

# **Reaction Mechanism Analysis Simulation Software - User Manual**

# Introduction

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This software simulates the impedance plot for a few reaction kinetics. The impedance spectra of an electrochemical system can yield a lot of information about the system. If you are not familiar with the terms "impedance", "electrochemical impedance spectroscopy" (EIS), please learn them before proceeding.

## Simulation using Electrical Equivalent Circuits

If there is an electrochemical reaction occurring on the electrode-electrolyte interface, then the impedance spectra, particularly in the low frequency regime, will depend on the reactions. Electrical equivalent circuits (EEC) are often used to model the data. While there are a lot of options to simulate the impedance for a given electrical circuit (commercial and free), there does not seem to be any publicly available software (free or commercial) to simulate the spectra for different kinetics. Therefore I tried to create a software for that and hope that it can act as a starting point. This software does NOT simulate using electrical equivalent circuits.

## Using Reaction Kinetics

In these reaction kinetics, "Langmuir isotherm" and "Tafel-like potential dependence" are assumed. You can refer to google or journal articles dealing with them to know the details better. If you already have an idea, you can proceed and will be able to benefit by using this software. With this software, you can simulate the impedance spectra for a given mechanism. I have included only a few mechanisms in this. But since the source code is available, and the building software is free (Visual Basic Express Edition 2005), you should be able to add any mechanism you want, as long as you use Windows(R) operating systems. I have not tested these but I hope that it will work with later versions of Visual Studio also.

## Customization

With this software, if you want to simulate spectrum for a mechanism that is already in the list, then it is trivial. If you want to add a few more mechanisms, you need to make an effort.

Usually, the difficulty is in writing the equations for a given mechanism. If the equations are written, any decent programming environment like Matlab (R) or Mathcad (R) or Mathematica (R) can be used to simulate the spectrum. Yet, it is not that user friendly. Giving the inputs is not as easy as it is here. And you will need that software (Matlab etc) to simulate. This software makes it very easy for even a beginner to 'get a feel' for the various types of spectra that may arise from various mechanisms.

## Getting Started

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There are three windows in this program.

1. main window
2. Bode plot window and
3. Complex plane plot window.

When you start the program, only the main window will be visible. You have to select a mechanism and then fill in the various [input values](#). If you click the 'Run' button, the program will run and give the impedance [data](#) in the box in the right side of the main window. The other two [graph](#) windows will also open and show the impedance in the corresponding formats.

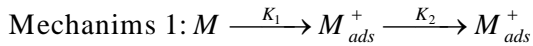
# Reaction Mechanisms

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The derivation of impedance for various reaction mechanisms are available in the literature. An example is given here.

Consider the reaction

Metal (M) --> Metal-ion-in-solution + electron.



with a reaction rate constant given by  $k_1 = k_{10}e^{bV}$  In this the exponent b is given by  $b = \pm \frac{\alpha F}{RT}$

The rate constant increases exponentially with the applied voltage.

The current is given by

$$i = Fk_1(1-\theta) \quad \text{where } F \text{ is the Faraday's constant}$$

When the electrode is held at a DC potential of  $V_{DC}$  and an ac potential  $V_{AC}$  is applied on top of it, the effective potential is given by

$$V = V_{DC} + V_{AC0} \sin(\omega t)$$

Hence the rate constant will also vary with time, as given by

$$k = k_0 e^{(b\{V_{DC} + V_{AC0} \sin(\omega t)\})}$$

The mass balance of the adsorbed species is written as

$$\tau \frac{d\theta}{dt} = k_1(1-\theta) - k_2\theta$$

Here  $\tau$  is the number of moles for a monolayer coverage and  $\theta$  is the surface coverage of the adsorbed species.

$$\theta_{ss} = \frac{k_1}{k_1 + k_2}$$

The steady state surface coverage is given by

When we neglect nonlinear terms, it can be shown that the derivative of surface coverage is

$$\frac{d\theta}{dV} = \frac{(b_1 - b_2)k_2\theta_{ss}}{k_1 + k_2 + j\omega\tau} \quad \text{where } j \text{ is the square root of } -1 \text{ and } \omega = 2\pi f \text{ is the angular frequency.}$$

The admittance (inverse of impedance) is given by taking the derivative of the current with respect to potential and using only linear terms.

$$\frac{di}{dV} = Fb_1k_1(1-\theta_{ss}) - Fk_1 \frac{d\theta}{dV} \quad \text{This gives the Faradaic impedance, which is in parallel with the double layer capacitance. The overall impedance can be calculated from this.}$$

You can play with different values for each parameter. For mechanism 1, try the cases with  $b_1 = b_2$ ,  $b_1 < b_2$  and  $b_1 > b_2$ . What do you see? Why?

