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A Numeric Symbolic Solution for Impedance Response of Electrochemical Devices

I. Introduction of the Method

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A numeric symbolic solution technique is introduced for the simulation of ac impedance response of electrochemical devices. The proposed method is numerical in the spatial coordinates and yields a closed form symbolic solution in the system parameters. The system of algebraic equations obtained by the spatial discretization is written in matrix form and solved symbolically. Although this method is capable of simulating ac impedance data for systems with multiple coupled partial differential equations, the method and its advantages over classical methods are illustrated using diffusion in a planar electrode.
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Various transport and reaction limitations restrict the cost effectiveness, utilization, and efficiency of electrochemical devices. AC impedance is a powerful technique used by various researchers to understand electrochemical systems.[1-4] Understanding and extracting useful information from ac impedance data is a formidable task. The main drawback with using circuit approach for simulating ac impedance response is that it only gives lumped-parameters for the system of interest and does not involve all of the meaningful quantitative system parameters such as the Fickian diffusion coefficient, rate constants, etc. Rigorous physics based models for simulating ac impedance response involves solving multiple partial differential equations (PDEs) in multiple domains making the models prohibitive because of numerical and computational constraints.[4] Typically, only single PDE has been solved analytically in the literature. Recently, an analytical solution was reported for two coupled PDEs.[3] For more than one PDE, obtaining an analytical solution involves complicated eigenvalue and cumbersome matrix calculations. Analytical solutions may not be easily separable to real and imaginary parts.

The purpose of this paper is to develop a numeric symbolic solution (NSS) for simulating ac impedance response of electrochemical devices. The methodology consists of applying finite differences for the spatial coordinate and a symbolic matrix inversion method for solving the resulting system of linear algebraic equations. Thus the NSS is numerical in the spatial coordinate and closed-form in all the system parameters. In this paper, this scheme is demonstrated by simulating diffusive impedance response of a planar electrode. This approach will be extended in the future to multiple PDEs in multiple spatial coordinates in multiple domains that govern the electrochemical behavior of various devices. The efficiency and superiority of NSS is compared with both analytical and numerical solutions.

Example – Diffusive Impedance

Diffusion in a planar electrode is given by Fickian diffusion as

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad [1]$$

The boundary conditions are

$$\text{at } x = 0, \quad c = 0$$

$$\text{at } x = L, \quad D\frac{\partial c}{\partial x} = \frac{i(t)}{nF} \qquad [2]$$

The electrode is in contact with the bulk-liquid at $x = 0$ and the electrochemical behavior is governed by the surface concentration at $x = L$. The electrochemical reaction takes place at the electrode surface. Because impedance experiments are performed about an operating point with a small perturbation, c in Eq. 1 can be thought of as a perturbation in concentration with initial condition being zero.

To get the ac impedance response for the electrode, Eq. 1 is converted from the time domain to the Laplace domain s, and expressed in dimensionless form as

$$\frac{d^2C}{dX^2} = SC \qquad [3]$$

with the boundary conditions

$$X = 0,\ C = 0 \quad \text{and} \quad X = 1,\ \frac{dC}{dX} = \delta(S) \qquad [4]$$

where $X = x/L$, $C = c/c_{\text{ref}}$, $\delta(S) = i(s)L/nFDC_{\text{ref}}$, and $S = sL^2/D$ is the dimensionless Laplace variable. Various approaches for the simulation of diffusive impedance response of planar electrode (Eq. 3 with the boundary conditions Eq. 4) are described below.

