

PRACTICAL ASPECTS ASSOCIATED WITH THE USE OF JACOBI POLYNOMIALS IN THE SIMULATION OF QUASI-REVERSIBLE ELECTRODE PROCESSES WITH LINEAR POTENTIAL SCAN AND DIFFUSIONAL CONTROL IN ONE DIMENSION

Dan DRAGU* and Mihai BUDA

Department of Applied Physical Chemistry and Electrochemistry, Faculty of Applied Chemistry and Materials Science, "POLITEHNICA" University of Bucharest, Calea Grivitei 132, 010737, Bucharest, ROMANIA

Received March 8, 2008

This paper emphasizes some practical aspects regarding orthogonal collocation techniques as used for model of a cyclic voltammetry experiment for a quasi-reversible electrode process with one-dimensional diffusion control. The influence of model's parameters is underlined and their influence over simulation accuracy is discussed.

The main model's parameters taken into account are the number of collocation points and their distribution for various types of Jacobi orthogonal polynomials. The influence of the number of potential/time discretization points and the length of diffusion limit layer is also discussed.

The differences between explicit and implicit discretization and the importance of the method used for computing the orthogonal constants are underlined.

INTRODUCTION

A system of differential equations with boundary conditions can be solved numerically through a wide range of techniques. It has long been known that one of the most efficient methods is the orthogonal collocation, provided the model's functions can be reasonably well approximated by a polynomial.

The advantages of this technique were underlined by Villadsen and Stewart,¹ while Michaelsen and Villadsen² described a simplified procedure for computing the constants associated with the collocation points. A particular case was further adapted to electrochemical experiments by Whiting and Carr,³ and developed later by Speiser.⁴⁻⁶

Both Whiting and Carr and Speiser use in their simulations Legendre polynomials, a particular case of Jacobi polynomials. A very good description of orthogonal collocation methods used in electrochemical experiments can be found in Britz.⁷

THEORETICAL ASPECTS

The orthogonal collocation method for solving a differential equation is based on approximating a given function with a polynomial. This is where both the strength and the weakness of the method lie: for well-behaved functions, (*i.e.*, functions that can be reasonably well approximated by a polynomial), orthogonal collocation will give accurate results even with only a few discretization points, whereas for ill-behaved functions (*e.g.* exponentially varying functions, which are not well described by a polynomial), the method will generally fail even with a large number of discretization points. The chosen polynomial will give the exact value of the function at the collocation nodes; care must be taken that the polynomial's roots, which give the collocation nodes, are to be found in the interval of interest, or else a change of variable may be required (such as for the shifted Legendre polynomials).

For a given function $f : [a; b] \rightarrow R$, with the boundary conditions $f'(a) = y_1$ and $f'(b) = y_2$ one can find a polynomial approximation as follows:

* Corresponding author: dandragu@yahoo.com

$$f(x) \approx P(x) = \sum_{j=0}^{n+1} a_j \cdot x^j; \quad f(x)|_{x_i} = P(x_i) = \sum_{j=0}^{n+1} a_j \cdot x_i^j;$$

$$\frac{\partial f(x)}{\partial x} \approx P'(x) = \sum_{j=0}^{n+1} j \cdot a_j \cdot x^{j-1}; \quad \left. \frac{\partial f(x)}{\partial x} \right|_{x_i} = P'(x_i) = \sum_{j=0}^{n+1} j \cdot a_j \cdot x_i^{j-1};$$

$$\frac{\partial^2 f(x)}{\partial x^2} \approx P''(x) = \sum_{j=0}^{n+1} j \cdot (j-1) \cdot a_j \cdot x^{j-2}; \quad \left. \frac{\partial^2 f(x)}{\partial x^2} \right|_{x_i} = P''(x_i) = \sum_{j=0}^{n+1} j \cdot (j-1) \cdot a_j \cdot x_i^{j-2};$$

where x_i are the collocation nodes, $i=0..n+1$ ($x_0 = a$ and $x_{n+1} = b$). The degree of the polynomial $P(x)$ is thus $n+2$ and can be written as $P(x)=(a-x)(b-x)P_n(x)$, where the polynomial $P_n(x)$ has the degree n and n real and distinct roots over the interval $(a;b)$.

The above equations can be written as $F = Q \cdot v$;

$\frac{dF}{dX} = R \cdot v$; $\frac{d^2F}{dX^2} = S \cdot v$, where F is the vector of the function values at each collocation node, v is the vector of containing the a_j coefficients, and Q is a Vandermonde matrix having as elements the roots of the orthogonal polynomial P_n . Equation $F = Q \cdot v$ is equivalent with $Q^{-1} \cdot F = Q^{-1} \cdot Q \cdot v = v$.

We can write:

$$\frac{dF}{dX} = R \cdot Q^{-1} \cdot F = A \cdot F \tag{1}$$

and

$$\frac{d^2F}{dX^2} = S \cdot Q^{-1} \cdot F = B \cdot F \tag{2}$$

Thus, it is enough to calculate the collocation points x_i only, without calculation of a_j coefficients. As P_n is an orthogonal polynomial it will have exactly n real distinct roots in the orthogonality interval.

Michelsen and Villadsen² proposed another approach for $P_n(x)$ based on Lagrange interpolation

$$P'_i(x) = (x - x_{i-1}) \cdot P'_{i-1}(x)$$

$$P''_i(x) = (x - x_{i-1}) \cdot P''_{i-1}(x) + 2P'_{i-1}(x)$$

$$P'''_i(x) = (x - x_{i-1}) \cdot P'''_{i-1}(x) + 3P''_{i-1}(x) \text{ with } P'_1(x) = 1; P''_1(x) = 0; P'''_1(x) = 0.$$

One of the main advantages of this method is the high stability of solution when computing the coefficients for large n values.

In any approach, one has to compute the roots of an n degree orthogonal polynomial. The roots are usually computed using a Newton algorithm. The initial guess of x_i is chosen between the two

formula. Thus, $P_n(x) = \prod_{i=1}^n (x - x_i)$, and the initial $n+2$ degree polynomial $P(x)$ becomes $P(x) = \prod_{i=0}^{n+1} (x - x_i)$. The target function f can be approximated as:

$$f(x) \approx \sum_{j=0}^{n+1} \frac{P(x)}{(x - x_j) \cdot P'(x_j)} \cdot f(x_j). \tag{The}$$

equations (1) and (2) are still valid, but their coefficients are calculated through an explicit formula and not through inverse matrix Q^{-1} :

$$\text{For } i=j: a_{i,i} = \frac{1}{2} \cdot \frac{P''(x_i)}{P'(x_i)} \quad b_{i,i} = \frac{1}{3} \cdot \frac{P'''(x_i)}{P'(x_i)}$$

and

$$\text{For } i < j: a_{i,j} = \frac{1}{x_i - x_j} \cdot \frac{P'(x_i)}{P'(x_j)}$$

$$b_{i,j} = \frac{1}{x_i - x_j} \cdot \left(\frac{P''(x_i)}{P'(x_j)} - 2 \cdot a_{i,j} \right)$$

