Letter to the Editor

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

Responses to Comments by B. Speiser

L. K. Bieniasz[†] and D. Britz[*]

Institute of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

In our recent paper[1] we reported a comparative study of the finite difference (FD) and orthogonal collocation (OC) algorithms of electrochemical kinetic simulations.[2] We found that OC is a quality method, capable of great accuracy and efficiency; we found also some negative aspects, apparently hitherto neglected or overlooked. Speiser[3] has recently presented critical comments on our study. In this letter we reply to these comments.

(1) Speiser[3] criticises our choice of algorithms, stating that the worst OC variant has been compared with one of the best FD techniques, which may be regarded unfavourable for OC. We agree that out of the various OC algorithms suggested in the electrochemical literature the selected standard OC variant is the least satisfactory. This has been plainly stated in our paper.[1] It may be debatable, however, whether the considered FD algorithms are really the best. Actually, we have worked with the simplest possible, classic explicit (EX) and Crank–Nicolson implicit (CN) FD methods, assuming temporal two-level and spatial three-point discretizations, as well as with the explicit Runge–Kutta second-order (RK2) method of lines. A variety of more advanced FD techniques exists based, for example, on the multilevel temporal discretization,[4,5] five-point spatial discretization,[5-7] deferred correction,[7] predictor–corrector integration,[5,8] other composite solution methods,[5] implicit methods of lines,[9] etc. These techniques are known to be more accurate and/or efficient than the simple FD algorithms considered by us. Another improvement may be brought

by the adaptive grid FD strategies.[10] It may also be debatable whether Rudolph's matrix solution technique[11] used in our work represents the best possible way of handling coupled FD equations arising in the CN method. In fact, our results indicate that this technique is very slow, the most accurate CN method becoming in some instances less efficient than the less accurate EX method or the comparably accurate RK2 integration (cf. Figs. 4a, 5a and 5b in Ref. 1). A variety of algorithms for solving sparse systems of equations is known,[12] and some of these methods may prove to be more efficient, although we have not explored this possibility.

(2) A certain amount of criticism about the reliability of OC, expressed in our paper,[1] results not only from the numerical tests (of the standard OC variant) presented therein, but also from the observation that the practical use of this method usually involves some kind of heuristic argumentation[13] which does not seem to have a fully rigorous formal justification. This refers as well to the more advanced variants employed by Speiser.[3] For example, essential factors such as the choice of orthogonal polynomials most suitable for a given problem, the number of collocation nodes, etc., must be specified by trial and error rather than based on rigorous convergence and/or stability criteria.[14] It is difficult to ascertain that a given choice is adequate, since general theorems regarding the accuracy and numerical stability of OC seem either not available or fragmentary,[15] although some development of the theoretical basis for collocation methods is observed.[16] Out of the finite-element methods, OC is relatively rarely used and discussed in the field of numerical analysis, apparently not being highly regarded,[15] despite the fact that a few comparative studies indicate[17] that in the area of application close to the needs

---

[†] On leave from the Institute of Physical Chemistry of the Polish Academy of Sciences, Molten Salts Laboratory, ul. Zagrody 13, 30-318 Cracow, Poland.
[*] To whom correspondence should be addressed.

of electrochemistry its performance may be similar to the better known Galerkin method. More attention has been paid to the theoretical principles and development of the Galerkin method.[18] With regard to FD methods, a large number of studies on the convergence and stability of these methods has been performed over the past decades and these properties are now relatively well understood.[19-21]

(3) The purpose of our study was not to provide solutions to problems for which solutions or solution algorithms do not exist, as one might infer from the conclusion by Speiser.[3] Our goal was to obtain answers to basic questions regarding the relative efficiency and reliability of the OC and FD methods, using simple examples and simple algorithms, since this facilitates conclusions. This goal has been achieved within the limitations imposed by the scope of our study. Our conclusions[1] regarding the advantages and disadvantages of OC relative to the FD methods are close to the conclusions obtained in other, non-electrochemical but similar, applications of these methods.[22,23] The discussion by Speiser[3] brings a useful extension to our work, showing the advantage of the modified OC algorithms over the standard OC variant, as already documented.[24,25] However, in order to obtain more complete conclusions about the reliability of various algorithms, it would also be interesting to see a comparison of the advanced OC variants with FD algorithms modified in a similar way. For example, a time-dependent, pre-defined transformation of the space variable could probably also be used with the FD algorithms.

References

1. Bieniasz, L. K. and Britz, D. *Acta Chem. Scand. 47* (1993) 757.
2. Britz, D. *Digital Simulation in Electrochemistry*, Springer, Berlin, Heidelberg 1988, and references cited therein.
3. Speiser, B. *Acta Chem. Scand. 47* (1993) 1238.
4. Lees, M. *Math. Comp. 20* (1966) 516.
5. See, for example, Lapidus, L. and Pinder, G. F. *Numerical Solution of Partial Differential Equations in Science and Engineering*, Wiley, New York 1982 and references cited therein.
6. Douglas, J., Jr. *J. Math. Phys. 35* (1956) 145.
7. See, for example, Smith, G. D. *Numerical Solution of Partial Differential Equations: Finite Difference Methods*, 3rd edn. Clarendon Press, Oxford 1985 and references cited therein.
8. See, for example, Ramos, J. I. *Int. J. Comput. Math. 18*, (1985) 141.
9. See, for example, Dekker, K. and Verwer, J. G. *Stability of Runge–Kutta Methods for Stiff Nonlinear Differential Equations*, Elsevier, Amsterdam 1984.
10. Bieniasz, L. K. *J. Electroanal. Chem. 360* (1993) 119.
11. Rudolph, M. *J. Electroanal. Chem. 314* (1991) 13.
12. See, for example, Østerby, O. and Zlatev, Z. *Direct Methods for Sparse Matrices*, Springer, Berlin 1983.
13. Ramkrishna, D., *Chem. Eng. Sci. 28* (1973) 1362.
14. Yen, S. C. and Chapman, T. W. *J. Electroanal. Chem. 135* (1982) 305.
15. Michelsen, M. L. *Personal communication*, 1993.
16. See, for example, Douglas, J., Jr. and Dupont, T. *Collocation Methods for Parabolic Equations in a Single Space Variable*, Springer, Berlin 1974.
17. See, for example, Michelsen, M. L. and Villadsen, J. In: *Foundations of Computer Aided Chemical Process Design, Proceedings, Henniker, New Hampshire, 1980*, Engineering Foundation, New York 1981, p. 341.
18. See, for example, Fairweather, G. *Finite Element Galerkin Methods for Differential Equations*, Dekker, New York 1978.
19. Richtmyer, R. D. and Morton, K. W. *Difference Methods for Initial-value Problems*, Interscience, New York 1967.
20. Mitchell, A. R. and Griffiths, D. F. *The Finite Difference Method in Partial Differential Equations*, Wiley, Chichester 1985.
21. Thomée, V., In: Ciarlet, P. G. and Lions, J. L., Eds. *Handbook of Numerical Analysis*, Vol. I, *Finite Difference Methods (Part 1) – Solution of Equations in $\mathbb{R}^n$ (Part 1)*, Elsevier, Amsterdam 1990, p. 7.
22. Finlayson, B. A. *Chem. Eng. Sci. 26* (1971) 1081.
23. Hossain, M. A. and Yonge, D. R. *J. Environ. Eng. 118* (1992) 238.
24. Hertl, P. and Speiser, B. *J. Electroanal. Chem. 217* (1987) 225.
25. Urban, P. and Speiser, B. *J. Electroanal. Chem. 241* (1988) 17.