

1-1-1994

A Finite-Difference Method for Pseudo-Two-Dimensional Boundary Value Problems

Z. Mao

University of South Carolina - Columbia

Ralph E. White

University of South Carolina - Columbia, white@cec.sc.edu

Follow this and additional works at: http://scholarcommons.sc.edu/eche_facpub



Part of the [Chemical Engineering Commons](#)

Publication Info

Journal of the Electrochemical Society, 1994, pages 151-156.

© The Electrochemical Society, Inc. 1994. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS). The archival version of this work was published in the *Journal of the Electrochemical Society*.

<http://www.electrochem.org/>

Publisher's link: <http://dx.doi.org/10.1149/1.2054675>

DOI: 10.1149/1.2054675

A Finite-Difference Method for Pseudo-Two-Dimensional Boundary Value Problems

Z. Mao* and R. E. White*

Department of Chemical Engineering, University of South Carolina, Columbia, South Carolina 29208

ABSTRACT

A finite-difference method is presented for solving pseudo-two-dimensional boundary-value problems. The sparse and nearly block tridiagonal properties of the matrices generated by using the finite-difference method for problems of this type are fully utilized and maintained, which yields a method that is highly efficient in the use of storage space and computation. An example shows that the central process unit time required by the method is significantly less than that required by an alternative method.

Pseudo-two-dimensional boundary-value problems often appear in chemical and electrochemical reactor analysis.¹⁻³ They can also appear in adsorption bed design problems.⁴ In this type of problem, there exist multiple phases or regions where different transport processes occur in each phase. The transport processes in one phase interact with those in another phase only at the interface between the phases. The schematic presented in Fig. 1 represents these kinds of problems. In region I, the transport processes are usually described by n partial differential equations which are normally simplified to be functions of the spatial coordinate x and time t only, but depend on the values of the variables of the Y phase at the interface ($y = 0$). These equations are of the form

$$F_{I,i} \left[\frac{\partial^2 C_I}{\partial x^2}, \frac{\partial C_I}{\partial x}, \frac{\partial C_I}{\partial t}, C_I, \frac{\partial C_Y}{\partial y} \Big|_{y=0}, C_{Y|y=0} \right] = 0 \quad i = 1, 2, \dots, n \quad [1]$$

where C_I and C_Y represent vectors of variables in regions I and Y

$$C_I = (C_{I1}, C_{I2}, \dots, C_{In})^T \quad [2]$$

$$C_Y = (C_{Y1}, C_{Y2}, \dots, C_{Ym})^T \quad [3]$$

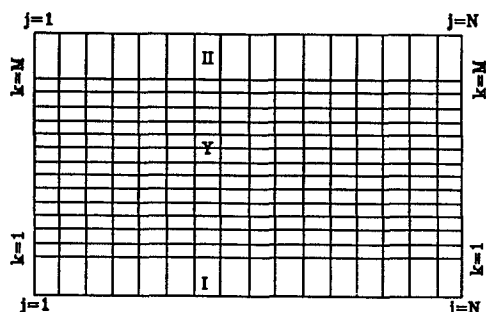
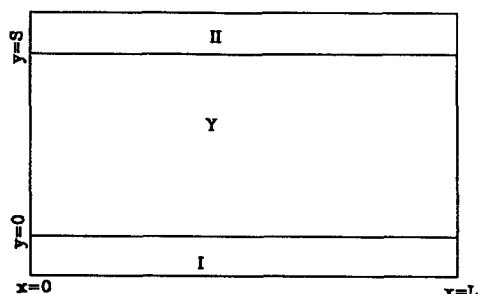


Fig. 1. (a, top) Schematic view of model regions, (b, bottom) finite difference grids for the model regions.

