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Recent Developments in Digital Simulation of Electroanalytical Experiments*

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This review covers developments in digital simulations of electroanalytical experiments, since 1996. Over the period of time considered, a number of new techniques has been applied. Among them are: the method of lines approach using the differential algebraic equations formulation, extrapolation and Rosenbrock time integrators, multipoint and high-order compact spatial discretisations, finite-element-like methods, adaptive techniques and sensitivity analysis. More simulation software is now also available.

Key words: computational electrochemistry, digital simulation, electrochemical kinetics, electroanalysis, transient methods, microelectrodes

1. Introduction

In connection with electroanalytical kinetic experiments [1], digital simulation [2,3] plays an increasing role. This review covers developments in the field after 1996. That is, it covers advances that were made after reviews published at about that time [4,5]. There have also been, at roughly the same time, more specific survey-type articles reviewing, for example, the "fast implicit finite difference" (FIFD)** method [6] and on theory (and some simulation) at ultramicroelectrodes (UMEs) [7,8]. Recently, a chapter on digital simulation has also appeared in the Encyclopaedia of Electrochemistry [9] and a brief review section is seen in [10], as an introduction to the available methods. It will be seen that a considerable number of new contributions has been published since these works appeared.

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

** Abbreviations used:
ADI – alternating direction implicit; AE – algebraic equation; BDF – backward differentiation formula; BI – backward implicit; CN – Crank-Nicolson; DAE – differential-algebraic equation; ECL – electrochemical luminescence; FD – finite difference; FEM – finite element method; FIFD – fast implicit finite difference; FIRM – fully implicit Richtmyer modification; HOC – high order compact; MOL – method of lines; NUMOL – numerical method of lines; ODE – ordinary differential equation; PDE – partial differential equation; RK – Runge-Kutta (method); SA – sensitivity analysis; SAGE – single alternating group explicit; SECM – scanning electrochemical microscope; UME – ultramicroelectrode.

The structure of the review is as follows. In section 2 we comment on the changing role and position of digital simulation in electroanalytical chemistry. In sections 3–5 we describe new developments related to the spatial and temporal discretisations used in electrochemical simulations. Section 6 lists various new developments of the simulation methodology, from the point of view of specific classes of problems or application types. Section 7 mentions miscellaneous new numerical methods applied to electroanalytical chemistry, but not belonging to the mainstream of simulation methods. Finally, section 8 describes those new developments that are aimed towards automating the various simulation practices. This includes a discussion of new simulation software.

A decision which papers to cite in a review is always somewhat subjective. For example, in the present case it is difficult to draw a clear dividing line between electrochemical kinetics and, let us say, electrochemical engineering, or other sub-fields of electrochemistry that require simulation. We apologise to all those authors whose important works may have been omitted due to our decisions.

2. Digital Simulation as a Part of Computational Electrochemistry

For several decades, digital simulation in electroanalytical chemistry has functioned as a modest addition to the theory of steady-state and transient electrochemical methods. With the overall changes in the methodology of natural sciences, caused by the increasing availability, power, and application scope of digital computers, the role and importance of digital simulation is now changing. It is justified to notice and consciously stimulate the emergence of a new branch of electrochemistry that might best be called Computational Electrochemistry. A recent paper by Bieniasz [11] has discussed in much detail the rationale for, tentative definition of, and research objectives for Computational Electrochemistry. It has been argued that Computational Electrochemistry should use computer experiments as an operational method of studying electrochemical phenomena, and that it should be complementary and non-reducible to the traditional fields of Experimental Electrochemistry (which uses physical experiments) and Theoretical Electrochemistry (which uses mathematical models and theories). One of the basic activities of Computational Electrochemistry should be the conception and development of Problem Solving Environments for electrochemistry, *i.e.* highly automated advanced software systems serving for a wide spectrum of computer-aided research activities in electrochemistry. Within Computational Electrochemistry, digital simulation gains a position of both one of the central subjects of study, and a basic research method, together with computer-based electrochemical data storage and analysis, development of computerised electrochemical instrumentation, and other possible uses of computers and computational methods. In order to achieve the ambitious goals posed for Computational Electrochemistry [11], the simulation methodology needs to be advanced to a much higher degree than ever in the past, including improvements in accuracy, efficiency, and automatism. Noticeable progress leading in this direction is documented below.

3. The Method of Lines and the Differential-Algebraic Equation Approach

Many simulation methods can be conveniently classified as examples of the so-called Method of Lines (MOL). A standard text on MOL is by Schiesser [12], who calls it NUMOL. The most common MOL approach (the longitudinal one) consists of what is called semidiscretisation of the initial value problems, that is, discretisation only of the spatial derivatives, leaving the time derivatives to be dealt with later. Thus, one can combine various spatial discretisations with various discrete time integrators. In the simplest case, the spatial discretisation results in a set of ordinary differential equations (ODEs), that can then be solved by any of a number of methods for these. Such a method was used, and called explicitly MOL, by Lemos and co-workers [13], who used explicit Runge-Kutta (RK) time integration. However, as the boundary conditions are often algebraic equations (AEs), a more general approach is to consider the spatially discretised problem as a set of differential-algebraic equations (DAEs), for which a number of time integrators is available, too. The DAE approach has been advocated by Bieniasz [14–16], partly because, apart from the boundary conditions, additional AEs or DAEs (associated for example with adsorption processes) may accompany the partial differential equations (PDEs) of electrochemical kinetics, so that the DAE approach allows one to consider such systems consistently. For those who do not wish to program their own solver, the formulation of the given DAE system, followed by solving with a general solver such as DASSL [17], might be the method of choice, as has indeed been used by Lasia and Grégoire [18] and Zhang and Cheh [19]. DASSL has also been included in the ELSIM 3.0 program (see section 8.3).

4. Developments in Finite Difference Discretisations

Considerable effort has been expended to investigate new finite difference (FD) discretisations, not previously implemented in electrochemical digital simulations. These can dramatically increase the efficiency of simulations. Also, improvements of formerly used FD discretisations have been reported.

