Electrochemistry

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1 Introduction

An electrochemical reaction is a chemical reaction caused by an externally supplied current, such as oxidation-reduction reactions. Linear sweep and cyclic voltammetry represent the most common types of potentiodynamic electrochemical measurement[1]. In the case of linear sweep voltammetry, the potential is swept linearly with time whereas in the case of cyclic voltammetry, after the pre-determined potential is reached, the working electrode's potential is swept in the opposite direction to return to the initial potential.

2 Chronoamperometry

2.1 Equations

I consider mass transport of chemical species to the electrode to be a one-dimensional diffusion process[2], which can be expressed as:

$$\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} \tag{1}$$

where x is the distance from electrode surface, t is time, $c_s(x,t)$ is the concentration of chemical species and D_s is the diffusion constant. Assume initially only one chemical species of A exists and oxidation reaction occurs at the electrode surface

$$A - e^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \tag{2}$$

where k_1, k_2 are rate constants that depend on the applied potential. Intuitively the current at the electrode surface is given by

$$I(t) = \left(\frac{\partial a}{\partial x}\right)_{x=0} \tag{3}$$

In the case of Chronoampermetry, the potential is stepped at $t = 0$ to ensure complete conversion of A to B at the electrode surface. Therefore I have the following set of equations:

$$\frac{\partial a}{\partial t} = D_a \frac{\partial^2 a}{\partial x^2} \ , \ \frac{\partial b}{\partial t} = D_b \frac{\partial^2 b}{\partial x^2} \tag{4}$$

$$D_a \frac{\partial a}{\partial x} = -D_b \frac{\partial b}{\partial x} \quad \text{at } x = 0 \tag{5}$$

$$a(x,0) = a^* \ , \ b(x,0) = 0 \tag{6}$$

$$a(x,t) \to a^* \ , \ b(x,t) \to 0 \quad \text{as } t \to \infty \tag{7}$$

$$a(0,t) = 0 \tag{8}$$

If I assume $D_a = D_b$ and nondimensinoalise the model, I obtain

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial x^2} \tag{9}$$

$$a(x,0) = 1 \tag{10}$$

$$a(x,t) \to 1 \quad \text{as } x \to \infty \tag{11}$$

$$a(0,t) = 0 \tag{12}$$

$$a + b = 1 \tag{13}$$

b can be easily computed once a is solved

2.2 Exact Solutions

The analytic solution of a can be obtained via similarity solution, setting

$$a = f(\eta) \ , \ \eta = \frac{x}{\sqrt{t}} \tag{14}$$

substitute this into the set of equations above, I obtain:

$$f'' + \frac{\eta}{2} f' = 0 \tag{15}$$

$$f(\eta) \to 1 \quad \text{as } \eta \to \infty \tag{16}$$

$$f(0) = 0 \tag{17}$$

therefore

$$a(x,t) = f(\eta) = \frac{2}{\sqrt{\pi}} \int_0^{\frac{\eta}{2}} e^{-s^2} ds = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{t}}} e^{-s^2} ds \tag{18}$$

Alternatively I could use the method of Laplace transform. Let $\tilde{a}$ denote the Laplace transform of a. If I apply Laplace transform on equation (9) I have:

$$\frac{\partial^2 \tilde{a}}{\partial x^2}(x,s) - s\tilde{a}(x,s) = -1 \tag{19}$$

therefore

$$\tilde{a}(x,s) = A(s)e^{\sqrt{s}x} + B(s)e^{-\sqrt{s}x} + \frac{1}{s} \tag{20}$$

Substituting boundary conditions:

$$a(0,t) = 0 \Rightarrow \tilde{a}(0,s) = 0 \Rightarrow A(s) + B(s) + \frac{1}{s} = 0 \tag{21}$$

$$\lim_{x\to\infty} a(x,t) = 1 \Rightarrow \lim_{x\to\infty} \tilde{a}(x,s) = \frac{1}{s} \Rightarrow A(s) = 0\,, B(s) = -\frac{1}{s} \tag{22}$$

$$a(x,0) = 1 \Rightarrow \lim_{s\to 0} \tilde{a}(x,s) = \lim_{s\to 0} \frac{1}{s}(1 - e^{-\sqrt{s}}x) = \frac{1}{s} \tag{23}$$

