\cdot E_m \tag{4}$$

The Mathcad files continue by defining the critical voltammetric dimensionless parameters, which govern the voltammetric features of each electrode mechanism, such as: the *dimensionless electrode kinetic parameter related to the electron transfer step*, $\mathrm{K} := \mathrm{k_s}\ (\tau)^{0.5}\ (\mathrm{D})^{-0.5}$ (applied to all three mechanisms); the *dimensionless chemical kinetic parameter* $\mathrm{K_{chem}} := (\mathrm{k_f} + \mathrm{k_b})\ \tau$ (applied to both CE and EC mechanisms); $\mathrm{K_{chem}} := (\mathrm{k_c})\ \tau$ (applied to EC' mechanism only); and the *equilibrium constant of the chemical reaction*, $K_{eq} := k_f / k_b$ (applied to the CE and EC mechanisms, in which reversible chemical reactions are assumed to occur).

The numerical method for deriving recurrent formulae for the simulation of the voltammetric response includes numerical integration parameters, which are defined as follows:[15]

$$S_m := \sqrt{m} - \sqrt{m-1} \tag{5}$$

$$M_m := \mathrm{erf}\left(\sqrt{\mathrm{Kchem}\cdot\frac{m}{25}}\right) - \mathrm{erf}\left[\sqrt{\mathrm{Kchem}\cdot\frac{(m-1)}{25}}\right] \tag{6}$$

These numerical integration parameters are functions that account for diffusion memory (Eq. 5) and for the effect of chemical kinetics (Eq. 6) in the recurrent formulae used for the calculation of currents in cyclic staircase voltammetry.[15] They come from discretising the specific, so-called convolutive integrals into stepwise sums.[15] It was important to underscore that in the simple electrode reaction (without coupled chemical reaction), only the parameter S (Eq. 5) matters; while in EC, CE and EC' catalytic electrode mechanisms, the M parameter was critical, as it accounts for the effect of the chemical rate parameter K_{chem}. These parameters form the backbone of the numerical integration scheme.

The recurrent formulae (Eqs. 7 and 8 in the provided Mathcad Supplementary files) are step-by-step recursive relations: each current value Ψ_m (Eq. 8 in the provided Mathcad Supplementary files), corresponding to a particular serial number of the time increment, depends on the values that precede it. The very first current value Ψ_1 (Eq. 7) gives the current at the very first potential step. In numerical simulations, this serves as the "initial condition" that anchors the iterative process. These defined values then enter the summations and recurrence expressions, making the calculation of Ψ_m mathematically feasible.

Once the currents Ψ_m are calculated using the corresponding recurrent formulas, the currents at specific points within each potential step – typically the last or 25th point – are extracted in order to construct the cyclic staircase voltammogram. For this operation, the serial number of potential steps *p* across the entire scan interval is required (Eq. 9 in the Mathcad Supplementary files). Then, the extraction of the last current point from each potential step is performed by means of Eq. 10. Finally, Eq. 11 in Mathcad Supplementary Files defined the potential values of each potential step, against which the currents of the cyclic staircase voltammogram are plotted, as shown in the graph below Eq. 11 in the Mathcad files.

Once the value of the dimensionless current function Ψ_m in each time increment is calculated, the real current is determined by considering the following relation: $I = \Psi A$, where *A* is the so-called amperometric constant. The value of the amperometric constant depends on particular experimental conditions: $A = nFSc^*(D/\tau)^{0.5}$, where *S* was the working electrode surface area and c^* was the bulk concentration of the initially present electroactive reactant Red (other parameters retain the same meaning as explained above).

Finally, graphs of the calculated cyclic voltammogram (Fig. 3) are generated in Mathcad, displaying characteristic features for each of the considered mechanisms.

