



# Implementing high performance voltammetry simulation using the implicit parallel algorithm



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## ABSTRACT

The numerical simulation of voltammetry and amperometry at a microdisc electrode is implemented with a parallel algorithm using GPU (CUDA in C++) and adapting the implicit finite difference approximation with the ADI method. This leads to high performance simulation of the current response whilst maintaining the high standard of accuracy required for such electrochemical systems. We gained a maximum speed-up of 20 times with a standard graphic card specifications (Quadro K4000) in comparison to a single core of 3.2 GHz CPU. The simplified allocation and data flow allows an accessible code which produces a starting point for researchers to manipulate the code to study new problems in electrochemical and surface reaction systems that require high performance simulation.

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## 1. Introduction

The numerical modelling of the current-time response from electrodes in physico-chemical systems is key to understanding mass transport and kinetics in electrochemical cells [1–3]. One of the strongest tools is voltammetry, where a scanning potential applied to an electrode allows the investigation of surface kinetic processes and determination of the diffusion coefficient of electroactive species. In another important technique, amperometry, the investigation of mass transport and especially diffusion can be achieved by holding the electrode at a fixed potential to measure current over time from the oxidation or reduction of adsorbing or reacting entities.

Experimental electrochemical systems are known to be accurate and are widely used as sensitive and quantitative analytical methods, and with conjunction of accurate simulation, physical parameters can be extracted. These include diffusion coefficients, reaction mechanisms, kinetic constants, adsorption and catalytic parameters [4,5]. Finite difference algorithms are widely used for the latter purpose, especially among researchers, due to the easy manipulation of the code to get a deep understanding of subtle effects on the transport, but in general, it involves the modelling of relatively simple geometries.

Performance and accuracy are a significant part of the modelling methods, and uncompromising space grids or time steps [1,6], can make calculations be very long, even for relatively simple routine investigations for example, extraction of kinetic parameters and reaction mechanism with a non-linear boundary condition problem [3,7] or

studying the life cycle of thousand charge/discharge processes in a multi-dimensional battery cell [8,9]. Therefore, high performance simulation is important for making the problems practicable for study and application.

Recently, the simulation of voltammetry using the graphic processor unit (GPU) was introduced for the solution of the finite difference problem via the explicit method [10]. Although the explicit method is a natural parallel problem, it is numerically unstable in comparison for the implicit method as shown for voltammetry problems by Bieniasz et al. [11]. Thus, finite difference studies generally use the implicit method to avoid inaccuracy, and sometimes utilize the interface OpenMP (Open Multi-Processing) or the high performance implementation of MPI (Message Passing Interface) to gain a fair performance [6]. However, with growing interest in parallel algorithms using GPU, very recent computational studies show that changing the naturally sequential Thomas algorithm to solve the dominant diagonal matrix with the a less efficient but inherently parallel algorithm 'Parallel Cyclic Reduction' (PCR), enables high performance in recent GPU architectures [12–14]. GPU implementations were reported for heat transfer [13] and are popular for fluid dynamics calculations [15], however, they have not yet introduced for electrochemical and surface kinetics either for research or applications.

We here introduce the finite difference simulation using the GPU for the implicit case of voltammetry at a disc electrode, using a two dimensional grid and kinetic boundary conditions for charge transfer in the case of redox reaction between species with equal diffusion coefficients. We also provide a simulation for the case of amperometry. The code provides a starting point for many other modelling systems that can be achieved by modifying and altering the code, such as

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complex simulation of multi-species with unequal diffusion coefficients, multi-reaction mechanism, adsorption problems and non-linear boundary conditions, or arrays. The code itself is written in an accessible way using CUDA with C++. That said, we optimize the code to be easy to understand rather than to be fully performance optimized. The results were also tested in comparison to the serial code with the Thomas algorithm and the analytical theoretical values for voltammetry.

## 2. Physical model

We model a representative electrochemical system of statistical diffusion towards a disc electrode. This case is generally assumed a full supporting electrolyte, where migration is negligible [16]. On the electrode surface, we use a kinetic and thermodynamic boundary condition with the widely used Butler–Volmer expression for the reaction mechanism on the disc surface [5].

The geometry is illustrated in Fig. 1a. Using axial symmetry around  $r=0$  (Fig. 1b), we can solve Fick's second law for a cylindrical space [17]:

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{\partial^2 c}{\partial z^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) \quad (1)$$

where  $r$  and  $z$  are the cylindrical coordinates, as shown in Fig. 1b.  $D$  is the diffusion coefficient,  $c$  is the concentration of the active species in an electrochemical cell with the redox couple (A and B). We define two distances in the  $r$  direction, the disc electrode radius ( $r_d$ ) and the surface radius ( $r_s$ ) as illustrated in Fig. 1.

