

BASIC DISCRETISATION TECHNIQUES USED IN CYCLIC VOLTAMMETRY NUMERICAL SIMULATIONS. COMPARISONS AND PRACTICAL ASPECTS

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The numerical methods studied in this paper are explicit discretisation, Laasonen implicit discretisation, Crank-Nicolson semi-implicit discretisation. Both equal and unequal discretisation steps are considered. A classical approach of discretisation techniques, the Box Method proposed by Feldberg, is also considered. The simulated data are validated through comparison with experimental data taken using the $\text{Co}(\text{bipyridin})_3^{2+}/\text{Co}(\text{bipyridin})_3^{3+}$ couple. The software package used for simulation is available for free use at (<http://cycsim.chfiz.pub.ro>).

INTRODUCTION

There are numerous studies over digital simulation techniques for cyclic voltammetry experiments, and the literature devoted to this subject is vast.¹ The simplest method is the explicit discretisation of space in equal intervals.² The more advanced implicit discretisation techniques are mainly the Laasonen³ and Crank-Nicolson⁴ ones. A very good review on numerical methods used in electrochemistry is due to Josplin and Pletcher.⁵ Feldberg later proposed a different approach which involves the discretisation of fluxes rather than space discretisation.⁶ This technique was further improved by Rudolph.⁷

EXPERIMENTAL

The software package DraguSim is written in C++. The executable is run on a Pentium 4 3.2GHz machine, with 512 MB of RAM.

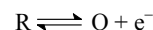
The redox couple used for checking the simulations was $\text{Co}(\text{bipyridin})_3^{2+}/\text{Co}(\text{bipyridin})_3^{3+}$, because of its simple outer-sphere kinetic, without complications due to adsorption, being also a moderately fast reaction⁸, which allows further study of the electrode kinetics using the developed simulation package. $\text{Co}(\text{bpy})_3^{2+}$ was obtained according to ref.⁹ The CVs were measured using a classical three-electrode cell, using as a reference electrode a 3M KCl Ag/AgCl and a thick Pt wire as counterelectrode, with the solution purged with high-purity argon for 15 minutes prior to each set of experiments (during the experiment the solution was kept under an argon blanket).

The working electrode was a platinum disk, which was carefully cleaned before each set of measurement using emery paper (grit 1000, 2000 and 4000, followed by 0.2 μm alumina) and then cycled in 1M H_2SO_4 (50-75 cycles at 200 mV/s between the onsets of hydrogen and oxygen evolution potentials)¹⁰. The surface was considered to be clean enough when the hydrogen adsorption-desorption peaks were clearly visible on the reduction scan (see Figure 1). For each CV, a "background run" was also performed, running a CV scan in pure 1M KCl and using exactly the same experimental setup.

Simulation data for the oxidation of $\text{Co}(\text{bpy})_3^{2+}$ are: start potential, $E_i = -0,15$ V; switch potential, $E_s = 0,3$ V; surface area, $A = 0,00265$ cm^2 ; temperature, $T = 303$ K; formal potential, $E^{0'} = 0,086$ V; standard rate constant, $k^0 = 0,02$ cm/s; transfer coefficient, $\alpha=0,4$; initial concentration of the oxidized species $c_O = 0,35$ mM; diffusion coefficient of the oxidized species $D_O = 1,45 \times 10^{-6}$ cm^2/s ; initial concentration of the reduced species, $c_R = 4,45$ mM; diffusion coefficient of the reduced species $D_R = 1,65 \times 10^{-6}$ cm^2/s . Note that c_O is not exactly equal to zero, since a small amount of $\text{Co}(\text{bpy})_3^{2+}$ is oxidized by the oxygen present in solution when the solution was prepared.

Model:

The electrode reaction is assumed to be a simple one, with no adsorption involved:



where for our system $\text{R} = \text{Co}(\text{bpy})_3^{2+}$ and $\text{O} = \text{Co}(\text{bpy})_3^{3+}$. For a cyclic voltammetry experiment one can write:

$$E(t) = E_i - v \cdot t;$$
$$\frac{c_O(0,t)}{c_R(0,t)} = f(t) = \exp\left[\frac{z \cdot F}{R \cdot T} \cdot (E_i - v \cdot t - E^{0'})\right];$$

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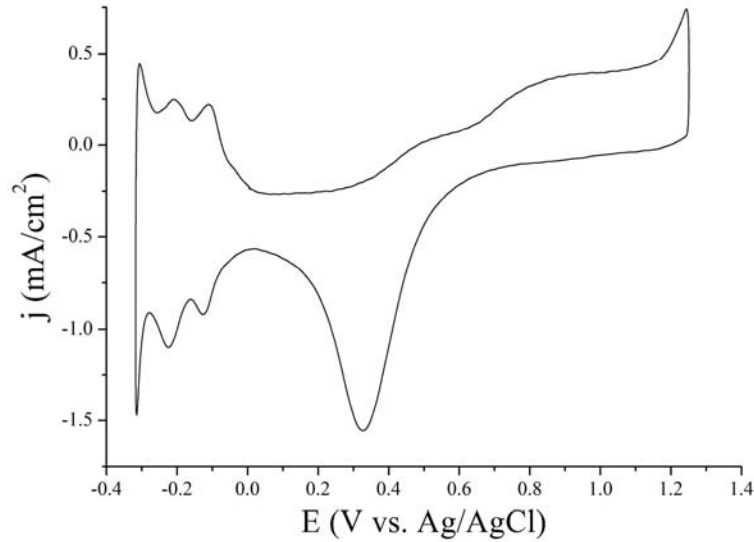


Fig. 1 – Characteristic voltammogram for a clean platinum electrode.