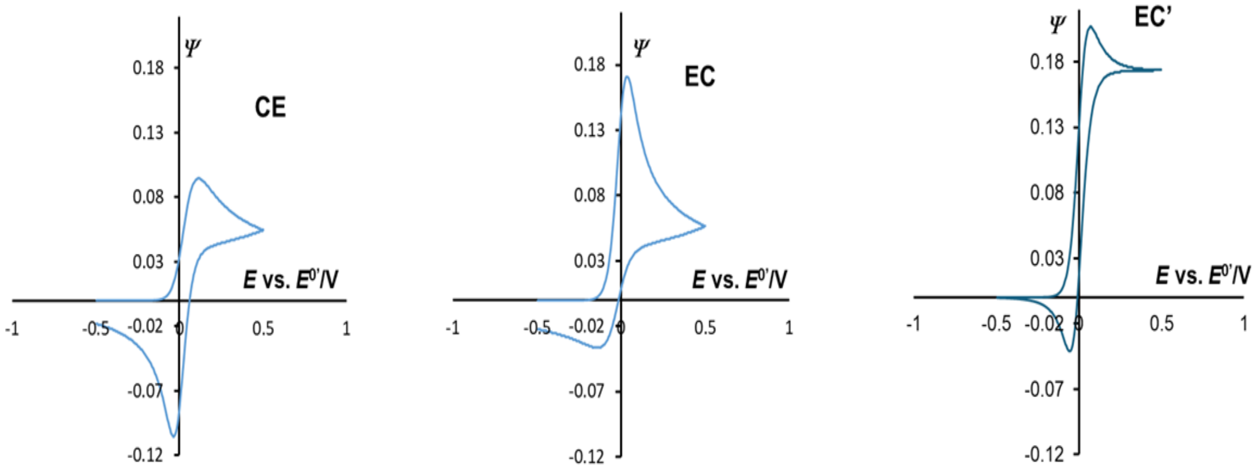

Fig. 3. Representative patterns of dimensionless cyclic staircase voltammograms simulated on the Mathcad platform for quasi-reversible CE, EC, and EC' mechanisms. In all cases, the simulated voltammograms feature the effect of the chemical reaction rate.

5. CONCLUSIONS AND PRACTICAL NOTES ON PERFORMING SIMULATIONS OF CYCLIC STAIRCASE VOLTAMMETRY IN MATHCAD

Once all relevant parameters outlined above are specified in the Mathcad working sheet, the potential ramp is constructed according to the staircase waveform, and the recurrent formulas for calculating the dimensionless currents are established, the file is prepared for initiating simulations. For any given electrode mechanism – whether coupled to a preceding, follow-up, or regenerative chemical reaction – the simulation is configured so that only one parameter of interest (e.g., the standard rate constant k_s, the chemical rate constant k_f, the electron transfer coefficient α, etc.) is varied, while all other parameters remained constant. This approach enables clear attribution of observed changes in the voltammetric response to the chosen variable. This method ensures that variations in the voltammograms arise solely from the intended parameter change, thereby providing robust mechanistic insights into the role of the chemical or electrochemical step under study.

One must not overlook the difference between the dimensionless current function Ψ and the real current I, and the relation between them ($I = \Psi nFSc^*(D/\tau)^{0.5}$). Although theoretical simulations focus on the features of the dimensionless function Ψ, only the real current I was directly comparable to the experimentally measured current. It is essential to emphasise that the time parameter τ, determined by the selected values of the scan rate v and the step potential increment dE, simultaneously influences the dimensionless current function Ψ (through the dimensionless kinetic parameters K and K_{chem}), and additionally affects the real current through the relation $I = \Psi nFSc^*(D/\tau)^{0.5}$.

When the simulations are performed by varying the values of a particular rate constant (e.g. the standard rate constant) for a given value of the scan rate, the outcome corresponds to the comparison of a series of different electrode reactions characterized by different standard rate constants. Conversely, if simulations are carried out by varying the scan rate for a given set of kinetic parameters, the outcome corresponds to the analysis of a single electrode reaction under varying scan rate.

Both types of simulations are unified by studying the effect of a particular dimensionless kinetic parameter (e.g. $K = k_s(\tau/D)^{0.5}$), whose values are varied either by changing the rate constant or the scan rate (i.e. τ). That effect was why such dimensionless kinetic parameters are critically important for understanding complex voltammetric behaviour, which is influenced by different sources.

In comparing simulated and experimental data, two approaches are possible: following calculation of the dimensionless function Ψ, the real current I is calculated and compared with the experiment; alternatively, the experimentally measured current is transformed into the dimensionless current, by means of the relation $I = \Psi nFSc^*(D/\tau)^{0.5}$.

In the analysis of simulated cyclic voltammograms, attention is directed to the positions of the anodic and cathodic peaks along the potential axis, the peak-to-peak separation, the magnitudes of the anodic and cathodic peak currents, the ratio of anodic to cathodic peak currents, and the overall shape and symmetry of the peaks, as well as the features of the baseline currents beyond the peak regions. These parameters collectively provide insight into whether the process was electrochemically reversible, quasi-reversible, or involves an electron transfer step coupled to a preceding, regenerative, or follow-up chemical reaction.

For any further enquiries or difficulties experienced during the simulations, readers are encouraged to contact the authors for assistance. The simulations require Mathcad version 14 or higher, and a 30-day free trial of Mathcad 15 is available at:
https://support.ptc.com/products/Mathcad/Mathcad-15-0/free-trial?refid=cadventure

In addition, the guide for users of Mathcad 15 is available for free download at:
https://lmal.zut.edu.pl/fileadmin/Wyklady_i_cwiczenia/techniki_komputerowe/Materialy/Literatura/Mathcad%20Users%20Guide%2015.pdf.[17]

A practical framework for simulations of voltammetric theories in Mathcad is also presented in references[15,16] in the Supplementary material, we provide three original Mathcad files (in free open-access format) configured to simulate CE, EC and EC' mechanisms in cyclic staircase voltammetry.

Acknowledgment: RG gratefully acknowledges the Goce Delčev University, Štip, N. Macedonia, for continued support. RG and VM jointly acknowledge the Alexander von Humboldt Foundation (Germany) for support through the Research Group Linkage Project (Ref 3.4 - 1070534 - MKD – IP).

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