Simulation of Impedance Spectra

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A Computational and Electrochemical Exercise for University Students

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During the last 20 years, electrochemical impedance spectroscopy (EIS) has become one of the most widespread tools for studying the electrochemical processes that take place on the electrode surface. In particular, the possibility of applying a wide range of frequencies to electrodes allows one to obtain separate information on processes that occur at different relaxation times (*1, 2*). The technique is very useful in studying physicochemical processes in electroactive films (*3–10*), electrode surfaces (*11, 12*), electrodeposition (*13*), composite materials (*14, 15*), mass transport through the concrete (*16, 17*), corrosion (*18–20*), and performance of organic coatings (*21*). However, students often have difficulty understanding the fundamentals of the impedance spectroscopy technique as well as the way the impedance spectrum is obtained and the usual methods of analyzing the results.

The best way to introduce all these subjects is via a laboratory exercise. Another, complementary, way is by simulation of the impedance spectra. One possibility would be to calculate the global impedance of an equivalent circuit as a function of the frequency, thus obtaining the global value of impedance for several frequencies. An interesting paper describing an exercise like this can be found in ref *22*. Here we present a different procedure. Obtaining an impedance spectrum requires a computer, which analyzes the experimental dependence of current and potential on time and obtains the modulus and phase of the impedance. We created simulation software (MULON98) that gives the time dependence of the current and potential, and from these data students can evaluate the impedance. Carrying out this exercise after the explanation of the EIS technique and the simpler equivalent circuits improves the students' understanding of the fundamentals of EIS.

The requirements for carrying out this exercise are very simple. The simulation program works under MS-DOS, even on an 80386 PC. A graphics package is also needed, and a spreadsheet is optional. Two sessions of three hours each are enough for the students to do this exercise. The first session includes a theoretical introduction and the simulation of the impedance spectra. The EIS data are analyzed in the second session.

Procedure for This Exercise

The simulation software MULON98 allows students to find the dependence of the current, i, and potential, E, on time, t. This process will take no longer than a few seconds on a PC (MS-DOS). The teacher should have a diskette containing the different equivalent circuits (the software includes some well-known equivalent circuits), which are unknown to the students, and the student should select the amplitude of the potential sinusoidal perturbation and the frequencies needed to analyze the results. The program saves the results of the i–E vs t curves in different files, one for each frequency studied, which can be read easily by most commercial graphics packages.

Once the student has the files containing the i–E vs t curves, there are two ways of evaluating the impedance, graphical and numeric.

Graphical Method. From a plot of E and i vs time it is possible to quickly obtain a value for the impedance modulus as the ratio between the amplitude of sinusoidal waves of potential and current. The phase angle is evaluated from the difference between the maxima of the two curves—or even better, from the difference between the curves' intercepts with the time axis. This graphical method is very intuitive and instructive, but the error that could accompany the evaluated impedance is sometimes important.

Numeric Method. This method requires a computer and a spreadsheet. We worked with Lotus 123 version 2, although any more advanced spreadsheet is also valid. The dependence of current on time can be expanded and expressed like this:

$$i(\omega t) = B\sin(\omega t + \phi) = B\cos(\phi)\sin(\omega t) + B\sin(\phi)\cos(\omega t) \qquad (4)$$

where B is the current amplitude, ϕ is the phase difference between current and potential, and ω is the angular frequency ($\omega = 2\pi f$, where f is the frequency). This equation allows one to obtain the values of B and ϕ by a multiparametric linear fitting procedure, where the measured current is the dependent variable and $\sin(\omega t)$ and $\cos(\omega t)$ are the two independent variables. This fit can be easily made with the spreadsheet or with our C programmed routine AZON98, which gives the B and ϕ values. It is the teacher's decision whether to supply this software to the students. This way, the two coefficients evaluated are $B\cos(\phi)$ and $B\sin(\phi)$, and from these data one can immediately obtain B and ϕ. The modulus of the impedance is the A/B ratio, where A is the amplitude of the potential sinusoidal perturbation.

After the students have the modulus, $|Z|$, and phase of the impedance for all the selected frequencies, they find it valuable and interesting to prepare at least the following four diagrams of impedance:

1. Bode plot of log ($|Z|$) and phase vs log(f).
2. Plot of log(Z_{re}) and log(Z_{im}) vs log(f), where Z_{re} and Z_{im} are the real and imaginary part of the impedance, respectively.

3. Nyquist plot of Z_{re} vs Z_{im}.
4. Cole–Cole or complex plane capacitance plot of C_{re} vs C_{im}.

The shape of these plots should help students to identify their equivalent circuit problem among a few possibilities. We suggest that the student could know that the equivalent circuit is one of only a few of the possibilities that the teacher can choose from. From these plots students should evaluate the parameters of this equivalent circuit.

[W]Supplemental Material

The following supplemental material for this article is available in this issue of *JCE Online*:

Theoretical introduction on the fundamentals of EIS.

Software (MULON98, AZON98, GRAFITA, Lotus 123 spreadsheet) and some examples of equivalent circuit files.

Directions for use of the software (programmed in C++).

Explained examples of the graphical determination of magnitudes.

All the software will be also provided free of charge via email when requested from the corresponding author.

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