Therefore $\tilde{a}(x,s)$ is given by:

$$\tilde{a}(x,s) = \frac{1}{s}(1 - e^{-\sqrt{s}}x) \tag{24}$$

Apply inverse Laplace transform I obtain:

$$a(x,t) = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{t}}} e^{-s^2} ds \tag{25}$$

which is same as equation (18).

2.3 Numerical Solution

The numerical solution of a and b can be solved by the method of finite differences. Plots of a and b are given in Figure 1 and Figure 2 respectively.

3 Linear Sweep Voltammetry

3.1 Equations

Now I consider the case that the applied potential varies linearly with time. In such case, after the nondimensionalisation procedure, at the point of $x = 0$ I have

$$\frac{\partial a}{\partial x} = k_1 a - k_2(1 - a) \tag{26}$$

where

$$k_1 = k_0 e^{(1-\alpha)(E(t)-E_0)} \tag{27}$$

$$k_2 = k_0 e^{-\alpha(E(t)-E_0)} \tag{28}$$

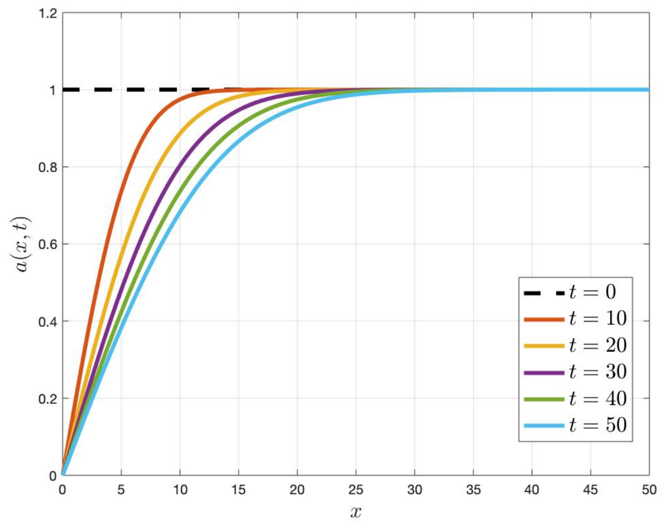

Figure 1: Plot of a at different times in chronoamperometry

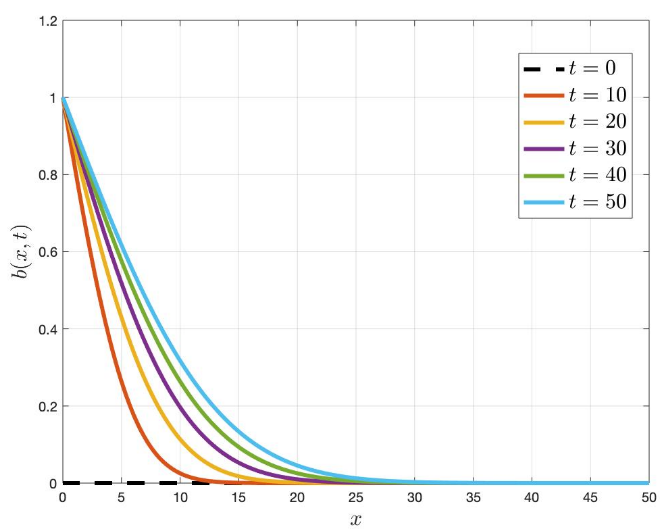

Figure 2: Plot of b at different times in chronoamperometry

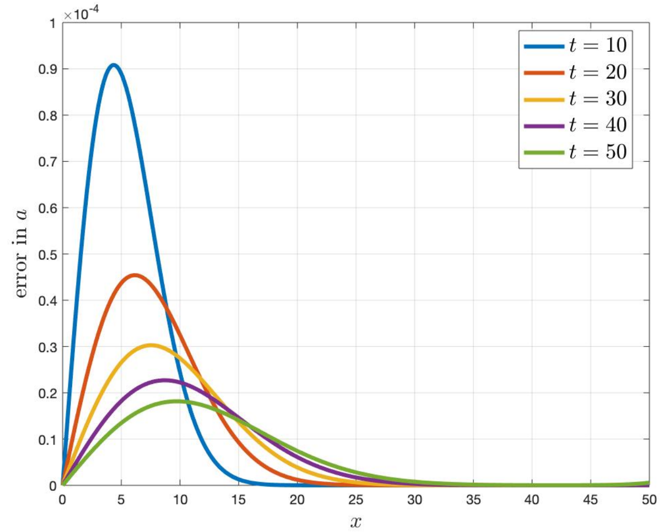

Figure 3: Absolute error between analytic and numerical results of a in chronoamperometry