* Electrochemical Society Active Member.

where n and m represent the number of dependent variables in regions I and Y, respectively. Similarly, n_1 general equations are given for region II

$$F_{II,i} \left[\frac{\partial^2 C_{II}}{\partial x^2}, \frac{\partial C_{II}}{\partial x}, \frac{\partial C_{II}}{\partial t}, C_{II}, \frac{\partial C_Y}{\partial y} \Big|_{y=S}, C_{Y|y=S} \right] = 0 \quad i = 1, 2, \dots, n_1 \quad [4]$$

where C_{II} represents a vector with n_1 dependent variables in region II

$$C_{II} = (C_{II1}, C_{II2}, \dots, C_{II n_1}) \quad [5]$$

The transport processes that are important within region Y are normally assumed to occur in the y direction only and are described by m equations for the m dependent variables

$$F_{Y,i} \left[\frac{\partial^2 C_Y}{\partial y^2}, \frac{\partial C_Y}{\partial y}, \frac{\partial C_Y}{\partial t}, C_Y \right] = 0 \quad i = 1, 2, \dots, m \quad [6]$$

The boundary conditions at $x = 0$ and at $x = L$ for Eq. 1 and 4 are generally given as follows

$$f_{I,i} \left[\frac{\partial C_I}{\partial x}, \frac{\partial C_I}{\partial t}, C_I \right] = 0 \quad i = 1, 2, \dots, n \quad [7]$$

$$f_{II,i} \left[\frac{\partial C_{II}}{\partial x}, \frac{\partial C_{II}}{\partial t}, C_{II} \right] = 0 \quad i = 1, 2, \dots, n_1 \quad [8]$$

The boundary conditions at $y = 0$ and $y = S$ for Eq. 6 contain local variables in regions I and II and derivatives of C_Y at these interfaces

$$f_{Y,i} \left[C_I, \frac{\partial C_Y}{\partial y} \Big|_{y=0}, C_{Y|y=0} \right] = 0 \quad i = 1, 2, \dots, m \quad [9]$$

$$f_{Y,i} \left[C_{II}, \frac{\partial C_Y}{\partial y} \Big|_{y=S}, C_{Y|y=S} \right] = 0 \quad i = 1, 2, \dots, m \quad [10]$$

Some examples of the physical regions represented by regions I, Y, and II are given next. For a packed-bed chemical reactor, *e.g.*, the n variables in region I would represent reactant and product concentrations, pressure, temperature, etc. in the axial direction, and the m variables in region Y would represent reactant and product concentrations and temperature within the porous catalyst particles. Region II in Fig. 1 would not be needed to model this type of reactor. For electrochemical reactors (*e.g.*, batteries), region I would represent an electrolyte phase within a porous electrode with the dependent variables being concentrations of ionic species, potential, electrolyte velocity, etc., region Y would represent a thin layer of insoluble solid active material on a metal substrate in which diffusion and migration of holes, electrons, and protons may occur simultaneously,⁵ and region II would represent the metal substrate. In a fuel-cell model, regions I and II would represent the anode and cathode gas channels, respectively, and region Y would represent the cross section of the cell (anode/separator/cathode, see Ref. 6, *e.g.*). These examples are referred to here as pseudo-two-dimensional boundary-value problems. To the best of our knowledge, there is no efficient

Table I. Comparison of CPU times.

Method	CPU time ^a (s)				No. of nodes
	CRAY-YMP ^b	VAX-8650 (DP) ^c	VAX-8650 (QP) ^d	SUN/SPARC	
PTWO	0.5725×10^{-2}	0.1000	0.3200	6.000×10^{-2}	$N = 21$
BAND	4.4100×10^{-2}	1.6400	4.5200	7.7500	$M = 21$
PTWO	2.8309×10^{-2}	0.5100	1.5900	0.3100	$N = 51$
BAND	0.8306	—	136.22	61.590	$M = 51$
PTWO	6.0667×10^{-2}	1.1700	2.6600	0.6300	$N = 101$
BAND	1.2023	—	257.82	161.34	$M = 51$

^a Estimated by using the IMSL function CTIME().
^b The programs were run with single precision.
^c The programs were run with double precision.
^d The programs were run with quadruple precision.

The governing equations for the electrolyte phase (Eq. 45 and 46) contain a derivative of the variable in the solid phase at the solid surface ($y = S$), the governing equation for the solid phase (Eq. 51) does not contain any variable of the electrolyte phase, but its boundary condition (Eq. 53) is strongly coupled with the variables of the electrolyte phase. The equations in this problem can be solved easily using the algorithm presented above. First, the model equations are discretized using three-point finite-difference equations for both the first and second derivatives and the Crank-Nicolson approximation is used to obtain $(\Delta t)^2$ accuracy in time. The resulting sets of nonlinear, coupled algebraic equations are solved using the Newton-Raphson method and the procedure presented here.

