EIS Model Fitting and Analysis

CASE STUDY
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1 Introduction

This document contains a tutorial on using electrochemical impedance spectroscopy (EIS) to fit equivalent circuit models (ECM) for lithium-ion battery applications. EIS is a technique commonly used in electrochemistry to characterize materials and electrochemical processes. The details of the EIS measurement conditions are discussed in section 2. Section 3 describes two battery models, how to parametrize them and discusses the fitting results.

The tutorial in this document is accompanied by a set of MATLAB files which contain the experimental dataset, functions for the model equations, and scripts to perform model fitting and generate the figures. A guide to the MALTAB companion code is given in section 0.

2 EIS Measurement

The data associated with this tutorial was collected using a Bio-logic SP150 potentiostat and a Samsung INR21700-50E cylindrical lithium-ion battery. The measurement was conducted in potentiostatic mode, which means voltage sine waves are applied at different frequencies and the battery current was measured. To satisfy the linearity requirement for valid EIS measurement, the voltage amplitude was kept small at 10 mV. A frequency range of 30 kHz to 30 mHz was applied, however, the data used in this tutorial was shortened for simplicity to a range of 700 Hz to 400 mHz. The frequencies were logarithmically spaced with 10 points per decade, and 4 periods were measured and averaged at each frequency. The EIS measurement was obtained after fully charging the battery and letting it rest for three hours to ensure the stability of the system.

3 MODEL FITTING

The first model is represented by the circuit shown in Figure 1 consisting of two RC-parallel pairs in series with a resistance R_o and an inductance L. In the second model, the first RC branch is replaced by a ZARC element (Resistor in parallel with a constant phase element (CPE)) and the second RC branch by a CPE (Figure 2) [1]. The inductance models the inductive behaviour of the cables used for the measurement and R_0 models the Ohmic resistance of the battery for both models. The RC branches of the R-RC-RC model create two, ideal semi-circles for the impedance spectrum. For the second model, the ZARC element creates a depressed semi-circle and the CPE an angled line.

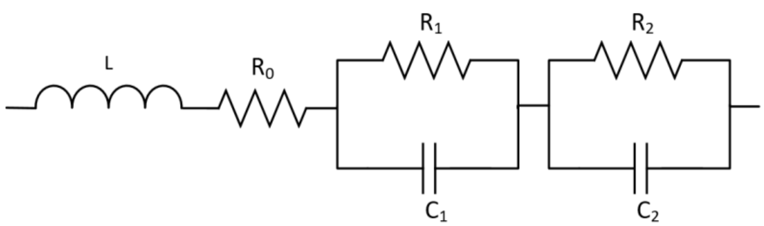

Figure 1: R-RC-RC model circuit

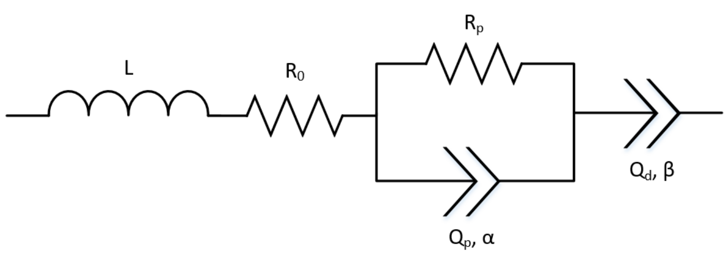

Figure 2: R-ZARC-CPE model circuit

The impedance of the R-RC-RC model is given by Equation 1 and the impedance of the R-ZARC-CPE model by Equation 3.