A recurrence formula can thus be found for polynomials $P(x)$:

$$P_i(x) = (x - x_{i-1}) \cdot P_{i-1}(x); \quad P_0(x) = 1; \quad i=1..n+1;$$

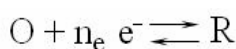
In a similar way, a recurrence formula can be found for derivatives also for $i=2..n+1$ (the derivatives must be equal to zero at $x=x_{i-1}$):

roots of the immediately inferior degree polynomial. A simplified algorithm, which doesn't require the computation of the roots for all polynomials with degree smaller than n , can be found in.⁹

The system of differential equations to be solved numerically using orthogonal collocation is:

$$\left\{ \begin{aligned} \frac{\partial c_O(x,t)}{\partial t} &= D_O \cdot \frac{\partial^2 c_O(x,t)}{\partial x^2}; & J_O(x,t) &= -D_O \cdot \frac{\partial c_O(x,t)}{\partial x} \\ \frac{\partial c_R(x,t)}{\partial t} &= D_R \cdot \frac{\partial^2 c_R(x,t)}{\partial x^2}; & J_R(x,t) &= -D_R \cdot \frac{\partial c_R(x,t)}{\partial x}; \\ & & J_O(0,t) &= -J_R(0,t); \\ & & J_O(0,t) &= k_1 \cdot c_O(0,t) - k_2 \cdot c_R(0,t); \\ & & k_1 &= k^0 \cdot \exp\left(-\alpha \cdot \frac{n_e F}{RT} \cdot (E(t) - E^0)\right); \\ & & k_2 &= k^0 \cdot \exp\left((1-\alpha) \cdot \frac{n_e F}{RT} \cdot (E(t) - E^0)\right); \end{aligned} \right.$$

which accounts for the electrode reaction for a planar electrode, in a diffusional controlled process:



Once the above system is solved, the electrical current associated to the electrode process with can be calculated as $I(t) = n_e F A J_O(0,t)$.

$$E(t) = \begin{cases} E_i - v \cdot t, & t \leq t_s, & E(t_s) = E_s \\ E_s + v \cdot t, & t > t_s \end{cases} \text{ is the}$$

applied potential function and the target functions are $c_O(x,t)$ and $c_R(x,t)$. To the first boundary condition already described (for $x=0$, i.e. the electrode), a second one is added, corresponding to the semi-infinite diffusion condition, $x \rightarrow \infty$: $c_O(\infty,t) = c_O^*$, $c_R(\infty,t) = c_R^*$, and two initial conditions, $c_O(x,t_0) = c_O^*$, $x \in [0, \infty)$, $c_R(x,t_0) = c_R^*$, $x \in [0, \infty)$. For the significances of the terms see the Annex 1.

The second boundary conditions is given for $x \rightarrow \infty$. In fact, following a redox reaction at the electrode, the concentrations of the species involved will alter significantly only in the limit

imposed by the thickness of diffusion layer, x_L . Beyond this limit, the concentrations can be considered to remain constant. Therefore, the interval for the target functions $c_O(x,t)$ and $c_R(x,t)$ can be redefined as $[0,L]$, where $L=x_L$, or further on, $[0,1]$ if one uses x_L as a parameter to render the differential equations dimensionless. Thus, in order to be able to use orthogonal polynomials with roots in a different interval, a change of variable is needed to shift their zeroes in the $[0,1]$ interval.

The general Jacobi polynomials are defined as:

$$g(x) = \int_{-1}^1 (1-x)^\alpha \cdot (1+x)^\beta \cdot P_n(x) \cdot P_m(x) dx = 0$$

and have roots in the $[-1,1]$ interval. Mapping the polynomials to the $[0,1]$ interval requires the change in variable $X=0.5(x+1)$, so as the "shifted" Jacobi polynomials become:

$$g(X) = \int_0^1 (1-X)^\alpha \cdot X^\beta \cdot P_n(X) \cdot P_m(X) dX = 0.$$

The coefficients of the Jacobi polynomial are further normalized in order to transform the leading coefficient $a_0 x^0$ equal with $(-1)^n$. The recursive calculation formulas for $P_n(x)$ and $P'_n(x)$ become:²

$$P_n(x) = (c_n - x) \cdot P_{n-1}(x) - d_n \cdot P_{n-2} \text{ and } P'_n(x) = (c_n - x) \cdot P'_{n-1}(x) - P_{n-1}(x) - d_n \cdot P'_{n-1}(x),$$

$$c_1 = \frac{\beta + 1}{\alpha + \beta + 2}, c_j = \frac{1}{2} \cdot \left(1 - \frac{(\alpha + \beta)(\alpha - \beta)}{(\alpha + \beta + 2j)(\alpha + \beta + 2j - 2)} \right), j=2..n;$$

$$d_1 = 0, d_2 = \frac{(\alpha + 1)(\beta + 1)}{(\alpha + \beta + 3)(\alpha + \beta + 2)^2},$$

$$d_j = \frac{(j-1)(j+\alpha-1)(j+\beta-1)(j+\alpha+\beta-1)}{(2j+\alpha+\beta-1)(2j+\alpha+\beta-2)^2(2j+\alpha+\beta-3)}, j=3..n.$$

$$P_{-1}(x) = 0, P_0(x) = 1, P'_0(x) = 0, P'_1(x) = -1.$$

The target functions $c_O(x,t)$ and $c_R(x,t)$, will be defined thus in the dimensionless interval $[0,1]$. Recommended value¹⁰ for maximum distance where concentration changes still took place is $L = 6\sqrt{D \cdot T_m}$, where T_m is necessary time for a full cycle of potential scanning between E_i , a switch value E_s , and again to E_i .

$$\left\{ \begin{array}{l} \frac{\Delta c_O(X)}{\Delta T} = \frac{D_O}{L^2} \cdot \frac{\partial^2 c_O(X)}{\partial X^2}; \quad J_O(x) = -\frac{D_O}{L} \cdot \frac{\partial c_O(X)}{\partial X} \\ \frac{\Delta c_R(X)}{\Delta T} = \frac{D_R}{L^2} \cdot \frac{\partial^2 c_R(X)}{\partial X^2}; \quad J_R(x) = -\frac{D_R}{L} \cdot \frac{\partial c_R(X)}{\partial X}; \\ J_O(0) = -J_R(0); \\ J_O(0) = k_1 \cdot c_O(0) - k_2 \cdot c_R(0); \\ k_1 = k^0 \cdot \exp\left(-\alpha \cdot \frac{n_e F}{RT} \cdot E\right); \\ k_2 = k^0 \cdot \exp\left((1-\alpha) \cdot \frac{n_e F}{RT} \cdot E\right); \end{array} \right.$$

Where $\Delta c = c' - c$, c = concentration at the moment t , c' = concentration at the moment $t + \Delta T$, $\Delta T = T_m / N_p$.

