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BROOKHAVEN NATIONAL LABORATORY

Final Progress Report
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Project Title:

Development of Simulators for Electrochemical Responses: Experimental and Pedagogical Applications

BNL PIs and Collaborators:

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Industrial Partner:

Bioanalytical Systems, Inc. (BAS)

Abstract:

The work carried out in this CRADA addressed the development of computational algorithms to simulate the responses for commonly used electrochemical techniques. The goal was the incorporation of these algorithms into DigiSim®, a generalized simulator for cyclic voltammetry (CV). CV, a ubiquitously applied electroanalytical technique used by nonelectrochemists as well as electrochemists, is sometimes referred to as "electrochemical spectroscopy". The latest version, DigiSim® 2.1, is now being sold by the industrial partner, Bioanalytical Systems, Inc. The response of the electrochemical community to this latest program (as well as its predecessors, DigiSim® 2.0 and the DOS version; versions 2.0 and 2.1 are for Windows), has been uniformly positive and numerous publications are now appearing which feature its application.

Benefits to the Industrial Partner:

DigiSim® has been of great benefit to BAS in a number of areas, including instrument sales, workshops, teaching experiments and basic R&D. The additional capabilities of DigiSim® developed during this project will greatly enhance the usefulness of DigiSim®.

BAS has made extensive use of DigiSim® in various workshops aimed at teaching the fundamentals of electrochemistry to users of BAS instruments, who frequently have little previous experience with electrochemistry. These workshops have been conducted at BAS and customer facilities, as well as at national scientific meetings. In contrast to the more traditional mathematical approach of teaching

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electrochemistry, DigiSim® has provided a highly visual method for illustrating the effects of mass transport, electron transfer kinetics, and chemical reaction kinetics. The use of DigiSim® has also been incorporated into a number of undergraduate and graduate teaching experiments, one of which has been published in the BAS journal, Current Separations (other experiments are currently in preparation). In addition, DigiSim® has been a valuable tool in the BAS R&D laboratories for the initial characterization of potential BAS products (e.g., biosensors for glucose). The new capabilities of DigiSim® that have been developed as part of this project (chronoamperometry, thin-layer and two-dimensional diffusion) will be of great benefit to BAS for both teaching and basic R&D.

DigiSim® has also contributed to the sales of other BAS instruments. In light of this success, BAS has been developing new instrumentation to be directly interfaced with DigiSim® in order to take full advantages of the capabilities of the simulation software. Three software engineers, one hardware engineer, and one electrochemist are devoted to completing these instruments, which should be available by the start of the next calendar year.

Technical Highlights and Accomplishments:

In addition to simulation of standard CV protocols, work during the course of this CRADA has produced a unique simulation of the cyclic voltammetric response in thin layers (e.g., films) and a very efficient and accurate simulation of the CV responses at the rotating disk electrode. The thin layer simulation, for example, permits modeling of complex electrochemical sensor systems based on immobilized membranes- currently a major area of research and development. These two algorithms are now incorporated into DigiSim® 2.1, a simulation program sold by Bioanalytical Systems. A novel algorithm has been developed to efficiently solve two dimensional diffusion problems. The focus here has been on disk and band geometries which are the popular geometries for ultramicroelectrodes (the critical dimension, r_o, which is the radius of the disk or the half-width of the band, will be of the order of microns or less). Our goal is an algorithm which exhibits the same generality, robustness and computational efficiency as the algorithm we've developed to simulate the one-dimensional problems. This work is still being refined. Once that goal has been achieved the disk and band simulations will be incorporated into the commercial DigiSim® code. Simulation of an array of disks, an electrode configuration that is becoming of increasing interest to the electrochemical community, will be a rather simple extension of this work and will be a welcome addition to the simulation package. In addition, we produced the prototype of DigiSim® 3.0, a WINDOWS 95 version of DigiSim®. This will include the option for simulating chronoamperometric as well as cyclic voltammetric experiments.

Publications:

Three publications summarize some of the important aspects of technical progress:

#1. Feldberg, S.W. and Goldstein, C.I. Examination of the behavior of the fully implicit finite difference algorithm with the Richtmyer modification: Behavior with an exponentially expanding time grid. *J. Electroanalytical Chem. 397*, 1-10 (1995).

#2. Feldberg, S.W., Goldstein, C.I. and Rudolph, M. A stability criterion for accurate simulation of electrochemical diffusion/kinetic phenomena at the rotating disk electrode and implications for simulation of diffusion/migration and other problems. *J. Electroanalytical Chem., 413*, 25-36 (1996).

#3. Goldstein, C.I. Rudolph, M. and Feldberg, S.W. A computationally efficient, fully implicit algorithm for two-dimensional implicit finite difference simulations: I. Diffusion. In preparation (awaiting final refinements).

Publication #1 deals with a simulation methodology that will be particularly applicable to simulation of chronoamperometric responses of systems involving a wide dynamic range of rate constants. With the approach described in this paper the time scale is exponentially expanded with each iteration effecting very efficient and very accurate simulation of a wide dynamic time range. The fully implicit algorithm is very robust and can be applied to simulation of very complex systems. One of our goals is the development of a generalized chronoamperometric simulator; this algorithm would be the most effective approach for that.

Publication #2 addresses an interesting stability problem which evolves in the simulation of electrochemical responses at a rotating disk electrode. The difficulty arises because of the hydrodynamic terms, a difficulty which is compounded by idiosyncracies of the exponentially expanding space grid which is essential for dealing with fast homogeneous kinetics. An interesting consequence of this work is the possible explication and alleviation of a stability problem associated with simulation of diffusion/migration problems. The improved algorithm is now incorporated into the DigiSim® program; a small bug was also discovered and corrected.

Publication #3 addresses the most difficult challenge: simulation of 2-dimensional problems. The objective here is development of efficient simulation of disk and band electrode geometries (of great interest to those working with micro- and ultramicroelectrode configurations). The fundamental problem here is that the fully implicit finite difference algorithm applied to one-dimensional or quasi-one-dimensional problems readily produces an easily and efficiently solved tri-diagonal matrix for even the most chemical complex systems. Two-dimensional diffusion does not produce a tridiagonal matrix. The traditional approach has been to use some form of alternating-direction-implicit simulation, effectively a mixed implicit-explicit operation which suffers from some serious stability problems as the analogous Crank-Nicholson simulation (discussed in Publication #1). The approach we have taken invokes the use of a perturbation method which allows the two-dimensional problem to be treated in a fully implicit (and therefore stable) manner and still produce a tridiagonal matrix. The methodology has been developed to deal with diffusional problems, but no homogeneous kinetics. The next step will be introduction of homogeneous kinetics. The methodology, if successful will then be incorporated into the DigiSim® program, probably for simulations of disk, band, and disk-array systems.

General Comments and Future Goals:

The DigiSim® CV simulator has impacted dramatically on the way in which many groups carry out their electroanalytical research. The unraveling of complex organic and inorganic reaction mechanisms involving coupled electrochemical and chemical reactions once required graduate-student-years of effort to develop the requisite computational analysis- with no guarantee that the theoretical results would really explain the experimental results. With DigiSim® those computations can be carried out in minutes.

The use of DigiSim® as a teaching tool has also been extremely effective. Numerous universities now routinely use DigiSim® to explicate fundamental electrochemical phenomena and to give students a hands-on feeling for how electrochemical systems work. One of the most popular features of the program is "CV- the Movie" which shows how concentration profiles in solution change with time and how those changes are affected by the various operative electrochemical and chemical parameters.

Acknowledgment:

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