4.1 Some notation. In what follows, various symbols will be used, and they are here defined. Time is denoted as t, space coordinates as x and y. The symbol λ, defined by $\lambda = D\,\delta t/h^2$, where D is a diffusion coefficient, δt is a time step size and h is the spatial mesh spacing, will be used. It is sometimes called the dimensionless diffusion coefficient, and it impinges seriously on the stability of a given method.

4.2 Time integrators. Following the MOL philosophy, outlined in section 3, we first discuss developments in discrete time integration, postponing the spatial discretisations until sections 4.3 and 5.

4.2.1 Crank-Nicolson oscillations controlled. The popular Crank-Nicolson method (CN) [20] can be viewed as an MOL combining a conventional second-order accurate FD discretisation of the second spatial derivatives with the trapezium rule integration in time. The method is attractive owing to the second order accuracy of the trapezium rule integrator. However, its provable absolute stability against all λ values (except in some extreme conditions [21–23]) is to some extent irrelevant in practice, because for potential

step simulations, that is, when a sharp transient is applied at zero time, CN responds with oscillations. This is because mathematically, the trapezium rule is only A-stable but not L-stable [24]. The greater a value λ has, the worse these oscillations become; this is unfortunate because large λ values are desirable to ensure a satisfactory resolution of local spatial variations of the concentrations. The oscillations (almost) always decay, but if at the end of a given simulation, there still are oscillations of appreciable magnitude, then CN is unsuitable as such.

There are, however, ways to largely eliminate the oscillations, and the problem has recently been studied [25,302]. There are several options. One of them is to divide the first time steps into a number of sub-steps, either equally or in an expanding sequence. Exponentially expanding sub-intervals have been suggested and used [26,27]; Svir and co-workers routinely use a number of doubling intervals for their UME simulations [28,29], which was later found not to be the best method [25]. The method of Pearson [30], which divides the first interval into a number of equal intervals, was found very effective and was first used in electrochemistry by Fang and Yen [31]. The number of subintervals should ideally be such that the sub-λ is about unity [25]. For large λ, this can mean many substeps, and in such cases, exponentially expanding substeps can reduce the number; however, the expansion factor should not be too great, see [25] for details of this rather complicated situation.

There is another, much simpler and very effective method. If one begins the simulation with a small number (1–4) of steps by means of the backward implicit (BI) method of Laasonen [32] before commencing with CN, it is found that the oscillations are largely damped, because CN is presented with a less sharp transient than that which exists at zero time, and BI does not cause oscillations because it makes use of the implicit Euler time integrator, which is L-stable [24]. This was devised by Rannacher [33] and has been studied since (see [25] for further literature). In [25], a single step was favoured but up to 4, as suggested by Rannacher and co-workers, can be useful. The replacement of CN by BI at the first time steps does compromise the actual accuracy to some extent, but that might be acceptable, given the convenience of CN. The method was found particularly effective for UME simulations using CN or the alternating direction implicit (ADI) method [34], used by Svir and co-workers [28]. The traditional ADI method, as proposed by Peaceman and Rachford (see a thorough discussion of several alternating direction schemes in Lapidus and Pinder [35]) behaves much like CN, showing oscillations unless these are suppressed. A single BI step often suffices to suppress these in UME simulations.

The disadvantage of this technique is that a given program must have both a BI routine as well as a CN routine or, in the case of subdivision of the first step, a separate section for that first step. This can be weighed up against the inconveniences of BDF, extrapolation or Rosenbrock (see the next sections), which require extra data storage.

4.2.2 New findings on BDF. The MOL consisting of the combination of the second order accurate conventional FD space discretisation with the backward differentiation formulae (BDF) for time integration, was brought into electrochemistry in 1994 [36], under the name fully implicit Richtmyer modification (FIRM), because Richtmyer [37]

suggested the three-point BDF variant for use in the solution of PDEs. The method thus does not belong to the time period of this review. What does belong, however, is a finding about the properties of the simple start-up used by Mocak *et al*. [36]. With BDF, there is the problem of the non-existence of values before time zero. Mocak et al. initially simply set all "past" values to the initial values, and then step forward. This clearly introduces an error. A more rational start is normally used in numerical studies outside electrochemistry, where one begins with BI (Laasonen method [32]), then uses three points, then four, *etc*., until the required number of points in time exist, continuing from there with that number. It is known that this starting protocol reduces the solution's accuracy order with respect to the time step size, so that a better method might be desirable. There have been experiments with high-order accurate starts, such as one that can be derived from the simulation method of Kimble and White [38]. This was found inefficient for PDEs [39]. This would probably also apply to the recent new method of Wu and White [40], which the authors suggest as a BDF start. An interesting feature emerged, however [39]. Mocak *et al*. [36] used, without any justification, a time correction at each step. That is, after n steps of δt, they assign the value of $(n - 0.5)\delta t$ to the time, rather than the normal value $n\delta t$. This is reminiscent of Feldberg's original subtraction of half a time step, also without justification at the time [2]; the only justification in both cases was that it seemed to work rather well. Britz examined the problem [41] and found that there appeared to be a time shift inherent in BDF with this simple start-up, the shift converging with high accuracy to $-0.5\delta t$. Later it was found that there is a mathematical reason for this phenomenon. It was shown [42,43] that the use of the simple start indeed introduces a time shift that converges in this manner. Therefore, the Feldbergian correction is fully justified in this case. It turns out [39] that rather accurate solutions are achieved using the simple start with the correction, and it appears that the optimum BDF variant might be the second-order three-point one, with the simple start and correction. One reason for not using higher-order BDF variants is that the rational start-up limits the accuracy order of the subsequent BDF operation, so not much is gained from higher order BDF applied subsequently. As well, at about five points, BDF begins to show oscillations [36,44], which are to be avoided. This is because only the two-point BDF variant (corresponding to the implicit Euler time integrator [24] is L-stable, and the method becomes entirely unstable for more than seven points [24].

4.2.3 Extrapolation. The various techniques of extrapolation date back to Richardson [45,46]. Lawson, Morris and Gourlay [47,48] developed a PDE method, in which extrapolation in time is applied to the BI method [32]. In other words, an extrapolated implicit Euler time integrator is combined with a second order accurate conventional FD spatial discretisation. This method has been introduced to electrochemistry by Strutwolf and co-workers [49,50].