The differential equation system (unidimensional) for a plane electrode (with the electrode at $x = 0$):
 a voltammetric experiment with diffusion control of transport at

$$\left\{ \begin{array}{l} \frac{\partial c_O}{\partial t} = D_O \cdot \frac{\partial^2 c_O}{\partial x^2}; \quad J_O = -D_O \cdot \frac{\partial c_O}{\partial x} \\ \frac{\partial c_R}{\partial t} = D_R \cdot \frac{\partial^2 c_R}{\partial x^2}; \quad J_R = -D_R \cdot \frac{\partial c_R}{\partial x}; \\ J_O(0, t) = -J_R(0, t); \\ J_O(0, t) = k_1 \cdot c_O(0, t) - k_2 \cdot c_R(0, t); \\ k_1 = k^0 \cdot \exp\left(-\alpha \cdot \frac{F \cdot z}{R \cdot T} \cdot (E(t) - E^{0'})\right); \\ k_2 = k^0 \cdot \exp\left((1 - \alpha) \cdot \frac{F \cdot z}{R \cdot T} \cdot (E(t) - E^{0'})\right); \end{array} \right. \quad (1)$$

Initial condition:

$$c(x, t_0) = c^*, x \in [0, \infty);$$

The boundary condition at infinite distance from the electrode:

$$c(\infty, t) = c^*;$$

Abbreviations:

D_O – diffusion coefficient for O;

D_R – diffusion coefficient for R;

J_O – flux for O;

J_R – flux for R;

k^0 – rate constant;

α – transfer coefficient;

F – Faraday constant;

R – ideal gas constant;

z – number of electrons transferred;

T – temperature;

$E^{0'}$ – formal potential;

I – the electrical current, $I = nFAJ_O$.

Mathematical aspects:

In order to solve the differential equations described above, the most common approach is the discretisation of time and space.

Usually, the for the space discretisation, the length of the diffusion-limiting region is used, which is given by the general

relation: $X = 6 \cdot \sqrt{T_m \cdot D}$; where T_m is the duration of experiment and D is diffusion coefficient^{1, 2, 5, 6, 7}. Through discretisation this length is split into N discrete intervals, the distance x_k ($k = 1, 2, \dots, N$) being the distance from the electrode ($x_0 = 0$) to point k . For equally spaced grid-points, the distance between two consecutive points is $h = x_k - x_{k-1}$; $k = 1, 2, \dots, N$. For the unequally spaced grid-points, a growing exponential grid was chosen, with the minimum distance $h = x_1 - x_0$ and the distance between two consecutive points, $h_k = x_k - x_{k-1} = h_1 \cdot \exp((k-1)\beta)$; where $k = 2, \dots, N$, and β is a positive arbitrary constant. Obviously for $\beta \rightarrow 0$ the grid points will be equally spaced.

Accordingly we have $x_k = \sum_{i=1}^k h_i = h_1 \cdot \frac{\exp(k \cdot \beta) - 1}{\exp(\beta) - 1}$.

Time discretisation is made through N_p equal intervals, each one has the length Δt .

An important constant in the description of discretisation techniques is MDC (Model Diffusion Coefficient)^{1, 2, 5, 6, 7}, and from this one we define an expression for an easier description of the unequal space grid relations $E(k)$.

$$MDC = \frac{D \cdot \Delta t}{h^2}; \quad E_k = 2 \cdot MDC \cdot \frac{\exp(\beta)}{\exp(\beta) + 1} \cdot \frac{1}{(\exp(k \cdot \beta))^2};$$

The Box Method^{6,7} substitutes space discretisation with flux discretisation, the space being split in discrete volumes as follows:

$$J(x, t) = -D \cdot \frac{\partial c(x, t)}{\partial x}; \quad J_k = -D \cdot \frac{c_{k+1} - c_k}{\bar{x}_{k+1} - \bar{x}_k};$$

$$\bar{x}_k = h_1 \cdot \frac{\exp(\beta \cdot (k - 1/2)) - 1}{\exp(\beta) - 1} = \text{nod in the middle of volume } k;$$

$$\bar{x}_{k+1} - \bar{x}_k = h_1 \cdot \exp((k - 1/2) \cdot \beta);$$

$$\frac{\Delta c_k}{\Delta t} = - \frac{A_k \cdot J_k - A_{k-1} \cdot J_{k-1}}{V_k};$$

$$V_k = A_k \cdot (x_k - x_{k-1}) = A_k \cdot h_k;$$

$$\text{for a plane electrode } A_k = A_{k-1} : \frac{c'_k - c_k}{\Delta t} = \frac{D}{h_k} \cdot \left(\frac{c_{k+1} - c_k}{\bar{x}_{k+1} - \bar{x}_k} - \frac{c_k - c_{k-1}}{\bar{x}_k - \bar{x}_{k-1}} \right);$$

Also, one may define additional parameters, for easier implementation:

$$D_{2,k} = MDC \cdot \exp(2 \cdot \beta \cdot (3/4 - k));$$

$$D_{1,k} = MDC \cdot \exp(2 \cdot \beta \cdot (5/4 - k)); \quad k > 1;$$

$$D_{1,1} = MDC \cdot \frac{\exp(\beta) - 1}{\exp(\beta/2) - 1}; \quad k = 1; \quad (\bar{x}_0 = 0)$$