The electron transfer electrochemical reaction on the electrode  $r \leq r_d$ :



The kinetics of the reaction on the electrode is defined by the boundary condition as shown below. Assuming equal diffusion coefficients for both species, A and B, and a single step reaction of A to B, we can solve Eq. (1) only for species A, and determine the concentration of species B by:

$$1 = \frac{[B] + [A]}{[B]^* + [A]^*} \quad (3)$$

where  $[A]^*$  is the initial concentration of species A, and  $[B]^*$  is the initial concentration of B.

In the work reported below,  $[B]^*$  is assumed to be zero.

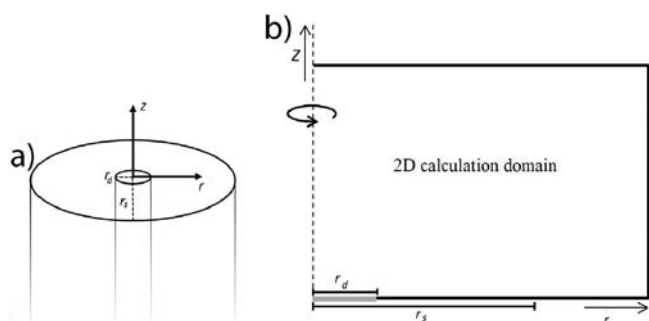


Fig. 1. 3D illustration of the microdisc electrode surrounded by an insulator (a) and the 2D system in the simulation model (b).

### 2.1. Boundary conditions

In voltammetry, the scanned potential ( $E/V$ ) is applied on the electrode with a scan rate  $\nu(V/s)$ . At  $z=0$  we define the kinetics at the adsorbing surface ( $r_d < r \leq r_s$ ), and the electrode boundary condition ( $r \leq r_d$ ). At the disc electrode, the letter is set to be the flux of each species related to the electrode potential ( $E/V$ ) according to the Butler–Volmer Eq. (5):

$$t \geq 0 \\ 0 < r \leq r_d \left( \frac{\partial c_{A(r,0)}}{\partial z} \right)_{z=0} = k^0 \left[ c_{A(r,0)} e^{-\frac{\alpha F}{RT} E} - (1 - c_{A(r,0)}) e^{\frac{\beta F}{RT} E} \right] \quad (4)$$

$F$  is the Faraday constant, and  $R$  and  $T$  are the gas constant and temperature, respectively.  $k^0$  is the kinetic constant, and  $\alpha$  and  $\beta$  are the transfer coefficients for the reaction.

In the case of voltammetry,  $E$  depends on the potential scan rate ( $\nu$ ) which is applied on the electrode via:

$$\begin{aligned} \text{Forwardscan } E_{\min} \rightarrow \phi_{\max} E(t) &= E\nu + E_{\min} \\ \text{Backwardscan } E_{\max} \rightarrow \phi_{\min} E(t) &= E_{\max} - E\nu \end{aligned} \quad (5)$$

$E_{\min, \max}$  are the lowest negative and highest positive potentials in the (cyclic) voltammetry, respectively. The maximum time ( $t_{\max}$ ) is chosen to be a full time of one cycle in the cyclic voltammetry:

$$t_{\max} = \frac{2(E_{\max} - E_{\min})}{\nu} \quad (6)$$

In the case of amperometry, we adjust the potential to a constant high potential where no kinetic barrier exists and the current is then driven only by diffusion. In the case of high potential, very small time steps should be included due to the large gradients in concentration adjacent to the electrode. However, since the long time steady state behaviour is of interest we must use an expanding time grid to solve the problem for short and long time, bearing in mind that this can be a source of instability [11] and thus the expanding factor should be adjusted carefully.

On the other boundaries of the cell, we define a wall/insulation boundary condition for A and B:

$$t \geq 0 \\ r_d < r, z = 0 \left( \frac{\partial [A]}{\partial z} \right) = \left( \frac{\partial [B]}{\partial z} \right) = 0 \quad (7)$$

where  $r_{\max}$  and  $z_{\max}$  are set to be the cell boundaries which is generally far enough to affect diffusion in the time scale of experiment. Invariably, we chose  $r_{\max}$  and  $z_{\max}$  to be larger size than  $6\sqrt{Dt_{\max}}$  in both directions ( $r, z$ ), to simulate an "infinite cell" [5].

From symmetry, the flux across the  $z$  axes can be set to zero:

$$\left( \frac{\partial [A]}{\partial z} \right)_{r=0} = \left( \frac{\partial [B]}{\partial z} \right)_{r=0} = 0 \quad (8)$$

Finally, the edges in the outer space of the simulation set to the bulk concentration of species A:

$$c_{r_{\max}} = [A]^*, c_{z_{\max}} = [A]^* \quad (9)$$

### 2.2. Current calculation

The flux inward the disk electrode is given by:

$$0 < r \leq r_d \quad j = \left( \frac{\partial [A]}{\partial z} \right)_{z=0} \quad (10)$$

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