The BI (Laasonen) method [32] has some attractive features, chief among them its unconditional numerical stability and the way it converges smoothly without any oscillations to the true solution with increasing numbers of time steps, that is, it is L-stable [24]. Contrary to the CN method [20], as the factor λ increases, BI performs better, whereas CN becomes more and more oscillatory (although see section 4.2.1).

The drawback of BI, however, is that it is first-order accurate with respect to δt, which results in long computation times for a given target accuracy. Extrapolation improves the order, and thus renders simulations more efficient.

To explain this, let the result of taking a single BI step be u_1, and the result of two steps with half the former step size be u_2. BI being a first-order method, we know that, to a good approximation, the error in u_2 is only half that in u_1. Therefore, the extrapolation expression $2u_2–u_1$ clearly eliminates the error – to a good approximation. The approximation lies in the fact that there are higher-order terms in the error, which are not eliminated. But the remaining error is now second-order, which is an improvement. Higher order schemes, using increasingly more complicated combinations and more partial steps, exist [49,50] but the second-order variant might be the most reasonable, as it matches the spatial accuracy of the BI method.

Extrapolation as described above, that is, based on BI, has all the convenient stability and smooth convergence properties of BI and a much improved accuracy. It is in principle possible to extrapolate on the basis of other schemes than BI, such as the explicit or CN methods; but this is not done.

Extrapolation, then, is an alternative to BDF. One drawback of extrapolation is that it necessitates a larger number of computations for a single step forward, and intermediate concentration values that must be stored, perhaps together with coefficient matrices, whereas BDF only requires a single coefficient matrix in addition to past concentrations (these matrices are sparse but become banded as one increases the number of points used in the spatial discretisation, or with two-dimensional systems, and then require sparse matrix techniques for solution). For problems where a single step entails the use of a sparse matrix that has been LU-decomposed once and for all, this means that a number of such decomposed matrices must be stored in the case of extrapolation, which can be inconvenient. In the case of second-order extrapolation, there are only two such matrices, which is not a great problem. Extrapolation does not have the start-up problem of BDF, previously mentioned. BDF has the drawback of being limited to second order accuracy with a practical start, whereas extrapolation can be driven to higher orders with no such limitations. The choice will rest on individual preference.

4.2.4 Rosenbrock. Bieniasz [15] suggested the use of Rosenbrock methods [51] for time integration. This group of time integration schemes has a lot to offer, such as increased error order (hence, better accuracy), and the ability to handle non-linear PDEs and boundary conditions without the need for iteration. Briefly, Rosenbrock schemes are all implicit RK integration methods. They are a good alternative to BDF or extrapolation methods, often used to solve ODEs or DAEs within the MOL approach (see section 3). As with explicit RK methods, one computes a set of changes and combines them using weighting coefficients. With explicit RK, the changes are evaluated one (set) after the other, whereas with implicit RK, they must normally be evaluated together as a linear system. With Rosenbrock schemes, the equations have been arranged such that one is able to evaluate the changes one (set) by one, even though this constitutes an implicit RK scheme. The reader is referred to [15] for the implementation in electrochemistry. There are second-order schemes for DAEs, for example ROS2 [52], but Bieniasz prefers the

ROWDA3 scheme of Roche [53], later developed into a more convenient form by Lang [54] because the method has third-order accuracy and proves particularly efficient (more so than second order accurate extrapolation). Both these schemes have a smooth response to transients, without oscillations. That is, they are L-stable. Similar to extrapolation, Rosenbrock schemes are one-step schemes, so that they do not have start-up problems and are well suited to rapid solution changes, typical of electrochemical kinetics. However, some of them (such as ROWDA3) cannot be used at temporal discontinuities in the boundary conditions, typical of step transients. The method deserves more attention than it has received.

4.3 Space discretisations. We now move to discussing new FD spatial discretisations that have been proposed for simulations since 1996.

4.3.1 Multi-point spatial discretisation. The seminal work of Kimble and White [38], although itself being nontrivial to program for the solution of PDEs, and inefficient as a start-up for BDF, did suggest that using more than the usual three points for the approximation to the second spatial derivative might be of advantage. Also, it makes little sense to use the higher-order time integration made possible by BDF, extrapolation or Rosenbrock, without at the same time raising the order of the spatial discretisation. Thus the use of five points (six at the edges, to keep the order at fourth) was systematically examined, combined with various time integration techniques such as BDF [55], extrapolation [56] and explicit RK [57]. These experiments showed that indeed, the multipoint approach was useful. It was also clear that uniform spatial meshes have limited use in electrochemistry, so the method was applied directly to arbitrarily spaced spatial meshes [58], using direct discretisation rather than coordinate transformation [58] (see section 4.3.3). In the work [58], it was concluded that an asymmetric four-point second spatial derivative discretisation, coupled with a second-order time discretisation such as extrapolation or BDF, might be ideal. The four-point approximation allows the use of the Thomas algorithm [59], modified appropriately, and thus avoids the use of a less efficient sparse matrix solver. This work goes on, recently having been applied to the two-dimensional case of the UME [60], using direct discretisation on an unequally spaced grid. This was seen to be better than discretisation on a conformally mapped grid and equally spaced grid, at small time values.

4.3.2 Hermitian schemes. As an alternative to multipoint FD spatial discretisations, high-order compact (HOC) schemes have been introduced into electrochemical simulation. Their essence is in every case, that one draws a higher order out of a few points than is normally the case. These schemes have a long history in the numerical literature, where they are mostly called HOC, or in some cases Hermitian. The latter term was used in the English translation of the book by Collatz [61], referring to its origin in Hermite interpolation [62]. The term has come to mean an approximation in general, that not only uses function values at grid points, but also derivative values. As will be seen below, the first of these to be applied to electrochemistry is the Numerov method for the second spatial derivative, followed by a Hermitian method for the flux approximation, a first spatial derivative. Outside electrochemistry, articles on HOC schemes are numerous, recent examples being [63,64]; few papers refer explicitly to the Hermitian method [65].

