Letter to the Editor

Electrochemical Simulations. Part 15.¹
Advanced Orthogonal Collocation Techniques in Problem Situations of the EC\textsubscript{cat} Mechanism


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Electrode reactions are in general composed of several steps including diffusion, electron transfer, adsorption and other processes. For the analysis of experimental results, simulations of theoretical models are performed in which the governing partial differential equations (PDEs) are solved by approximating numerical methods. Bieniasz and Britz have recently compared finite difference (FD) and orthogonal collocation (OC) simulation schemes, as regards efficiency and reliability.² Chronoamperometric and cyclic voltammetric responses of two reaction mechanisms involving electron transfers and homogeneous kinetics were considered.

Taking into account several FD variants³⁴ and the classical OC algorithm,⁵⁶ they conclude that OC may be more effective than FD and yield better accuracy. Inaccuracies were, however, identified for fast homogeneous chemical kinetics and for discontinuous boundary conditions.

For their comparison, Bieniasz and Britz used advanced FD algorithms such as Rudolph’s matrix solution technique⁴ as improved by Britz.⁸ On the other hand, in the case of OC they employed the original formulation.⁵⁶ It is known that this simple technique does not perform well in the problem cases mentioned above. This has been documented¹⁰¹¹ and the reason has been identified: in OC the concentration profiles in the diffusion layer (space coordinate 0 ≤ x ≤ L; L is a distance from the electrode at which diffusion effects can be neglected during the entire simulation) are represented by a finite set of polynomials result in a set of ordinary differential equations from each PDE (spatial discretization). Only a small number N of ‘nodes’ (collocation points) is used, and the method only claims that exact concentration values at these points are calculated.⁶¹³ The distribution of the collocation points along x is determined by the type of polynomials used.⁶ If, in a particular case, only one or no collocation point is situated in a certain range of interest within the diffusion layer, the accuracy will drop drastically, since the corresponding effects will be ‘missed’. For example, if a fast homogeneous reaction is coupled to the electron transfer, a thin reaction layer is formed close to the electrode, whose thickness is much smaller than L. Then, the reaction layer may extend from the electrode (x = 0) to a point in solution which is closer to x = 0 than the innermost collocation point, and the effect of the fast reaction is not ‘seen’ by the simulation. Similar problems are found if a sudden change of the concentration is imposed at x = 0, as in chronoamperometric simulations. If one distributes the collocation points in such a way that a good representation is expected near the end of the simulation, it may well be that the diffusion layer at the beginning does not reach the first collocation point. Again, incorrect results will be found.

Improved algorithms to overcome these problems have been suggested and successfully tested for both cases [spline collocation (SOC);¹¹ temporally expanding simulation space¹²]. Although Bieniasz and Britz recognize these techniques in their paper, they see the comparison of the most simple variant as the most stringent test for OC. Under these circumstances, however, their results only prove that the worst OC variant has some advantages and some disadvantages over some of the best FD techniques. Thus it might be of interest to demonstrate the drastic improvements brought about by the more advanced OC algorithms mentioned.

Results of OC simulations with and without these
Table 1. Potential results (half-peak or half-wave potential, referred to \( E^\circ \)) in mV for EC_{cat} simulations under CV conditions; tabulation stepwidth: 1 mV.

| \( \kappa \) | OC   | |
|--------------|------|------|------|
|              | \( N = 6 \) | \( N = 8 \) | \( N = 10 \) | SOC   | \( N = 6 \) | \( N = 8 \) | \( N = 10 \) |
| 0            | 28   | 28   | 28   | 28   | 28   | 28   | 28   |
| 0.1          | 26.7 | 26   | 26   | 26   | 26   | 26   | 26   |
| 1            | 11.2 | 12   | 12   | 11   | 11   | 11   | 11   |
| 10           | 1.0  | 8    | 5    | 3    | 1    | 1    | 1    |
| \( 10^2 \)   | 0    | 12   | 10   | 9    | 0    | 0    | 0    |
| \( 10^4 \)   | 0    | 194  | 194  | 194  | 0    | 0    | 0    |
| \( 10^8 \)   | 0    | 194  | 194  | 194  | 0    | 0    | 0    |

features generated with our program EASI\textsuperscript{14} (integrator, DDEBDF; mainframe computer, CONVEX C3850) for the EC_{cat} mechanism \( A \rightleftharpoons B \pm e^- \) (characterized by the formal potential \( E^\circ \)), \( B \rightarrow A \) (characterized by the normalized rate constant \( \kappa \), as defined e.g. in Ref. 2) will be compared. For chronoamperometry this corresponds to problem 1 of Bieniasz and Britz, for cyclic voltammetry to their problem 2.