Analytical approach.— Equation 3 can be analytically solved using a standard classical technique and a closed-form solution for C as a function of S (s, D, and L) is obtained as[5]

$$C_{\text{analytical}} = \frac{\delta(S)\sinh(X\sqrt{S})}{\sqrt{S}\cosh(\sqrt{S})} \qquad [5]$$

The surface concentration, C_s gives the overpotential and hence the impedance. C_s at the boundary $X = 1$ is obtained as (without losing generosity δ is assumed to be 1)

$$C_{S_{\text{analytical}}} = Z_{\text{analytical}} = \tanh(\sqrt{S})/\sqrt{S} \qquad [6]$$

The impedance response or the Nyquist plot is obtained by substituting $S = I\Omega$ (Ω is the dimensionless frequency and is obtained by multiplying frequency ω by L^2/D) in Eq. 6 and by separating the real and imaginary parts. The separation of the total impedance as real and imaginary parts is simple for this case as the analytical expression does not contain complicated eigenfunctions and eigenvalues.[3]

Numerical approach.— A numerical solution to solve Eq. 3 is performed by applying finite difference or other discretization methods in the spatial direction, X. Because one has to find both real and imaginary parts, Eq. 3 is typically converted to real and imaginary parts before implementing a numerical procedure. By substituting $S = I\Omega$, Eq. 3 is separated for real and imaginary parts as

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$$\frac{d^2C_{re}}{dX^2} = -\Omega C_{im}$$

$$\frac{d^2C_{im}}{dX^2} = \Omega C_{re} \quad [7]$$

The boundary conditions are also separated for real and imaginary parts as

$$X = 0,\ C_{re} = 0;\quad C_{im} = 0$$

$$X = 1,\ \frac{dC_{re}}{dX} = 1;\quad \frac{dC_{im}}{dX} = 0 \quad [8]$$

For a particular value of frequency Ω, the set of equations given in Eq. 7 is solved numerically with appropriate boundary conditions given by Eq. 8. By consecutively finding C_{re} and C_{im} at the surface ($X = 1$) for various values of Ω numerically, the Nyquist plot is obtained. For this purpose, Maple's dsolve numeric command is used.[6]

Numeric symbolic solution.— The numeric symbolic solution approach to solve Eq. 3 involves applying finite differences in the spatial direction, as the primary step. Then Eq. 3 is converted to discrete-form (system of algebraic equations) for N number of interior node points as

$$\frac{C_{i-1} - 2C_i + C_{i+1}}{h^2} = SC_i;\quad h = \frac{1}{N+1} \quad [9]$$

where $i = 1 \ldots N$. The boundary conditions governing the exterior node points are also converted to discrete-form as

$$C_0 = 0 \quad [10]$$

$$C_{N+1} = -\frac{1}{3}C_{N-2} + \frac{4}{3}C_{N-1} + \frac{2h}{3} \quad [11]$$

The above system of algebraic equations can be rewritten and solved in matrix form as[7]

$$\mathbf{AY} = \mathbf{B} \Rightarrow \mathbf{Y} = \mathbf{A}^{-1}\mathbf{B} \quad [12]$$

where $\mathbf{Y}$ is the dependent variables vector, $\mathbf{Y} = [C_1\ C_2\ C_3 \cdots C_N]^T$ (for all the variables in all the interior node points), $\mathbf{A}$ is the coefficient matrix and $\mathbf{B}$ is the forcing function vector, $\mathbf{B} = [0\ 0\ 0 \cdots -2/3h]^T$. If $N = 2$ interior node points are used the coefficient matrix $\mathbf{A}$ is given as

$$\mathbf{A} = \begin{bmatrix} -\frac{2}{h^2} - S & \frac{1}{h^2} \\ \frac{1}{3h^2} & -\frac{2}{3h^2} - S \end{bmatrix} \quad [13]$$

The simulation of the system is completed by inverting $\mathbf{A}$ matrix symbolically as a function of the system parameters (S or s, D and L). A flow chart describing the NSS is presented in Fig. 1. When $N = 2$ interior node points are used, the resulting expression for impedance response is

$$Z_{NSS} = \frac{1 + \frac{4}{27}\left(\frac{sL^2}{D}\right) + \frac{1}{243}\left(\frac{sL^2}{D}\right)^2}{1 + \frac{4}{9}\left(\frac{sL^2}{D}\right) + \frac{1}{54}\left(\frac{sL^2}{D}\right)^2} = \frac{1 + \frac{4}{27}S + \frac{1}{243}S^2}{1 + \frac{4}{9}S + \frac{1}{54}S^2} \quad [14]$$

