Development of Impedance Analysis Software Implementing a Support Function to Find Good Initial Guess Using an Interactive Graphical User Interface

Kiyoshi KOBAYASHI* and Tohru S. SUZUKI

Research Center for Functional Materials, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

*Corresponding author: KOBAYASHI.kiyoshi@nims.go.jp

ABSTRACT

We developed an impedance analysis software implementing new function for finding an appropriate initial parameter set for impedance spectrum analysis using an interactive graphical user interface (GUI). This new function can be applied without limitation of the equivalent circuits on the basis of a measurement model. The initial parameter values of an equivalent circuit model, which is represented by a peculiar script, can easily be obtained by selecting a data point using a cursor on the logarithm of frequency versus imaginary part of impedance plot by GUI operation and setting a partial impedance element on the graphic control panel. The partial impedance elements include a resistor, capacitor, inductor, a resistor parallely connected to a capacitor, Warburg impedance, Gerischer impedance, and Havriliak-Negami impedance. Calculating and setting the initial values of the parameters are performed through GUI control, that is, by simply dragging a cursor and clicking buttons. On the basis of this GUI function, users can easily avoid the divergence of complex nonlinear least square process because the calculation can start from an adequate initial guess.

Keywords : Impedance Analysis, Software, Graphical User Interface, Supporting Function

1. Introduction

Electrochemical impedance spectroscopy is widely used for the analysis of various electrochemical processes in batteries, fuel cells, solar cells, corruptions, etc.1 The most popular software used for such analyses implement a three-step procedure: (1) loading and displaying the spectrum data, (2) making the equivalent circuit model and entering the initial guess values of the model parameters, and (3) executing a complex nonlinear optimization scheme and displaying the optimized results. Difficulty in the analysis is encountered at procedure (2), particularly the setting of the initial guess values. If the initial values are significantly different from the answer, it is impossible to attain the answer due to trapping of the local minimum or divergence during complex nonlinear least squares calculation.2 To avoid this phenomenon, researchers are investigating to apply new nonlinear least squares algorithms that are insensitive to the initial guess values.3–9 Even after employing a new optimization algorithm, it is impossible to avoid trapping of the local minimum and/or divergence when the initial guess is significantly different from the answer.

Another way to find a good initial guess is to deconvolute the partial impedance spectra under the assumption of a measurement model.10–12 On the basis of the measurement model, equivalent circuits are presented by serial connections of partial impedance elements, namely resistor, capacitor, inductor, constant phase element, and resistor connected to capacitor in parallel, among others.10–12 Although the measurement model is intuitively easy to imagine, it is sometimes necessary to use equivalent circuits which are impossible to present by the measurement model such as Randles circuit. Furthermore, specialized software is necessary for conveniently using measurement model11 in addition with the mathematical relations. From the view point of analysis using equivalent circuit models, easy method to find a good initial guess does not exist. Hence, it is necessary to develop a new and easy method for finding an initial guess that is close to the answer in order to eliminate the difficulty in the analysis for various type of equivalent circuit.

In this research, we successfully developed new software that implements a support function to easily find an appropriate initial guess based on a visual process. This function is based on the application of an interactive graphical user interface (interactive GUI). By using this function, users can easily find a good initial guess visually by comparing the target spectrum with the calculated one on the displayed graphs using a proportionality factor explained below.

2. Necessary Software and Platform

To implement the GUI based supporting function, we selected the Igor Pro software (Wavemetrics Inc., USA) and its macro language as a platform. The required version of the software must be higher than 6.36, but version 8 is preferable. Regarding to the operating system, not only the Windows® but also macOS© are supported if the software is installed in the computer. Required display resolution is full HD or higher for windows and WXGA+ or higher for macOS.

3. Script for the Equivalent Circuit Modeling

In this software, the equivalent circuit model is represented by a script, similar to the process for several commercial and free software.13–15 However, we did not employ Circuit Description Code (CDC)13–15 because some implicit restrictions exist because of its specification. For example, users cannot set linear constraints to make some elements in the equivalent circuit to have the same value because the CDC is constructed under the assumption that all the elements are independent. Though this rule does not require a discriminant symbol for each element, users cannot attempt to fit
using an approximated transmission line model, namely a model constructed by several elements that have the same parameter values. Moreover, the parameter table becomes illegible since elements with the same names are arrayed.

To enhance expandability, we developed a description code for the equivalent electrical circuit model. The names of the circuit elements and circuit connection symbols are listed in Table 1. How to insert the discriminant label of each circuit element is represented by the addition of integer numbers after the element name, as presented in Table 1. For example, a Randles circuit containing a traditional Warburg impedance is represented in this script by “R1".

