Acta Chemica Scandinavica, 1993: 47: 757–767
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Efficiency of Electrochemical Kinetic Simulations by Orthogonal Collocation and Finite Difference Methods. A Comparison

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Bieniasz L. K. and Britz D., 1993. Efficiency of Electrochemical Kinetic Simulations by Orthogonal Collocation and Finite Difference Methods. A Comparison. – Acta Chem. Scand. 47: 757–767.

The efficiency and reliability of electrochemical kinetic simulations by orthogonal collocation and finite difference methods have been examined quantitatively in calculations, using typical examples of homogeneous reaction–diffusion kinetic problems. Orthogonal collocation has been found to be more efficient than finite difference methods, but a proper selection of the integrator for ordinary differential equations and a careful choice of method parameters is essential for this. On the other hand, finite difference methods seem more reliable in problems with discontinuous boundary conditions and homogeneous reactions, especially those of second order.

Numerical solution of partial differential equations (PDEs) is frequently used to obtain theoretical predictions to kinetic problems in electroanalytical chemistry.[1] Among various direct numerical techniques which have been suggested for this purpose, finite difference (FD) methods[2] and orthogonal collocation[3] (OC) seem to be the most popular. An intensive use of finite difference calculations in electrochemical kinetics has been initiated by Feldberg,[4] and since that time various FD schemes have been proposed and explored.[1,5–10] Orthogonal collocation, initially suggested for electrochemical simulations by Whiting and Carr,[11] has been extensively utilized and improved by Speiser and co-workers,[12–23] as well as other authors[24–26] (only references to most prominent papers dealing with kinetic problems in one-dimensional geometry are given here).

The applications of OC to electrochemical kinetic problems are sometimes accompanied by claims that this method is faster than, and in many aspects superior to, FD calculations.[11,24,26] However, the arguments reported in the electrochemical literature to support these claims are not fully convincing, despite the fact that a few comparative studies of FD and OC methods have already been performed.[27,28] For example, Magno *et al.*[27] found OC to perform worse than simple explicit FD calculations with nonuniform space integration steps. The conclusions of these authors seem to disagree with the later study by Su and Speiser,[28] who compared computational times required for the simulation of cyclic voltammograms by the Crank–Nicolson and spline OC methods and who found OC to be rather more efficient.

A clarification of the above issue appears to be important in our search for the best numerical methods suitable for the solution of a large class of electrochemical kinetic problems. A comparison of the quality of various numerical algorithms is also useful for the development of general programs for electrochemical kinetic simulations.[9,29–33] Therefore, in the present work an attempt has been undertaken to provide some answers to the above question. In particular, the essential matter of the relative efficiency of the FD and OC methods has been discussed quantitatively. The problem of the reliability of the considered algorithms has also been addressed.

Selection of problems

In any comparative study there occurs the difficulty of selecting representative examples on which the comparisons are to be made. In the case of electrochemical kinetic problems there is a considerable number of physical phenomena which may occur and which, if taken into account, can have an influence on the results of the comparisons: diffusion, homogeneous reactions, convection, migration, adsorption and various types of electrode reactions. Other factors may also be important, such as the kind of simulated transients, geometry of the electrodes, etc.[1]

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In the present work the discussion has been arbitrarily restricted to problems involving diffusional transport coupled with homogeneous reactions of first and second order only. Such a selection results from the conviction that this is the class of problems to which the numerical methods considered are most frequently applied. In addition, the usual difficulties associated with the homogeneous reactions (formation of thin reaction layers) provide a severe test for any numerical method.

As an example of first-order homogeneous kinetics the standard pseudo-first-order catalytic mechanism (1) and (2)[34] has been selected, which involves formally two

$$A + e^- \rightleftharpoons B \tag{1}$$

$$B \underset{\kappa_b}{\overset{\kappa_f}{\rightleftharpoons}} A \tag{2}$$

species A and B and requires a solution of two corresponding PDEs. For this mechanism analytical solutions are available, which simplifies the accuracy comparisons. Two kinds of transients have been simulated: the potential-step chronoamperometric transient (CA) under limiting current conditions and the linear potential scan voltammetric transient (LSV).[34] Simulation of the potential-step transients is a difficult test for numerical techniques, owing to the discontinuous boundary conditions at the initial time moment $t = 0$.

As an example of second-order homogeneous kinetics the system of Pedersen and Svensmark[35] has been chosen. In a simplified version of this mechanism (Ref. 1, p. 146 and Ref. 35) four species: A, B, C and D are involved in three reactions (3)–(5). A steady state is assumed[35] for the

$$A + e^- \rightleftharpoons B \tag{3}$$

$$B + C \rightarrow A + D \qquad \text{(SET)} \tag{4}$$

$$B + D \rightarrow \text{products} \qquad \text{(fast coupling)} \tag{5}$$

transitory species D. Consequently, the kinetic PDEs for only the first three species need to be solved. The reader is referred to the original work[35] for the details of the derivation. For this system LSV curves only were simulated.

Semi-infinite diffusion conditions and planar electrodes have been assumed in both examples. In the following text, the CA calculations for mechanism (1) and (2), the LSV calculations for mechanism (1) and (2) and the LSV calculations for the mechanism (3)–(5) will be referred to as problem 1, problem 2 and problem 3, respectively.

Selection of methods

Another difficulty which is inherent in the present study is that OC is a rather complicated method, as compared with FD algorithms. There are many more factors that can have an influence on its overall efficiency. In particular, various trial polynomials can be selected, various algorithms for integrating sets of stiff ordinary differential equations (ODEs) arising in this method can be chosen and various input parameters for these algorithms can be assumed.[11–29]

For the present study the simplest variant of the OC has been accepted, i.e. the collocation using Legendre polynomials,[3,11,24] based on a fixed set of collocation nodes with the first node at the electrode surface and the last one at the minimal distance L from the electrode, at which practically no concentration changes can be expected during the time interval of interest on the basis of the estimated diffusion rate (Ref. 1, pp. 14 and 40). Since this variant seems to possess the worst numerical properties, as compared with other proposed modifications,[11–28] its comparison with FD provides the most stringent test for OC. The principles and equations according to which the discretization of the kinetic PDEs has to be performed and corresponding ODEs derived are described in detail in Refs. 12 and 24. This discretization has been applied here.

