Defining all relevant parameters in MATHCAD protocol that are needed to simulate cyclic voltammograms

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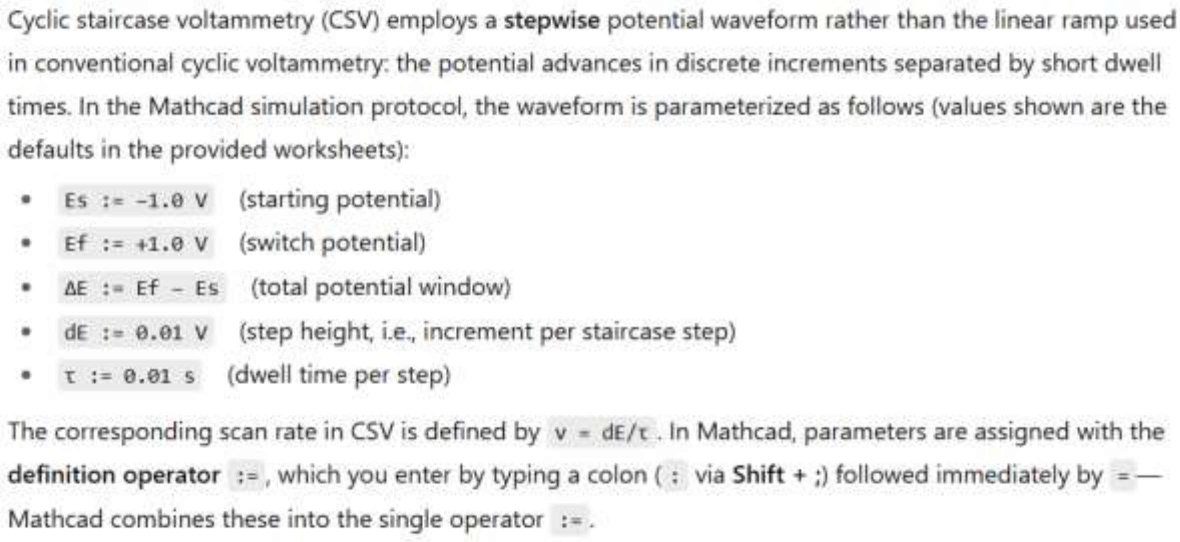
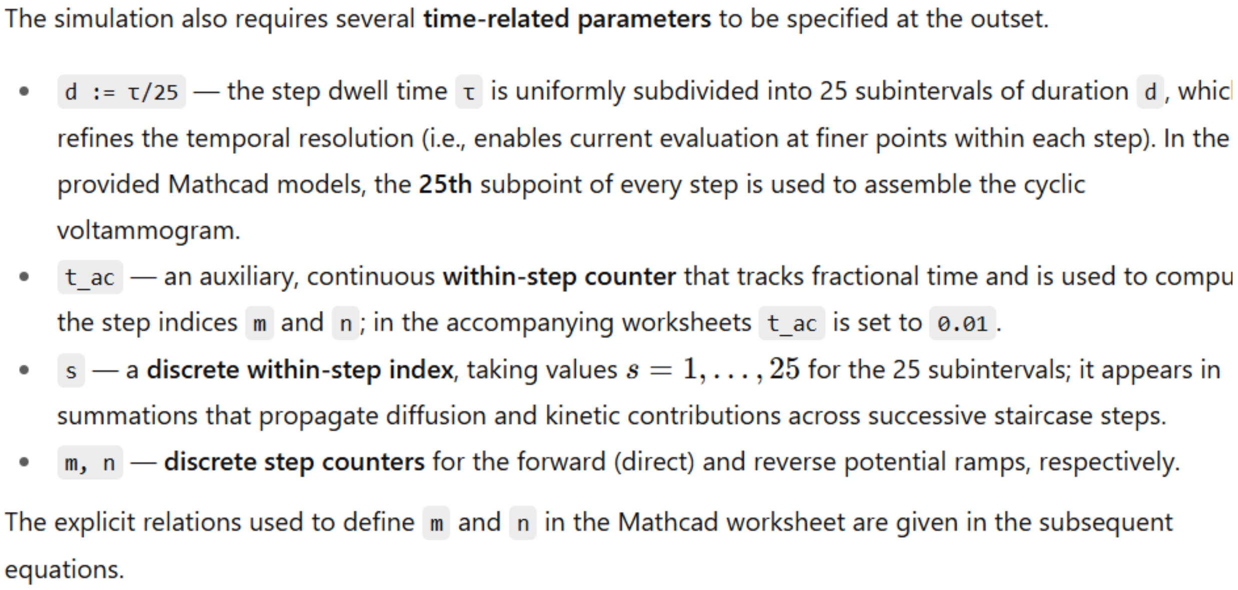