In all the following equations $k = 1, 2, 3, \dots, N$;

boundary condition at infinite distance from the electrode).

c' is the concentration at $t + \Delta t$;

$c_{n+1} = c^*$ = the bulk concentration (equal to the initial concentration) for each species (corresponding to the

Explicit discretisation:

The discretized diffusion equation is written as:

$$\frac{c'_k - c_k}{\Delta t} = D \cdot \frac{\frac{c_{k+1} - c_k}{x_{k+1} - x_k} - \frac{c_k - c_{k-1}}{x_k - x_{k-1}}}{\frac{x_{k+1} - x_{k-1}}{2}};$$

(a) Equally spaced grid (abr. EqExp):

$$c'_k = MDC \cdot c_{k-1} + (1 - 2 \cdot MDC) \cdot c_k + MDC \cdot c_{k+1} \quad (2.1)$$

(b) Exponentially spaced grid (abr. ExExp):

$$c'_k = E_k \cdot \exp(\beta) \cdot c_{k-1} + (1 - E_k - E_k \cdot \exp(\beta)) \cdot c_k + E_k \cdot c_{k+1}; \quad (2.2)$$

(c) Box method (abr. BExp):

$$c'_k = D_{1,k} \cdot c_{k-1} + (1 - D_{1,k} - D_{2,k}) \cdot c_k + D_{2,k} \cdot c_{k+1}; \quad (2.3)$$

The explicit discretisation is conditionally stable¹, therefore MDC should not exceed 0.5.

Laasonen implicit discretisation:

The discretized diffusion equation is written as:

$$\frac{c'_k - c_k}{\Delta t} = D \cdot \frac{\frac{c'_{k+1} - c'_k}{x_{k+1} - x_k} - \frac{c'_k - c'_{k-1}}{x_k - x_{k-1}}}{\frac{x_{k+1} - x_{k-1}}{2}};$$

(a) Equally spaced grid (abr. EqLaa):

$$c_k = -MDC \cdot c'_{k-1} + (1 + 2 \cdot MDC) \cdot c'_k - MDC \cdot c'_{k+1} \quad (3.1)$$

(b) Exponentially spaced grid (abr. ExLaa):

$$c_k = -E_k \cdot \exp(\beta) \cdot c'_{k-1} + (1 + E_k + E_k \cdot \exp(\beta)) \cdot c'_k - E_k \cdot c'_{k+1}; \quad (3.2)$$

(c) Box method (abr. BLaa):

$$c_k = -D_{1,k} \cdot c'_{k-1} + (1 + D_{1,k} + D_{2,k}) \cdot c'_k - D_{2,k} \cdot c'_{k+1}; \quad (3.3.)$$

Crank-Nicolson semi-implicit discretisation:

The discretized diffusion equation is written as:

$$\frac{c'_k - c_k}{\Delta t} = \frac{D}{2} \cdot \left(\frac{\frac{c_{k+1} - c_k}{x_{k+1} - x_k} - \frac{c_k - c_{k-1}}{x_k - x_{k-1}}}{\frac{x_{k+1} - x_{k-1}}{2}} + \frac{\frac{c'_{k+1} - c'_k}{x_{k+1} - x_k} - \frac{c'_k - c'_{k-1}}{x_k - x_{k-1}}}{\frac{x_{k+1} - x_{k-1}}{2}} \right);$$

(a) Equally space grid (abr. EqCN):

$$\begin{aligned} -MDC \cdot c'_{k-1} + (1 + 2 \cdot MDC) \cdot c'_k - MDC \cdot c'_{k+1} &= \\ &= MDC \cdot c_{k-1} + (1 - 2 \cdot MDC) \cdot c_k + MDC \cdot c_{k+1} \end{aligned}; \quad (4.1.)$$

(b) Exponentially spaced grid (abr. ExCN):

$$A(k, c'_{k-1}, c'_k, c'_{k+1}) = B(k, c_{k-1}, c_k, c_{k+1}); \quad (4.2.)$$

$$\begin{aligned} A(k, c'_{k-1}, c'_k, c'_{k+1}) &= -\frac{E_k}{2} \cdot \exp(\beta) \cdot c'_{k-1} + \left(1 + \frac{E_k}{2} + \frac{E_k}{2} \cdot \exp(\beta) \right) \cdot c'_k - \frac{E_k}{2} \cdot c'_{k+1}; \\ B(k, c_{k-1}, c_k, c_{k+1}) &= \frac{E_k}{2} \cdot \exp(\beta) \cdot c_{k-1} + \left(1 - \frac{E_k}{2} - \frac{E_k}{2} \cdot \exp(\beta) \right) \cdot c_k + \frac{E_k}{2} \cdot c_{k+1}; \end{aligned}$$

(c) Box method (abr. BCN):

$$\begin{aligned} -D_{1,k} \cdot c'_{k-1} + (2 + D_{1,k} + D_{2,k}) \cdot c'_k - D_{2,k} \cdot c'_{k+1} &= \\ = D_{1,k} \cdot c_{k-1} + (2 - D_{1,k} - D_{2,k}) \cdot c_k + D_{2,k} \cdot c_{k+1}; \end{aligned} \quad (4.3.)$$

When explicit techniques are used, the system (1) becomes a system with 4 algebraic equations:

$$\begin{cases} J_O = -D_O \cdot \frac{c_{O,1} - c_{O,0}}{\Delta x}; \\ J_R = -D_R \cdot \frac{c_{R,1} - c_{R,0}}{\Delta x}; \\ J_O = -J_R; \\ J_O = k_1 \cdot c_{O,0} - k_2 \cdot c_{R,0}; \end{cases} \quad (5)$$

J_O – flux of species O at the moment t ;
 J_R – flux of species R at the moment t ;
 $c_{O,0}$ – concentration of species O at the surface of the electrode at the moment t ;
 $c_{R,0}$ – concentration of species R at the surface of the electrode at the moment t ;

Further, the concentration profiles at the moment $t + \Delta t$ are calculated with either one of the equations (2.1.), (3.1.), (4.1.).