$E(t)$ is the applied potential, E_0 is the formal potential which depends on the chemical species, k_0 is the heterogeneous rate constant and α is the charge transfer constant. In the case of linear sweep voltammetry

$$E(t) = E^* + t \tag{29}$$

where E^* denotes the initial potential. If a cyclic voltammetry is applied, where $E(t)$ is given by:

$$E(t) = \begin{cases} E^* + t & 0 \le t \le t^* \\ E^* + 2t^* - t & t^* \le t \le 2t^* \end{cases} \tag{30}$$

I expect the current to show cyclic behaviour as Figure 5 shows.

3.2 Integral Equation

I posit that the following equation holds:

$$\frac{\sqrt{\pi}}{1 + e^{-(E(t)-E_0)}} = \int_0^t \frac{I(\tau)}{\sqrt{t-\tau}} d\tau \tag{31}$$

This is the integral equation and I shall prove its validity. In the case of linear sweep voltammetry, $I(0) = 0$. Integrating the right hand side of the equation by parts:

$$\int_0^t \frac{I(\tau)}{\sqrt{t-\tau}} d\tau = \int_0^t 2\sqrt{t-\tau} I'(\tau) d\tau \tag{32}$$

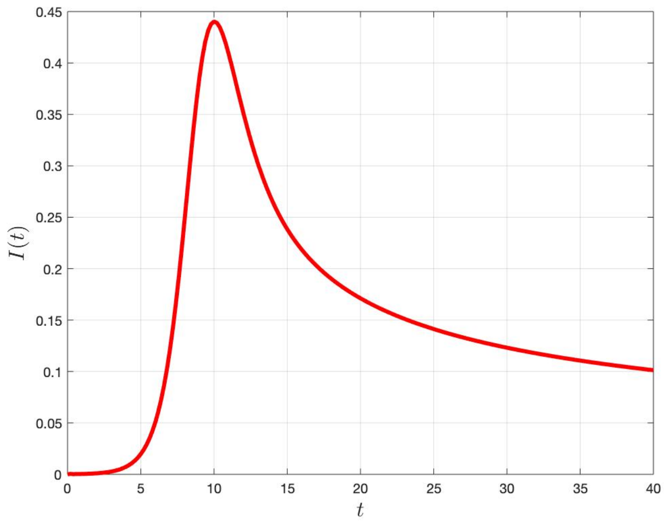

Figure 4: Current with respect to time when a linear sweep voltammetry is applied, $(E^*, E_0, k_0, \alpha) = (-10, -1, 35, 0.5)$