Cyclic staircase voltammetry (CSV) employs a **stepwise** potential waveform rather than the linear ramp used in conventional cyclic voltammetry: the potential advances in discrete increments separated by short dwell times. In the Mathcad simulation protocol, the waveform is parameterized as follows (values shown are the defaults in the provided worksheets):

- `Es := −1.0 V` (starting potential)
- `Ef := +1.0 V` (switch potential)
- `ΔE := Ef − Es` (total potential window)
- `dE := 0.01 V` (step height, i.e., increment per staircase step)
- `τ := 0.01 s` (dwell time per step)

The corresponding scan rate in CSV is defined by `v = dE/τ`. In Mathcad, parameters are assigned with the **definition operator** `:=`, which you enter by typing a colon (`:` via **Shift** + ;) followed immediately by `=`— Mathcad combines these into the single operator `:=`.

a) Defining the time indexing parameters



The simulation also requires several **time-related parameters** to be specified at the outset.

- `d := τ/25` — the step dwell time `τ` is uniformly subdivided into 25 subintervals of duration `d`, whic refines the temporal resolution (i.e., enables current evaluation at finer points within each step). In the provided Mathcad models, the **25th** subpoint of every step is used to assemble the cyclic voltammogram.
- `t_ac` — an auxiliary, continuous **within-step counter** that tracks fractional time and is used to compu the step indices `m` and `n`; in the accompanying worksheets `t_ac` is set to `0.01`.
- `s` — a **discrete within-step index**, taking values $s = 1, \ldots, 25$ for the 25 subintervals; it appears in summations that propagate diffusion and kinetic contributions across successive staircase steps.
- `m, n` — **discrete step counters** for the forward (direct) and reverse potential ramps, respectively.

The explicit relations used to define `m` and `n` in the Mathcad worksheet are given in the subsequent equations.

$$s := 1 .. \frac{tac}{d}$$

Equations for defining of **m** and **n** parameters in the MATHCAD file are as follows:

$$m := \frac{tac}{d} + 1 .. \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} \qquad (3)$$

$$n := \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} + 1 .. \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{tac}{d} \right) \qquad (4)$$

b) *Definition of the parameters of potential ramps*

The potential at given step **m** (**Em**) is defined as:

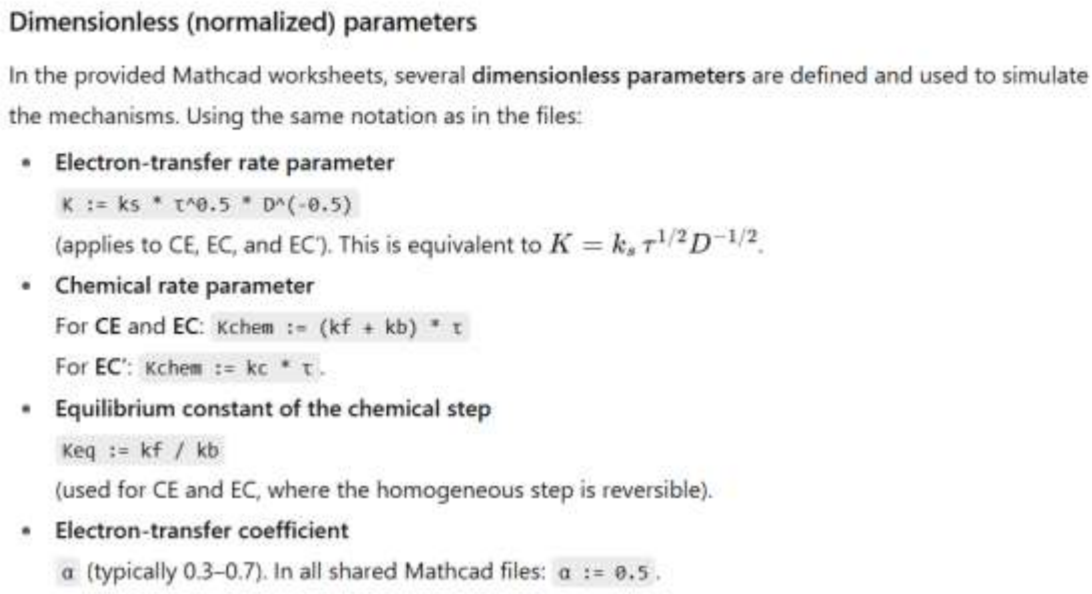
$$E_m := Es + \left(\mathrm{ceil}\left(\frac{m - \frac{tac}{d}}{25} \right) \cdot dE - dE \right) \qquad (5)$$

This equation applies during the *forward scan*.