In case of implicit techniques, some observations must be made. The equations for evaluating concentration profiles (2.2.), (2.3.), (3.2.), (3.3.), (4.2.), (4.3.) are forming tri-diagonal systems. These systems are easily transformed in bi-diagonal systems¹¹ and the system (1) becomes:

$$\begin{cases} a \cdot c'_{O,0} + b \cdot c'_{O,1} = c; \\ m \cdot c'_{R,0} + n \cdot c'_{R,1} = p; \\ J_O = -D_O \cdot \frac{c'_{O,1} - c'_{O,0}}{\Delta x}; \\ J_R = -D_R \cdot \frac{c'_{R,1} - c'_{R,0}}{\Delta x}; \\ J_O = -J_R; \\ J_O = k_1 \cdot c'_{O,0} - k_2 \cdot c'_{R,0} \end{cases} \quad (6)$$

a, b, c, m, n, p – coefficients for the bi-diagonal systems obtained accordingly previous observations;

J_O – flux of species O at the moment $t + \Delta t$ at the surface of the electrode;

J_R – flux of species RO at the moment $t + \Delta t$ at the surface of the electrode;

$c'_{O,0}$ – concentration of species O at the surface of the electrode at the moment $t + \Delta t$;

$c'_{R,0}$ – concentration of species R at the surface of the electrode at the moment $t + \Delta t$;

$c'_{O,1}$ – concentration of species O in the first discretisation point at the moment $t + \Delta t$;

$c'_{R,1}$ – concentration of species R in the first discretisation point at the moment $t + \Delta t$;

Δx from the systems (5) and (6) is either h_1 or $h_1/2$ for space discretisation techniques, and $h_1 \times \frac{\exp(\beta) - 1}{\exp(\beta/2) - 1}$ for

flux discretisation techniques, with h_1 being the minimum distance between the electrode surface and first point of discretisation.

Model vs. experimental data

In order to avoid complications due to the disk geometry of the electrode, the CVs taken at 300 mV/s was chosen for extensive comparison with the simulated data, taking care to subtract the background current before comparing with the simulated CVs. The accuracy of the simulations will be checked using the following peak parameters, taken from the experimental CV: $I_p = 2.2015 \mu A$, $E_p = 0.123 V$ and $E_{p2} = 0.064 V$. Due to the small currents, the ohmic drop can be neglected.

The equally spaced grid is fully described by N_p (number of discretisation points per semicycle) and MDC. For unequally spaced grids the adjustable parameter β may be varied.

In the following tables, N_x represent the number of space discretisation nodes and t represents computational time for simulation of a half cycle.

The parameters for each technique can be more or less optimized, so as to obtain a better superposition with the experimental data.

From tables 1 to 4 is easy to notice that the errors do not exceed 4%, which can be considered as acceptable for most common situations.

Table 1

General comparison between discretisation techniques approached and experimental CV at **200 mV/s**
($I_p = 1.842 \mu\text{A}$, $E_p = 0.122 \text{ V}$ and $E_{p/2} = 0.064 \text{ V}$)

	MDC	N_p	N_x	Beta	$I_p [\mu\text{A}]$	$\epsilon I_p [\%]$	$\epsilon E_p [\%]$	$\epsilon E_{p/2} [\%]$	t [m:s]
Eq Exp	0.4	500	120	-	1.86274	+1.1	-0.8	0	0:0.6
Eq Laa	5	500	424	-	1.83155	+0.5	0	+1.5	0:0.7
Eq CN	5	500	424	-	1.83194	+0.5	0	0	0:0.6
Ex Exp	0.4	500	27	0.1	1.866205	+1.3	-0.8	0	0:0.7
Ex Laa	5	500	39	0.1	1.83343	+0.4	0	+1.5	0:0.2
Ex CN	5	500	39	0.1	1.83381	+0.4	0	0	0:0.2
B Exp	0.4	500	114	0.001	1.85761	+0.8	-0.8	0	0:0.2
B Laa	5	500	354	0.001	1.84398	+0.1	-0.8	0	0:0.9
B CN	5	500	354	0.001	1.84425	+0.1	-0.8	0	0:0.9

Table 2

General comparison between discretisation techniques approached and experimental CV at **250 mV/s**
($I_p = 2.0051 \mu\text{A}$, $E_p = 0.123 \text{ V}$ and $E_{p/2} = 0.064 \text{ V}$)