Applying collocation method, the equations

$$\frac{\Delta c_{O,R}(X)}{\Delta T} = \frac{D_{O,R}}{L^2} \cdot \frac{\partial^2 c_{O,R}(X)}{\partial X^2}$$

$$c'_{O,R}(X_i) - c_{O,R}(X_i) = \frac{\Delta T \cdot D_{O,R}}{L^2} \cdot \left(b_{0,i} \cdot c_{O,R}(0) + b_{n+1,i} \cdot c_{O,R}(1) + \sum_{j=1}^n b_{j,i} \cdot c_{O,R}(X_j) \right),$$

while for the implicit one:

$$c'_{O,R}(X_i) - c_{O,R}(X_i) = \frac{\Delta T \cdot D_{O,R}}{L^2} \cdot \left(b_{0,i} \cdot c'_{O,R}(0) + b_{n+1,i} \cdot c'_{O,R}(1) + \sum_{j=1}^n b_{j,i} \cdot c'_{O,R}(X_j) \right)$$

A further important point to be discussed is the results validation. We chose as reference the dimensionless current function $\chi(\sigma)$ proposed by Nicholson and Shain.⁸ This values are calculated for a reversible electrode reaction. Therefore we chose $k^0 = 1$, enough to accomplish reversible criteria of Bard,¹⁰ $\Lambda > 10$, $\Lambda = \frac{k^0}{\sqrt{D \cdot v \cdot n_e F / RT}}$.

The relation between $\chi(\sigma)$ and I is $\sqrt{\pi} \cdot \chi(\sigma) = I(t) \cdot \frac{1}{n_e \cdot F \cdot A \cdot c_o^* \cdot \sqrt{D_o \cdot \sigma}}$. The

values for $\sqrt{\pi} \cdot \chi(\sigma)$ are tabulated in the literature. Other simulation data are: start potential

In order to eliminate time dependence for a simplified equation system, we choose to discretize potential values through N_p equal discretization points, where N_p has a conveniently chosen value (see below).

$$\text{become } \frac{\Delta c_{O,R}(X)}{\Delta T} = \frac{D_{O,R}}{L^2} \cdot B \cdot C_{O,R}.$$

The form for an explicit approach is:

$E_i = 0,5$ V; switch potential $E_s = 0,0$ V; surface area, $A = 0,01$ cm²; scan rate $v = 0.1$ V/s; temperature, $T = 298$ K; formal potential, $E^{\circ'} = 0,025$ V; transfer coefficient, $\alpha = 0,5$; initial concentration of the oxidized species $c_O = 1$ mM; initial concentration of the reduced species, $c_R = 0$ mM; diffusion coefficients of the species $D_O = D_R = 1.0 \times 10^{-5}$ cm²/s.

RESULTS AND DISCUSSION

We shall discuss first the solutions obtained using particular forms of Jacobi polynomials (Legendre, Chebyshev I, Chebyshev II, Gegenbauer). The results are shown in Figures 1-5.

The particular case of Legendre polynomials will be discussed more extensively, since these

polynomials are most often used in literature and give the best results.