For the *reverse scan*, the potential at given step **n** (**En**) is defined as:

$$E_n := Ef - \left[\mathrm{ceil}\left[\frac{n - \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} \right)}{25} \right] \cdot dE - dE \right] \qquad (6)$$

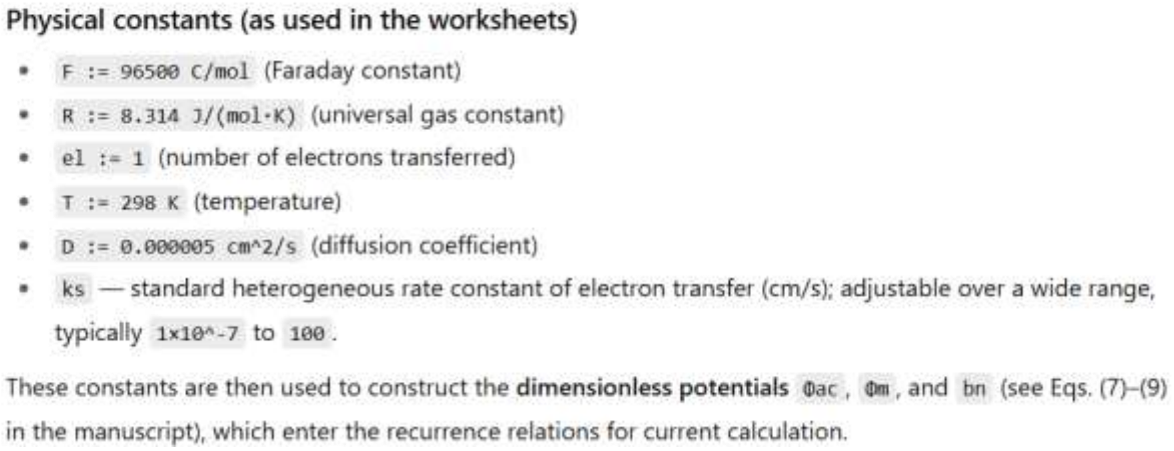
d) *Definition of dimensionless parameters related to electrode reaction and the coupled chemical reactions*



Dimensionless (normalized) parameters

In the provided Mathcad worksheets, several **dimensionless parameters** are defined and used to simulate the mechanisms. Using the same notation as in the files:

- **Electron-transfer rate parameter**
  `K := ks * τ^0.5 * D^(-0.5)`
  (applies to CE, EC, and EC′). This is equivalent to $K = k_s \tau^{1/2} D^{-1/2}$.
- **Chemical rate parameter**
  For **CE** and **EC**: `Kchem := (kf + kb) * τ`
  For **EC′**: `Kchem := kc * τ`.
- **Equilibrium constant of the chemical step**
  `Keq := kf / kb`
  (used for CE and EC, where the homogeneous step is reversible).
- **Electron-transfer coefficient**
  `α` (typically 0.3–0.7). In all shared Mathcad files: `α := 0.5`.



Physical constants (as used in the worksheets)

- `F := 96500 C/mol` (Faraday constant)
- `R := 8.314 J/(mol·K)` (universal gas constant)
- `el := 1` (number of electrons transferred)
- `T := 298 K` (temperature)
- `D := 0.000005 cm^2/s` (diffusion coefficient)
- `ks` — standard heterogeneous rate constant of electron transfer (cm/s); adjustable over a wide range, typically `1x10^-7` to `100`.