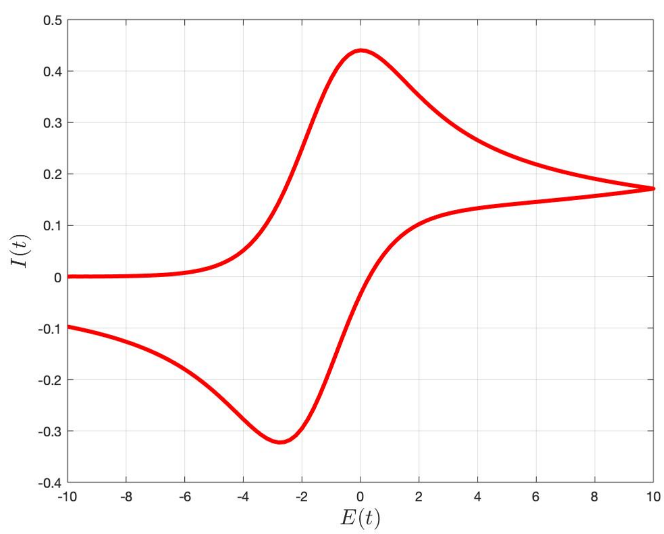

Figure 5: Current with respect to time when a cyclic voltammetry is applied, $(E^*, E_0, k_0, \alpha) = (-10, -1, 35, 0.5)$

Taking Laplace transform of equation (32) and apply the convolution theorem I have:

$$L[2\sqrt{t} * I'(t)] = 2L[\sqrt{t}]L[I'(t)] = \tilde{I}(s)\sqrt{\frac{\pi}{s}} \tag{33}$$

where $\tilde{I}(s)$ denotes the Laplace transform of $I(t)$ and $*$ denotes convolution. The Laplace transform of the current is given by:

$$I(t) = \left(\frac{\partial a}{\partial x}\right)_{x=0} \Rightarrow \tilde{I}(s) = \left(\frac{\partial \tilde{a}}{\partial x}\right)_{x=0} \tag{34}$$

The general form of $\tilde{a}(x,s)$ is given by equation (20), apply the far field boundary condition:

$$\lim_{x\to\infty} a(x,t) = 1 \Rightarrow \lim_{x\to\infty} \tilde{a}(x,s) = \frac{1}{s} \Rightarrow A(s) = 0 \tag{35}$$

Hence $\tilde{I}(s)$ is given by:

$$\tilde{I}(s) = \left(\frac{\partial \tilde{a}}{\partial x}\right)_{x=0} = -\left(\sqrt{s}B(s)e^{-\sqrt{s}x} + \frac{1}{s}\right)_{x=0} \tag{36}$$

Therefore

$$B(s) = -\frac{\tilde{I}(s)}{\sqrt{s}} \tag{37}$$

Combining equation (31) and equation (37) gives:

$$\tilde{a}(0,s) = -\frac{\tilde{I}(s)}{\sqrt{s}} + \frac{1}{s} \tag{38}$$

Apply inverse Laplace transform to equation (38) and use the relation given by equation (33) I obtain:

$$L^{-1}[\tilde{a}(0,s)] = -\frac{1}{\sqrt{\pi}}\int_0^t \frac{I(\tau)}{\sqrt{t-\tau}}d\tau + 1 \tag{39}$$

Moreover, equation (26) can be rearranged to show that:

$$a(0,t) = \frac{1}{e^{E(t)-E_0} + 1} \tag{40}$$

Equating equation (39) and equation (40) I obtain the integral equation.

3.3 Numerical Solution of Integral Equation

Remember that the integral equation is given by:

$$\frac{\sqrt{\pi}}{1+e^{-(E(t)-E_0)}} = \int_0^t \frac{I(\tau)}{\sqrt{t-\tau}} d\tau \tag{41}$$

where $E(t)$ is a known function and $I(0) = 0$. Integrate the right hand side of the equation gives:

$$\int_0^t \frac{I(\tau)}{\sqrt{t-\tau}} d\tau = \int_0^t 2\sqrt{t-\tau} I'(\tau) d\tau \tag{42}$$

I notice that the right hand side of equation (42) is a Volterra integral equation of the first kind:

$$f(t) = \int_0^t K(t,\tau)\phi(\tau)d\tau \tag{43}$$

where

$$f(t) = \frac{\sqrt{\pi}}{1+e^{-(E(t)-E_0)}}\,, \quad K(t,\tau) = 2\sqrt{t-\tau}\,, \quad \phi(\tau) = I'(\tau) \tag{44}$$