For the solution of the system of stiff ODEs two integrators have been chosen: the STIFF3 program, reported by Villadsen and Michelsen[3] and recommended for electrochemical simulations by Pons,[24] and the STINT program, written by Tendler *et al.*[36,37] and recommended by Rice.[38] The main reason for this selection is that the source texts of both these programs are available, which makes them accessible to every electrochemist willing to include them in a program. The STIFF3 integrator is based on the semi-implicit Runge–Kutta integration method of Caillaud and Padmanabhan,[39] but it involves, in addition, a simple automatic integration step-size selection mechanism. This program is fairly simple and easy to understand. However, it is not very efficient, since it requires frequent Jacobian matrix evaluations for the ODE system. Its other disadvantage is that analytical expressions for the Jacobian matrix have to be provided (Ref. 3, p. 322) and that time has to be treated as a dependent variable in these expressions (Ref. 3, p. 320). This makes its use for most electrochemical kinetic problems impractical (with the possible exception of the modelling of the CA transients), owing to very cumbersome expressions for the Jacobian matrix, arising in problems with time-dependent boundary conditions. STINT uses a variable-step and variable-order cyclic composite method,[36] and it is much more complicated than STIFF3. It can evaluate the Jacobian matrix by numerical differencing, which is very convenient in practice. The A-stability of the STIFF3 integrator (Ref. 3, p. 319) and the stiff stability of STINT[36] are good reasons to believe that these integrators do not impose constraints on the values of the β-parameter arising in the OC discretization.[12,13,24] Hence, one can select this parameter simply on the basis of the physical rationale for the considered kinetic problems (see later). There are not many other integrators available for stiff ODEs. Library packages such as DDEBDF, LSODA or METAN, used by Speiser,[29] are probably somewhat more efficient than STINT, which is considered to be a moderately efficient integrator.[36] Owing to the above circumstances, in the

present work the STIFF3 program has been used only in conjunction with problems 1 and 2. STINT was applied to all the problems. For problem 3 only numerical evaluation of the Jacobian matrix was used.

Out of the FD methods the following algorithms have been selected for the comparisons: the classic explicit[1,2] (EX), Runge–Kutta second-order[7] (RK2) and Crank–Nicolson[40] with the matrix solution technique suggested by Rudolph[41] (CNR). The "point" formulation of these FD algorithms (Ref. 1, p. 31) has been assumed. "Parallel" calculation of diffusional and homogeneous chemical reaction terms (Ref. 1, p. 143) has been used in the EX and RK2 methods. Among the traditionally used FD techniques the selected algorithms are potentially of the greatest importance, due either to their simplicity (classic explicit and Runge–Kutta) or to their accuracy (Crank–Nicolson). The application of the Rudolph technique[41] of solving the set of coupled linear equations for the concentrations of the reacting species at new time levels in the CNR algorithm followed the description by Britz,[42] including the implicit calculations of the concentrations at the electrode.[43] Five-point approximations for the gradients (Ref. 1, p. 63) at the electrode have been utilized. Linearized expressions (Ref. 1, p. 150) for second-order kinetic terms of the mechanism (3)–(5) have been assumed in the CNR algorithm.

The computer programs corresponding to all the above algorithms have been written in the "C" language[44] and compiled using the TURBO C++ compiler (v. 1.01) for an IBM-compatible PC. The integrators STIFF3 and STINT, as well as other FORTRAN procedures necessary for the OC method and presented in Ref. 3, have also been translated into "C". The calculations have been performed using an IBM-compatible PC with an Intel 80386 processor and a 80387 math co-processor, operating at 25 MHz, under MS DOS.

Computational

In the case of the catalytic mechanism (1) and (2) the reversibility of both reactions (1) and (2) has been assumed in the programs. However, $\kappa_b = 0$ was used as an input value in all the calculations.

In problem 1 the dimensionless time $T = t/\tau$ has been introduced, where t is the physical time variable and τ is an observation time (Ref. 1, p. 17). Consequently, the dimensionless rate constant was $K_f = \kappa_f \tau$. The determined quantity was $G_A/G_A^{anal} - 1$, where G_A was the calculated dimensionless concentration gradient of species A at the electrode and G_A^{anal} was the analytical expression (6) for this gradient, given by Delahay and Stiehl.[45]

$$G_A^{anal} = (\pi T)^{-1/2} \exp(-K_f T) + K_f^{1/2} \operatorname{erf}[(K_f T)^{1/2}] \qquad (6)$$

The value of $\log |G_A/G_A^{anal} - 1|$ corresponding to $T = 1$ was considered as a measure of the solution error in most of the calculations, in a way analogous to that in Ref. 1. The concentrations were normalized by the bulk concentration c_A° of A. Thus the initial concentration values of A were equal to 1 and those of B were equal to zero. In the case of FD calculations this initial condition was modified for the space grid point at the space coordinate $x = 0$ (i.e. at the electrode), where a concentration of A equal to zero and a concentration of B equal to unity were assumed. Such a formulation of initial conditions obtains accurate results in the FD calculations of the CA transients in limiting current conditions.[46]

In problem 2 the dimensionless time was $T = Fvt/RT$, as usually defined in the theory of the LSV method,[34] where v is the potential scan rate and F, R and T have their usual meaning. Consequently, the dimensionless rate constant was $K_f = \kappa_f/(Fv/RT)$. Since the LSV curves for the catalytic mechanism do not exhibit a peak (except at small κ_f), it was not possible to discuss the accuracy of the calculations in terms of the peak parameters obtained by various methods. Instead, the value of $\log |G_A/G_A^{anal} - 1|$, corresponding to $T = 16$, was selected as a measure of the error. Simultaneously, the dimensionless starting potential (Ref. 3, p. 49) of $+6.5$ was taken. It was assumed arbitrarily that with these parameters the stationary state, characteristic for the catalytic mechanism,[47] is already reached at $T = 16$ (which corresponds to the dimensionless potential of -9.5), at least when $K_f \geqslant 1$, so that, according to Ref. 47, G_A^{anal} is given by eqn. (7). Most of

$$G_A^{anal} = K_f^{1/2} \qquad (7)$$

the calculations for problems 1 and 2 have been performed assuming $K_f = 1$, in a manner analogous to that in Ref. 1.

In the case of problem 3 similar normalizations to those of problem 2 were used (a normalized set of kinetic equations is given and described in Ref. 1, p. 146). Reversibility of the electrode reaction (3) has been assumed. The dimensionless homogeneous rate constant of the (coupled) reactions (4) and (5) $K = 1$, the ratio of bulk concentrations $c_C^\circ/c_A^\circ = 3$ and an initial dimensionless potential of $+8$ were taken for the calculations. Under these conditions the calculated LSV curves were peak-shaped. A heavy run was performed with the OC method in order to obtain maximally accurate values of the peak parameters: $T_p^{acc} = 8.630\,224\,0473$ and $\chi_p^{acc} = 0.437\,369\,062\,26$, where χ is a nondimensional current function, defined in the usual way.[34] Therefore, the quantities: $\log |T_p/T_p^{acc} - 1|$ and $\log |\chi_p/\chi_p^{acc} - 1|$, where T_p and χ_p are simulated peak parameters, were used as measures of the error involved in the calculations. The above values of T_p^{acc} and χ_p^{acc} are probably accurate to about 7–9 significant digits.