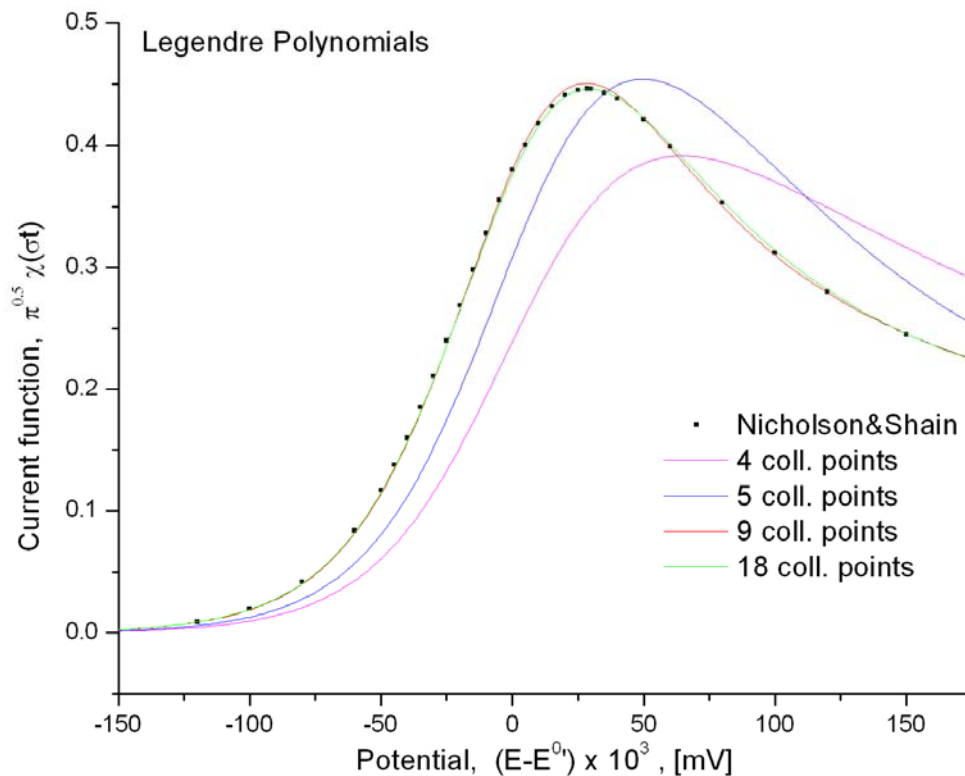


Fig. 1

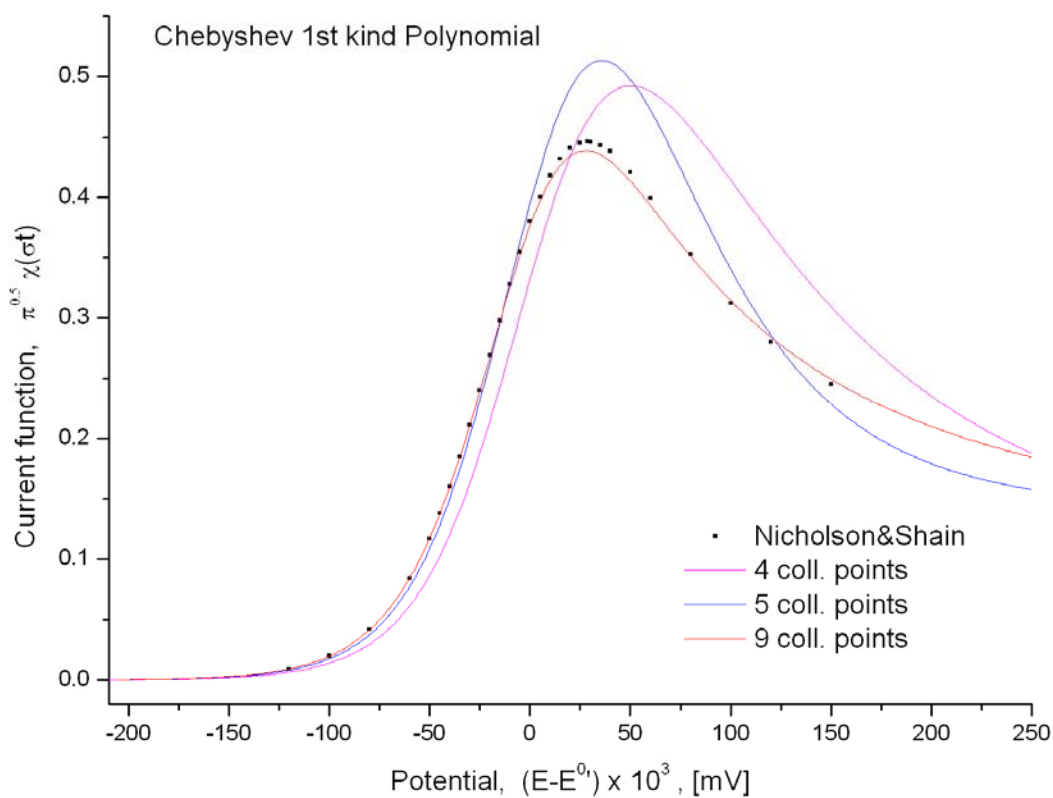


Fig. 2

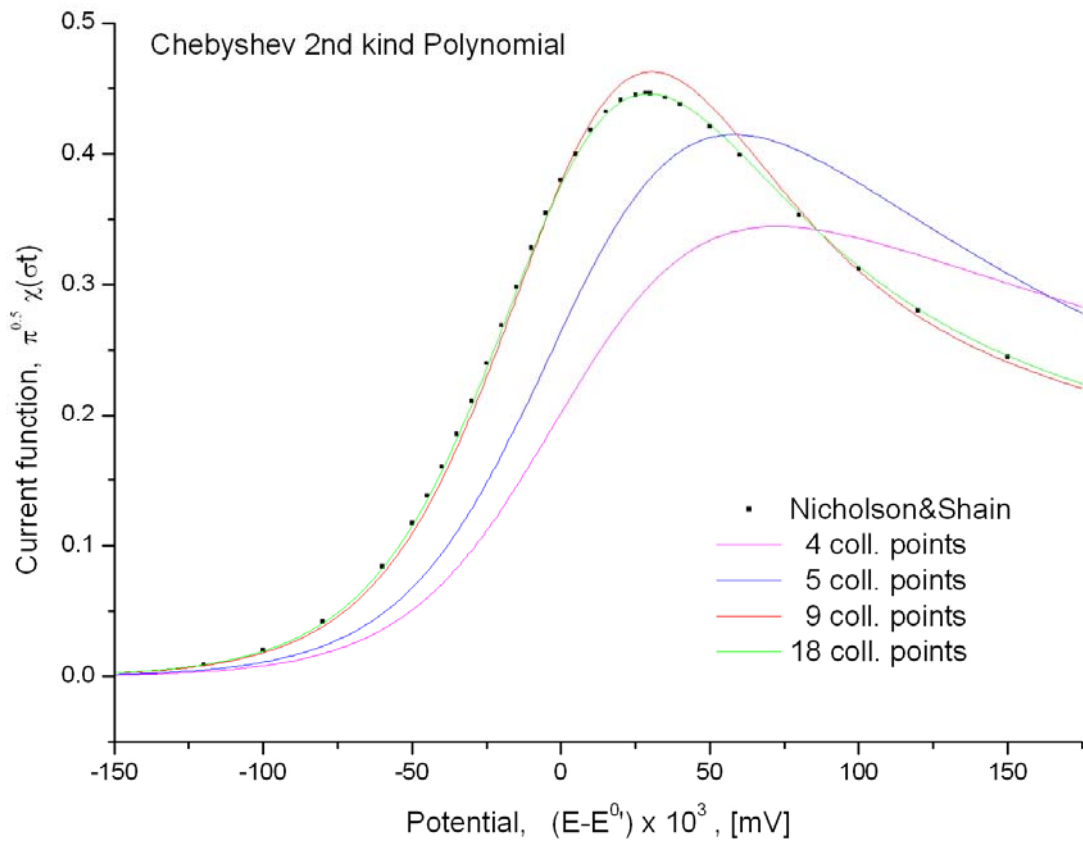


Fig. 3

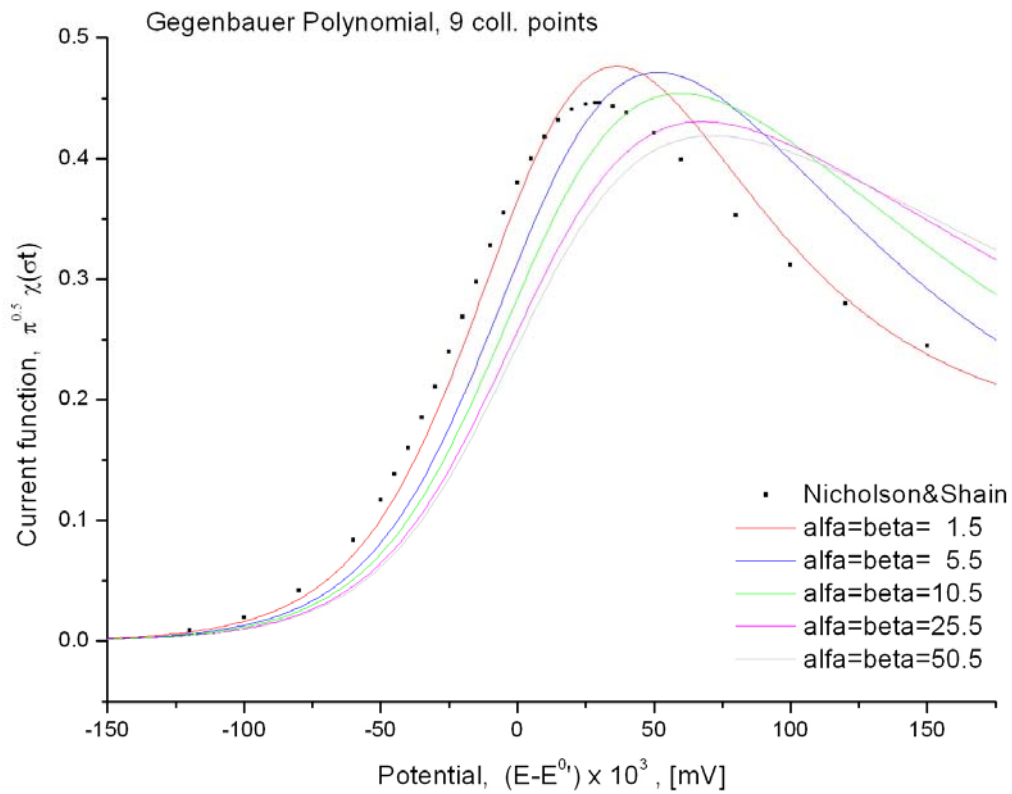


Fig. 4

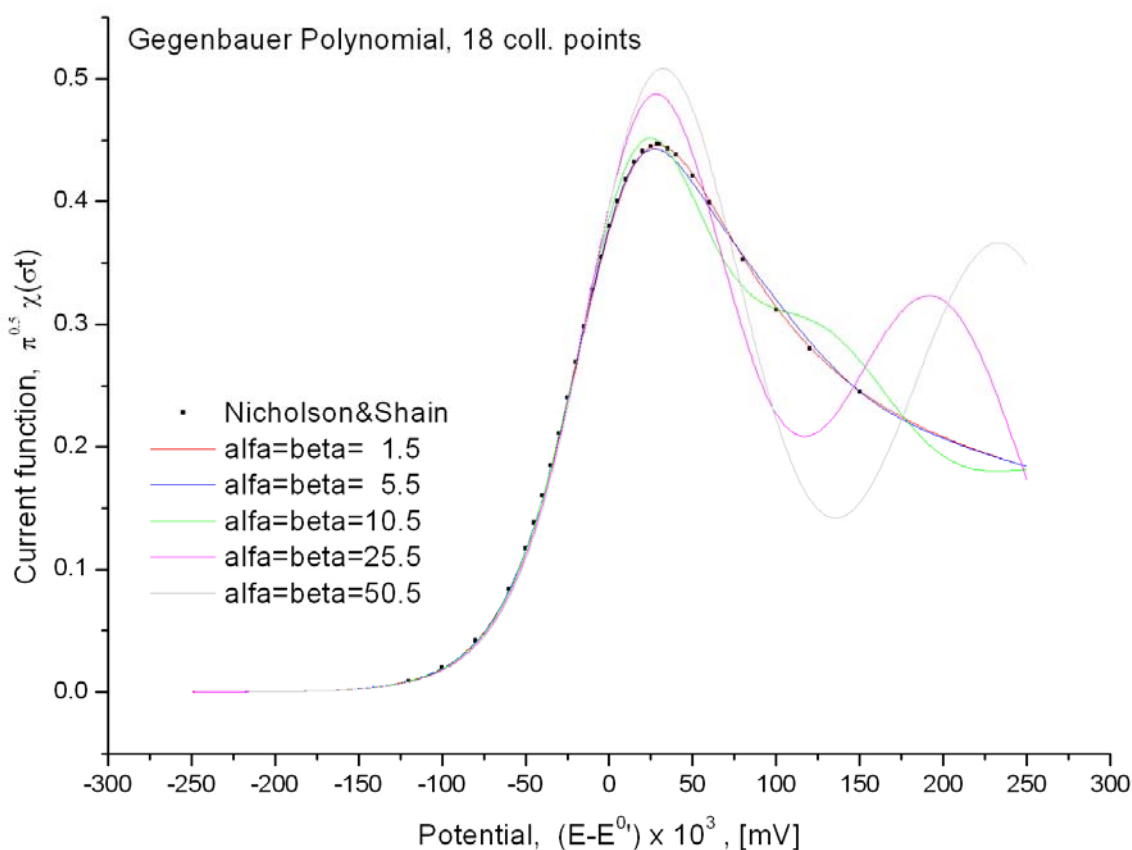


Fig. 5

Legendre polynomials will give very good results even when using just 9 collocation nodes. For Chebyshev polynomials, up to 18 collocation nodes are required. However, the solution tends to become unstable for Chebyshev polynomials of 1st kind. Increasing the number of collocation nodes doesn't lead to improve performances of Gegenbauer polynomials with large values of α and β .

The main reason for these results lie in the distribution of the collocation nodes. When the collocation nodes are concentrated closer to $x=0$, the accuracy of the solution is improved. This is a direct consequence of the fact that the concentrations change mostly close to $x=0$. For Gegenbauer polynomials, when $\alpha = \beta$, the nodes are evenly distributed around 1/2; increasing the values of α and β , the nodes tend to be concentrated around 1/2 (Figure 6). If only the value for α is increased, the nodes are concentrating closer to $x=0$, while an increase of β concentrates the nodes towards $x = 1$ (Figure 7). 5 collocation points may still provide reasonable

accuracy, as long as the nodes are concentrated at $x=0$ (Figure 8), even if the errors increase slightly for longer times (the right part of potentials domain): this is to be expected, since for longer experimental times, the concentration profile will start to change significantly further away from $x = 0$.

Under certain circumstances, the solution is prone to oscillations (Figure 9). These oscillations are mostly eliminated with increasing of the value for N_p . In the absence of the oscillations, small errors are obtained for a relative small value of N_p (Figure 10), and a slightly increased value for N_p over a reasonable limit, doesn't affect considerable the accuracy of the solution (Table 1). The oscillations appear because increasing values for α and β on one hand, and increasing number of collocation points on the other. Another important factor generating oscillations is the method used for calculation of the coefficients for matrixes A and B . From this point of view, the recursive method is better when large number of collocation points are used (Table 2).