4.3.2.1 The Numerov method. Numerov (using the French transliteration of his name, Noumerov) wrote a paper in 1924 [66] describing a numerical correction by which a second derivative approximation, using only three points, which normally, for equally spaced spatial grids, has an $0(h^2)$ error, can be brought to have an $0(h^4)$ error. This was adapted for use in the solution of parabolic PDEs by Douglas (mentioned in the monograph of Smith [67]) and was recently fully explained and adapted to electrochemical simulations by Bieniasz [68,69,303] (to which the reader is referred for details). The method can be highly efficient, especially if coupled to a matching high-order time integrator such as BDF, extrapolation or Rosenbrock.

4.3.2.2 A better current approximation. Bieniasz has also used a Hermitian approach [70] to achieve a high-order accurate FD formula for the concentration gradient approximation at the electrode. The gradient is often related to the electric current. The usual n-point expressions [71] have truncation errors that can be expanded in Taylor series. By using the information inherent in the PDE to be solved, some of these terms can be corrected for (perhaps approximately), and the result is a HOC approximation using only a few points. In particular, this is very useful for improving two-point approximations, as up to third-order accuracy can be achieved, using two points. The method is thus far limited to uniform space grids with the exception of the simplest, two-point HOC approximation. Also, the governing PDE cannot involve first spatial derivatives. The reader is referred to [70] for a detailed explanation of how this works.

4.3.3 Non-uniform space grids – direct discretisation or transformation? It has long been considered that in cases where an unequally spaced spatial grid is of advantage (for example in the cases of thin reaction layers or hydrodynamic layers at the electrode), it is better to transform the grid to another space, divided into equally spaced intervals, that correspond to the original uneven grid. In the numerical literature, the work of Kálnay de Rivas [72] is often cited to support this position. This has also been accepted until recently by electrochemists, who often transform space for this reason. The Feldberg approach of exponentially expanding boxes [73] was applied to a set of points in the form of a transformation of x- into y-space, with discretisation taking place on the y-space grid and transformed transport equation. Rudolph [74], however, showed that direct FD discretisation on an unequally (exponentially expanding) grid is in fact superior to using transformation. This was partially contested by Bieniasz [75], pointing out that the discretisation used by Rudolph in the transformed space could easily be modified to achieve better accuracy; Rudolph [76] then also independently derived a similar improvement. Comparisons in two-dimensional systems such as the UME suggest that the superiority of one approach over the other may depend on the time-scale to be simulated over, that is, at short electrolysis times, the direct approach is better, the conformal map approach taking over at longer times [60]. Gavaghan [77,78] experimented with the direct approach with UMEs and found poor performance. This is due to the edge effect on the UME, and extreme expansions must be used here and the use of more points for the second space derivative approximation is indicated [60].

There are some subtleties to be noted in this context: Rudolph favours the Feldberg box method which, he argues, is a finite volume rather than a FD method. He emphasises

the flux-conservative property of the box method, which may not be shared by some of the FD variants on the transformed spatial grids. This may be one of the reasons for the difficulties observed.

Direct discretisation also motivates the search for efficient means of obtaining the coefficients for the discretisation formulae. Explicit formulae for arbitrary spacing become quite complicated [58] with increasing numbers of points included in a given approximation. A few formulae, both for first and second derivatives, are available from other authors [74,77,79]. For this reason, an algorithm and subroutine were devised [80], that returns a derivative value as well as the coefficients to generate it. Recently, some simpler explicit formulae were shown for the special (and most used) case of an exponentially expanding grid [81]. An efficient recursive general algorithm has also been known for some time [82].

4.4 Numerical stability studies. Assessment of the numerical stability of the various simulation algorithms is an important, although often neglected problem. Work on these issues is progressing.

Britz [83] analysed the stability of the Kimble and White [34] method, which appeared puzzling. Essentially, it uses a five-point central first time derivative and, when used in a marching fashion, this is known to be unstable [84], but they write all time steps into one large linear system. Then, at the first few steps, asymmetric formulae must be used, as also at the end, where for the very last step a BDF form is used. These few asymmetric forms render the whole system stable, as was shown.

Britz [44] confirmed the stability of BDF [36] for electrochemical PDEs, for up to the seven-point formula. At about five points, oscillations are seen, becoming worse at six and seven points.

The use of multipoint spatial derivatives (section 4.3.1) can change the stability conditions of a given method. For example, with the explicit method, the upper limit for λ when using three-point approximations is 0.5 for pure diffusion, but it decreases to 0.375 for five-point approximations; a similar decrease was seen for the explicit RK method [57], although the actual limiting λ values depend on the number of RK stages used (the more, the larger the λ limit). With BDF, however, stability is retained under the same conditions, and also for extrapolation, as shown by Britz and Strutwolf [55,56].

5. Developments in Finite-Element-like Methods

Apart from the FD spatial discretisations, discussed above, there is a group of techniques such as the finite element method (FEM) [85] and other related methods, that suggest themselves to simulation where the geometry dictates fine space grids in some regions and coarser grids in others. With FEM, one places node points where one wants them, and solves for the entire region in a variety of ways. Stevens *et al*. wrote a general description of the application of FEM to a variety of electrochemical simulations [86]. FEM has been applied to UME simulations [87–90], to scanning electrochemical microscope (SECM) studies [91], convective systems [92,93], in particular channel flow systems [93–95] and the wall tube system (a wall jet impinging on a small electrode) [96–98], tubular flow [99,100], as well as to current distribution studies (Laplace

equation, steady state) [101]. Gooch *et al*. [102] simulated channel flow systems with modulated flow, using FEM, and Gooch *et al.* [103] simulated liquid/liquid transfer (without migration effects). Some authors [94,104] use available FEM solvers. FEM has also been developed to an adaptive method (see below, section 8.1). For steady state simulations, the boundary integral element method [105,106] can be even better, requiring only node points around the boundary, and has been used recently for SECM studies [107–111], for current distribution computation [112], for steady state UME simulations [113,114], a 3D study of a distorted UME [106] and even for a time-marching UME simulation [115].