Table I presents a comparison of CPU times for one iteration in solving the above problem with the subroutines BAND using the method of Nguyen and White¹⁰ and with PTWO on three different computers: a SUN workstation, a VAX-8650, and a CRAY-YMP. Although the differences in the CPU times used by PTWO and by BAND depend on the number of nodes, as shown in Table I, PTWO required less CPU time than BAND by at least one hundred times on the SUN workstation. The CPU time spent by PTWO on the VAX-8650 was fourteen to ninety-seven times less than that by BAND when the programs were run with quadruple precision. When the number of nodes was increased and the programs were run with double precision on the VAX-8650, an error occurred in BAND due to overflow, which did not occur in PTWO. It is interesting to note that both BAND and PTWO required less CPU time on the SUN workstation than on the VAX-8650. On the CRAY-YMP, the CPU time used by PTWO was seven to twenty-nine times less than that by BAND. For the example problem given above, it was found that use of a large number of nodes is essential to obtain an accurate solution, and an actual simulation would require approximately three thousand time steps.¹⁵ Consequently, the CPU time would be prohibitively large if the problem were to be solved using BAND on a SUN workstation or on a VAX-8650, whereas PTWO provided accurate results for an affordable CPU time.

Conclusions

Pseudo-two-dimensional problems can be solved by using the finite-difference method presented in this work with much less computation time and storage space than that required by a full two-dimensional solver.¹⁰ This is because in this method the vectors of variables are arranged so that the Jacobian coefficient matrix for the system of equations and the submatrices for each node are nearly block tridiagonal. The highly sparse and nearly block tridiagonal properties of these matrices are utilized to reduce the storage and CPU time by using LU factorization to solve these systems of equations.

Acknowledgments

The authors are grateful for the support of this work by the Office of Research & Development, Hughes Aircraft Company, the Center for Space Power at Texas A&M University, and for the computer time on the Cray-YMP super-

conductor at Texas A&M received through a grant from Cray Research, Inc.

Manuscript submitted July 8, 1993; revised manuscript received Sept. 27, 1993.

The University of South Carolina assisted in meeting the publication costs of this article.

APPENDIX A

LU factorization of B_i^1 .

The block matrices $b_{nm}^1, b_{mn}^1, b_y^1(1, k)$ ($k = 2, 3, \dots, M$), and b_i^1 in the lower triangular matrix in Eq. 44 are the same as those in Eq. 30. The other nonzero block matrices in the lower and upper block triangular matrices are calculated as follows

$$b_{nn}^1 b_{nm}^u(i) = b_{nm}(i) \quad i = 1, 2, 3 \quad [A-1]$$

$$b_{nm}^1 b_r^u = b_r \quad [A-2]$$

for $k = 1$

$$b_y^1(1, 1) = b_y(1, 1) - b_{mn} b_{nm}^u(1) \quad [A-3]$$

$$b_y^1(1, 1) b_y^u(i, 1) = b_y(i, 1) - b_{mn} b_{nm}^u(i) \quad i = 2, 3 \quad [A-4]$$

$$b_y^1(1, 1) b_i^u(i, 1) = -b_{mn} b_r^u \quad [A-5]$$

for $k = 2$

$$b_y^1(2, k) = b_y(2, k) - b_y(1, k) b_y^u(2, k - 1) \quad [A-6]$$

$$b_y^1(2, k) b_y^u(3, k) = b_y(3, k) - b_y(1, k) b_y^u(3, k - 1) \quad [A-7]$$

$$b_y^1(2, k) b_i^u(k) = -b_y(1, k) b_i^u(k - 1) \quad [A-8]$$

for $3 \leq k \leq M$

$$b_y^1(2, k) = b_y(2, k) - b_y(1, k) b_y^u(3, k - 1) \quad [A-9]$$

$$b_y^1(2, k) b_y^u(3, k) = b_y(3, k) \quad [A-10]$$

$$b_y^1(2, k) b_i^u(k) = -b_y(1, k) b_i^u(k - 1) \quad [A-11]$$

for $k = M$

$$b_y^1(2, k) = b_y(2, k) - b_y(1, k) b_y^u(3, k - 2) \quad [A-12]$$

$$b_y^1(3, k) = b_y(3, k) - b_y^1(2, k) b_y^u(3, k - 1) \quad [A-13]$$

$$b_y^1(3, k) b_{mn}^u = b_{mn1} - b_y(1, k) b_i^u(k - 2) - b_y^1(2, k) b_i^u(k - 1) \quad [A-14]$$