$$Z_{R-RC-RC} = j\omega L + R_0 + \frac{R_1}{1+j\omega\tau_1} + \frac{R_2}{1+j\omega\tau_2} \tag{1}$$

$$\tau_i = R_i C_i \tag{2}$$

$$Z_{R-ZARC-CPE} = j\omega L + R_0 + \frac{R_p}{1+\left(j\omega\tau_p\right)^a} + \frac{1}{Q_d(j\omega)^b} \tag{3}$$

$$\tau_p = \left(R_p Q_p\right)^{\frac{1}{a}} \tag{4}$$

To parameterize the models with a dataset, optimization algorithms can be used to fit the data to the models. Optimization algorithms typically require an objective function to minimize. The sum of squares S of the difference in measured and calculated real and imaginary components of the impedance may be used as an objective function for EIS data and is shown as Equation 5. Here, N is the number of measured impedance data points, Z_i' is the measured real part of the impedance, $Z_{i,calc}'$ the calculated real part, and Z_i'' and $Z_{i,calc}''$ the measured and calculated imaginary parts of the impedance, respectively. For some impedance spectra it is useful to implement a form of weighting as described by Lasia [2]. In this tutorial, unity weighting is used, therefore, the weights are $w_i' = w_i'' = 1$.

$$S = \sum_{i=1}^{N} \left\{ w_i' [Z_i' - Z_{i,calc}']^2 + w_i'' [Z_i'' - Z_{i,calc}'']^2 \right\} \tag{5}$$

The most common optimization algorithm used for EIS data is the damped non-linear least squares method or Levenberg-Marquardt (LM) algorithm. However, this method is heavily dependant on the quality of the initialization parameters. Therefore, if little is known about the parameters, the LM algorithm my only find local minima. Alternatively, a more advanced optimization method may be used. In this tutorial, the particle swarm optimization (PSO) method is also used. The PSO is not gradient based, which allows it to search past local minima, and upper and lower bounds may be set on each model parameter to narrow the search space.

The real part of the impedance is commonly plotted against the imaginary part in the complex plane for EIS analysis. This plot is known as a Nyquist plot and is shown in Figure 3 for the data used here. By convention, the imaginary part is multiplied by -1 ($-Z''$). Figure 3 also contains some additional annotations which show how R_0 and R_1 can be estimated [3]. These estimates may then be used as initial values for the optimization algorithms. Another way to visualize impedance data is with Bode magnitude and phase plots shown in Figure 4 for the measured EIS data. Bode plots provide additional insight into the EIS response as it changes with frequency, and can particularly be useful if the impedance differences are large between different frequency ranges. In this case, semi-circles may be missed when only considering the Nyquist plot. Furthermore, Bode plots provide another method for validating model fits.