Equal diffusion coefficients, D, of all the species considered have been assumed for simplicity in all the calculations. The dimensionless space coordinate $X = x(D\tau)^{-1/2}$ was introduced in the CA case and $X = x(DRT/vF)^{-1/2}$ in the LSV case.

In the FD calculations constant integration steps H and δT for the space and time coordinates were used, except for the Crank–Nicolson method in problems 1 and

2, where calculations based on the grid of unequal spatial integration steps (Ref. 1, p. 90 and Ref. 48) have also been performed. The transforming function (8) suggested by Feldberg,[49] with $a = 1$, was applied in that case. The

$$y = \ln(1 + ax) \tag{8}$$

integration step-size H was determined from the input values of δT and the assumed values of the dimensionless diffusion coefficient $\lambda = \delta T/H^2$, which were 0.4 for the EX and RK2 methods, 1 for the CNR method with uniform space integration steps, and 3 for the CNR method with non-uniform space integration steps (in the latter case this was the maximal λ-value for the first integration step at $X = 0$). The necessary number of integration steps along the X-coordinate was obtained, based on the assumed simulation layer L for the whole time interval T_{max} considered.

Taking into account the estimated rate of diffusion (Ref. 1, pp. 14 and 40), the assumed thickness of the simulation layer (in X-units) was $L = 6T_{max}^{1/2}$ in problems 1 and 2 and $L = 3T_{max}^{1/2}$ in problem 3. The corresponding β-parameter in the OC discretization[12,13,24] was $\beta = L^{-2}$. The values of T_{max} were $T_{max} = 1$ for problem 1, $T_{max} = 16$ for problem 2 and $T_{max} = 10$ for problem 3. The computational times given below represent the duration of the solution processes within the entire intervals T_{max} of T.

Results and discussion

The accuracy and speed of the accepted variant of the OC method depend on the following factors: the number N of the internal collocation points, which (together with the number of kinetic PDEs) determines the dimension of the ODE set to be solved, the initial integration step-size δT_0 along the T-coordinate, the tolerance parameter ε, which determines the desired accuracy for a single ODE integration step, and the number of tabulation points N_t, i.e. the number of (usually equidistant) time instances at which one wishes to determine concentrations and their gradients at $X = 0$. Such parameters form a typical set of input data for the ODE solvers with automatic integration step-size selection algorithms, and have also to be specified in the case of the integrators STIFF3 and STINT. However, the way in which these parameters are used by the ODE solvers can be different in different programs. Therefore, their influence on the results has to be recognized in every particular case. In the STIFF3 integrator, for example, the desired number of tabulation points has an effect on the integration step-size used, since in every call to the program the end of the last integration step is forced to coincide with the current tabulation point. In STINT the grid of integration steps is entirely independent of the grid of tabulation points, and interpolation on the integration grid is used to obtain tabulated results. The error test parameter ε also has a somewhat different meaning in both programs. During the integration this parameter is compared with some estimates for the errors of the components of the ODE set, taken with appropriate weighting factors. Both the error estimates and weighting factors are different in different methods. For example, in STIFF3 the error weighting factors equal to unity have been assumed on input for all the components of the ODE sets. STINT calculates such factors automatically. The effect of the above parameters on the accuracy and efficiency of the calculations is analysed below.

Effect of δT_0 *on accuracy.* Since the ODE systems emerging from the OC discretization are stiff, the initial step-size δT_0 should preferably be of the order of the

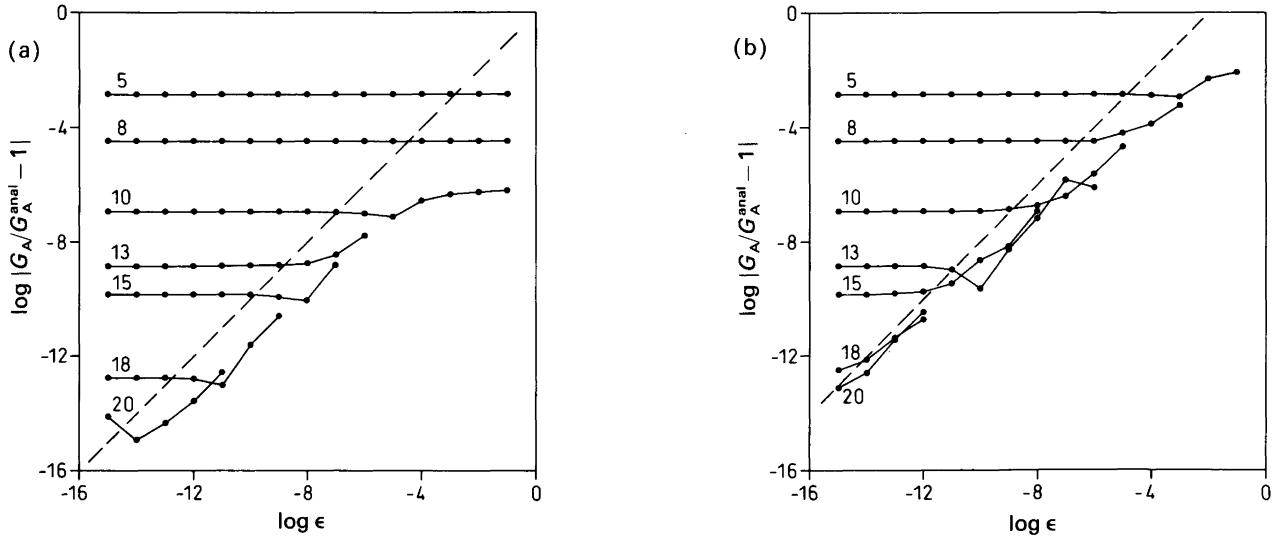

Fig. 1. Dependences of the relative error of the gradient at $X = 0$ and $T = 1$ on ϵ, obtained for problem 1 with the OC method and the STIFF3 integrator (a) or the STINT integrator (b). Values of N are indicated in the figure. The broken line joins points on the curves for which ϵ is optimal (see text).