These constants are then used to construct the **dimensionless potentials** `Φac`, `Φm`, and `bn` (see Eqs. (7)–(9) in the manuscript), which enter the recurrence relations for current calculation.

$$\Phi ac := el \cdot \frac{F}{R \cdot T} \cdot Es \qquad (7)$$

$$\Phi_m := el \cdot \frac{F}{R \cdot T} \cdot \left(E_m\right) \qquad (8)$$

$$b_n := el \cdot \frac{F}{R \cdot T} \cdot \left(E_n\right) \qquad (9)$$

Parameter **k** defined as $k := 1 .. 2 \cdot \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d}\right)$ is the discrete index for simulation of cyclic staircase voltammograms. It spans all potential steps (forward and reverse) and includes sub-divisions inside each step, while ensuring fine resolution of the potential waveform and current response. This parameter (**k**) is needed for the definition of numerical integration parameters $S1_k$ and S_k that are defined as follows:

$$S1_k := \sqrt{k} - \sqrt{k - 1} \qquad (10)$$

$$S_k := \mathrm{erf}\left[\left(Kchem \cdot \frac{k}{25}\right)^{0.5}\right] - \mathrm{erf}\left[\left[Kchem \cdot \frac{(k - 1)}{25}\right]^{0.5}\right] \qquad (11)$$

These parameters are the backbone of the numerical integration scheme. They translate continuous diffusion-reaction integrals into discrete, computable sums, thus ensuring that the recurrent current formulas in cyclic voltammetry simulations remain accurate and physically meaningful.

f) *Definition of recurrent formulas needed to calculate dimensionless currents*

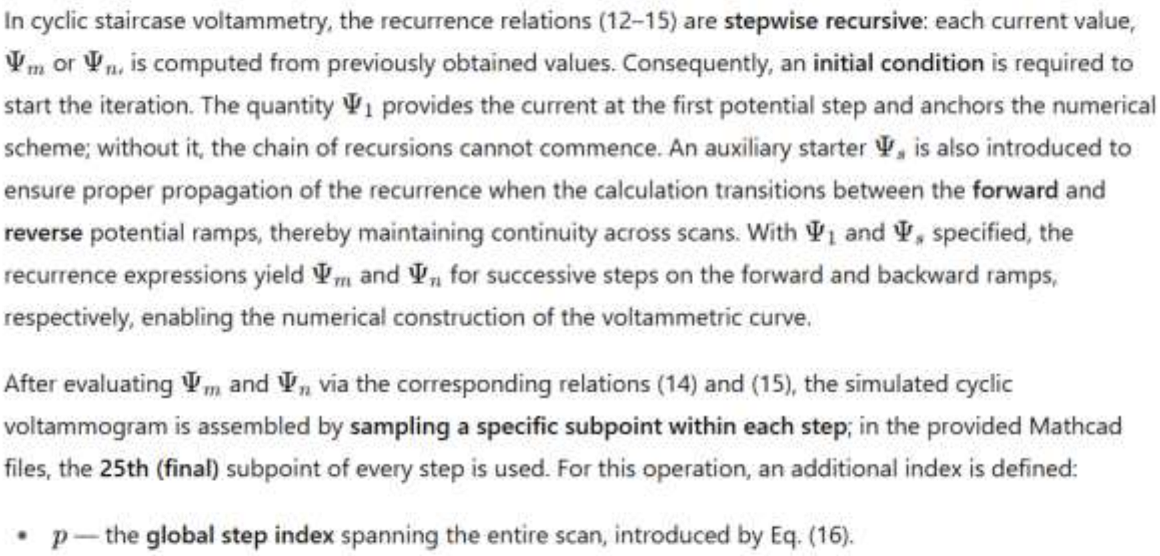
Once the above parameters have been specified in the worksheet, the Mathcad simulation proceeds to define the **recurrence relations** used to compute the currents at each increment of the staircase potential. For illustration, in the **CE mechanism** the calculation employs the set of recurrence relations given in **Eqs. (12–15)**, exactly as implemented in the original Mathcad worksheet.

$$\Psi_1 := \frac{K\cdot e^{\alpha\cdot\Phi_1}\cdot\left[\frac{Keq}{1+Keq}-\frac{2\cdot e^{-\alpha\cdot\Phi_1}}{\sqrt{25\cdot\pi}}\cdot 0-1\cdot\left(\frac{Keq}{1+Keq}\right)\cdot\left[\frac{2}{(25\cdot\pi)^{0.5}}\right]\cdot 0-1\cdot\frac{1}{\sqrt{Kchem}}\cdot\frac{1}{(Keq+1)}\cdot 0\right]}{1-K\cdot e^{\alpha\cdot\Phi_1}\left[\left(\frac{Keq}{1+Keq}\right)\cdot 1-0-0\right]} \tag{12}$$

