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FAST QUASI-EXPLICIT FINITE DIFFERENCE SIMULATION OF ELECTROCHEMICAL RESPONSES INITIATED BY A DISCONTINUOUS PERTURBATION

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Computer simulation is an invaluable tool when an analytic solution is unavailable. Commencing in the early '60s the application of explicit finite difference (EFD) methods to the analysis of electrochemical problems paralleled the development and availability of fast, main-frame, digital computers. The appeal of the EFD method has been its simplicity of principle and of application. EFD algorithms, however, are notoriously inefficient for solving certain types of "stiff" problems (e.g., problems involving a wide dynamic range of time constants). Although phenomenal increases in computational speed over the past 25 years have softened these limitations, many problems of interest still remain outside the range of the EFD method.

In this presentation I will discuss the principles and some applications of a fast quasi-explicit finite difference (FQEFD) method in which the computational speed is enhanced, by many orders of magnitude in some cases, without compromising the "user friendliness" which has popularized the EFD method. The method is designed to treat electrochemical responses to a discontinuous (e.g., chronoamperometric) perturbation and utilizes the DuFort-Frankel algorithm (1) with exponentially expanding space (2) *and* exponentially expanding time grids. (A previously published version of the FQEFD method (3,4) was designed to treat electrochemical responses to a continuous (e.g., cyclic voltammetric) perturbation and utilizes the DuFort-Frankel (3) algorithm in conjunction with an exponentially expanding space grid and a uniform time grid. The development of the basic FQEFD equations was presented there.) The protocol for introducing the expanding time grid is straightforward and will be discussed.

Some specific examples will demonstrate the versatility and power of the method, e.g., simulation of the chronoamperometric response for classic Cottrellian diffusion,

$$A + e \rightarrow B \qquad (a_{x=0} = 0) \qquad (1)$$

for the (catalytic) EC mechanism,

$$\begin{array}{lll} A+e \rightarrow B & (a_{x=0}=0) & \\ B \rightarrow A & (k_{1f}) & (2) \end{array}$$

for the CE mechanism,

$$\begin{array}{lll} C \rightleftharpoons A & (k_{1f}, k_{1b}) & \\ A+e \rightarrow B & (a_{x=0}=0) & (3) \end{array}$$

and for the ECE mechanism,

$$\begin{array}{lll} A + e \rightarrow B & (a_{x=0}=0) & \\ B \rightarrow C & (k_{1f}) & \\ C + e \rightarrow D & (c_{x=0}=0) & (4) \\ B + C \rightleftharpoons A + D & (k_{2f}, k_{2b}) & \end{array}$$

The EC, CE, and ECE mechanisms involve myriad rate processes and, under certain conditions, can be examples of very stiff problems. Criteria for stability and accuracy are examined (e.g., parameters of spatial and temporal grid expansion, computational precision) along with the role of propagational adequacy (5). Simulation results are compared with analytic solutions whenever possible.

The effectiveness of the FQEFD method for solving stiff problems is demonstrated by the simulation of the ECE mechanism (scheme 4, above) with second order rate constants which are fast enough to maintain the equilibrium of the cross reaction. Four sets of values of k_{1f}, k_{2f} and k_{2b} are considered (Cases #1 - #4, Table 1). The relationships between n_{app} and $\log_{10}[k_{1f}t]$ for Cases #1 - #4 are presented in Figure 1 and are virtually identical to previous EFD simulations utilizing some simplifying assumptions and limited to K_{2eq} = 0/0, ∞, 1, and 0 (6). The computational "times" for the EFD and FQEFD methods are also shown in Table 1 (τ_{EFD} and τ_{FQEFD} are in arbitrary units and normalized for a simulation to $k_{1f}t = 10^3$). For Cases #2 - #4, which are very stiff since they involve a dynamic range of 10^5 in operative rate constants, the FQEFD method is more than 10^5 faster than the EFD method. Case #1 corresponds to the classic Alberts and Shain ECE with no cross reaction (7).

Table 1

#	$k_{2f}c_A/k_{1f}$	$k_{2b}c_A/k_{1f}$	K_{2eq}	τ_{EFD}	τ_{FQEFD}
1	0	0	0/0	6.6×10^6	9.6×10^4
2	10^5	1	10^5	1.0×10^{12}	1.8×10^6
3	10^5	10^5	1	1.0×10^{12}	1.8×10^6
4	1	10^5	10^{-5}	1.0×10^{12}	1.8×10^6

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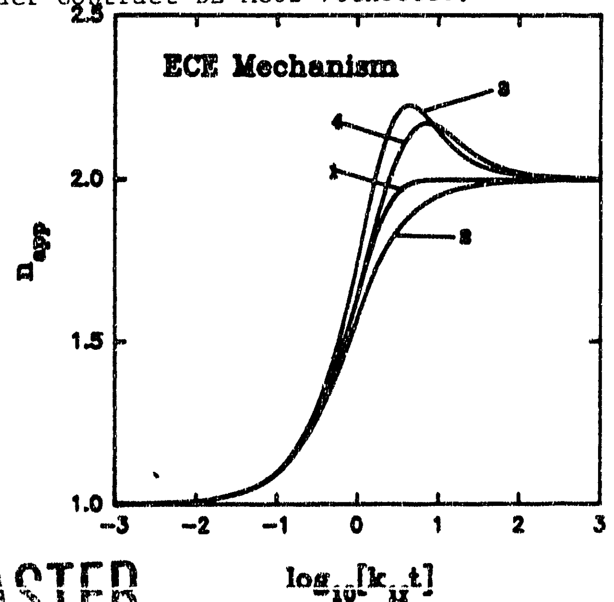

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