After entering the equivalent circuit script and clicking the read equivalent circuit button displayed by “Read Equiv. Circ.”, the corresponding parameter list is generated on the parameter table, as shown in Fig. 1. At this stage, the software automatically translates the script for the equivalent circuit into a numerically calculable function on the basis of the script analysis algorithm. It is necessary to note that our circuit script cannot represent circuits with bridge type connections and transmission line model without common earth line similar to the CDC.15-17

4. Supporting Function to Find an Initial Guess

Estimation of the initial guess is performed using the selected data point on the logarithm of frequency (log f) versus imaginary part of impedance (Zimag) plot and selection of the name of the partial impedance circuit from the popup in the control panel by users. Types of partial impedance circuits and their corresponding equations are listed in Table 2. The relationships guiding each partial impedance circuit are described in another paper.11

The basic concept of a supporting function is that initial parameter values of the equivalent circuit model, which is set by
users, are approximately estimated from combinations of spectrum data, the partial impedance circuit, and proportionality factor. 

Users can select the partial impedance circuit by checking a feature of the spectrum data. For example, if the \( Z_{\text{imag}} \) versus \( \log f \) plot shows an inverted peak shape, a user recognizes that combination of R//C or R//CPE partial impedance circuit is selected to guess the initial parameters. On contrary, calculated spectrum on the basis of estimated initial guess by the sampling data and partial impedance circuit only shows an unignorable deviation from the measured data because other partial impedance components are convoluted on the sampling \( Z_{\text{imag}} \) data or the partial impedance circuit used is different from the equivalent circuit used for the analysis. Hence, tuning function is necessary to adjust the calculated spectrum to the measured spectrum. The proportionality factor (pf) is worked for the tuning function. When the proportionality factor is set as less than 1 or larger than 1, apparent \( Z_{\text{imag}} \) value can change by multiplication of \( Z_{\text{imag}} \) and pf. By this treatment, peak intensity of the calculated spectrum by partial impedance elements on the log-\( f \)-\( Z_{\text{imag}} \) plot can change with fixed peak position in the case of R//C, R//CPE, Warburg impedance, and Gerischer impedance. Using the tuning function, users can easily adjust a good initial guess by interactive-GUI operation by checking the displayed plots.

Actual estimation of initial guess can be carried out by the selection of the corresponding R, C, and CPE elements in the equivalent circuit setting by users. The cursor is used to select typical data points that users want to employ. When the magnitude of the calculated curve is different from the data, users can adjust it using the proportionality factor. By implementing these functions using the graphic user interface, users can estimate a good initial guess by a combination of analyzing the plotted graphs on display and mouse operation. The following represents two concrete examples.

For the Randles circuit spectrum shown in Fig. 2, the spectrum is approximately represented by an R//C connected in series with a traditional Warburg impedance. It is assumed that the Randles circuit is described by “C1/(R1 + W.old)”, the R//C circuit element is selected from the popup menu (Mov.S1 in the Supporting Information). Then, the initial guess assistant window is opened. In new this window, the desired parameter set can be selected from a popup menu (Fig. 1). For the Randles circuit model, the R and C that are selected are the “R1” and “C1,” respectively. Next, the \( \text{cursor mark is placed close to the peak-top position in the log-} f \text{-}\ Z_{\text{imag}} \text{plot, which corresponds to the top of the semicircle on the impedance plot (real part of the impedance (} \text{Re} \text{) versus} \text{Im} \text{plot). The calculated spectrum is drawn on three plots (log-} f \text{-}\ Z_{\text{imag}} \text{plot, which the “Read from the Graph Cursor” button is clicked. Following this procedure, the spectrum data (} f, \text{ Re} \text{, and} \text{Im} \text{) values on the } \text{cursor are read and the corresponding parameter values calculated automatically.

Similar to R//C estimation, estimation of the initial guess is carried out from the “W.old” assistant after putting the \( \text{cursor on the lowest frequency data position in the log-} f \text{-}\ Z_{\text{imag}} \text{plot. The final impedance spectrum calculated using the estimated initial guess show a little difference from the spectrum data; however, it is enough to converge the complex nonlinear least squares using the Levenberg-Marquardt algorithm.}

The second example involves the fitting of two semicircle shaped impedance spectrum, shown in Fig. 3. It is known that this spectrum can be fitted by four equivalent circuit models, as shown in Figs. 3(d) to (g). The corresponding equivalent circuit descriptions are “R1//C1+R2//C2,” “C1/(R1+C2)/R2),” “C1//R1// (R2+C2),” and “R1//(C1+(R2+C2)),” respectively. In the case of the “R1//C1+R2//C2” model, it is easy to guess the parameters using the data at the two peak positions in the log-\( f \)-\( Z_{\text{imag}} \) plot by the R1 and C1 pair, and R2 and C2 pair, respectively.
replacing the parameter pair between R1, C1 pair and R2, C2 pair has no effect on the fitted results.