By trapezium rule the Volterra equation can be approximated by:

$$\int_0^t K(t,\tau)\phi(\tau)d\tau \approx \frac{\Delta t}{2}[K(t,0)\phi(0) + 2K(t,\tau_1)\phi(\tau_1) + 2K(t,\tau_2)\phi(\tau_2) + \ldots + K(t,\tau_n)\phi(\tau_n)] \tag{45}$$

where

$$0 < \tau_1 < \tau_2 < \cdots < \tau_n = t\,, \quad \Delta t = \tau_{i+1} - \tau_i \tag{46}$$

Therefore I have a system of equations given by:

$$f(\tau_1) = \frac{\Delta\tau}{2}[K(\tau_1,0)\phi(0) + K(\tau_1,\tau_1)\phi(\tau_1)] \tag{47}$$

$$f(\tau_2) = \frac{\Delta\tau}{2}[K(\tau_2,0)\phi(0) + 2K(\tau_2,\tau_1)\phi(\tau_1) + K(\tau_2,\tau_2)\phi(\tau_2)] \tag{48}$$

$$\ldots \tag{49}$$

$$f(\tau_n) = \frac{\Delta\tau_n}{2}[K(\tau_n,0)\phi(0) + 2K(\tau_n,\tau_1)\phi(\tau_1) + 2K(\tau_n,\tau_2)\phi(\tau_2) + \ldots + K(\tau_n,\tau_n)\phi(\tau_n)] \tag{50}$$

Since $K(\tau_i,\tau_i) = 0$, denoting $K(\tau_i,\tau_j)$ by $K_{i,j}$, then the above system can be written as:

$$\begin{pmatrix} f(\tau_1) \\ f(\tau_2) \\ f(\tau_3) \\ \vdots \\ f(\tau_n) \end{pmatrix} = \frac{\Delta\tau}{2} \begin{pmatrix} K_{1,0} & & & & \\ K_{2,0} & K_{2,1} & & & \\ K_{3,0} & K_{3,1} & K_{3,2} & & \\ \vdots & \vdots & \vdots & \ddots & \\ K_{n,0} & K_{n,1} & K_{n,2} & \cdots & K_{n,n-1} \end{pmatrix} \begin{pmatrix} \phi(0) \\ \phi(1) \\ \phi(2) \\ \vdots \\ \phi(\tau_{n-1}) \end{pmatrix} \tag{51}$$

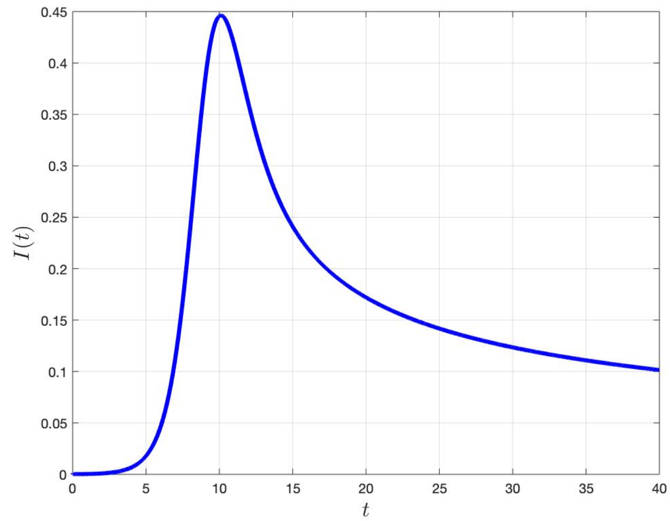

Figure 6: Plot of current with respect to time when a Linear Sweep Voltammetry is applied, solved by using the integral equation. $(E^*, E_0, k_0, \alpha) = (-10, -1, 35, 0.5)$

which can be solved via forward substitution to obtain $\phi(0), \phi(1), \ldots, \phi(\tau_{n-1})$. Given $I'(0), I'(1), \ldots, I'(\tau_{n-1})$, I can use trapezium rule to compute I by this way:

$$I(0) = 0 \tag{52}$$

$$I(\tau_1) = \frac{\Delta\tau}{2}[I'(0) + I'(\tau_1)] \tag{53}$$

$$\vdots \tag{54}$$

$$I(\tau_n) = \frac{\Delta\tau}{2}[I'(0) + 2I'(\tau_1) + \cdots + I'(\tau_n)] \tag{55}$$

From Figure 6 I can see that numerical solution by integral equation match nicely with the numerical solution computed by finite difference method in Figure 5.