$$\Psi_s := \frac{K\cdot e^{\alpha\cdot\Phi ac}\cdot\left[\frac{Keq}{1+Keq}\cdot\left[1-\frac{2}{(25\cdot\pi)^{0.5}}\cdot\sum_{j=1}^{s-1}\left(\Psi_j\cdot S1_{s-j+1}\right)\right]+1\cdot\frac{1}{\left(\sqrt{Kchem}\right)}\cdot\frac{1}{(Keq+1)}\cdot\sum_{j=1}^{s-1}\left(\Psi_j\cdot S_{s-j+1}\right)-\frac{2\cdot e^{-\Phi ac}}{(25\cdot\pi)^{0.5}}\cdot\sum_{j=1}^{s-1}\left(\Psi_j\cdot S1_{s-j+1}\right)\right]}{1-K\cdot e^{\alpha\cdot\Phi ac}\left[\frac{-2\cdot Keq\cdot S1_1}{(25\cdot\pi)^{0.5}\cdot(1+Keq)}+\frac{S_1}{\sqrt{Kchem}\cdot(1+Keq)}-\frac{2\cdot e^{-\Phi ac}\cdot S1_1}{(25\cdot\pi)^{0.5}}\right]} \tag{13}$$

$$\Psi_m := \frac{K\cdot e^{\alpha\cdot\Phi_m}\cdot\left[\frac{Keq}{1+Keq}\cdot\left[1-\frac{2}{(25\cdot\pi)^{0.5}}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot S1_{m-j+1}\right)\right]+1\cdot\frac{1}{\left(\sqrt{Kchem}\right)}\cdot\frac{1}{(Keq+1)}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot S_{m-j+1}\right)-\frac{2\cdot e^{-\Phi_m}}{(25\cdot\pi)^{0.5}}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot S1_{m-j+1}\right)\right]}{1-K\cdot e^{\alpha\cdot\Phi_m}\left[\frac{-2\cdot Keq\cdot S1_1}{(25\cdot\pi)^{0.5}\cdot(1+Keq)}+\frac{S_1}{\sqrt{Kchem}\cdot(1+Keq)}-\frac{2\cdot e^{-\Phi_m}\cdot S1_1}{(25\cdot\pi)^{0.5}}\right]} \tag{14}$$

$$\Psi_n := \frac{K\cdot e^{\alpha\cdot\Phi_n}\cdot\left[\frac{Keq}{1+Keq}\cdot\left[1-\frac{2}{(25\cdot\pi)^{0.5}}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot S1_{n-j+1}\right)\right]+1\cdot\frac{1}{\left(\sqrt{Kchem}\right)}\cdot\frac{1}{(Keq+1)}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot S_{n-j+1}\right)-\frac{2\cdot e^{-\Phi_n}}{(25\cdot\pi)^{0.5}}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot S1_{n-j+1}\right)\right]}{1-K\cdot e^{\alpha\cdot\Phi_n}\left[\frac{-2\cdot Keq\cdot S1_1}{(25\cdot\pi)^{0.5}\cdot(1+Keq)}+\frac{S_1}{\sqrt{Kchem}\cdot(1+Keq)}-\frac{2\cdot e^{-1\cdot\Phi_n}\cdot S1_1}{(25\cdot\pi)^{0.5}}\right]} \tag{15}$$

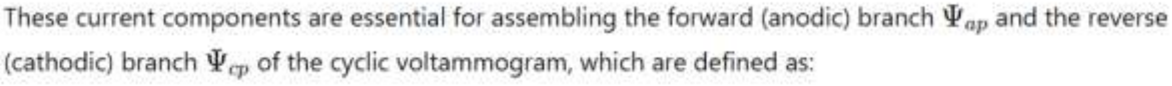


In cyclic staircase voltammetry, the recurrence relations (12–15) are **stepwise recursive**: each current value, Ψ_m or Ψ_n, is computed from previously obtained values. Consequently, an **initial condition** is required to start the iteration. The quantity Ψ_1 provides the current at the first potential step and anchors the numerical scheme; without it, the chain of recursions cannot commence. An auxiliary starter Ψ_s is also introduced to ensure proper propagation of the recurrence when the calculation transitions between the **forward** and **reverse** potential ramps, thereby maintaining continuity across scans. With Ψ_1 and Ψ_s specified, the recurrence expressions yield Ψ_m and Ψ_n for successive steps on the forward and backward ramps, respectively, enabling the numerical construction of the voltammetric curve.