Conversely, there is a restriction of the parameter order in the case of the “C1//(R1+C2)//R2)” model. However, the initial guess assistance is still useful in this model if two log$f$-$Z_{\text{imag}}$ peaks with higher and lower frequencies are assigned by R1, C1 pair and R2, C2 pair, respectively.

For the “C1//R1//(R+C2)” model, an empirical rule should be applied. The higher and lower frequency peaks on the log$f$-$Z_{\text{imag}}$ plot are assigned by R2, C1 pair and R1, C2 pair, respectively. The estimated spectrum is considerably different from the target data if only this estimation is used (Fig. 3 and Mov. S2 in the Supporting Information). Hence, the adjustment procedure is required before the fitting. The adjustment can be made by combination of the estimation procedure using the proportionality parameter presented in Fig. 1 and Table 1. The actual process is found in Mov. S2 in the Supporting Information file. First, the estimated R2 and C1 values are read from position A in Fig. 3. Then, the proportionality factor is set to a value of 1.1 to increase the magnitude of the $Z_{\text{imag}}$ peak on the log$f$-$Z_{\text{imag}}$ plot around the A position. For the C1//R1// (R2+C2) circuit, the magnitude of both peaks around the A and B positions can be modified by changing the estimated value of R2 by clicking the “Recalculate” button several times. This behavior indicates that both the log$f$-$Z_{\text{imag}}$ peaks around the A and B positions are strongly correlated to the value of R2. To reduce the magnitude of $Z_{\text{imag}}$, the proportionality factor is set to a value less than 1. Next, the log$f$-$Z_{\text{imag}}$ peak around B position is adjusted in a similar manner. Figure 3 shows a rough estimation using the R//C partial impedance circuit. This result was obtained using the R2, C1 pair with the proportionality factor at 2 for the peak A, and R1, C2 pair with the proportionality factor at 2 for the peak B, respectively. Following this adjustment, appropriate values of the initial guess can be found that can be used for the complex nonlinear least squares sets based only on the GUI operation.

Though it is common for many electrochemists to access only the impedance plot ($Z_{\text{real}}$ versus $Z_{\text{imag}}$ plot), the plot of log$f$ versus $Z_{\text{imag}}$ is found to be more convenient for estimating the initial guess, as explained above and as shown in Table 2 since the parameter values can be estimated from the value set with $f$ and $Z_{\text{imag}}$. If estimation of the initial guess from the impedance plot only is required, the user must select a frequency region, not single point. However, a part of the total spectrum is obtained through convolution of several elements in the actual spectrum, thereby reducing the validity of the guessed parameters. Even if the proportionality factor is introduced, users might find it inconvenient because the values of $Z_{\text{real}}$ and $Z_{\text{imag}}$ change simultaneously with changes in the proportionality factor. In contrast, a user can decide to adjust only the log$f$ versus $Z_{\text{imag}}$ curve using our method, because the log$f$ versus $Z_{\text{real}}$ curve automatically approaches the data due to the Kramers-Kronig transformation relationship.
It is impossible to use this support function to accurately evaluate parameter values when the equivalent circuit is not represented by a serial connection of the partial impedance elements. However, it is useful to set the initial guess values within the accuracy range for converge of the complex nonlinear least square process. Furthermore, users can check the degree of fit by graphically evaluating the \( \log(f) - Z_{\text{imag}} \) and \( \log(f) - Z_{\text{real}} \) plots in parallel. Moreover, users can experience how to graphically manipulate each parameter in the total spectrum. This experience will assist users to develop their analytical skills through reading the spectrum plots and data.

5. Conclusions

We developed new software for impedance analysis by implementing a GUI supporting function for the initial guess. The initial guess was set by reading data point values selected by users on a GUI and using equations obtained from the partial impedance circuits. Though it is difficult to accurately evaluate parameter values using this supporting function, the guessed parameter values are sufficient to apply the complex nonlinear least squares method to avoid a divergence or the trap of a local minimum. Moreover, users can learn how to influence each parameter in the total spectrum by manipulating the GUI supporting function.
Supporting Information

The Supporting Information is available on the website at DOI:
https://doi.org/10.5796/electrochemistry.19-00058.

Acknowledgment

This macro program will be opened by free of charge for usage after agreement with simple license. If you have the Igor Pro software and want to use this program, please contact to the corresponding author.

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