The real and imaginary parts are obtained as

$$Z_{re} = \frac{2[13122 + 567\Omega^2 + \Omega^4]}{9[2916 + 468\Omega^2 + \Omega^4]} \quad [15]$$

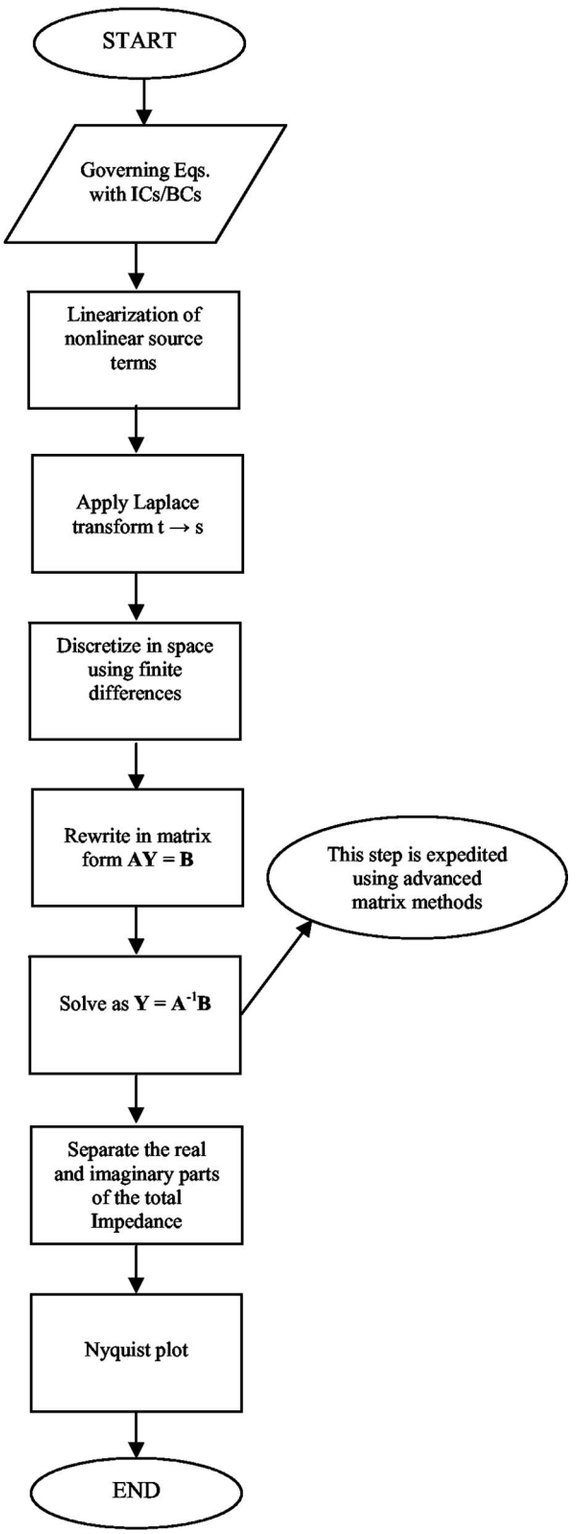

Figure 1. Computational procedure for numeric symbolic solution (NSS).

$$Z_{im} = \frac{8\Omega[324 + \Omega^2]}{3[2916 + 468\Omega^2 + \Omega^4]} \quad [16]$$

It can be noted from Eq. 14 that the NSS technique yields a closed-form solution as a function of all the system parameters (S or