reciprocal of the largest eigenvalue of the Jacobian matrix of the ODE system at $T=0$ (Ref. 3, p. 324). Then unnecessary automatic time-step adjustments are minimized and possible troubles with the numerical stability (for too high δT_0) avoided. The determination of the eigenvalues is not a simple task for the present calculations, owing to the rather large dimensions of the ODE sets and their complexity. Therefore, various δT_0-values were tested, by trial and error, and it was found that the computational time did not significantly depend on this choice, but a smaller δT_0 produced somewhat more accurate results. Therefore, $\delta T_0 = 10^{-14}$ was assumed for further calculations. This is about the smallest acceptable value, at least for the STINT integrator, for the following reason. In calls to STINT the minimal and maximal allowable time step sizes have additionally to be specified. The minimal step size should be much smaller than any expected value of the integration step, in order to avoid problems with the automatic step size selection when the error criterion is not met in a single iteration. Therefore, 10^{-2} times the initial integration step (i.e. 10^{-16}) was taken for this purpose. Such a small value is on the verge of machine accuracy. The maximal allowable time step ten times larger than the tabulation interval was arbitrarily assumed. The maximal allowable order of 7 of the integration method in STINT was assumed in all the calculations, in order to utilize fully the capabilities of this program.

Effect of ε *and* N *on accuracy.* The accuracy of the OC computations was found to depend strongly on two parameters: the number N of internal collocation points and the tolerance parameter ε. This result is rather obvious, since N reflects the quality of the representation of the concentration profiles by the orthogonal polynomial expansions in X, while ε determines the accuracy

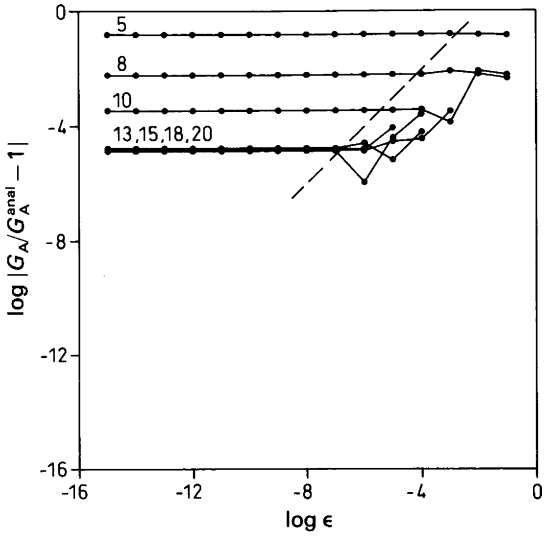

Fig. 2. Dependences of the relative error of the gradient at $X=0$ and $T=16$ on ϵ, obtained for problem 2 with the OC method and the STINT integrator. Values of N are indicated in the figure. The broken line joins points on the curves for which ϵ is optimal (see text).

of the ODE integration in T. Figures 1–3 show the dependences of the calculation errors on ε at various N. It can be seen that for any fixed N-values these errors generally decrease with decreasing ε, if initially a large ε is selected, until a minimal error, allowed by a given N, is reached. It can also be seen that higher N allows better accuracy to be achieved. However, in Fig. 2 one does not observe a further decrease of the errors with N for $N \geqslant 13$. Apparently, this reflects the fact that eqn. (7) does not give a fully correct gradient value in that case, i.e. the steady-state limiting current is not, in fact, yet attained at $T=16$, as was assumed.

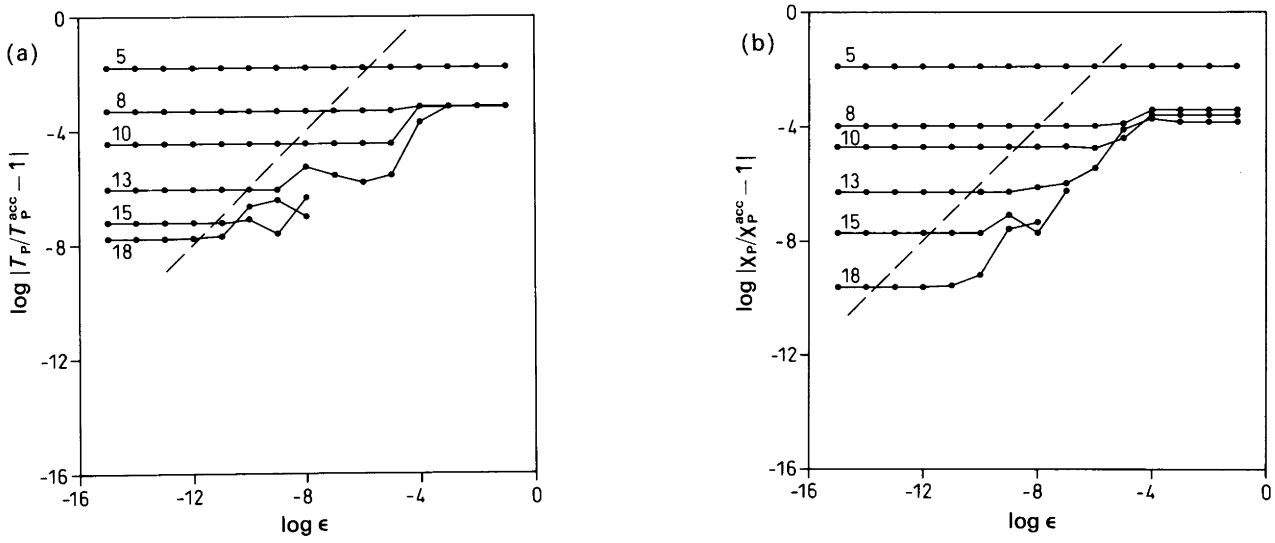

Fig. 3. Dependences of the relative error of the LSV peak position (a) or LSV peak height (b) on ϵ, obtained for problem 3 with the OC method and the STINT integrator. Values of N are indicated in the figure. The broken line joins points on the curves for which ϵ is optimal (see text).

The smaller the value of ε is taken, the better accuracy of ODE integration can be achieved, but the greater the computational time becomes. Therefore, an optimal ε_{opt}-value for computations can be defined as a maximal ε-value for which the minimal error allowed by a given N is already reached. The broken lines in Figs. 1–3 indicate that in the case of the STIFF3 integrator and problems 1 and 2, ε_{opt} is roughly equal to the error reached in the calculations. For STINT it is about 100 times lower. For problem 3, ε_{opt} is about 10^4 times lower than the errors. Concrete values of ε_{opt} used in further calculations are collected in Table 1. In the case of problem 2 the optimal ε values for $N \geqslant 15$ have been determined by linear extrapolation of the ε_{opt}-values for $N < 15$, assuming a linear dependence of the error on N. Such a dependence is fairly well obeyed for the data from Fig. 1.