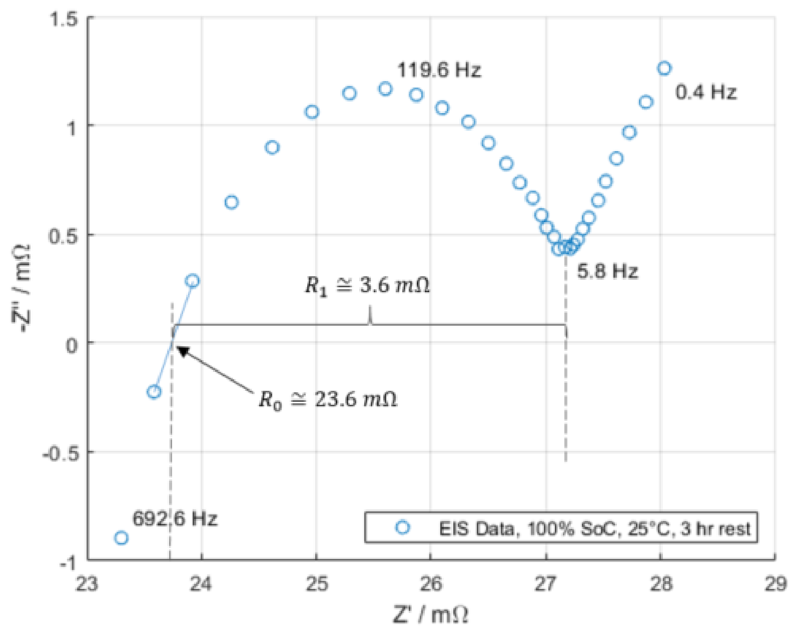

Figure 3: Nyquist plot

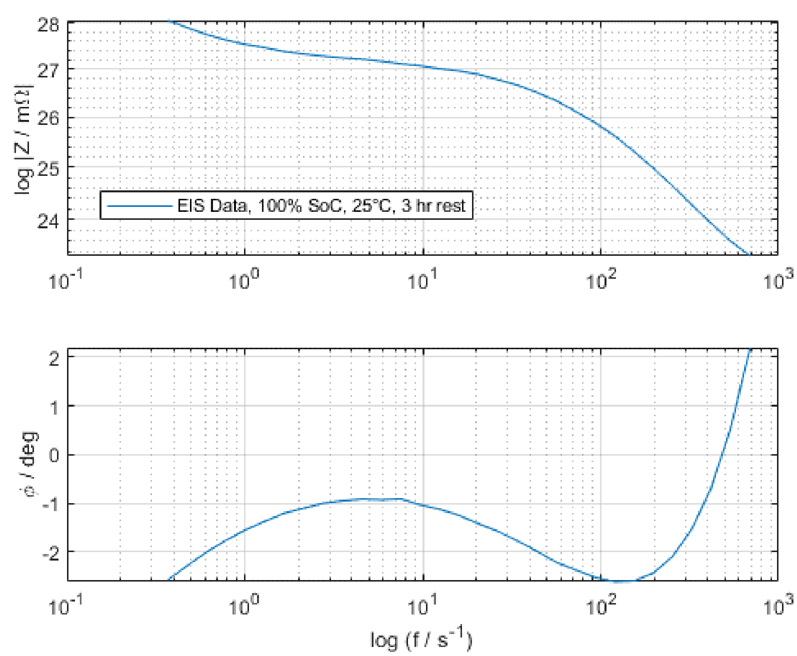

Figure 4: Bode plot

Figure 5 shows the Nyquist plots of the R-RC-RC and R-ZARC-CPE models and how they compare to the measured EIS data. The R-RC-RC model attempts to fit the data with two semi-circles, but since the data does not follow ideal behavior, the fit does not match the data very well. The R-ZARC-CPE model, on the other hand, results in a much closer fit due to its ability to model non-ideal behaviour. The fitting errors as calculated by Equation 5 are shown in Table 1. Figure 6 shows the bode plots for the two models, and it is evident that the R-ZARC-CPE indeed follows both the phase and magnitude response.

