Possible Extensions to Electrochemistry Project

Case Studies in Scientific Computing

Non-uniform Mesh

Use an expanding spatial mesh to solve the problem, i.e.

- set $x_0 = 0$
- set $x_i = x_{i-1} + h_i$ for $i = 1, \ldots N$
- here $h_1 = 0.025$ (say) and $h_i = rh_{i-1}$ for $i = 2, \ldots N$ with $r = 1.01$ (say).

You will need to choose N so that x_N is large enough.

What will the finite difference scheme be on this non-uniform mesh?

Non-uniform Mesh via Mapping

The alternative way to generate a mesh with more points clustered near $x = 0$ is to use a map, for example

$$y = \exp(-\rho x) ,$$

for some $\rho > 0$. Use the chain rule to work out the partial differential equation and boundary conditions in the (y, t) variables and then solve using a uniform mesh in (y, t) space.

Verifying Properties of the Peak Current

Demonstrate numerically that the peak ac current varies linearly with ΔE.

To do this take $\omega = \frac{\pi}{2}$, π, 2π, 4π, 8π, 16π, 32π and $\Delta E = 0.05 : 0.05 : 1$. Compute the ac current by working out the total current minus the dc current.

Also demonstrate numerically that the peak of the ac wave is a linear function of $\omega^{1/2}$. Use $\Delta E = 0.1$.

More Complex Reaction Mechanism

Solve a more complex reaction mechanism, such as the ECE reaction mechanism:

$$\begin{aligned} A + e^- &\rightarrow B \,, \\ B &\xrightarrow{k} C \,, \\ C + e^- &\rightarrow D \,. \end{aligned}$$

Assuming equal diffusion coefficients, this is modelled in dimensionless variables by

$$\frac{\partial a}{\partial t} = \frac{\partial^2 a}{\partial x^2} \,, \quad \frac{\partial b}{\partial t} = \frac{\partial^2 b}{\partial x^2} - kb \,, \quad \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} + kb \,, \quad \frac{\partial d}{\partial t} = \frac{\partial^2 d}{\partial x^2} \,,$$

for $0 < x < \infty$ and for $t > 0$.

More Complex Reaction Mechanism

The initial and boundary conditions are given by

$$
\begin{array}{lll}
a(x,0) = 1\ , & b(x,0) = c(x,0) = d(x,0) = 0\ , & 0 \le x < \infty\ , \\
a(x,t) \to 1\ , & b(x,t),\ c(x,t),\ d(x,t) \to 0\ , & \text{as } x \to \infty,\ t > 0\ , \\
\frac{\partial a}{\partial x} + \frac{\partial b}{\partial x} = 0\ , & \frac{\partial c}{\partial x} + \frac{\partial d}{\partial x} = 0\ , & \text{at } x = 0,\ t > 0\ .
\end{array}
$$

The specific boundary conditions for voltammetry are

$$
\begin{aligned}
\frac{\partial a}{\partial x} &= k_0^1 \left(a\mathrm{e}^{(1-\alpha_1)(E(t)-E_a^0)} - b\mathrm{e}^{-\alpha_1(E(t)-E_a^0)} \right)\ , \\
\frac{\partial c}{\partial x} &= k_0^2 \left(c\mathrm{e}^{(1-\alpha_2)(E(t)-E_c^0)} - d\mathrm{e}^{-\alpha_2(E(t)-E_c^0)} \right)\ ,
\end{aligned}
$$

at $x = 0$, for $t > 0$ where $E(t) = E_{\mathrm{start}} + t$.

More Complex Reaction Mechanism

The current is then given by

$$I(t) \quad = \quad \left(\frac{\partial a}{\partial x} + \frac{\partial c}{\partial x}\right)_{x=0} \quad .$$

Show that d can be eliminated from this set of equations and then solve for a, b and c then compute and plot the current.
Experiment with the parameters E_a^0 and E_c^0. For example try

- $E_a^0 = E_c^0 = 0$,
- $E_a^0 = 0,\ E_c^0 = 5$,
- $E_a^0 = 5,\ E_c^0 = 0$.

Square Wave Voltammetry

Set the applied potential in ac voltammetry to be a linear sweep with a square wave superimposed so that

$$E(t) = E_{\mathrm{dc}} + E_{\mathrm{ac}} \ ,$$

with

$$\begin{aligned} E_{\mathrm{dc}} &= E_{\mathrm{start}} + t \ , \\ E_{\mathrm{ac}} &= \Delta E(-1)^{\lfloor \omega t \rfloor} \end{aligned}$$

Plot the power spectrum. You should find that only the odd harmonics are present. Why is this?
(If we let y be the FFT of the current then take the absolute value of the first half of y, this is the power.)

More Complicated Model

In linear sweep voltammetry we may write the boundary condition at the electrode surface as

$$\frac{\partial a}{\partial x} = k_{\mathrm{ox}} a - k_{\mathrm{red}} b,$$

where

$$\begin{aligned} k_{\mathrm{ox}} &= k_0 \mathrm{e}^{(1-\alpha)(E(t)-E^0)}, \\ k_{\mathrm{red}} &= k_0 \mathrm{e}^{-\alpha(E(t)-E^0)}. \end{aligned}$$

Now suppose we model resistance in the solution so

$$\begin{aligned} k_{\mathrm{ox}} &= k_0 \mathrm{e}^{(1-\alpha)(E(t)-R_u I(t)-E^0)}, \\ k_{\mathrm{red}} &= k_0 \mathrm{e}^{-\alpha(E(t)-R_u I(t)-E^0)}. \end{aligned}$$

Here $I(t)$ is the current so we have a nonlinear boundary condition. What does the solution look like now and what effect does the size of R_u have? (Try $R_u = 2.5$ initially.)

Inverse Problem

When $D_A = D_B$ so that $a + b = 1$, the voltammetry problem is

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

for $0 < x < \infty$ and for $t > 0$, with initial and boundary conditions

$$\begin{aligned} a(x,0) &= 1 , \\ a(x,t) &\to 1 , \quad \text{as } x \to \infty , \\ \frac{\partial a}{\partial x} &= k_0 \left(a\mathrm{e}^{(1-\alpha)(E(t)-E^0)} - (1-a)\mathrm{e}^{-\alpha(E(t)-E^0)} \right) , \quad \text{at } x = 0, , \end{aligned}$$

where $E(t) = E_{\text{start}} + t + \Delta E \sin \omega t$. The current is

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

In terms of chemistry, the chemist knows the applied potential, $E(t)$ (sometimes called the input signal) and can measure $I(t)$. Given this information, they would like to find k_0, α and E^0. This is the inverse problem.

Inverse Problem

Let $I_{\rm exp}(t)$ be a numerical approximation to the current (possibly with noise added) with a fixed set of parameters k_0, α and E^0. Then we want to minimise

$$L \quad := \quad \sum_{i=1}^{n} \left(I(t_i) - I_{\rm exp}(t_i) \right)^2$$

(where n is the number of timesteps) over k_0, α and E^0. There are constraints — we need $k_0 > 0$ and $\alpha \in (0, 1)$. These can be enforced by setting $L = 10^6$ if k_0 and α lie outside the required ranges. Then you should be able to solve the minimisation problem in Matlab using `fminsearch`.

Inverse Problem

If no noise is added, we expect perfect recovery of the parameters. Noise should be normally distributed with mean 0 and variance $\sigma^2 = 0.01 I_{\max}$ where $I_{\max} = \max |I(t)|$. Do the values of ΔE and ω have any effect on the recovery in this case?