# Inputs

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There are three windows in this software. When you start the program, the main window will be visible and will be almost blank (empty). When you choose a mechanism, the appropriate inputs will be visible. Default values are supplied there, but you should use your guesses to get a better feel for the software as well as to get a feel for the type of impedance curve that would arise for different values of the rate parameters.

The following are the inputs:

1. Potential, in volts. This is the potential above open circuit potential (OCP), for anodic dissolution reactions. If you are using this for deposition kinetics, then it is the potential below the OCP.
2. Minimum Frequency, in Hz
3. Maximum Frequency, in Hz.
4. Number of Frequencies where impedance is acquired
5. RSol - Solution resistance, in ohms
6. Cdl - Double layer capacitance, in micro Farads

Kinetic parameters

k10, k20 etc are pre exponents in the equation  $k1 = k10 * e^{b1 * \text{volt}}$ , in moles/s

km10 etc denote k-minus-one-zero and so on

b1, b2 etc denote the exponents in the above equation

Tau is the number of sites available in the electrode, in moles.

If you find a set of parameters that give interesting spectra, you can save them by choosing 'File--> Save'. Later, you can retrieve them using 'File--> Open'. The parameters as well as the mechanism chosen (along with unused parameters) are also saved as text file. The impedance values are not saved, but they can easily be generated by clicking the run button.

You can save the impedance data using 'copy' button and then pasting it to some other software such as Notepad or Excel.

You can also load 'experimental data'. The data **must** be a "\*.csv" file. It must have only 3 columns, Frequency, ZRe and ZIm. The names of the columns are not that important; e.g. you can write them as "x,y,z", but the first column is assumed to be frequency, second is assumed to be Zreal and third is assumed to be ZImaginary.

When experimental data is loaded **and** simulation is done for some mechanism / parameters, both experimental and simulated values are plotted.

## Results

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### Data

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The results are shown as data as well as graphs.

The data shows

1. Potential
2. Frequencies
3. Z Real part
4. - Z Imaginary part. Since the negative of Z-imaginary is usually plotted for EIS, I have given it here.
5. Z Imaginary part
6. Z-abs , i.e.  $\text{mod}(Z)$ , for Bode Plot
7. Phi, i.e. angle, for Bode plot

Even though only one potential is used, it is repeated so that the data can be easily copied and pasted to commercial software like Microsoft Excel (R) for plotting.

### Graphs

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The complex plane plots (also called as Nyquist plots) and Bode plots are shown for immediate viewing. The graphs were plotted using Zedgraph code, available under LGPL license terms.

You can zoom in by clicking the left mouse button, holding and dragging. You can right click to get various options such as 'copy', 'save image', 'un-zoom' (i.e. zoom out) and 'show point values' to see the values.

The complex plane plot shows the "negative of Z-Imaginary" vs "Z-real", since it is the usual method for EIS plots.

The first Bode plot shows log of absolute value of impedance vs log of frequency.

The second Bode plot shows the angle vs log of frequency. The natural log is used in the Bode plots .

Although both plots are shown in one window, they are two different plots. Hence if you want to copy them, you should click on each one of them and copy and paste separately.

## Contact

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This software is written in Visual Basic .NET 2005. As a matter of principle, I always give the source code. Even when it is ugly. Because the source code is available to you, it is possible to modify this program to suit your needs. Specifically, it is possible to add more mechanisms and simulate spectra for those mechanisms. Similarly, it is easier for you to find any bugs (and hopefully inform me so that I can fix them).

You can contact me at [srinivar@iitm.ac.in](mailto:srinivar@iitm.ac.in) for questions and comments.

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## Miscellaneous

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### **Work to be done**

This is not even a beta version, it is only an alpha version. Simulating the spectra for multiple potentials will be a useful option.

If the software can load experimental data and determine the 'best fit' for a given mechanism, it would be great. I am afraid that it will need something better than VB. The data fit will be done by complex nonlinear least square algorithm and the time it takes for convergence is very strongly dependent on initial values. Something in Fortran or C or C++ would be better. That is for another day.



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