	MDC	N_p	N_x	Beta	$I_p [\mu\text{A}]$	$\epsilon I_p [\%]$	$\epsilon E_p [\%]$	$\epsilon E_{p/2} [\%]$	t [m:s]
Eq Exp	0.4	500	120	-	2.07966	+3.7	-0.8	-1.5	0:0.6
Eq Laa	5	500	424	-	2.04488	+1.9	0	0	0:0.7
Eq CN	5	500	424	-	2.04528	+2.0	0	0	0:0.6
Ex Exp	0.4	500	27	0.1	2.08353	+3.9	-0.8	-1.5	0:0.7
Ex Laa	5	500	39	0.1	2.046968	+2.0	0	0	0:0.2
Ex CN	5	500	39	0.1	2.04736	+2.0	0	0	0:0.2
B Exp	0.4	500	114	0.001	2.07397	+3.4	-0.8	-1.5	0:0.2
B Laa	5	500	354	0.001	2.058759	+2.6	-0.8	-1.5	0:0.9
B CN	5	500	354	0.001	2.059162	+2.6	-0.8	-1.5	0:0.9

Table 3

General comparison between discretisation techniques approached and experimental CV at **300 mV/s**
($I_p = 2.2015 \mu\text{A}$, $E_p = 0.123 \text{ V}$ and $E_{p/2} = 0.064 \text{ V}$)

	MDC	N_p	N_x	Beta	$I_p [\mu\text{A}]$	$\epsilon I_p [\%]$	$\epsilon E_p [\%]$	$\epsilon E_{p/2} [\%]$	t [m:s]
Eq Exp	0.4	500	120	-	2.275398	+3.3	0	-1.5	0:0.6
Eq Laa	5	500	424	-	2.237241	+1.6	0	0	0:0.7
Eq CN	5	500	424	-	2.23776	+1.6	0	0	0:0.6
Ex Exp	0.4	500	27	0.1	2.27961	+3.5	0	-1.5	0:0.7
Ex Laa	5	500	39	0.1	2.23952	+1.7	0	+1.5	0:0.2
Ex CN	5	500	39	0.1	2.240045	+1.7	0	0	0:0.2
B Exp	0.4	500	114	0.001	2.269137	+3.0	0	-1.5	0:0.2
B Laa	5	500	354	0.001	2.25247	+2.3	0	-1.5	0:0.9
B CN	5	500	354	0.001	2.25286	+2.3	0	-1.5	0:0.9

Table 4

General comparison between discretisation techniques approached and experimental CV at **350 mV/s**
($I_p = 2.3826 \mu\text{A}$, $E_p = 0.124 \text{ V}$ and $E_{p/2} = 0.065 \text{ V}$)

	MDC	N_p	N_x	Beta	$I_p [\mu\text{A}]$	$\epsilon I_p [\%]$	$\epsilon E_p [\%]$	$\epsilon E_{p/2} [\%]$	t [m:s]
Eq Exp	0.4	500	120	-	2.454895	+3.0	0	0	0:0.6
Eq Laa	5	500	424	-	2.413727	+1.3	+0.8	0	0:0.7
Eq CN	5	500	424	-	2.414276	+1.3	0	0	0:0.6
Ex Exp	0.4	500	27	0.1	2.459448	+3.2	0	0	0:0.7
Ex Laa	5	500	39	0.1	2.416185	+1.4	+0.8	0	0:0.2
Ex CN	5	500	39	0.1	2.41674	+1.4	0	0	0:0.2
B Exp	0.4	500	114	0.001	2.448178	+2.7	0	0	0:0.2
B Laa	5	500	354	0.001	2.4302	+1.9	0	0	0:0.9
B CN	5	500	354	0.001	2.43071	+2.0	0	0	0:0.9

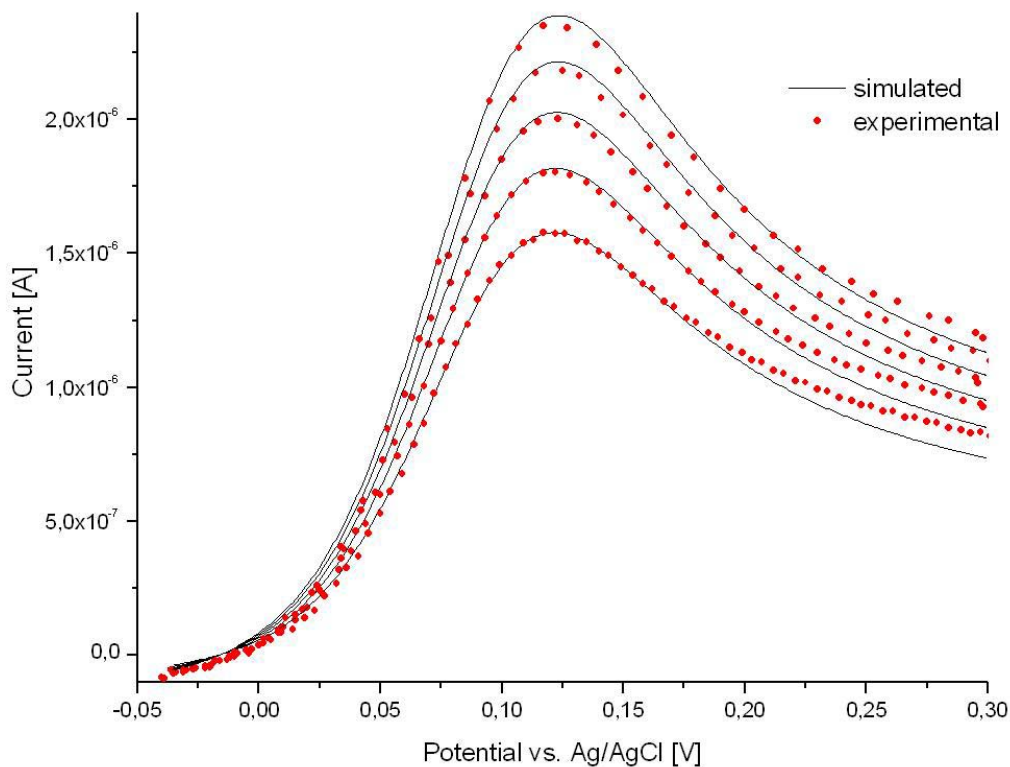


Fig. 2 – Cyclic voltammograms at 150, 200, 250, 300 and 350 mV/s.