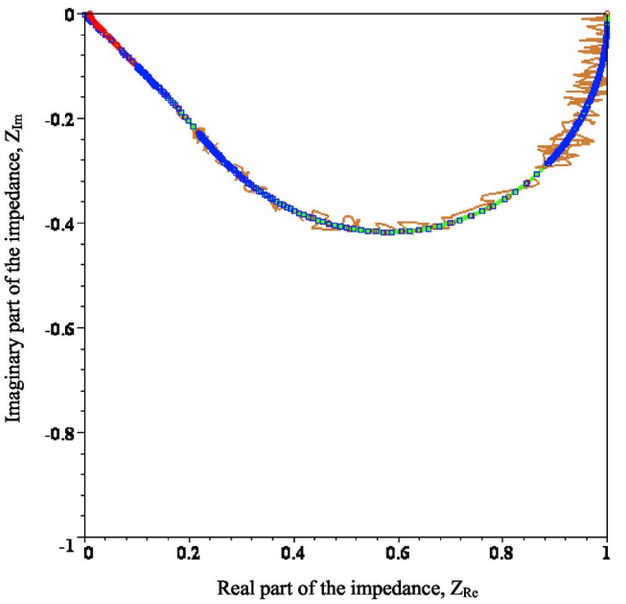

Figure 2. (Color online) Impedance response of diffusion in a planar electrode (Nyquist plot). Solid line denotes analytical method, dotted line (boxed) denotes numerical method, dotted line (circled) denotes numeric symbolic solution, and solid line (thin line) denotes synthetic experimental data. Numerical and NSS data points coincide.

ω or s, L, and D). For illustration, we showed the results obtained with two node points. For better accuracy we need to increase the number of node points. Note that the coefficient matrix in Eq. 12 can be a function of the Laplace variable S or the frequency, Ω. Maple can be used to invert **A** matrix. However, by following the pattern of eigenvalues an efficient code can be written for the inverse symbolically.[5,8] A user-friendly program has been written to obtain the matrix inverse, which does not take more than a minute to find the inverse even for $N = 100$ or 1000 node points. All the simulations in this paper are performed in a PC with 1.7 GHz processor and 1 GB RAM (running Windows XP).

Comparison of Various Approaches

The impedance responses obtained using the above three approaches are plotted in Fig. 2 and the corresponding simulation time required to obtain the curves are shown in Table I. The analytical solution (solid-line in Fig. 2) is a function of the system parameters (S or s, L, D, or ω) and hence the full curve is obtained by separating the real and imaginary parts in Eq. 6. The computation time to obtain the curve is just one second. The numerical approach (dotted line in Fig. 2) takes more than 45 s to generate the plot. This is inevitable, because there is a need to solve Eq. 7 repeatedly for every value of Ω to get one point in the curve (totally 300 points are evaluated to obtain a smooth curve). The NSS is a closed-form solution of the system parameters S or Ω and takes only 2 s to generate the entire curve; both the numerical and NSS solutions overlap with the analytical solution in Fig. 2.

Table I. Comparison of different approaches for the simulation of ac impedance response.

Method	Computation time (s)
Analytical method	1
Numerical method	45
Numeric symbolic solution	2

Table II. Comparison of estimated parameter values and computation time for different approaches.

Method	Estimated value of diffusivity (m^2/s)	Computation time
Analytical method	$1.002803726 \times 10^{-7}$	6 s
Numerical method	$1.005148577 \times 10^{-7}$	41 min
Numeric symbolic solution	$1.002811529 \times 10^{-7}$	35 s

NSS is useful for parameter estimation. There are two parameters involved in the model equations, the thickness of the electrode L, and the Fickian diffusion coefficient D. Fixing the thickness of the electrode as 10^{-6} m, the unknown parameter D is estimated using Gauss-Newton method from the synthetic experimental data. The experimental values are generated by distributing 5% randomness error to the analytical values for $D = 10^{-7}$ m^2/s by considering 300 data points. The expression used to generate experimental values using random error is

$$Z_{\text{experimental}} = Z_{\text{analytical}}[0.95 + 0.01(\text{Random number between 0 and 10})] \quad [17]$$