Roots distribution for $\alpha = \beta$

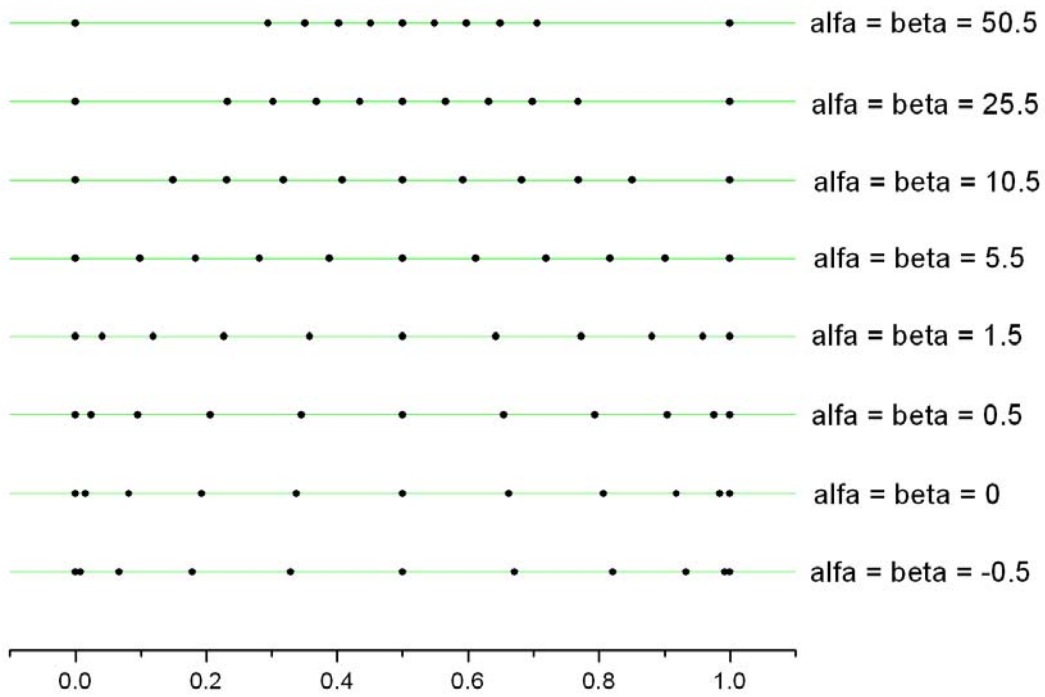


Fig. 6

Roots distribution for $\alpha \neq \beta$

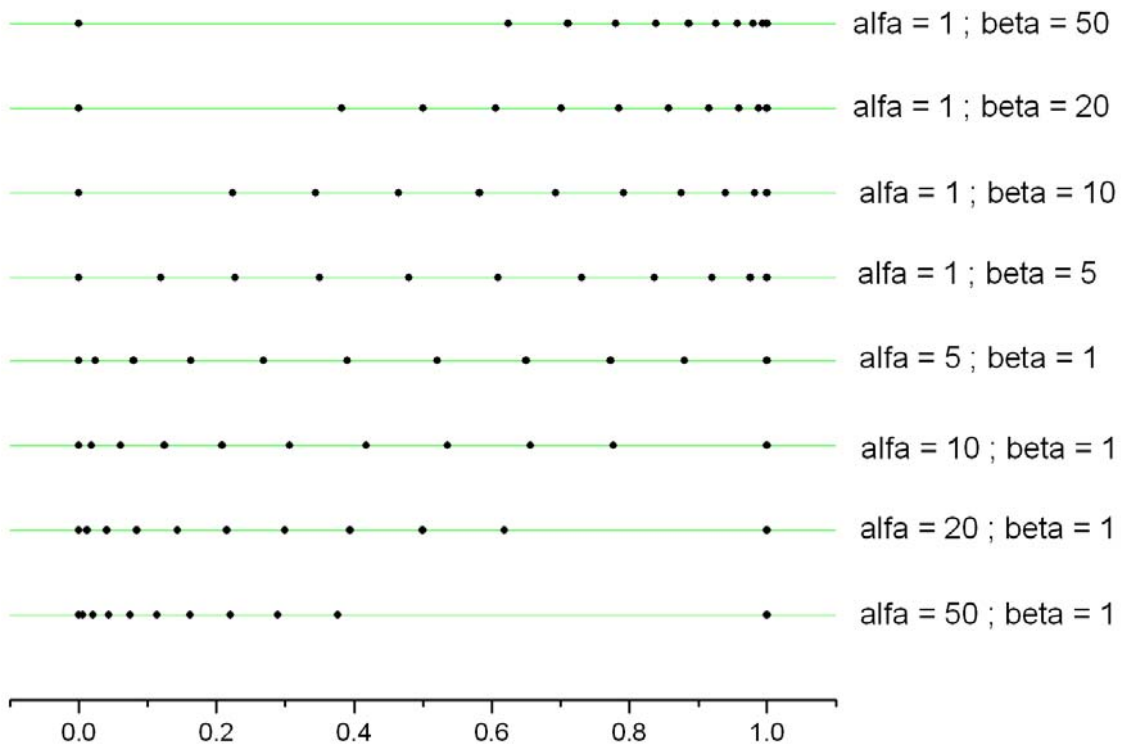


Fig. 7

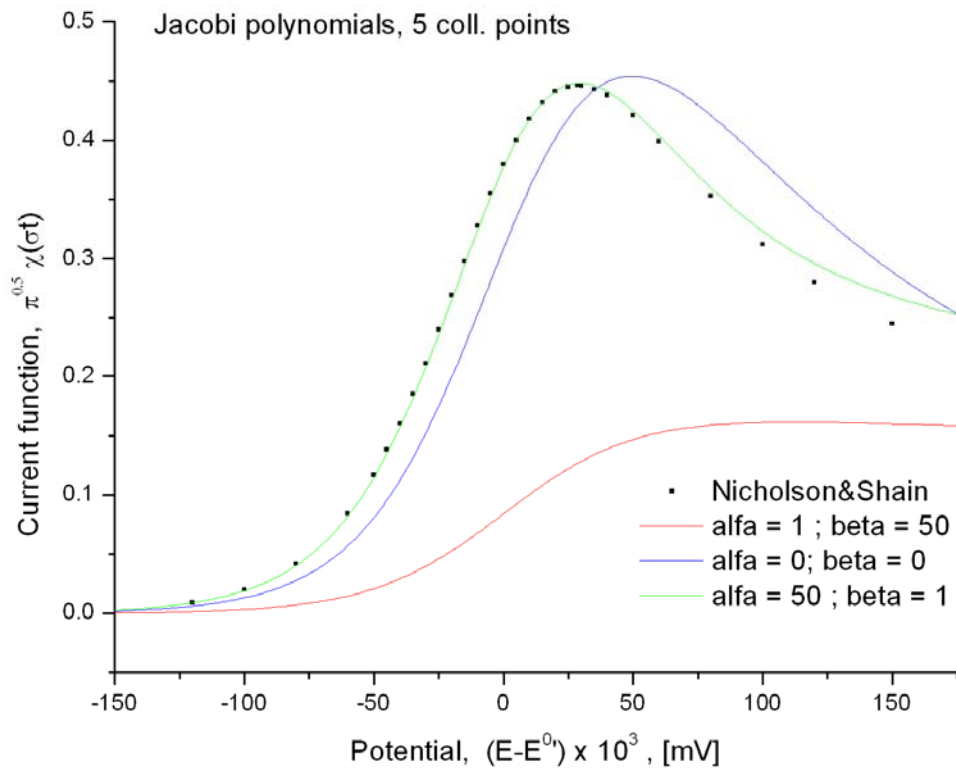


Fig. 8

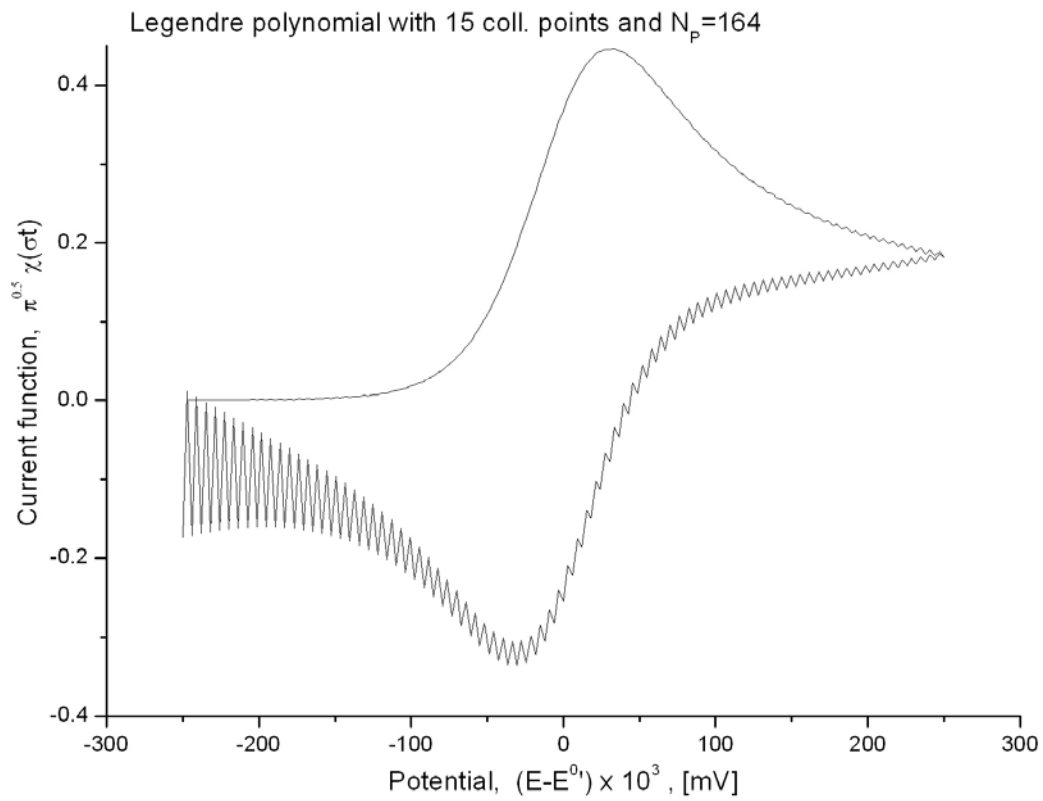


Fig. 9

Table 1 (continued)

40	438	-	-	+4		+3	+*
50	421	-	+*	+6	+*		-
60	399	+*	+**	+8	-		-*
80	353	+*	+*	+8		-3	
100	312	+*	+*	+7	-**		-*
120	280	+*	+*	+6	-*		-
150	245	-	+*	+4	-		+**

Table 2

Maximum number of collocation nodes as the result of the method of calculation of the matrix *B* coefficients (recursive or through Q^T):

	$N_p=500$	$N_p=1000$	$N_p=5000$	$N_p=10000$	$N_p=50000$
recursive, $\alpha=25, \beta=1$	18	23	30	30	30
inverse, $\alpha=25, \beta=1$	18	22	22	22	22
recursive, $\alpha=0, \beta=0$	19	23	35	42	50
inverse, $\alpha=0, \beta=0$	19	22	22	22	22

As for the thickness of the Nernst layer, *L*, large variations between $L = 1.5\sqrt{D \cdot T_m}$ and $L = 21\sqrt{D \cdot T_m}$ have not significant influence over the simulations. For a value of $L = 0.6\sqrt{D \cdot T_m}$ we record a slightly increase of errors in the right side of the potential range, and only an increase of $L = 40\sqrt{D \cdot T_m}$ generates significant errors (Figure 11). Similar results are obtained when Legendre polynomials are used. A variation of the scan rate between 10 and 1000 mV is equivalent with a variation of *L* between