A related method is the finite analytical method in which local analytical solutions are sought. This method is due to Chen [116], and has been applied by Jin *et al*. [117], to interdigitated microband arrays [118], the microring [119], and the UME [120,121].

6. Developments in Solving Specific Classes of Problems

A large group of simulation studies has been devoted more to solving specific problems or classes of problems, than to developing new discretisations or analysing old ones. Such studies are equally important for the overall progress in the simulation methodology, so that we list them in this section.

6.1 Multidimensional systems. One-dimensional systems have always been a convenient simplification (albeit quite applicable in many cases) but modern UMEs have forced us to go to more dimensions, mostly two. The most used is the flat disk UME, flush with an insulating plane, and simulation efforts are concentrated here; but other geometries are used and simulations have been carried out. Some examples of simulations performed on related electrode types are recessed and protruding UMEs [122–124] sphere-cap [125] conical [126], a microring electrode [119] which can be thought of as a special case of a microband; UME arrays [127]. Microband electrodes continue in use and simulation, with and without convection [118,128–139]. The work [133] dealt with chronopotentiometry at a microband electrode, which presents an interesting difficulty for simulation, owing to a non-local boundary condition preventing the use of the popular ADI methods. There has been recent interest in dual microband simulation [137–139] and interdigitated band arrays [118,134,136].

Microband electrodes in convective systems were simulated [123,130,140–153], mostly in the context of channel flow systems. Two interesting cases were that of Gooch *et al.* [102], who simulated a parallel dual channel system, separated by a semipermeable membrane and Fulian *et al*. [95], who allowed two channels to join in a confluence flow, the reaction producing a species that was detected by a microband electrode. The SECM is seeing increasing use, and simulations have been done [91,154–165].

In microdisk simulations, the most popular approach is to use one of several conformal maps to transform the cylindrical coordinates such that in effect, small spatial intervals are obtained at the disk edge, where there is a very large current density. This problem was already realised by Crank and Furzeland in 1977 [166], and Gavaghan [167] writes that this discontinuity renders all simulation results accurate to $0(h^{1/2})$. Gavaghan concluded that, for this reason, whether one uses trapezium or Simpson rule

integration of the current density over the electrode surface is not important, as the concentration values obtained from a given simulation are not highly accurate. He then examined the use of direct discretisation on an unequally spaced grid [77,78,168], and used spacings near the disk edge as small as 8×10^{-6} (the disk radius having been normalised to unity). This was recently compared with simulation on a conformally mapped grid [60], using higher-order accurate approximations to space derivatives, and it was found that at small times, the direct approach is better, while the transformed grid is better at longer times. This is somewhat surprising, given the Rudolph finding in one dimension [74], suggesting that direct discretisation on a non-uniform grid is best, but note the critique [75] and further discussion in section 4.3.3. The same study [60] concluded that an asymmetric four-point discretisation on the uneven grid is about optimal, giving second-order accurate derivative approximations. Gavaghan used three-point formulae, considering them second-order accurate, while in fact they are first-order accurate. However, in a private communication with one of us (DB) he explained that the constants in the error polynomial are such that the behaviour is more like second order, even though when one measures the order, it comes out as first-order. Nevertheless, a four-point approximation might be preferred, not being difficult to apply [60]. Amatore and Svir [169] tried a two-domain approach, using uniform spatial grids, but more closely spaced in a region close to the disk. This did seem to give rather good results.

Amatore *et al*. [170] studied the case of a microring electrode, varying the ratio of ring width to ring diameter. A "thick" ring (width comparable with diameter) was observed to behave much like a disk, while a "thin" ring behaved much like a microband.

Further developments for multidimensional systems are associated with the use of adaptive methods, see section 8.1.

All the work referred to above uses two-dimensional discretisation, which leads to sparse equation systems. This implies a search for an efficient sparse solver. One option is to use direct sparse solvers. Thus, for example, Y12M [171], available at the netlib site [172], has been used in [39,133], whereas Strutwolf and Britz used MA28 [173], available at the Harwell site [174]. The brute force approach, simply solving for the whole system and ignoring the zero elements [27], although it turned out not too demanding of computing time, is thus superseded. Other approaches to overcoming the banded nature of these system are the iterative methods, such as the Krylov methods, used by Alden *et al*. [175] and Welford *et al*. [176]. Alden *et al*. [177] and Bidwell *et al*. [147,148] also tried the strongly implicit method [178] and the multigrid method [179,180], comparing it with the Krylov methods, which were found best.

Despite the general character of the sparse matrix methods of solution, many authors still use splitting methods such as the ADI method [34] or hopscotch [181,182]. These both have the advantage of allowing either tridiagonal systems (ADI) or an explicit solution (hopscotch). However, it can be argued that both have rather severe disadvantages. ADI behaves much like the CN method, that is, it responds with oscillations to sharp initial transients (cf. section 4.2.1). Such oscillations are seen in Svir *et al*. [29]. Peaceman and Rachford [34] used small initial steps, possibly for this reason.

Hopscotch, too, is known to cause some initial oscillations under the same conditions [183], and it has the additional drawback of "propagational inadequacy" [184], which prevents the use of large time steps, the very goal in the use of stable techniques. Nevertheless, it seems that the attractions of tridiagonal systems outweigh the drawbacks for many workers, and ADI has been used for various 2D systems in the period covered [10,28,29,125,127,129,138,139,159–162,185–192], particularly in SECM simulations [154–157,159,163–165]. Hopscotch was also used, though not as often [131,169,193].

Some three-dimensional systems have been simulated. Myland and Oldham [304] simulated a hollow tube cell using BI (Laasonen), Beriet *et al.* [89] an UME array and Fulian *et al*. a distorted UME [194] the latter two groups using the FEM.