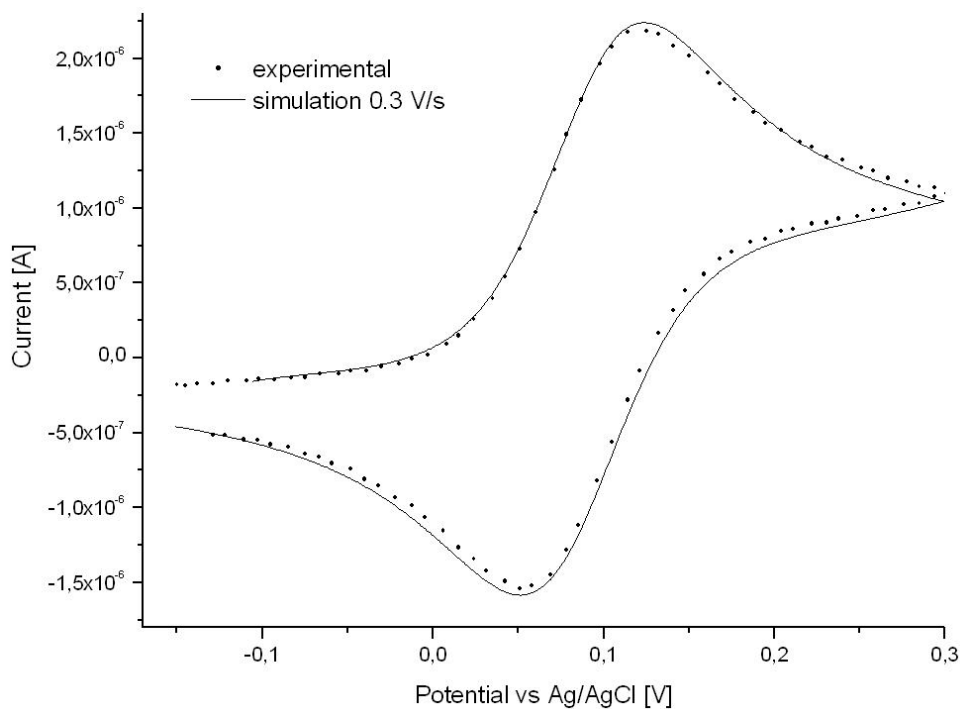


Fig. 3 – Comparison between full simulated CV and experimental data at 300 mV/s (ExLaa).

The value $N_p=500$ is considered a mark value for all discretisation techniques, as a suitable compromise between acceptable accuracy and small simulation times. Above a value of N_p of about 2000, further increase in N_p has little effect over the achieved accuracy. Acceptable accuracy may also be obtained for smaller value of N_p , but since the

simulation time is already very small, there is usually no reason to choose N_p below 500 (see Table 5).

An increase of MDC value strongly decrease the accuracy of the box method (Table 6). The same values have smaller effect for classical discretisation techniques (Table 7).

Table 5

Influence of N_p over accuracy of simulation (method ExLaa)

MDC	N_p	N_x	Beta	I_p [μ A]	ϵI_p [%]	ϵE_p [%]	$\epsilon E_{p/2}$ [%]	t [m:s]
5	100	31	0.1	2.19273	-0.3	+4.5	+6.0	0:0.1
5	500	39	0.1	2.239528	+1.7	+0.8	+1.5	0:0.2
5	5.000	50	0.1	2.264822	+2.8	-0.8	-3.0	0:1.6
5	50.000	62	0.1	2.272795	+3.2	-0.8	-4.6	0:18.5
5	100.000	65	0.1	2.27387	+3.2	-0.8	-4.6	0:40.3