Figure 2 compares the synthetic experimental values with theoretical values. The synthetic experimental values are then provided for parameter estimation algorithm along with an initial guess based on the value used for simulating the ac impedance response. The following steps are involved in the parameter estimation of impedance data[9]: (*i*) start with a good initial guess for parameters, $\mathbf{k}^{(0)}$ (*ii*) compute the real part, imaginary part and Jacobian of both real and imaginary parts at each data point and set up the vector with experimental values $\mathbf{Y}_{\text{exp}}$, predicted values $\mathbf{Y}_{\text{pre}}$, and the Jacobian matrix **J**, (*iii*) the correction factor is obtained by using the expression, $\Delta\mathbf{k} = (\mathbf{J}^T\mathbf{J})^{-1}\mathbf{J}^T(\mathbf{Y}_{\text{exp}} - \mathbf{Y}_{\text{pre}})$ for both real and imaginary parts of the impedance, (*iv*) using this, an improved parameter value can be obtained as $\mathbf{k}^{(i+1)} = \mathbf{k}^{(i)} + \Delta\mathbf{k}^{(i)}$, the predicted parameter for the next iteration is the arithmetic average of $\mathbf{k}^{(i+1)}$ values of real and imaginary parts. Steps (*ii*) to (*iv*) are repeated until a required accuracy is reached. The Jacobian matrix **J** is defined as

$$\mathbf{J} = \begin{bmatrix} \frac{\partial Y_1}{\partial k_1} & \cdots & \frac{\partial Y_1}{\partial k_m} \\ \cdots & \cdots & \cdots \\ \frac{\partial Y_n}{\partial k_1} & \cdots & \frac{\partial Y_n}{\partial k_m} \end{bmatrix} \quad [18]$$

where m is the number of parameters and n is the number of experimental data points.

The estimated parameter values based on the three approaches (analytical, numerical and numeric symbolic solution) are shown in Table II. The computation time associated with each approaches are also compared. It is clear from the simulation results that the numerical method requires more time to estimate a single system parameter. This is because the numerical approach needs additional time to solve additional differential equations (Jacobians **J**) associated with both real and imaginary parts of the impedance. The inefficiency of numerical codes for predicting parameters can be overcome by the NSS. Using the closed form of symbolic solution, the jacobians involved in the parameter estimation can be exactly calculated. The comparison of computation time shows that the NSS performs as efficiently as the analytical solution for parameter estimation. All three approaches are simulated in Maple. Maple programs to obtain the impedance response and to estimate the parameters using all the three approaches are available upon request from the corresponding author for academic and noncommercial purposes. The NSS program that takes less than 1 min to run based on advanced matrix inversion method is to be applied for software

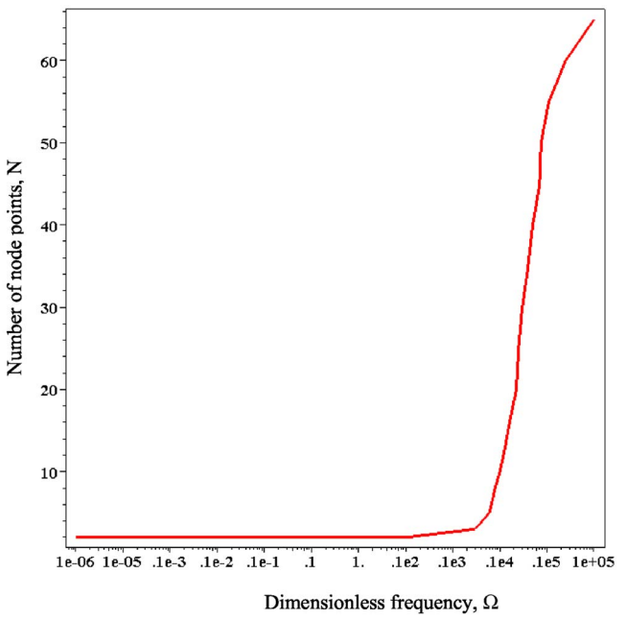

Figure 3. (Color online) Number of node points required for NSS for various values of Ω.

disclosure/patents. However, Maple's inbuilt matrix inversion command can be used to obtain the NSS (this program is available upon request).