Cyclic voltammograms were simulated with a tabulation stepwidth of 1 mV in the range 0 \( \rightarrow \) 0.5 V with \( E^\circ = 0.35 \) V, while \( \kappa \) was varied. Results for the peak or, in the case of the wave-shaped current/potential curves at higher \( \kappa \), half-wave potentials (both referred to \( E^\circ \)) are given in Table 1 and compared to literature reference values.

While simulations with OC do not give reliable results for the potential features at \( \kappa > 1 \), SOC may be used up to at least \( \kappa = 10^6 \) (Table 1). The number of nodes, \( N \), does not have an influence in the SOC case on the accuracy. Thus, even \( N = 6 \) is appropriate if the determination of a potential within 1 mV is desired.

With an increasing number of collocation points, the relative error\textsuperscript{2} of the current function in SOC calculations (Fig. 1) decreases from \( 10^{-3} \) \((N = 6)\) to \( 10^{-7.5} \) \((N = 10)\) owing to the increasingly better approximation of the concentration profiles in the reaction and diffusion layer. This parallels the observations for OC simulations.\textsuperscript{2}

An increase in \( \kappa \), however, has a negligible effect on the accuracy of the current function if SOC is used. The relative error remains almost constant at the values mentioned above between \( \kappa = 10 \) and \( \kappa = 10^6 \). For the OC and FD algorithms, on the other hand, a strong increase of the error was observed\textsuperscript{2} for \( \kappa > 1 \). The accuracy of the SOC simulations is based on the fact that the entire space coordinate is divided into two regions: (a) \( 0 \leq x \leq x_s \), the reaction layer, and (b) \( x_s \leq x \leq L \), the diffusion layer. In each region, \( N \) collocation points are distributed. The extension of the reaction layer, \( x_s \), is determined from the rate constant of the homogeneous chemical reaction.\textsuperscript{11}

This fact explains why the accuracy does not depend on the value of \( \kappa \).

It must be noted, however, that for \( N = 8 \) and \( N = 10 \) in the simulations employing the larger \( \kappa \)-values slight oscillations of the current are found in the limiting current region. These oscillations have absolute amplitudes around \( 10^{-10} \) at a current function of \( 10^5 \). Thus \( 10^{-13} \) seems to be the intrinsic limit of the relative accuracy of the SOC method in the present formulation, which can not be decreased even by an increase in \( N \). Clearly, this is below the experimentally accessible accuracy by many orders of magnitude.

It is concluded that SOC is an accurate method for the simulation of fast catalytic electrode reactions of the type considered here. In earlier publications, similar results have been obtained for other electrode reaction mechanisms.\textsuperscript{11,15}

For \( \kappa = 1 \) in chronoamperometric simulations concentration profiles at \( T' = 0.01, 0.1 \) and 0.5 (where \( T' \) is the time normalized to the pulse length)\textsuperscript{2} were compared for two cases: (a) OC and (b) OC with temporal expansion of the simulation space.\textsuperscript{12} Results are shown in Fig. 2 for \( N = 7 \) (species A). Classical OC (Fig. 2a) gives (as previously observed)\textsuperscript{2} strong oscillations at \( T' = 0.01 \), which abate at later times. Also, negative concentrations of B at the nodes are found even for \( T' = 0.5 \). With increasing \( N \) the effects decrease. In simulations with the improved technique, on the other hand, such oscillations are effectively damped even at early times for \( N = 7 \) (Fig. 2b).
profiles throughout the calculation. The functional relation defining the movement is derived from the temporal expansion of a diffusion layer (see e.g. Ref. 16). Although the results are considerably improved even with the use of such a rather rigid model, further advantages could possibly be gained from dynamically adjustable grid techniques such as proposed by Bieniasz,17 which take into account the actual development of the diffusion layer with $T'$. Consequently, for the problem cases identified by Bieniasz and Britz2 for OC simulations, solutions already exist. Although these algorithms may further be improved, their use leads to more accurate and reliable results.

References


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Fig. 2. Concentration profiles of species A during chronamperometric simulations of the EC1 mechanism; $\kappa = 1$, $N = 7$, profiles at $T' = 0.01$ (○), 0.1 (△) and 0.5 (∗); (a) OC, (b) OC with temporarily expanding simulation space; distance normalized to $L$ at the end of simulation.

Negative $c_a$-values have decreased to an absolute maximum of $8 \times 10^{-4}$ at $T' = 0.01$ and totally disappear for $T' > 0.01$.

In this algorithm, all $N$ collocation points are distributed in the thin diffusion layer near the electrode at the beginning of the simulation, and their location moves12 away from the electrode surface with $(T')^{1/2}$, maintaining a good representation of the concentration...