$L = 1.8\sqrt{D \cdot T_m}$ and $L = 19\sqrt{D \cdot T_m}$, T_m is experimental time for a scan rate of 100 mV/s.

When small values of *L* are used, the solution is strongly oscillating. Therefore, for $L = 0.6\sqrt{D \cdot T_m}$, a number of $N_p=50000$ was chosen for compensation, and for $L = 1.5\sqrt{D \cdot T_m}$, $N_p=25000$. The length of the diffusion layer has also influence over the maximum number of collocation points for a fix value of N_p (Table 3).

Table 3

Maximum number of collocation points as the result of the method of calculation of the matrix *B* coefficients (recursive or through Q^T) for different values of *L*:

	<i>A</i>	$L = x \cdot \sqrt{D \cdot T_m}$	$N_p=500$	$N_p=1000$	$N_p=5000$	$N_p=10000$	$N_p=50000$
recursive, $\beta=1$	25	$x=3$	10	13	25	29	29
inverse, $\beta=1$	25	$x=3$	10	13	16	16	16
recursive, $\beta=1$	50	$x=3$	-	9	17	17	17
inverse, $\beta=1$	50	$x=3$	-	9	13	13	13
recursive, $\beta=1$	25	$x=6$	18	23	30	30	30
inverse, $\beta=1$	25	$x=6$	18	22	22	22	22
recursive, $\beta=1$	50	$x=6$	12	16	17	17	17
inverse, $\beta=1$	50	$x=6$	12	16	17	17	17
recursive, $\beta=1$	25	$x=9$	24	30	30	30	30
inverse, $\beta=1$	25	$x=9$	24	27	27	27	27
recursive, $\beta=1$	50	$x=9$	17	17	17	17	17
inverse, $\beta=1$	50	$x=9$	17	17	17	17	17