Table 1: Model fitting error

Model Name	**Fit Error *S***
R-RC-RC	4.94E-5
R-ZARC-CPE	7.78E-7

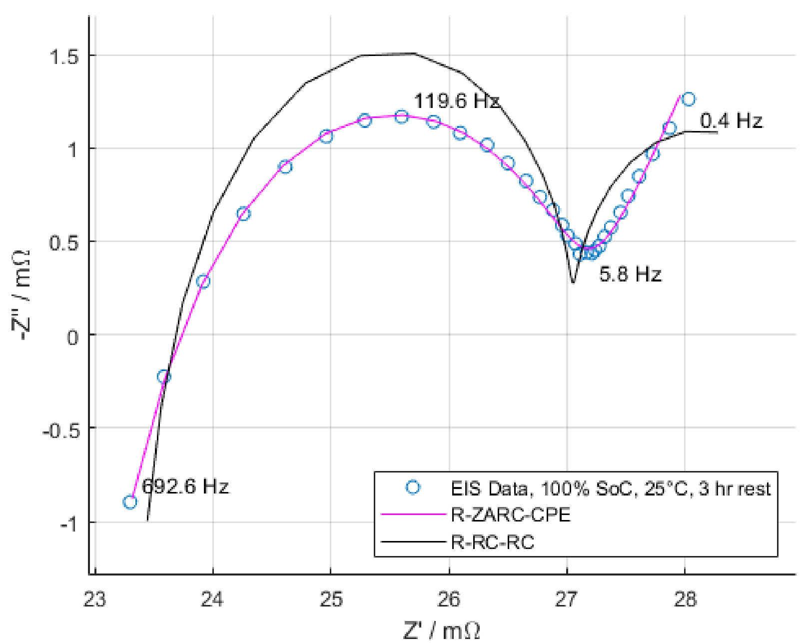

Figure 5: R-RC and R-CPE-CPE model fits Nyquist plot

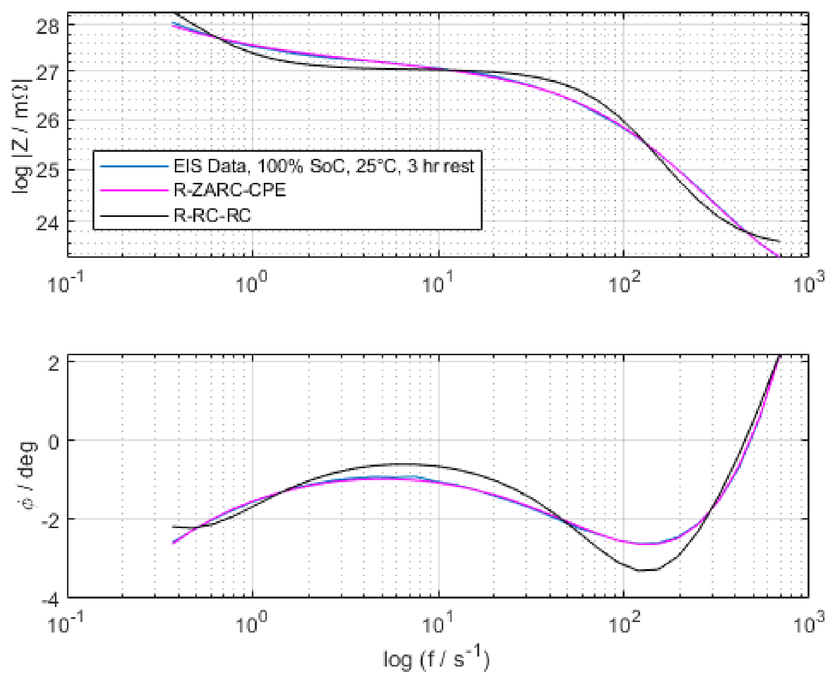

Figure 6: R-RC-RC and R-CPE-CPE model fits Bode plot

The model parameters for the R-RC-RC and R-ZARC-CPE models are shown in Table 2 and Table 3 respectively. The rows labeled *Initial* show the values used to initialize the optimization algorithms, *UB* denotes the upper bound and *LB* the lower bound. Using Equations 2 and 4, the time constants of the models can be calculated as follows.

$$\tau_1 = 0.0038 \times 0.2583 = 0.000982 \cong 1\,ms$$

$$\tau_2 = 0.0022 \times 173.41 = 0.3468 \cong 0.35\,s$$

$$\tau_p = (0.00509 \times 0.717)^{\frac{1}{0.760}} = 0.00062 \cong 0.62\,ms$$

The two time-constants τ_1 and τ_2 of the R-RC-RC model are several orders of magnitude different, which results in two clearly separated semi-circles in the Nyquist plot. The R-ZARC-CPE model only has one time constant for the parallel branch which is slightly small than τ_1.

Table 2: R-RC-RC model parameters

	L $[H]$	R_0 $[\Omega]$	R_1 $[\Omega]$	C_1 [F]	R_2 $[\Omega]$	C_2 [F]
Initial	1E-06	0.0236	0.0036	1E6	1	1E6
UB	1E-06	0.024	0.0060	1E6	1	1E6
LB	1E-08	0.022	0.0036	1E-4	1E-4	1E-4
Solution	4.23E-7	0.0232	0.0038	0.2583	0.0022	173.41