$$b_i^1(1) = -b_i b_{nm}^u(1) \quad [A-15]$$

$$b_i^1(2) = -b_i b_{nm}^u(2) - b_i^1(1) b_y^u(2, 1) \quad [A-16]$$

$$b_i^1(3) = -b_i b_{nm}^u(3) - b_i^1(1) b_y^u(3, 1) - b_i^1(2) b_y^u(3, 2) \quad [A-17]$$

$$b_i^1(i) = -b_i^1(i - 1) b_y^u(3, i - 1) \quad i = 4, 5, \dots, M - 3 \quad [A-18]$$

$$b_{n_{1m}}^1(1) = b_{n_{1m}}(1) - b_i^1(M - 3) b_y^u(3, M - 3) \quad [A-19]$$

$$b_{n_{1m}}^1(2) = b_{n_{1m}}(2) - b_{n_{1m}}^1(1) b_y^u(3, M - 2) \quad [A-20]$$

$$b_{n_{1m}}^1(3) = b_{n_{1m}}^1(3) - b_{n_{1m}}^1(2) b_y^u(3, M - 1) \quad [A-21]$$

$$b_{n_{1n_1}}^* = b_{n_{1n_1}}^1 - b_i b_r^u - \sum_{k=1}^{M-3} b_i^1(k) b_i^u(k) - b_{n_{1m}}^1(1) b_i^u(M - 2) - b_{n_{1m}}^1(2) b_i^u(M - 1) - b_{n_{1m}}^1(3) b_{mn_1}^u \quad [A-22]$$

Equations A-1, A-2, A-4, A-5, A-7, A-8, A-10, A-11, and A-14 in this Appendix have to be solved to obtain the

nonzero elements in the upper tridiagonal block matrix in Eq. 44. LU factorization is used here to solve these equations.

REFERENCES

1. G. F. Froment and K. B. Bischoff, *Chemical Reactor Analysis and Design*, 2nd ed., p. 477, John Wiley & Sons, Inc., New York (1990).
2. K. West, T. Jacobsen, and S. Atlung, *This Journal*, **129**, 1480 (1982).
3. J. Bouet, F. Richard, and Ph. Blanchard, in *Proceedings of the Symposium on Nickel Hydroxide Electrode*, D. A. Corrigan and A. H. Zimmerman, Editors, PV 90-4, p. 260, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1990).
4. C. D. Holland and A. I. Liapis, *Computer Methods for Solving Dynamic Separation Problems*, p. 389, McGraw-Hill, Inc., New York (1983).
5. M. Sinha, Ph.D. Thesis, University of California, Los Angeles (1982).
6. T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, in *Proceedings of the Symposium on Modeling of Batteries and Fuel Cells*, R. E. White, M. W. Verbrugge, and J. F. Stockel, Editors, PV 91-10, p. 209, The Electrochemical Society Proceedings Series, Pennington, NJ (1991).
7. W. E. Schiesser, *DSS/2: Fortran 77 Code for Systems of Ordinary and One, Two, and Three-Dimensional Partial Differential Equations*, Lehigh University and Naval Air Development Center, Lehigh, PA (1988).
8. T. Hailu, MS Thesis, Texas A&M University, College Station, TX (1990).
9. IMSL, MATH/LIBRARY User's Manual, p. 11, IMSL, Houston, TX (1987).
10. T. V. Nguyen and R. E. White, *Comput. Chem. Engng.*, **11**, 543 (1987).
11. B. A. Finlayson, *Nonlinear Analysis in Chemical Engineering*, p. 11, McGraw-Hill, Inc., New York (1980).
12. R. E. White, *Ind. Engr. Chem. Fundam.*, **17**, 367 (1978).
13. J. S. Newman, *Electrochemical Systems*, Appendix C, 2nd Ed., Prentice-Hall, Englewood Cliffs, NJ (1991).
14. R. M. Spotnitz, D. Zuckerbrod, S. L. Johnson, J. T. Lundquist, and R. E. White, in *Proceedings of the Symposium on Modeling of Batteries and Fuel Cells*, R. E. White, M. W. Verbrugge, and J. F. Stockel, Editors, PV 91-10, p. 88, The Electrochemical Society Proceedings Series, Pennington, NJ (1991).
15. Z. Mao and R. E. White, *J. Power Sources*, **43**, 181 (1993).