4 Sine Wave Voltammetry

In the case of Sine Wave Voltammetry:

$$E(t) = E_{dc}(t) + E_{ac}(t) \tag{56}$$

where

$$E_{dc}(t) = E^* + t\,, \quad E_{ac}(t) = \Delta E \sin(\omega t) \tag{57}$$

Here Δt and ω are controlled by the experiment. Similarly I could solve for $I(t)$ via finite difference method and an example is given in Figure 7.

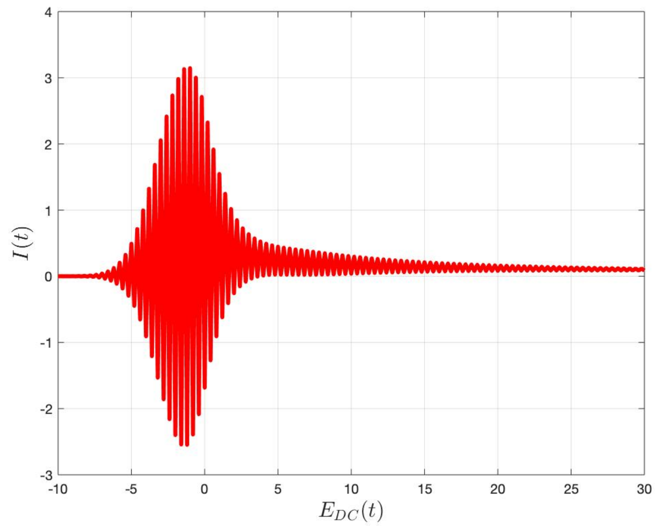

Figure 7: Plot of current with respect to time when a sine wave voltammetry is applied, $(E^*, E_0, k_0, \alpha, \Delta t, \omega) = (-10, -1, 35, 0.5, 2, 16)$

5 Inverse Problem

Suppose I are given experimental data $I(t_n)$ for $n = 1, 2, 3, \ldots, N$, along with parameters $E^*, \Delta E, \omega$, and I would like to find the parameters E_0, k_0, α from the data that I have. Firstly I can set up an objective function given by:

$$J(E_0, k_0, \alpha) = \sum_{n=0}^{N} (I_{exp}(t_n) - I_{num}(t_n, E_0, k_0, \alpha)) \tag{58}$$

where $I_{exp}(t_n)$ denote the experimental data and $I_{exp}(t_n) - I_{num}(t_n, E_0, k_0, \alpha)$ denote the numerical result when some (t_n, E_0, k_0, α) is used. One way to solve for parameters (E_0, k_0, α) is by using the fminsearch function in MATLAB to find the values that fit the best. However I need to make sure that k_0 is positive and $\alpha \in (0, 1)$. I will try to apply this method to the case where $(E_0, k_0, \alpha) = (0, 0.1, 0.5)$ and see if it works. First I generate $I_{num}(t_n, E_0, k_0, \alpha)$ using these parameter values, then I generate a noisy current by adding noise such that:

$$I_{exp}(t_n) = I_{num}(t_n, E_0, k_0, \alpha) + rI_{max}\Delta N \tag{59}$$

where $I_{max} = \max_{0 \le n \le N} I_{num}(t_n, E_0, k_0, \alpha)$, ΔN is sampled from a standard normal distribution and r denotes the percentage error. Then I apply fminsearch to $I_{exp}(t_n)$ to obtain parameter values and check if they are closed to the actual values. In this