Table 3: R-ZARC-CPE model parameters

	L $[H]$	R_0 $[\Omega]$	R_p $[\Omega]$	Q_p $[F]$	a	Q_d $[F]$	b
Initial	1E-06	0.0236	0.0036	1E3	1	1E3	1
UB	1E-06	0.024	0.0060	1E3	1	1E3	1
LB	1E-08	0.022	0.0036	0	0	0	0
Solution	5.31E-7	0.0220	0.00509	0.717	0.760	393.14	0.620

3.1 MATLAB Companion Code

This tutorial may be followed in MATLAB by first opening the *EISCaseStudy_Main.m* file. This file is best used by selecting the separate code blocks and clicking on the “Run Selection” button in the EDITOR panel to execute each block individually. The files included in this companion are listed in Table 4.

Table 4: Files required for MATLAB companion code

#	File Name	Description
1	EISCaseStudy_Main.m	Main script broken up into code blocks.
2	RRCRC_MDL.m	Function to calculate R-RC-RC model impedance.
3	R-ZARC-CPE,m	Function to calculate R-ZARC-CPE model impedance.
4	Objective.m	Function implementing the objective function (Equation 5) for optimization.
5	Optimization.m	Function used to perform either non-linear least squares optimization or PSO.
6	EIS_DATA.mat	Table containing EIS measurement data.

3.1.1 Load Data Block

The load data block initializes unit conversion constants, loads the experimental data from EIS_DATA.mat, and initializes vectors with model parameters for initialization as well as vectors already containing the optimized solution.

3.1.2 Model Fitting Block

This code block sets up two types of models for parameterization. The user may select between the two models by running either the R-RC-RC model block or the R-ZARC-CPE model block. Different vectors may be assigned to the *model_parameters* variable to see how the optimization algorithms behave when first initialized.

3.1.3 Run Optimization

The next code block first creates a function handle to the *Objective.m* function which implements Equation 5. It then calls the *Optimize.m* function which runs either non-linear least squares optimization or particle swarm optimization (PSO) depending on the last argument in the function call (1-least squares, 2-PSO). Both optimization methods call the *Objective.m* function via the previously created function handle. The impedance equations for the R-RC-RC and R-ZARC-CPE models are implemented in *RRCRC_MDL.m* and *RZARCCPE.m* functions respectively, and a provided to the *Objective.m* function via the MDL argument.

3.1.4 Plot Nyquist

After running the optimization, results can be plotted. This is done starting with the next block, which plots the measured EIS data as a Nyquist plot as shown in Figure 3.

3.1.5 Plot Nyquist Fit Results

With this block, the results of the optimization can be added to the Nyquist plot (assuming the previous block was executed once, and the figure was left open). If the figure is left open, a new optimization (for example with a different model) may be run using blocks 3.1.2 and 3.1.3 and the results of the new optimization may be added to the existing Nyquist plot again with the current block.

3.1.6 Plot Bode

This block behaves similarly to the previous block but generates Bode magnitude and phase plots (Figure 4).

3.1.7 Plot Bode Fit Result

With this block, optimization results may be added to existing Bode plots (similar to block 3.1.5 for the Nyquist case).

4 Conclusion

This document and the MATLAB companion files are intended to provide a simple tutorial for fitting equivalent circuit models to EIS data. The details of the EIS measurement are briefly described followed by an introduction to the battery ECMs and their model equations. Next, methods for parameterization and analysis are explained. Results of the model fitting are also shown. Finally, the features of the MATLAB companion files are described. The references included in this document may be consulted for further details on various aspects of EIS modelling.

5 References

[1] J. Schmitt, A. Maheshwari, M. Heck, S. Lux, and M. Vetter, "Impedance change and capacity fade of lithium nickel manganese cobalt oxide-based batteries during calendar aging," *J. Power Sources*, vol. 353, pp. 183–194, 2017.

[2] A. Lasia, *Electrochemical Impedance Spectroscopy EIS, and Corrosion*. 2011.

[3] R. Cottis and S. Turgoose, *Electrochemical Impedance and Noise*. Houston: NACE International, 1999.