The identification of the optimal ε-values is a simple task when exact solutions are known and plots such as presented in Figs. 1–3 can be made. In practice, one does not know the solutions (if one did, why do the simulations?), so that ε_{opt} have to be determined in a different way. For example, one can make calculations with gradually decreasing ε and observe how the ratios of the step-by-step calculated values of the quantity of interest converge to unity (or zero on the logarithmic scale). The value of ε for which further decrease of ε does not bring these ratios substantially closer to unity can be then selected as ε_{opt}.

Efficiency comparisons. The efficiency of a given integration method for the electrochemical kinetic PDEs can be conveniently characterized quantitatively by plotting its error vs. computational time (ct) involved.[1] Efficient methods produce small errors in short computational times. Figures 4 and 5 present such logarithmic efficiency plots obtained in the present work. The plots for the OC method have been obtained assuming the optimal values of the tolerance parameter ε from Table 1. As can be seen, the efficiency of the OC calculations strongly depends on the ODE integrator used and on the number of tabulation intervals N_t. STIFF3 is about 1–2 orders of magnitude less efficient than STINT. When using STINT, there is a slight difference between the calculations based on analytical Jacobian matrix evaluation and those which use numerical approximation for the Jacobian matrix. The first option is only marginally faster, owing to the fact that the Jacobian matrix evaluation was performed only rarely by STINT during the calculations. This also

Table 1. Optimal values, ϵ_{opt}, of the tolerance parameter ϵ, for various numbers, N, of the internal collocation points.[a]

	Problem 1		Problem 2		Problem 3
N	STIFF3	STINT	STIFF3	STINT	STINT
5	1.371E-3	1.371E-5	1.472E-1	1.472E-3	1.233E-6
8	3.192E-5	3.192E-7	5.768E-3	5.768E-5	1.047E-8
10	1.114E-7	1.114E-9	3.319E-4	3.319E-6	1.941E-9
13	1.429E-9	1.429E-11	1.556E-5	1.556E-7	5.035E-11
15	1.396E-10	1.396E-12	1.578E-6[b]	1.578E-8[b]	1.928E-12
18	1.811E-13	1.811E-15	5.093E-8[b]	5.093E-10[b]	2.410E-14
20	7.745E-15	7.745E-17	5.164E-9[b]	5.164E-11[b]	—

[a] xE-$y \equiv x \times 10^{-y}$. [b] Values obtained by linear extrapolation.

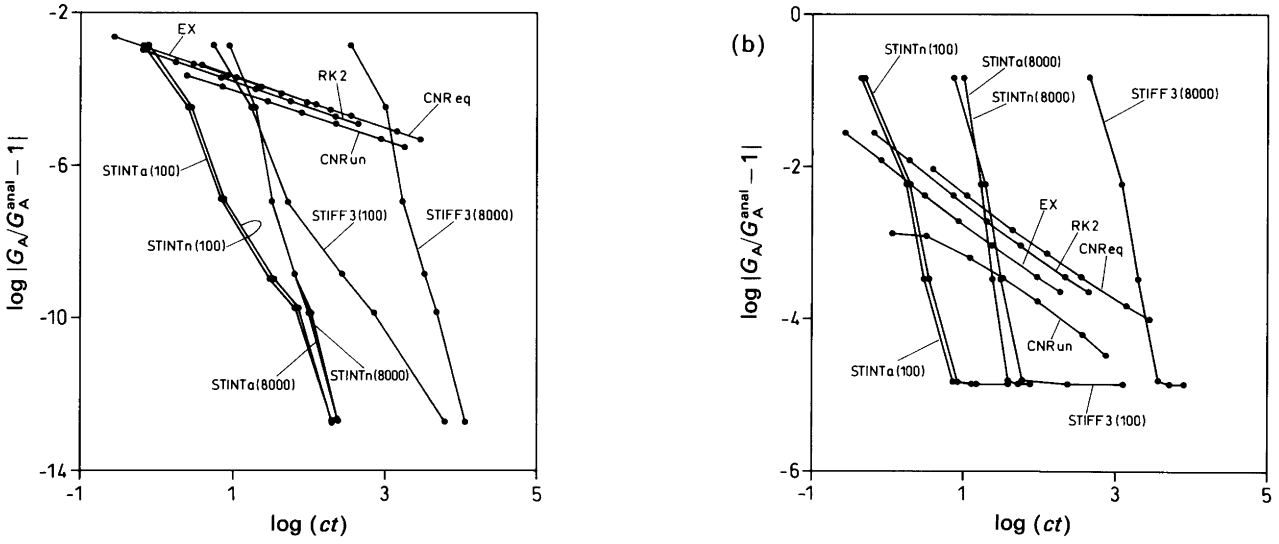

Fig. 4. Efficiency plots for the simulation of problem 1 (a) or problem 2 (b). Notation: EX, Classic explicit FD algorithm with equal space integration steps; RK2, Runge–Kutta second-order FD algorithm with equal space integration steps; CNReq, Crank–Nicolson FD algorithm with equal space integration steps; CRNun, Crank–Nicolson FD algorithm with unequal space integration steps; STIFF3, OC algorithm using the STIFF3 integrator; STINTa, OC algorithm using the STINT integrator with analytical Jacobian matrix evaluation; STINTn, OC algorithm using the STINT integrator with numerical Jacobian matrix evaluation. For a given FD algorithm, each point on the curve corresponds to a different number of integration steps along T: 100, 200, 500, 1000, 2000, 5000 or 8000. For a given OC algorithm, values of the number N_t of tabulation points are given in braces and each point on the curve corresponds to a different number N of internal collocation points: 5, 8, 10, 13, 15 or 18. The computational time is given in seconds.