After evaluating Ψ_m and Ψ_n via the corresponding relations (14) and (15), the simulated cyclic voltammogram is assembled by **sampling a specific subpoint within each step**; in the provided Mathcad files, the **25th (final)** subpoint of every step is used. For this operation, an additional index is defined:

- p — the **global step index** spanning the entire scan, introduced by Eq. (16).

$$p := 1 .. \frac{\Delta E}{dE} \qquad (16)$$



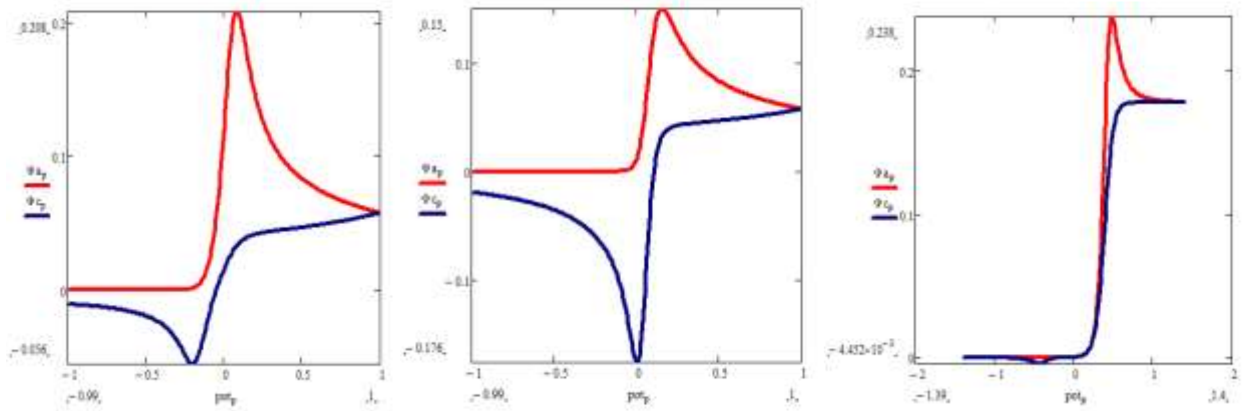
These current components are essential for assembling the forward (anodic) branch Ψ_{ap} and the reverse (cathodic) branch Ψ_{cp} of the cyclic voltammogram, which are defined as:

$$\Psi a_p := (\Psi)_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25} \qquad (17)$$

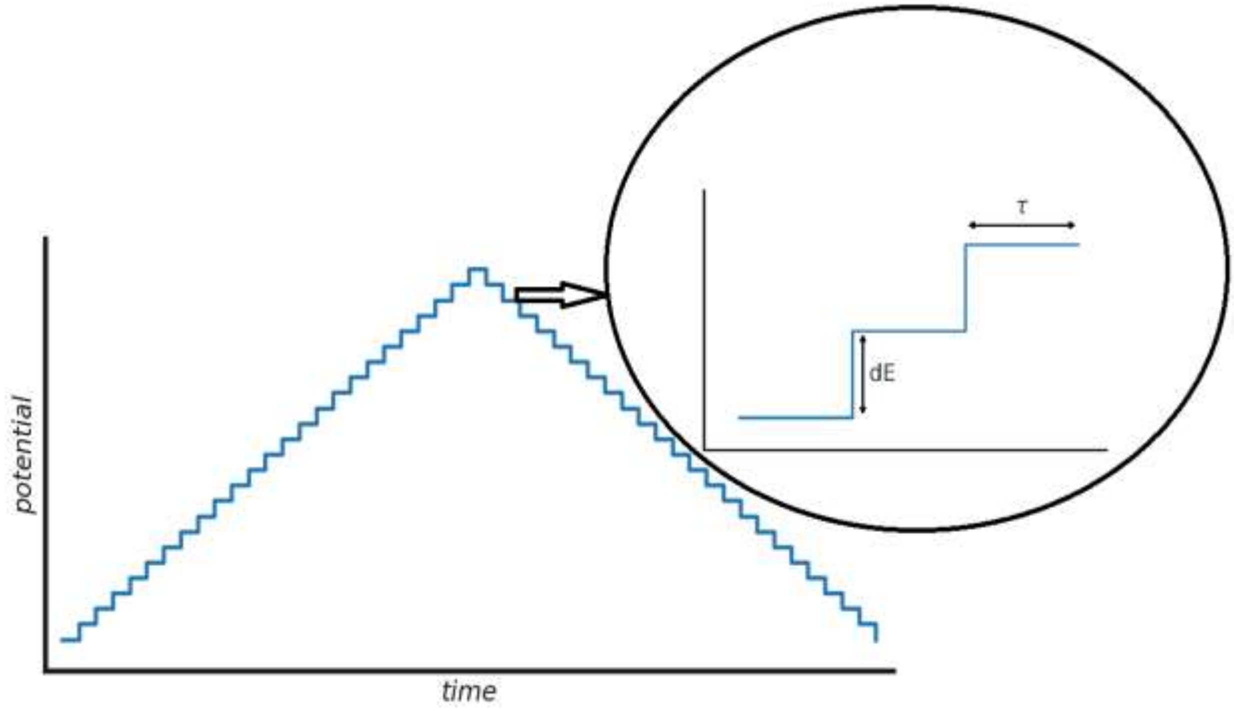
$$\Psi c_p := (\Psi)_{\left[\left[\frac{\Delta E}{dE}\cdot 2+\left(\frac{\tau}{25\cdot d}\right)\right]-p\right]\cdot 25} \qquad (18)$$