6.2 Migration. In previous books and reviews [2–11], the issues of simulating electric migration in addition to diffusion (and convection) transport, have been largely omitted, despite the importance and frequently practised simulation of migration in many areas of electrochemistry, bioelectrochemistry and technology (for example ionic membranes, cells, electrolyte junctions, biological ionic channels, electrochemical reactors, electrophoretic analysis, concrete technology, *etc.*). Mathematically analogous simulations are also intensively performed in the area of charge transport in semiconductors (drift-diffusion). Various simulation approaches to such problems have been described in numerous publications that deserve a separate and comprehensive review, substantially exceeding the volume acceptable for the present paper. For this reason, we list here only selected developments, applicable to transient simulations of kinetic or electroanalytical experiments performed in the absence or at low concentrations of the supporting electrolyte. This choice is dictated by the increasing popularity of such experiments, as was indicated by the available review [195]. Readers interested in the numerical methods published within a wider context of migrational systems can be guided by the partial review by Volgin and Davydov [196]. A fairly large number of references to numerical methods is also provided in Bieniasz [197].

Jaworski *et al*. [198] described an FD method for the simulation of chronoamperometry at hemispherical microelectrodes (one-dimensional) in the presence of a very low concentration of the supporting electrolyte. The solution of the highly non-linear boundary conditions has been simplified by a partially analytical reformulation, so that the method is not generally applicable. It was improved later by Hyk *et al.* [199]. The latter algorithm is based on the CN method and uses an exponentially expanding spatial grid. The electroneutrality condition was not explicitly imposed in the calculations, but the deviations from electroneutrality were controlled and considered to be negligible.

Feldberg *et al*. [200] discussed the susceptibility of their fully implicit simulation algorithm to non-physical oscillations (lack of a property termed "spatial stability" by the authors), when migration is present, and formulated criteria for avoiding such oscillations. The emphasis was on transient simulations at the rotating disc electrode.

Pfabe and Shores [201] developed a Sinc-Galerkin method to solve the second order boundary value problem with a non-local boundary condition, arising in the theory of chronoamperometry in the presence of migration. The method is not likely to be very

generally applicable to various kinetic models, but it has proven helpful in the mathematical analysis of chronoamperometry.

Stevens *et al*. [202] outlined an explicit FD method similar to that used earlier by Bond and Feldberg [203] in the presence of migration under local electroneutrality conditions. The method was found to be accurate, but very small discrete time steps, and consequently very large numbers of time levels are needed to ensure numerical stability.

Dan *et al.* [204] presented a method for solving migration-convection-diffusion with electroneutrality equations at the rotating disc electrode, which combines a finite volume spatial discretisation with their multi-dimensional upwinding method for the convection contribution, and trapezium rule time integration. The method applies to spatially one- and two-dimensional models. It has been tested on linear potential sweep and impedance simulations.

Myland and Oldham [205] have developed a convolution technique, to solve the problem of cyclic voltammetry in the presence of migration, when ohmic potential drop is included into boundary conditions. Convolution is often contrasted with digital simulation, being classified as a semi-analytical technique, but we mention it here, because the treatment of migration by this method necessitates some numerical integration.

A number of FD methods for solving migration-convection-diffusion + electroneutrality equations (including explicit, fully implicit and semi-implicit methods) has been discussed and compared by Volgin *et al*. [206]. The methods have been tested using examples of galvanostatic and cyclic voltammetric experiments in binary, ternary and quaternary electrolytes.

Bieniasz [197,207] has extended his patch-adaptive FD method (see section 8.1 below) to migrational problems, including Nernst-Planck-Poisson and Nernst-Planck-electroneutrality equations. The method has been tested (among other examples) on several models of potential step chronoamperometric and cyclic voltammetric experiments. The method works in a largely automatic way, but tends to be computationally rather expensive when migration is present. It has proven sufficiently robust to reveal inaccuracies in the convolution calculations by Myland and Oldham [205] (and other authors).

6.3 Other difficult problems. Orlik [208] used the explicit simulation method to match experimental data, in order to measure kinetic constants, including uncompensated resistance and double layer capacity effects, often neglected.

Orlik *et al*. [209–211] have applied the same method to the simulation of various oscillatory electrochemical systems. Numerical artefacts were observed, which are expected for this method, owing to the incompatibility of the stability conditions for the PDE and a simultaneous ODE of double layer charging [14]. To avoid such artefacts, one should use implicit methods, as was indeed demonstrated by Rudolph *et al.* [212] and Bieniasz [213].

Pedersen found (not using simulation) [214] that the often made assumption that related species, for example a substance and its reduction product, have the same diffusion coefficients, is doubtful. For a certain substance and its radical anion, there was

a ratio of 1.2 between the two diffusion coefficients, which should alert simulationists to the danger of the equality assumption. The non-negligible effect of the difference between diffusion coefficients has also been identified in migrational systems [215–218].

Not many simulation techniques are suited to sharp concentration changes away from the electrode. Svir *et al.* [219,220], simulating electrochemical luminescence (ECL) at an UME, simply used uniform spatial grids and the CN method, and were able to include the (rather broad) hump in the solution. Later [221], they used exponentially expanding space grids and BDF. This will only work if the hump is broad, and does not move, as was the case also with Leventis and Gao [222], who used the explicit method. Such humps or moving fronts generally require adaptive space grids, whereas analogous highly localised temporal variations require adaptive time grids (see section 8.1).

7. Miscellaneous Numerical Methods

A number of numerical approaches has found application in electrochemical kinetics, not all of them being easily classified as digital simulation, some falling more broadly under Computational Electrochemistry. Natarajan and Mohankumar [223] improved the evaluation of the Randles-Ševčík function, and Mocak [224,225] obtained some highly precise values, for all eight cases originally considered by Nicholson and Shain [226]. These authors used infinite series summation algorithms. The integral equation approach has been consistently taken by the Cope and Tallman group for the modelling of microband electrode behaviour; this work continues [227], also elsewhere [228–230]. Deng *et al.* [231] used a method called SAGE (single alternating group explicit), which in fact is a two-step Saul'yev variant [232] that has previously been found to behave rather like CN [233] in that it tends to oscillate. Also, Saul'yev can, under certain conditions, become unstable [234], as indeed can CN [21].