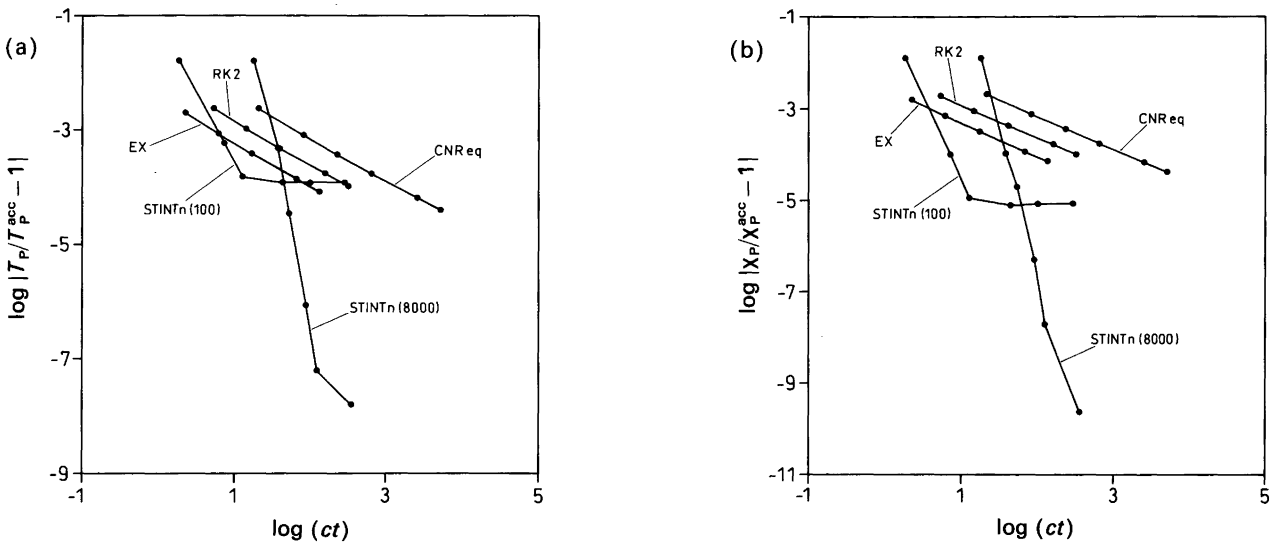

Fig. 5. Efficiency plots for the simulation of problem 3, error of the LSV peak position (a) or LSV peak height (b). Notation as in Fig. 4. The points for 100 (and 100 and 200) integration steps along T are not displayed for the CNR (and EX and RK2) algorithms, respectively. With such numbers of integration steps negative concentrations were observed in the calculations.

indicates that the stiffness of the ODE systems was not very pronounced in the present calculations. The effect of the number of tabulation intervals N_t is the most considerable when the number N of internal collocation nodes is small. When using a small N (such as for example $N = 5$), OC is evidently less efficient than all the FD methods taken for comparison. However, OC becomes superior when $N \geqslant 10$ and when a fast integrator, such as STINT, is used. It yields extremely small errors (e.g. relative errors 10^{-13} in Fig. 4a) which would not be possible to attain in the same ct by the FD algorithms. The high efficiency of the OC is particularly noticeable when small N_t is satisfactory for the applications of the results obtained, as is usually the case for the CA transients (Fig. 4a) and with the LSV curves for problem 2 (Fig. 4b). In the latter case the inadequacy already pointed out of eqn. (7) to provide accurate G_A^{anal}-values is also visible in Fig. 4b. This obscures to some extent the conclusions regarding the efficiency of the OC method in that case. However, it is rather clear that the higher efficiency of OC would be seen in Fig. 4b if the exact G_A^{anal}-values were known and could be used in the error analysis. OC performs more poorly when transient curve characteristics such as LSV peak parameters T_p and χ_p have additionally to be determined, as it is in the case of problem 3. In order to obtain these parameters one additionally has to interpolate between the tabulated transient curve values. In the present work the parameters T_p and χ_p were determined by a parabolic interpolation between the three maximal tabulated χ values, followed by an analytical calculation of the maximum of the parabola obtained. The accuracy of this procedure significantly depends on N_t. Small N_t values, such as $N_t = 100$ in Fig. 5, are not sufficient to assure an accuracy of the peak parameters comparable with that which, in principle, is possible for the tabulated transient curve values themselves. Therefore, at small N_t a further increase of N for $N \geqslant 10$ cannot improve the accuracy of the peak parameters in Fig. 5. Consequently, one has to use rather high N_t-values in such cases, which increases the ct necessary for the OC calculations. However, when one accepts expending more computational time, it can still be more profitable to use OC rather than FD methods, since with high N_t OC assures much smaller errors of the peak parameters than do the FD methods with the number of time integration steps equal to the number of OC tabulation steps N_t. When analysing Fig. 5 one has to remember that the values of T_p^{acc} and χ_p^{acc} are not perfectly accurate. They have been obtained assuming $N = 20$, $N_t = 8100$ and $\varepsilon = 10^{-15}$ (for STINT), i.e. extreme values which lie at the limit of technical possibilities of the programs used. Therefore, Fig. 5 provides the rates of convergence to T_p^{acc} and χ_p^{acc}, which can be achieved by the OC and FD methods, rather than true accuracies and efficiencies.

One should treat Figs. 4 and 5 with a certain caution. Complex algorithms can usually be programmed in many different ways, at different levels of generality, using different programming languages, different compiler optimizations, etc., as well as executed on different computers. This applies to OC and to more complicated FD programs, such as those for the CNR method. Therefore, the above results of the relative efficiency of the OC and FD methods do not have an absolute character, and some departures from them can occur in particular implementations.

Reliability for discontinuous boundary conditions. Efficiency is an important, but not the only, property required from the numerical solution methods in electrochemical kinetics. Another important feature is their

ability to cope with discontinuous boundary conditions. In the present study this difficulty occurs for problem 1. The potential step at $T=0$ leads, in the case of the reversible reaction (1), to the singularity of the concentration gradients, in accordance with eqn. (6). Neither FD nor OC methods can truly reproduce this singularity in the numerical solution, since both these methods are based on finite differencing in time, which can give only finite values of the gradient. Consequently, large errors are usually expected in the simulated gradient close to $T=0$. A reliable numerical method should quickly damp out these errors. Figure 6 shows how the errors of the gradient evolve in time in the case of the OC method and the CNR algorithm, which is the most accurate from the FD methods considered. It can be seen that in both cases the error is greatest initially and then, on average, decreases with time. Close to $T=0$ both the CNR and OC algorithms give poor results. When the number of internal collocation points is small ($N=5$) then in the whole time interval $T\in[0, 1]$ the OC method gives larger errors than the CNR method with a minimal number (100) of time steps used. However, when N is sufficiently large (e.g. the curve for $N=18$ in Fig. 6), the accuracy of the OC method within $T\in[0, 1]$ becomes better than that of the CNR method, with a maximal number (8000) of time steps used.