These current components (**Ψa_p** and **Ψc_p**) plotted *vs* **potential** (**pot_p**), that has a form (19):

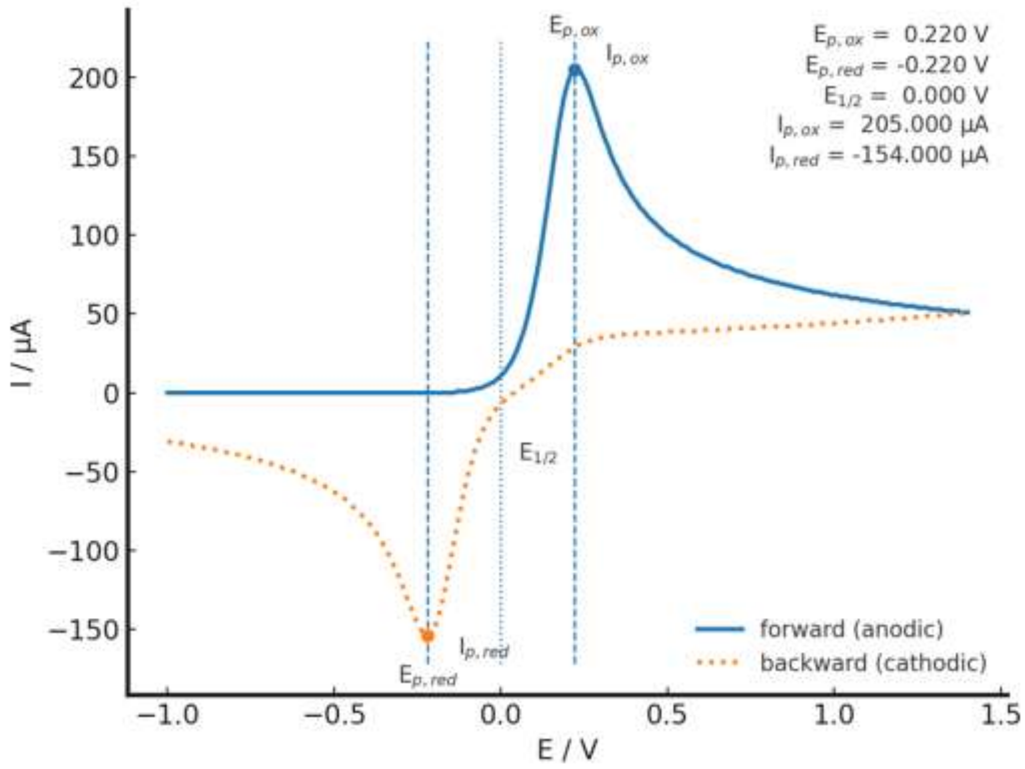
$$pot_p := Es + p\cdot dE \qquad (19)$$



Cyclic voltammograms simulated in MATHCAD platform for EC mechanism (left), CE mechanism (middle), and EC’ catalytic mechanism (right).



Potential ramps in Cyclic Staircase Voltammetry



Characteristic parameters of a cyclic voltammogram

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