Discussion

Numerical simulation of ac impedance models is not ideal for parameter estimation. This is true because for one PDE we need 100 node points in the *x*-axis for a numerical simulation (for a particular value of frequency). To simulate the complete impedance spectra, for 300 different values of frequency (in the entire domain), we solved two sets (one for real and another for imaginary part of total impedance) of 100 such equations numerically 300 times. When the numerical approach is used to predict one parameter (diffusion coefficient, *D*) from experimental data, there is a need to solve two more sets of 100 equations for the sensitivity variable in all the 100 node points. For a model with a single PDE and a single parameter we would need to solve $2 \times 100 + 2 \times 100 = 4 \times 200$ equations numerically 300 times. For estimating parameters numerically using a good initial guess, we are required to iterate 10 times. Hence, for a single PDE model with one parameter we have to solve $4 \times 200 = 800$ equations $300 \times 10 = 3000$ times.

As is evident from the previous sections, the only major step in NSS is inverting the coefficient matrix **A**. But, using advanced matrix methods, the matrix can be inverted symbolically as a function of *S*.[5,8] The matrix methods involve following the pattern of eigenvalues and eigenvectors of the matrix for $N = 2, 3, 4$ node points, etc. A recursive relationship is obtained to find the matrix inverse symbolically. Once the recursive relationship is obtained the matrix inverse step does not take more than 1 min to find the inverse of the matrix even for $N = 100$ or 1000 node points. Figure 3 shows the number of node points needed for NSS at different values of dimensionless frequency Ω, for the simulation of entire impedance response curve. This shows that at very low to fairly high values of frequency the number of node points needed is very small. Then, the number of node points steeply increases with Ω when $\Omega > 1000$.

The NSS can be separated into real and imaginary parts to simulate the ac impedance response without additional computation constraints. Even if more node points are used to obtain a closed form of symbolic solution, the NSS works well and simply separates the real and imaginary parts successfully. It is also interesting to realize that the computation time needed to obtain the ac impedance response using NSS is almost the same as that required by the analytical solution, whereas the computational time taken for the simulation of impedance response using numerical solution is 45 times greater than that of the analytical solution. The NSS is expected to be superior to analytical solutions for estimating transport and kinetic parameters if rigorous electrochemical models are considered. This means that, while rigorous analytical solutions must be resolved/re-derived for the rigorous models for batteries or other electrochemical devices, the NSS can provide a solution independent of the boundary conditions and geometry. The NSS can also provide solutions as a function of geometry factor if Eq. 3 has an additional term $p[dC/dX]$ with *p* being 0, 1, and 2 for rectangular, cylindrical and spherical coordinates or *D* or other parameters as a function of *X*.

The advantages of NSS have been validated by comparing the time taken to obtain an impedance response curve and one parameter using the NSS, numerical, and exact analytical solutions. The NSS exploits the properties of both analytical as well as numerical approaches. The computation time of NSS is several times superior to the numerical simulation.

Future work.— The proposed NSS method has been proven to be as good as the analytical solution and superior to the numerical simulation. Thus the method can be extended for the simulation of a rigorous physics based ac impedance model[4] for electrochemical devices such as batteries, fuel cells, capacitors, sensors, etc.[10] To better understand porous electrodes, it is important to consider the simultaneous phenomenon of coupled gradients of concentration and potential. Real experimental data can be obtained and used for the estimation of system parameters such as diffusion coefficient, electrolyte conductivity, or exchange current for the reaction. Future communication will address the development of this scheme for porous electrodes to estimate parameters for Li-ion batteries, PEM fuel cells, sensors, and other electrochemical devices. In addition, other discretization methods (collocation, etc.) are also pursued and will be discussed in future communications. The closed form solution obtained can also be thought as transfer functions, thus giving hope for real-time physics based control of electrochemical devices and real time simulation of stacks and hybrids. The use of NSS for process control, stack and hybrid system modeling and control, and for life cycle modeling will also be discussed in future communications.

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