Study of the Redox Process of Poly (2-Naphthol) Film Using *In Situ* Multiple Internal Reflection FTIR Spectroscopy

Minh-Chau Pham and Pierre-Camille Lacaze

Institut de Topologie et de Dynamique des Systemes de l'Universite Paris 7, 75005 Paris, France

ABSTRACT

Poly(NAP-2) is a novel conducting polymer film obtained by electrochemical oxidation of 2-naphthol. The polymer structure consists of polymers P and oligomers Q. The P structure comprises alternate naphthylene and furan rings while the Q structure bears quinonoid groups in the chain. The electrochemical oxidation-reduction of the two forms P and Q in poly(NAP-2) film was studied. The redox process of the furan groups in the polymer structure P is detected in neutral acetonitrile while that involving Q/H₂Q couple in Q structure is observed in acidic acetonitrile solution.

Recently, we showed that a novel electroactive and conducting polymer film, poly(2-naphthol) [poly(NAP-2)], was obtained by electrochemical oxidation of 2-naphthol in acetonitrile solution. The polymer structure and the electropolymerization mechanism were elucidated by *in situ* multiple internal reflection Fourier transform infrared spectroscopy (MIRFTIRS)¹ and *in situ* electron spin resonance (ESR) study.²

The proposed structure for poly(NAP-2) film is composed of two forms, P and Q. The polymer P comprises alternate naphthylene and furan rings analogously to poly(NAP-1) film³ while the Q structure involves oligomers bearing quinonoid groups

potential cycling between 0.2 and 1.5 V or between 0.2 and 2 V vs. SCE.

When the potential limit is 2 V, the formation of the quinonoid structure Q is favored while P structure formation is predominant when the potential limit is 1.5 V.²

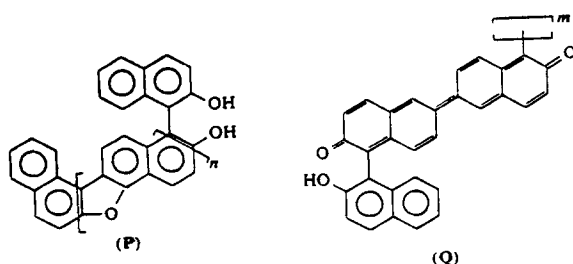
In the present paper, an investigation of the mechanism of the electrochemical oxidation-reduction process of poly(NAP-2) film is performed by electrochemical and MIRFTIRS studies.

Experimental

Materials.—2-Naphthol (Aldrich Chemical Company) was sublimed before use. The electrolytes, NBu₄ClO₄ and LiAsF₆ (Fluka), were used without further purification. Acetonitrile was provided by Aldrich (spectrophotometric grade).

Preparation of poly(NAP-2) film.—For the double potential step experiments, poly(NAP-2) films were prepared by electropolymerization of 2-naphthol (0.1M) in an acetonitrile solution containing 0.1M of the electrolyte (LiAsF₆ or LiClO₄) by potential scanning between 0.2 and 1.5 V or 2 V vs. SCE. The film thickness was measured by scanning electron microscopy (SEM). A strip of polymer was scratched out from a polymer film deposited on a Pt substrate to reveal a cross section of the film.

In the MIRFTIRS studies, in order to investigate the redox process of the film in the whole film thickness, the film



Polymer films can be deposited on Pt or glassy carbon electrodes at constant potential (1.5 or 2 V vs. SCE) or by