Table 6

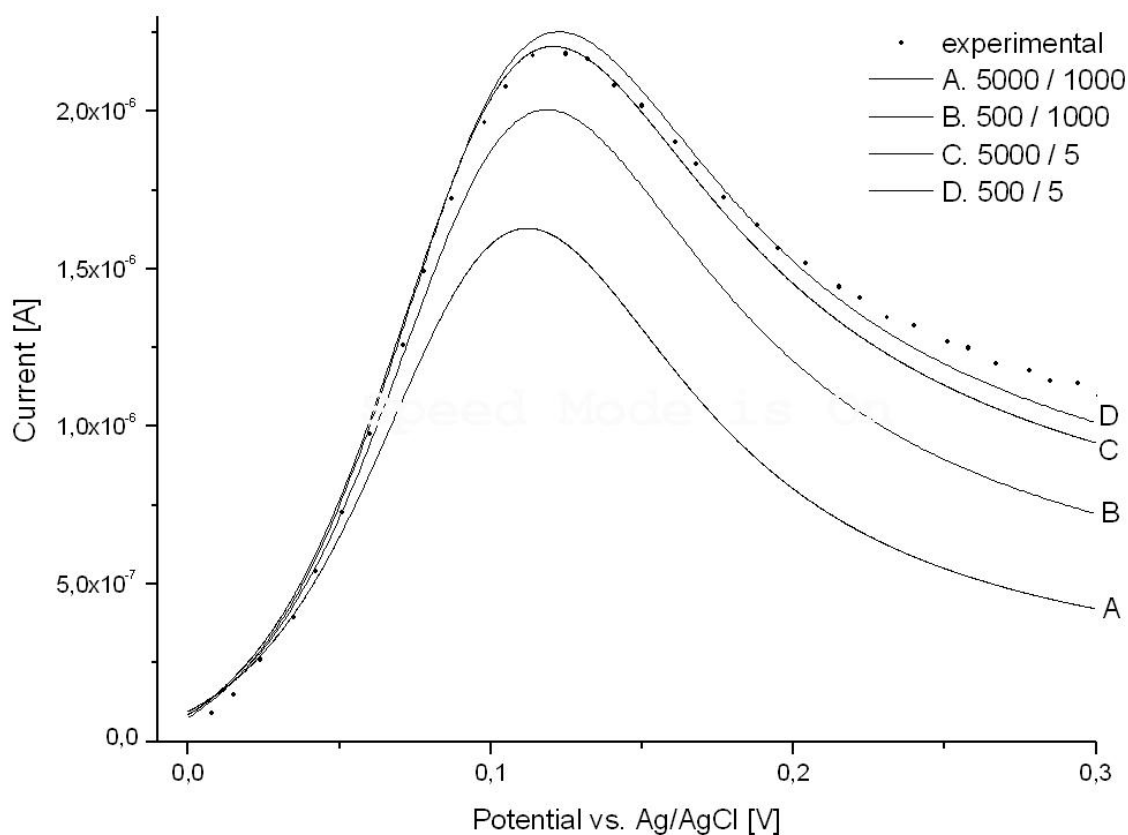
Influence of N_p and MDC over accuracy of box method through Laasonen discretisation

MDC	N_p	N_x	Beta	I_p [μ A]	ϵI_p [%]	ϵE_p [%]	$\epsilon E_{p/2}$ [%]	t [m:s]
1000	5000	2995	0.001	1.62929	-25.9	-8.9	-10.7	1:0.7
5	5000	852	0.001	2.206633	+0.2	-2.4	-3.0	0:17.5
5	500	354	0.001	2.25247	-2.2	-0.8	0	0:0.6
1000	500	1947	0.001	2.005161	+9.2	-4.0	-4.6	0:3.5

Table 7

Influence of N_p /MDC over accuracy of classic implicit Laasonen discretisation

MDC	N_p	N_x	Beta	I_p [μ A]	ϵI_p [%]	ϵE_p [%]	$\epsilon E_{p/2}$ [%]	t [m:s]
1000	5000	2995	0.001	2.274207	+7.2	-0.8	-3.0	1:40.8
5	5000	852	0.001	2.263141	+2.7	-0.8	-3.0	0:25.4
5	500	354	0.001	2.237251	+1.6	0	0	0:0.9
1000	500	1947	0.001	2.271943	+7.1	0	0	0:5.7

Fig. 4 – Influence of N_p and MDC for the box method (BLaa).

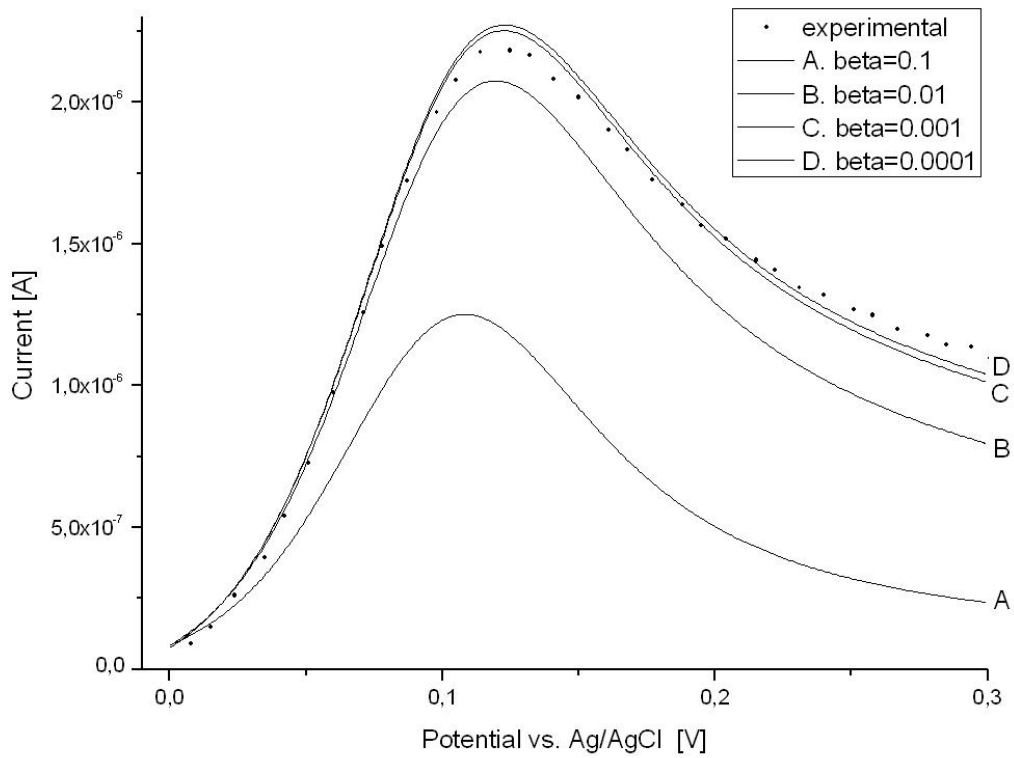


Fig. 5 – Influence of beta for the box method.