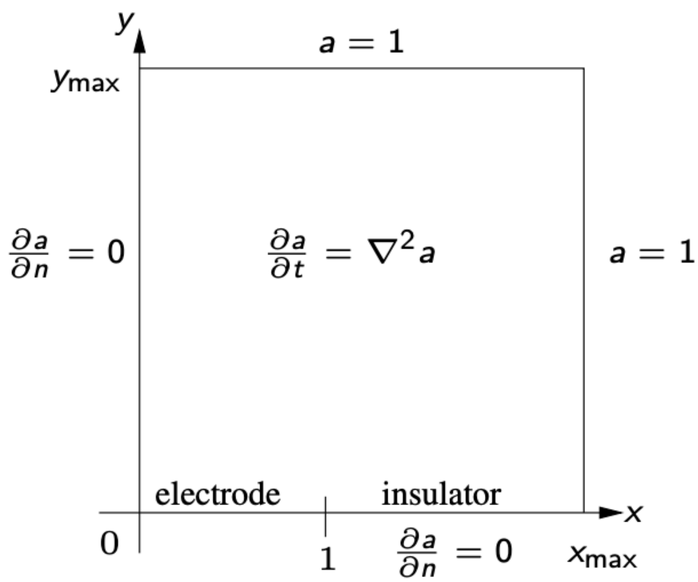

Figure 8: 2D problem

case I set $r = 0.05$ and apply 5 iterations of fminsearch, the result is given by the following table.

Error			
	error E_0	error α	error k_0
Linear	2.2758	0.11874	0.23088
Cyclic	0.10487	0.039065	0.015578
Sine	8.8764	0.037121	0.17398

Clearly the most accurate result is recovered when cyclic voltammetry is applied, followed by linear sweep voltammetry and lastly sine wave voltammetry. In general α and k_0 are recovered correctly whereas E_0 is recovered only when cyclic voltammetry is applied.

6 Extension

Now I consider a 2D problem of linear sweep voltammetry at a microband electrode assuming equal coefficient for A and B. Here the electrode is small so it is assumed that the effects from the electrode/insulator edge have an effect. The problem in a truncated domain is given by Figure 8. Here I can see that there exist two types of boundary conditions: Dirichlet boundary condition and zero Neumann boundary condition. Inside the domain a satisfies the heat equation. Here I consider a rectangular domain of $\Omega = [0,2] \times [0,2]$, the uniform mesh points are defined by

$$x_i = i\Delta x\,, \quad y_j = j\Delta y$$

for $i, j = 0, 1, 2 \ldots, N+1$ with meshsizes $\Delta x = \Delta y = 2/(N+1)$. Timestep is defined bt $t_m = m\Delta t$ for $m = 0, 1, 2, \ldots$ I use the approximation $A^m_{i,j}$ for $a(x_i, y_j, t_m)$ Consider the equation:

$$\frac{da}{dt} = \frac{d^2a}{dx^2} + \frac{d^2a}{dy^2} \tag{60}$$

By the Crank Nicolsan Method[3], equation (60) can be approximated by:

$$\frac{A^{m+1}_{i,j} - A^m_{i,j}}{\Delta t} = \theta \frac{A^{m+1}_{i+1,j} - 2A^{m+1}_{i,j} + A^{m+1}_{i-1,j}}{\Delta x^2} + (1-\theta)\frac{A^m_{i+1,j} - 2A^m_{i,j} + A^m_{i-1,j}}{\Delta x^2} \tag{61}$$

$$\tag{62}$$

$$+\theta \frac{A^{m+1}_{i,j+1} - 2A^{m+1}_{i,j} + A^{m+1}_{i,j-1}}{\Delta y^2} + (1-\theta)\frac{A^m_{i,j+1} - 2A^m_{i,j} + A^m_{i,j-1}}{\Delta y^2} \tag{63}$$

for $i, j = 1, 2, ..., N$, $m = 1, 2, ...$ and $\theta \in [0,1]$. Using θ-method subject to the boundary conditions I obtain a linear system:

$$(I - \theta M)\mathbf{A}^{m+1} = (I + (1-\theta)M)\mathbf{A}^m + \mathbf{f} \tag{64}$$

where

$$\mathbf{A}^m = (A^m_{1,1}, A^m_{1,2}, \ldots A^m_{1,N}, A^m_{2,1}, \ldots A^m_{N,N})^T \tag{65}$$