The poor reliability of the OC method with small N, when dealing with discontinuous boundary conditions, can also be seen in the concentration profiles. Figure 7 compares the concentration profiles of the species B in problem 1, obtained with the OC and CNR methods at three time instants. As can be seen, at each time instant the CNR algorithm gives concentration values which are

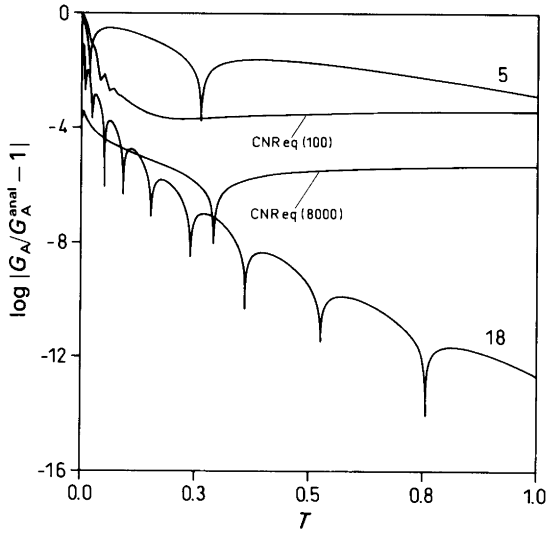

Fig. 6. Dependences of the relative error of the simulation of problem 1 on T, obtained with the Crank–Nicolson algorithm with equal space integration steps (CNReq) and the OC method with 1000 tabulation points N_t. Values of the number of integration steps for T variable in the CNR algorithm are given in braces. Values of N are provided at the respective OC curves.

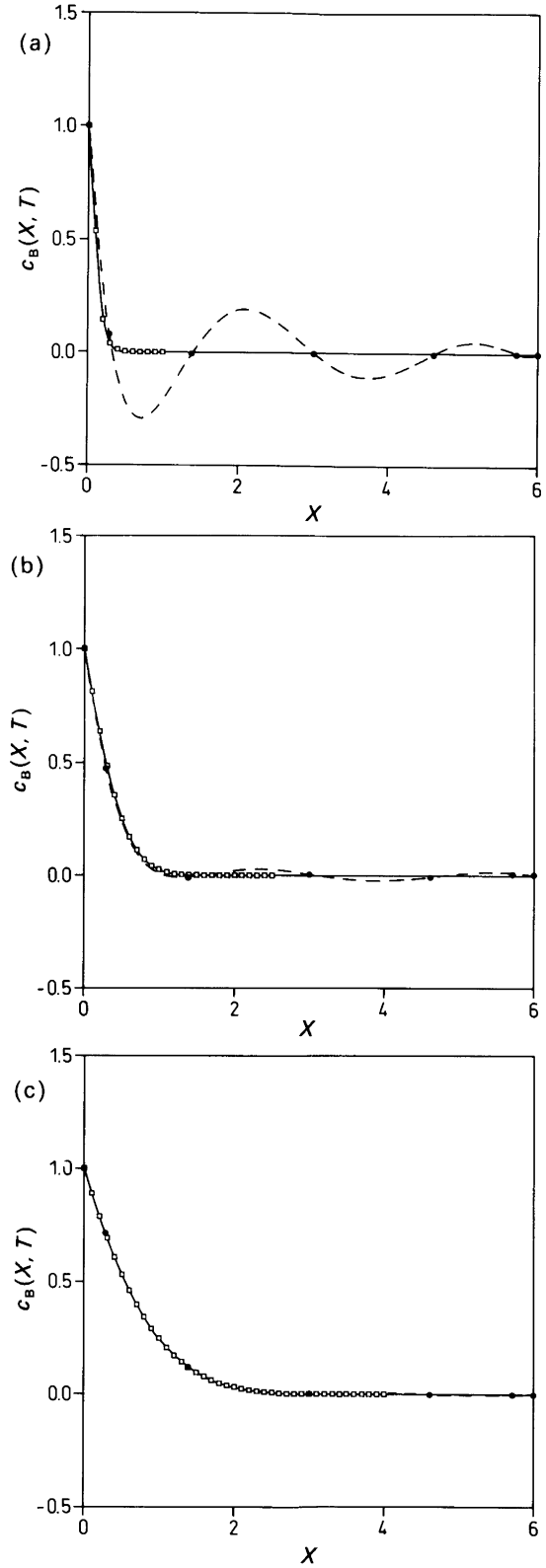

Fig. 7. Concentration profiles of species B in problem 1 at (a) $T=0.01$, (b) $T=0.1$ and (c) $T=0.5$. Notation: (——) analytical prediction based on eqn. (11) in Ref. 45; (– – • – –) results of the OC method with 5 internal collocation points; (□ □ □) results of the CNR method with equal space integration steps and 100 time integration steps along $T\in[0, 1]$.

very close to the accurate ones, even though the number of time integration steps is very small (100). No negative concentrations are observed. As opposed to this, the values obtained by the OC method with a small N are only roughly approximate at the collocation nodes, especially when T is small (Fig. 7a). In addition, concentration values between collocation nodes deviate considerably from the analytical prediction. Even at T as large as 0.5 (Fig. 7c) one still observes non-physical, oscillatory behaviour of the concentration profile. This behaviour is related to the inability of the finite set of collocation polynomials, resulting from the small, finite number N of collocation points, to represent rapid spatial changes of the concentration. The problem has already been pointed out by Whiting and Carr,[11] but apparently it has not been considered to be very serious, since for large T a good accuracy has been obtained. However, in the simulation of the potential-step transients, one should rather pay attention to the good accuracy for small T, when the most dramatic changes in the physical processes occur. A related and even more serious deficiency of the OC algorithm is that non-physical, negative concentrations are frequently observed, both at the collocation nodes and between them, as clearly seen in Figs. 7a and 7b. The quite large magnitudes of the negative concentrations at collocation nodes cannot be explained exclusively by the round-off errors occurring during the numerical integration. Use of higher N improves the accuracy of concentration profiles for small T, but the negative concentrations are observed even with $N = 18$ (Fig. 8). These problems also occur in more advanced OC algorithms, as observed by Speiser,[22] albeit in a less drastic form.

Reliability for fast homogeneous reactions. Another important property which determines the quality of the numerical methods used in electrochemical kinetic

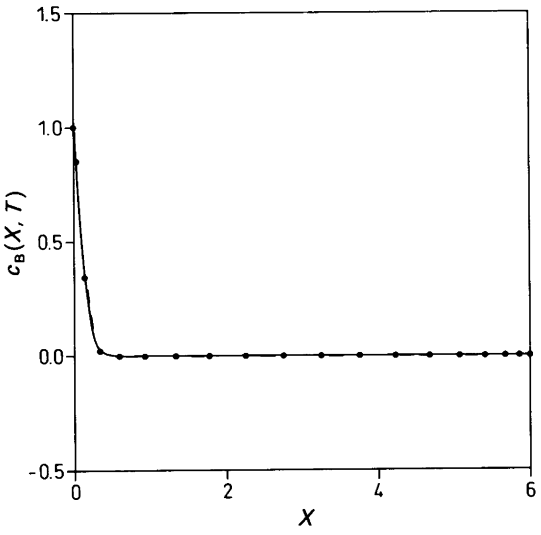

Fig. 8. Concentration profiles of species B in problem 1 at $T = 0.01$. Notation: (——) analytical prediction based on eqn. (11) in Ref. 45; (--•--) results of the OC method with 18 internal collocation points.