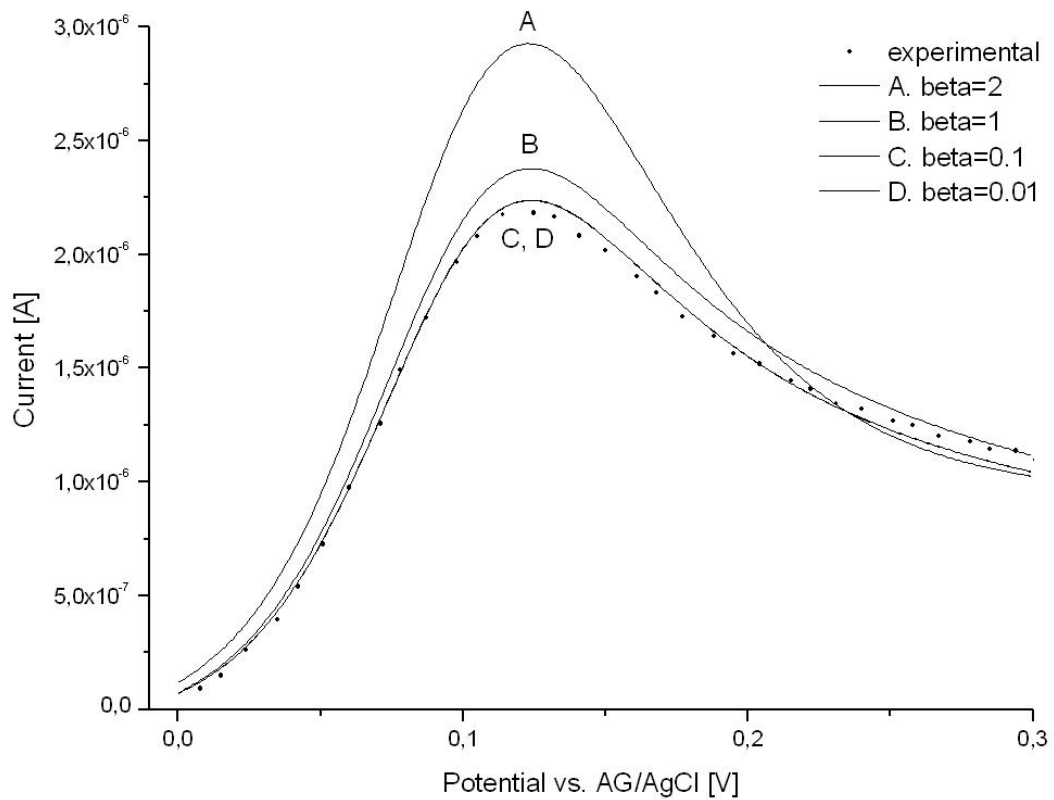


Fig. 6 – Influence of beta for the classic Laasonen discretisation.

Table 8

Influence of beta for box method through Laasonen discretisation

MDC	N_p	N_x	Beta	I_p [μ A]	ϵI_p [%]	ϵE_p [%]	$\epsilon E_{p/2}$ [%]	t [m:s]
5	500	39	0.1	1.251721	-43.1	-12.1	+33.8	0:0.2
5	500	167	0.01	2.07528	-5.7	0.2	-3.0	0:0.3
5	500	354	0.001	2.25247	-2.2	-0.8	0	0:0.6
5	500	416	0.0001	2.271943	+3.9	0	0	0:0.6

Table 9

Influence of beta over classical implicit Laasonen discretisation

MDC	N_p	N_x	Beta	I_p [μ A]	ϵI_p [%]	ϵE_p [%]	$\epsilon E_{p/2}$ [%]	t [m:s]
5	500	4	2	2.92771	+32.9	0	0	0:0.2
5	500	7	1	2.378107	+8.0	0	+1.5	0:0.2
5	500	39	0.1	2.239528	+1.7	+0.8	+1.5	0:0.3
5	500	167	0.01	2.23734	+1.6	0	0	0:0.5

CONCLUSIONS

The main discretisation techniques used in the simulation of electrochemical techniques are studied and compared for a typical cyclic voltammetry experiment.

All discretisation techniques studied offer a reasonably good approximation of experimental data. There are no significant differences between equal space grid and unequal space grid discretisation techniques.

For a simple electrochemical system the Laasonen and Crank-Nicolson discretisation techniques show very similar results, both in accuracy and computation times. However, Crank-Nicolson discretisation technique is prone to solution oscillations¹², whereas the Laasonen technique proved to be oscillation-free.

For simple electrochemical system, the implicit unequally spaced grid has a good precision even only when 40 discretisation space points. For the same precision the box method requires at least 150 points. The computation time is therefore an important issue for classical discretisation techniques.

Laasonen implicit discretisation is the best method, from the accuracy/simulation time point

of view ratio. The box method, despite being simple and straightforward, is interesting mainly for theoretical and educational purposes, as it needs a rather large number of grid points for good accuracy.

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