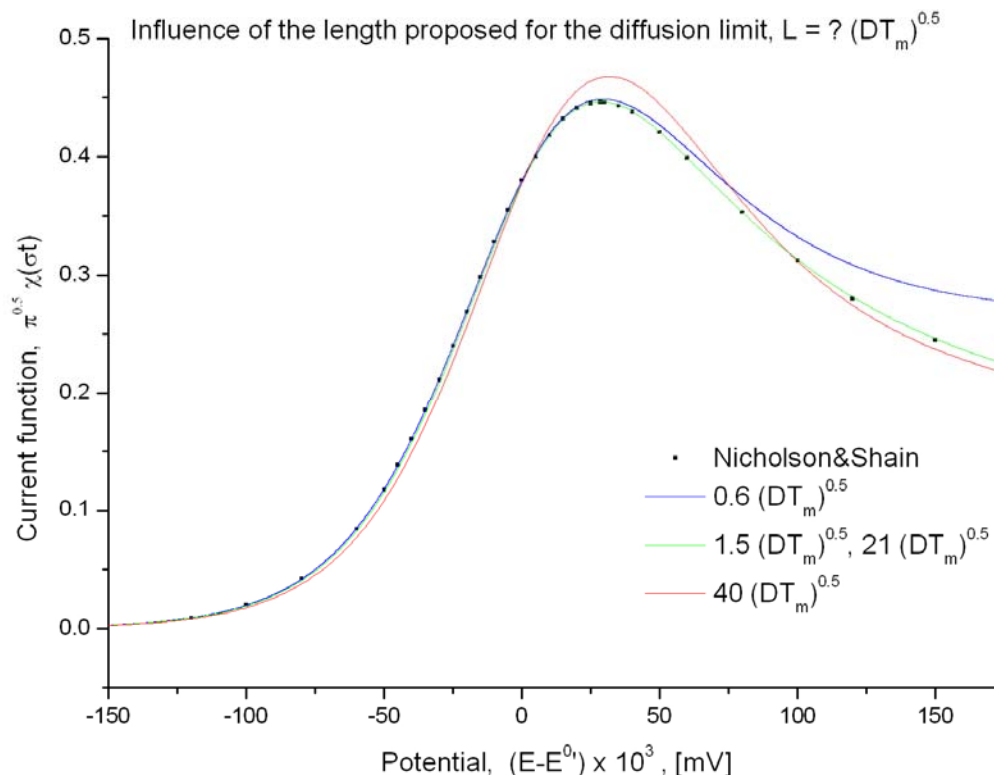


Fig. 11

For a fix set a values for the pair α and β , there is a maximum number of collocation points which allow for a stable solution. The increase of either N_p or diffusion limit L is not affecting this value (Table 3). From the tabulated data in Table 3 we can deduce an optimal set of values associated with collocation method for simulating an cyclic voltammetry experiment. Hence 9 collocation points and $N_p=1000$ discretization potential points are enough for covering bigger variation of values of the pair α and β and bigger variation of the length of the diffusion layer, L .

Implicit approach of the system brings no differences when $\alpha=25$ and $\beta=1$ comparing with the explicit approach. However, small differences are recorded when Legendre polynomials with small number of collocation points are used (Table 1).

The simulation time for collocation method rarely exceed 1 second. For an Jacobi polynomial with $\alpha=25$, $\beta=1$ $N_p=25000$ and 18 collocation points, the computation time on a Intel Core Duo processor with 2200 MHz is only 0.823 seconds. At least from this point of view, collocation methods are very efficient.

The software used for simulation was built in C++ and the source code is available on request. An important observation is that all variables used in program were defined in double precision.

CONCLUSIONS

The main advantage when the roots of a general Jacobi orthogonal polynomial is used for simulating a cyclic voltammetry process is given by the possibility to concentrate the collocation points closed to boundary $x=0$. When a simple electrochemical process is simulated, there are small differences between general Jacobi with $\alpha>\beta$ and widely used Legendre polynomials. For a more complex electrochemical process, it may become important to be able to choose a Jacobi type of polynomial. The oscillations associated with collocation method can be easily eliminated increasing the number of discretization points of potential (or time) domain. A reasonable variation of the diffusion layer L has very little influence over the accuracy of the method.

ABBREVIATIONS

v – potential scan rate;
 t – time;
 E_i – starting potential;
 E_s – switching potential;
 D_O – diffusion coefficient for O;
 D_R – diffusion coefficient for R;

J_O – flux for O;
 J_R – flux for R;
 k^0 – standard electrochemical rate constant;
 $k^{0'}$ – dimensionless rate constant;
 α – transfer coefficient;
 F – Faraday constant;
 R – ideal gas constant;
 n_e – number of electrons transferred;
 T – temperature;
 $E0'$ – formal potential;
 I – electrical current;
 L – length of the diffusion limit layer.

REFERENCES

1. J.V.Villadsen and W.E.Stewart, *Chem.Eng.Sci.*, **1967**, 22, 1483.
2. M.L.Michelsen and J.Villadsen, *Chem.Eng.J.*, **1972**, 4, 64.
3. L.F.Whiting and P.W.Carr, *J.Electroanal.Chem.*, **1977**, 81, 1.
4. B.Speiser and A.Rieker, *J.Electroanal.Chem.*, **1979**, 102, 1.
5. B.Speiser, *J.Electroanal.Chem.*, **1980**, 110, 69.
6. B.Speiser, S.Pons and A.Rieker, *Electrochim.Acta*, **1982**, 27, 1171.
7. D. Britz, "Digital Simulation in Electrochemistry", Springer, Berlin, 2005.
8. R.S.Nicholson and I.Shain, *Anal.Chem.*, **1964**, 36, 706.
9. Whilliam H.Press, Brian P.Flannery, Saul A.Teukolsky and William T.Vetterling, "Numerical Recipies in C: The Art of Scientific Computing", Cambridge University Press, 1992.
10. Allen J.Bard and Larry R.Faulkner, "Electrochemical Methods. Fundamentals and Applications", John Wiley&Sons, 2001.

ANNEX 1

Orthogonal polynomials

A sequence of polynomials P_0, P_1, \dots, P_n , are orthogonal one with each other, if

$$\int_{x_1}^{x_2} W(x) \cdot P_n(x) \cdot P_m(x) dx = 0 \text{ for } m < n$$
, where m and n are polynomials degree. The function $W : [x_1, x_2] \rightarrow \mathfrak{R}$ is the residual function, and the domain $[x_1, x_2]$ is the orthogonality interval.

The roots of every orthogonal polynomial lies strictly between the roots of the next degree polynomial in the sequence. Each n degree polynomial can be recursive expressed with the help of the smaller degree next two polynomial in the sequence:

$$b_1 \cdot P_n = (b_2 \cdot x + b_3) \cdot P_{n-1} - b_4 \cdot P_{n-2}.$$

The constants b_1, b_2, b_3 and b_4 are explicitly defined for every particular kind of orthogonal polynomial sequence.

Jacobi polynomials are orthogonal polynomials with $W : [-1, 1] \rightarrow \mathfrak{R}$, $W(x) = (1-x)^\alpha \cdot (1+x)^\beta$; $\alpha > -1$; $\beta > -1$ and recursive coefficients are:

$$b_1 = 2n(n + \alpha + \beta)(2n + \alpha + \beta - 2);$$

$$b_2 = (2n + \alpha + \beta - 2)(2n + \alpha + \beta - 1)(2n + \alpha + \beta);$$

$$b_3 = (2n + \alpha + \beta - 1)(\alpha + \beta)(\alpha - \beta);$$

$$b_4 = 2(n + \alpha - 1)(n + \beta - 1)(2n + \alpha + \beta);$$

More particular Jacobi polynomials can be obtained when:

$\alpha = \beta = 0$ (Legendre polynomials);

$\alpha = \beta = -1/2$ (Chebyshev 1st degree polynomials);

$\alpha = \beta = 1/2$ (Chebyshev 2nd degree polynomials);

$\alpha = \beta = \gamma - 1/2$, $\gamma > -1/2$ (Gegenbauer polynomials).