Horno and co-workers continue with their network approach, in which diffusion and a large variety of boundary conditions are modelled by a network of electrical elements (resistors, capacitors, current sources and sinks), to be solved by existing software for such networks [235–244]. One suspects that the work of expressing the transport equations in these terms is roughly equal to that of simply simulating them directly. Much of their work was devoted to simulating migration-diffusion problems in membranes and thin layer cells [236,239–243], rather than in classical electroanalytical experiments considered in section 6.2.

Rajendran [245,246] continues his work with Padé approximants to solutions of electrochemical transport problems; this might be called mathematical, rather than numerical, modelling.

Nagy *et al*. applied the random walk technique to diffusion [247,248]. While this has the attraction of mimicking diffusion as the stochastic process it is, results are rather rough and the simulations time-consuming.

8. Towards Automatic Simulations

A difficult task for computational electrochemists, still awaiting accomplishment, is the design of fully automatic simulation (as well as data analysis) methods, and the

creation of Problem Solving Environments for electrochemical kinetics, in agreement with the emerging paradigm of Computational Electrochemistry (*cf.* section 1). Efforts directed specifically towards this goal are listed in this section.

8.1 Adaptive grid methods. Automatic simulation methods should be capable of providing numerical solutions having a prescribed accuracy, without any need for intervention or simulation control by the electrochemist, and without any restriction on the physically justified values of model parameters. In numerical mathematics such methods are called adaptive grid methods, because they are based on the idea of dynamically adapting the spatial and temporal discrete grids used to the evolving features or local structures of the solutions obtained, without any *a priori* knowledge of their location or duration. Compared to other branches of natural sciences, such advanced methods are merely beginning to be used in electrochemistry.

In a continuing series of papers, Bieniasz [16,197,207,213,249–256] has pursued his efforts to design an adaptive method most suitable for electrochemical kinetic models in one-dimensional space geometry. The formerly considered moving grid method [79,257–259] has been replaced by a patch-adaptive FD strategy, in which a hierarchy of locally refined spatial grid patches is automatically constructed at every time level, to resolve spatial details of the solutions with a prescribed accuracy. The use of the ROWDA3 and extrapolation time integrators (see section 4.2) allows one easily to control time steps as well, by appropriately adjusting them to reduce time error estimates provided by the integrators. This strategy, described in [16], was initially applied to provide largely automatic solutions to kinetic models defined over single space intervals, and characterised by difficult-to-solve narrow solution features at the boundaries, such as reaction layers, hydrodynamic layers, and diffusion layers associated with discontinuous boundary conditions [249]. Later it was successfully applied to resolve thin moving homogeneous reaction fronts [250] and moving fronts caused by concentration-dependent diffusion coefficients in models of the redox switching of conducting polymers [251]. The advantage of time step adaptation has been demonstrated using an example of narrow current spikes in the model of linear potential sweep voltammetry for the EE-DISP mechanism [252]. Subsequently, the method was extended [253] onto models involving simultaneously distributed and localised (*e.g.* adsorbed) species [213], models defined over multiple space intervals, typical *e.g.* for amalgam electrodes, liquid/liquid systems or electrochemical biosensors [254], and models of moving fronts typical of the pattern formation at electrodes [255,256]. This necessitated a generalisation of the classical Thomas algorithm [59] used by the method, onto quasi-block-tridiagonal linear algebraic linear equation systems arising from the latter three kinds of kinetic models. The generalisation has been described in [260].

Finally, the strategy has been extended onto models involving electric migration ionic transport [197,207] (see also section 6.2). In this way, the performance of the patch-adaptive method has been comprehensively tested on practically all kinds of difficulties for simulation, occurring in one-dimensional models of electrochemical kinetics. The performance is generally quite satisfactory, but inefficiencies and error

control imperfections observed in single examples indicate that further development and improvement of the method is still required.

Nann and Heinze [261,262] introduced a different approach to adaptive electrochemical simulations based on the FEM (section 5). The validity of the method (devised for two-dimensional simulations) has been demonstrated on a few rather simple example models of steady-state experiments, potential-step chronoamperometry, cyclic voltammetry at UMEs, and SECM [262], assuming exclusively distributed species.

Harriman *et al.* [135,263–267] have presented another adaptive FEM for two-dimensional simulations with distributed species, using a sophisticated theory of FEM error estimators. The method has been initially applied to steady-state experiments at UMEs [135,263–266] but later extended to transient experiments for relatively uncomplicated reaction mechanisms [267].

Yet another adaptive FEM, thus far restricted to steady-state two-dimensional simulations, has been recently announced by Abercrombie and Denuault [88]. The method is argued to be simpler but more efficient than that of Harriman *et al.*

An important achievement of Refs. [88,135,261–267] is the demonstration of the power of adaptive FEMs in dealing effectively with the spatial edge effects that are a nightmare of conventional, fixed-grid two-dimensional simulations (*cf*. section 6.1). The methods are also well suited to simulations on arbitrarily shaped space domains. However, no evidence has yet been provided that these methods are capable of automatically resolving other, even more challenging difficulties, such as extremely thin boundary layers and moving fronts characteristic of electrochemical kinetics.

A commercial adaptive grid program PDEase2 has also been used by Shao and Mirkin [268] to simulate SECM, but without discussing the method. It is mentioned again by Mirkin [269].

8.2 Simulation and sensitivity analysis. One of the crucial questions posed in the modelling studies of electroanalytical experiments, is: what is the effect of various model parameters (reaction rate constants, diffusion coefficients, formal potentials, characteristic dimensions of the cells, *etc*.) on the results of the experiments? From the mathematical point of view, answering this question requires so-called sensitivity analysis (SA). Until recently, formal SA methods have been used on a large scale in certain areas of chemical kinetics [270,271], but have been relatively uncommon in electrochemistry, with the exception of the SA of electric circuits used in the electrochemical impedance studies, and limited applications in electrochemical engineering. Bieniasz *et al.* [272–274] have suggested the more routine use of the formal SA methods for the modelling of large amplitude transient methods. They have proposed using digital simulation for calculating the so-called local sensitivity coefficients, in addition to the usually simulated concentrations of the chemical species. The sensitivity coefficients represent derivatives of the concentrations with respect to the model parameters, and can be obtained by solving appropriately modified kinetic model equations. Such a direct derivation of the sensitivity coefficients from the model equations can be computationally less expensive than the indirect deduction of the sensitivity information by means of multiple simulation runs with various parameter combinations. It has been

demonstrated that the simulated sensitivity coefficients can be used to gain more insight into the behaviour of the kinetic models [272], for performing the model expansion or reduction [273], and for quantifying the statistical error/uncertainty propagation in simulation and in non-linear least-squares parameter estimation from large amplitude transients [274]. In this way, SA not only expands the application scope of conventional digital simulation, but also becomes a rigorous tool for coordinating the simulation practices, opening perspectives for more automated modelling and simulation activities of the future.