I is the $N^2 \times N^2$ identity matrix and M is a $N^2 \times N^2$ matrix of the form:

$$M = \begin{pmatrix} B' & C & & & & \\ C & B & C & & & \\ & C & B & C & & \\ & & \ddots & \ddots & \ddots & \\ & & & C & B & C \\ & & & & C & B \end{pmatrix} \tag{66}$$

where C,B',B are $N \times N$ matrices of the form:

$$C = \begin{pmatrix} \mu_x & & & \\ & \mu_x & & \\ & & \ddots & \\ & & & \mu_x \end{pmatrix} \tag{67}$$

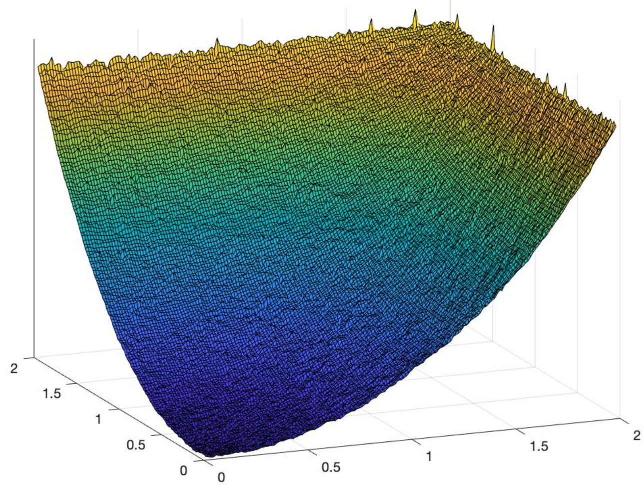

Figure 9: Numerical solution of a when $t = 10$

$$B' = \begin{pmatrix} -(\mu_x+\mu_y) & \mu_y & & & & \\ \mu_y & -(\mu_x+2\mu_y) & \mu_y & & & \\ & \mu_y & -(\mu_x+2\mu_y) & \mu_y & & \\ & \ddots & \ddots & \ddots & & \\ & & \mu_y & -(\mu_x+2\mu_y) & \mu_y \\ & & & \mu_y & -(\mu_x+2\mu_y) \end{pmatrix} \tag{68}$$

$$B = \begin{pmatrix} -(2\mu_x+\mu_y) & \mu_y & & & & \\ \mu_y & -2(\mu_x+\mu_y) & \mu_y & & & \\ & \mu_y & -2(\mu_x+\mu_y) & \mu_y & & \\ & \ddots & \ddots & \ddots & & \\ & & \mu_y & -2(\mu_x+\mu_y) & \mu_y \\ & & & \mu_y & -2(\mu_x+\mu_y) \end{pmatrix} \tag{69}$$

and $\mathbf{f}$ is of the form:

$$\mathbf{f} = (0, 0, \dots, \mu_y, 0, 0, \dots, \mu_y, \dots, 0, 0, \dots, \mu_y, \mu_x, \mu_x, \dots, \mu_x + \mu_y)^T \tag{70}$$

where $\mu_x = \frac{\Delta t}{\Delta x^2}$ and $\mu_y = \frac{\Delta t}{\Delta y^2}$. Plugging in intial values for a and run iterations I obtain a numerical solution of a showed by Figure 9.

7 Conclusion

In this paper I introduced one-dimensional diffusion of chemical species to the electrode in the case of chronoamperometry. Then I extend it to the case when linear sweep voltammetry is applied and derive the integral equation which can be solved numerically by trapezium rule. I also introduce the inverse problem where I recover unknown parameter values from experimental data by using fminsearch in MATLAB. Lastly I extend linear sweep voltammetry in a two-dimensional domain and compute the solution numerically by using the method of finite differences.

References

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