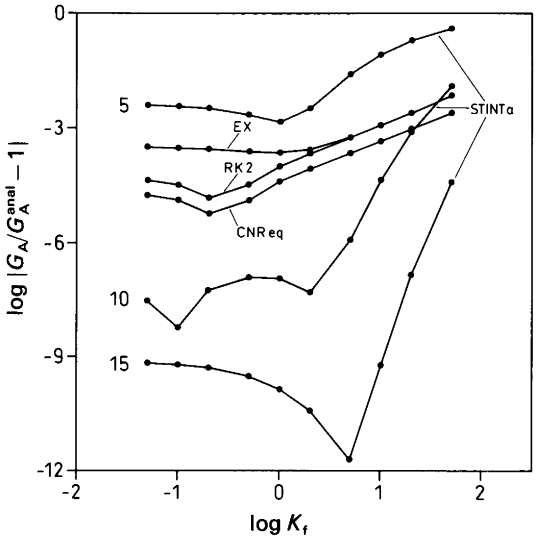

Fig. 9. Relative errors of the gradient at $X = 0$ and $T = 1$, in the simulation of problem 1, as a function of log K_f. Notation as in Fig. 4. The curves for FD algorithms refer to 1000 integration steps along T. For the OC method, values of N used are indicated in the figure.

simulations is their reliability in the solution of fast homogeneous reaction–diffusion problems. For such problems thin reaction layers occur, which is a serious difficulty. The above calculations have been performed assuming $K_f = 1$ or $K = 1$ for reactions (2) or (4) and (5). This is a rather small homogeneous rate constant, for which the above difficulty practically does not occur. Therefore, the investigation of the error behaviour for larger rate constants is relevant. Figure 9 compares dependences of the error on log K_f, obtained with various methods for problem 1. It can be seen that the considered variant of the OC method performs in a similar way to the FD methods, i.e. there is always a region of K_f (around 10^{-1}–10) in which the errors are minimal, but for K_f larger than some limiting value (around 10 in Fig. 9) there is a systematic error increase with K_f. Although the OC algorithm produces rather smaller errors, in a wide range of K_f, than do the FD methods, for large K_f it behaves equally poorly. This deficiency is significantly reduced in more elaborated variants of the OC method, such as spline collocation,[16] where K_f up to 10^{10} can succesfully be considered.[50]

Figure 9 gives useful information about the accuracy with which kinetic currents can be calculated in the presence of homogeneous reactions by the OC method. However, in view of the frequently observed negative concentrations the question of the reliability of such calculations arises, especially for fast second-order kinetics. For the first-order reactions the sign of a homogeneous kinetic term in a PDE changes in the same way as the sign of the time derivative for a concentration. Therefore, if the concentration becomes negative, such a kinetic term will act as a negative feedback in the respective ODE, tending to force the negative concentration

back to non-negative values. Similar behaviour occurs for second-order bimolecular kinetic terms if the concentration of only one species is negative. However, when both concentrations in a second-order kinetic term are negative, their product becomes positive and there is a positive feedback in the respective ODE, which may lead to the increase of the absolute value of the negative concentration, and consequently may destabilize the solution process. In the cases of sporadic occurrence of negative concentrations, when their magnitude is at the level of machine accuracy and when they clearly result from round-off errors, this problem can be eliminated by locally changing the sign of the kinetic term within the procedures of numerical integration, in order to impose realistic constraints on the values of the numerical solution.[22] However, such a strategy cannot be applied and physically justified in the cases when one observes larger negative concentrations, as it happens when the number of collocation points N is small. In such a case the negative concentrations apparently reflect the inherent properties of the solution of the ODE set, resulting from the low-order polynomial expansion of the concentration profiles, and are not associated with the errors of the numerical integration of this ODE set. Another reason can be the existence of multiple solutions to the ODE problem, when non-linear homogeneous kinetics are involved.[51] The numerical integration is likely to fail in such cases, oscillating between physical and non-physical solutions, especially when they lie close to each other. These problems appear to be a serious deficiency of the OC method, as opposed to FD calculations, where the occurrence of negative concentrations can successfully be eliminated,[32] and it leads to the question whether the good accuracy of this method is not, at least in some cases, fortuitous. This also raises certain doubts about the numerical stability of this method. Statements can be found in the literature[24] that the stability of solutions is inherent in the OC. Apparently, such statements result from the fact that one can use stable integrators for solving the ODE sets in this method. The above example of second-order homogeneous kinetics shows that this is only half of the truth. One is interested in obtaining stable solutions of the PDEs and not only those of the ODEs. For this, the polynomial expansions of the concentrations have also to be stable, in the sense that the difference between the solution of the resulting ODEs and the correct solution of the PDEs does not grow and remains sufficiently small for any time value. Stability, as understood in this way, seems to be difficult to examine and to prove in a general way for electrochemical kinetic problems.

Conclusions

The results obtained in the present work reveal that OC possesses both advantages and disadvantages, as compared with the FD algorithms for electrochemical kinetic simulations. The advantage of OC is that very high accuracy and efficiency of the simulations can be achieved with this method, if a proper ODE integrator and proper values of the parameters such as the number N of internal collocation points, tolerance parameter ε and the number N_t of tabulation steps, are chosen. The disadvantage is a rather doubtful reliability of this method in the simulation of discontinuous boundary conditions and homogeneous reactions. These features make OC simulations an art rather than routine. The successful use of the OC requires more experience and skill than do the FD calculations.

For practical applications of OC the following hints can be helpful. One should use a fast integrator for stiff ODEs, with δT_0 as small as possible and with ε close to optimal. The number of internal collocation nodes used should be at least 10. Certainly, $N = 5$ or 6 nodes by various authors[24] is not enough, if OC is to be competitive with FD methods and sufficiently reliable. One has to pay attention to negative concentrations and/or second-order homogeneous kinetic terms.

Acknowledgments. This work has been carried out as part of a project supported by the Danish Science Research Council Grant No. 11-9311. L. K. B. is grateful to Priv. Doz. Dr. Bernd Speiser of Tübingen University, Germany, for valuable discussions by email.

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Received December 23, 1992.