8.3 Simulation software. Speiser [4] has reviewed and compared a number of general simulation programs, available before about 1996. References to some other earlier known programs have also been provided in Bieniasz [11]. We therefore focus here exclusively on the software released after the discussion in Speiser [4]. The software runs on personal computers or workstations.

The latest, third version of ELSIM has been published by Bieniasz in 1997 [275]. The program incorporates new capabilities allowing one to solve kinetic equations associated with interfacial species. This refers both to equations entirely independent of spatial coordinates, and to equations in one-dimensional space geometry. Hence, user-defined controlled potential and controlled current transient experiments for reaction mechanisms involving distributed and adsorbed species (either separately or simultaneously) can be simulated by ELSIM, under conditions of diffusion and convection-diffusion transport. The program has been equipped with a specially developed reaction compiler [276], allowing the users to automatically translate their reaction mechanisms into corresponding systems of mathematical model equations. The equations can also be modified or re-edited by the users, prior to the simulation. Single simulated transient curves can be fitted to experimental transients. Despite having quite extended capabilities (see [11] and references cited therein) and an interactive user interface, ELSIM 3.0 suffers from the limitations inherent in the MS DOS operational system, for which it has been designed. An MS-Windows version is not yet available. The program is currently freely obtainable from the author.

The commercial code DigiSim for Windows, elaborated by Rudolph and Feldberg, and sold by BAS [277], has gained a noticeable popularity, and new versions have appeared, all having interactive, graphical user interfaces. The program simulates mostly cyclic voltammetry, for user-defined reaction mechanisms involving distributed species only, assuming one-dimensional space geometry. The simulation method and other algorithmic details have been described [6]. Although DigiSim is nominally limited to cyclic voltammetry, it is possible to force it to approximate the potential jump experiment by suitable adjustment of parameters, and Ketter *et al*. [278] found a way to use this program for calculating integrated ECL emission intensity. The simulation engine cooperates with the BAS (and some other) experimental data collecting software, and enables fitting of the simulated voltammograms to the experimental ones.

The commercial code POLAR by Huang [279] has been vigorously advertised in the electrochemical discussion lists on the Internet. The program is declared to simulate various types of voltammograms. We do not have experiences with using the latest

versions of this program, and we do not know of any published descriptions of the algorithms implemented in POLAR. However, a review of the program has appeared [280].

Kaczmarski and Sanecki [281,282] have developed the ESTYM_PDE code for the solution of and parameter estimation from coupled PDE/AE and PDE/DAE systems, including several electrochemical kinetic models in one-dimensional space geometry. The program uses spatial discretisation by orthogonal collocation, and temporal integration by Adams-Moulton or BDF methods. The program is written using the Delphi Pascal compiler and has a graphical Windows user interface (unfortunately, in Polish only). Data fitting options are available. Some information regarding the capabilities of ESTYM_PDE and methods implemented in this program can be deduced from Refs. [283–286]. The program is available from the author (K.K.).

Laouenan [287] released the VirtualCV program for simulating cyclic voltammetry experiments. The program performs simulated experiments that can be useful for teachers, students and researchers. The program can share input data with the older ESP code by Nervi [288] and uses a C++ translation of Gosser's simulation engine [289]. It is available from simtel [287].

A cyclic voltammetric simulator for Windows 95 or higher, has been announced by Vining *et al*. [290]. The program is intended as a tutorial, covering the fundamental concepts of cyclic voltammetry, including reaction kinetics and diffusion.

In addition to the above efforts to design fairly general simulation programs, a number of codes designed for specific models or problems has been presented in the electrochemical literature or on the web. Biader Ceipidor *et al*. [291] have described an EXCEL-based simulator for cyclic voltammetry and a CEC reaction mechanism. Martinet *et al.* [292] have reported software for the simulation of cyclic voltammograms for a two-step metal deposition with adsorption. These latter authors argued that problems with adsorption could not be solved by previously available software. This argument is not precise: as was already noted, ELSIM 3.0 has such capabilities. Ohtani [293] provided a Java-based online simulator on the web, serving as a simulator of quasi-reversible voltammetric responses of electrodes coated with electroactive monolayer films. The simulator uses the previously published theory [294]. Svir *et al.* [295] have developed ECL-PACKAGE, especially designed for the simulation of ECL at UMEs of various (one- and two-dimensional) geometries: sphere, microdisc, and channel double microband, during non-steady-state electrolysis. The package uses fixed-grid FD and FEMs with coordinate transformations. A graphical user interface is provided. A commercial code PIRoDE has been released by ELSYCA [296]. The code is designed for the simulation of transient experiments at the rotating disk electrode, under conditions of migration-convection-diffusion transport (dilute solution model of ionic transport). Intermediate adsorbed or deposited species can be handled. Options for parameter optimisation are also available. Graphical user interface is provided. Some information regarding the capabilities of PIRoDE and methods implemented in this program are available in Refs. [204,297,298].

Out of the above programs, only ELSIM has been specifically developed as a Problem Solving Environment for electrochemical kinetics, although features characteristic of such software systems are also found in other programs. The idea of building Problem Solving Environments has been recently undertaken by Speiser and co-workers, who started a long-term project called EChem++ [299]. They apply object-oriented analysis and the C++ language, to code the overall electrochemical data generation, analysis and interpretation processes in the form of an integrated software package. As an open source project, EChem++ is intended to be applied, extended, improved and tested freely by the electrochemical community. First building blocks of this package are currently in preparation [300,301], assuming a Linux platform.

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