Case Study: EIS Model Fitting & Analysis

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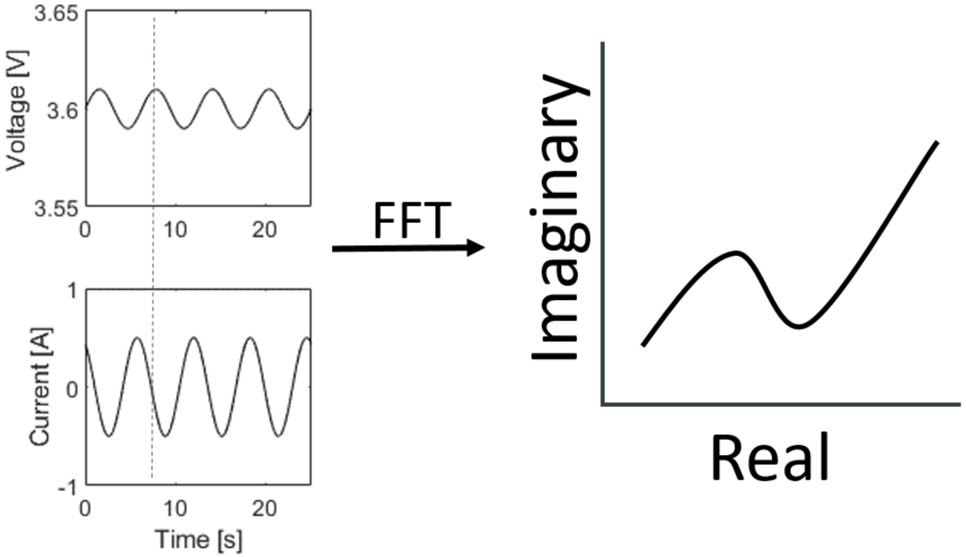
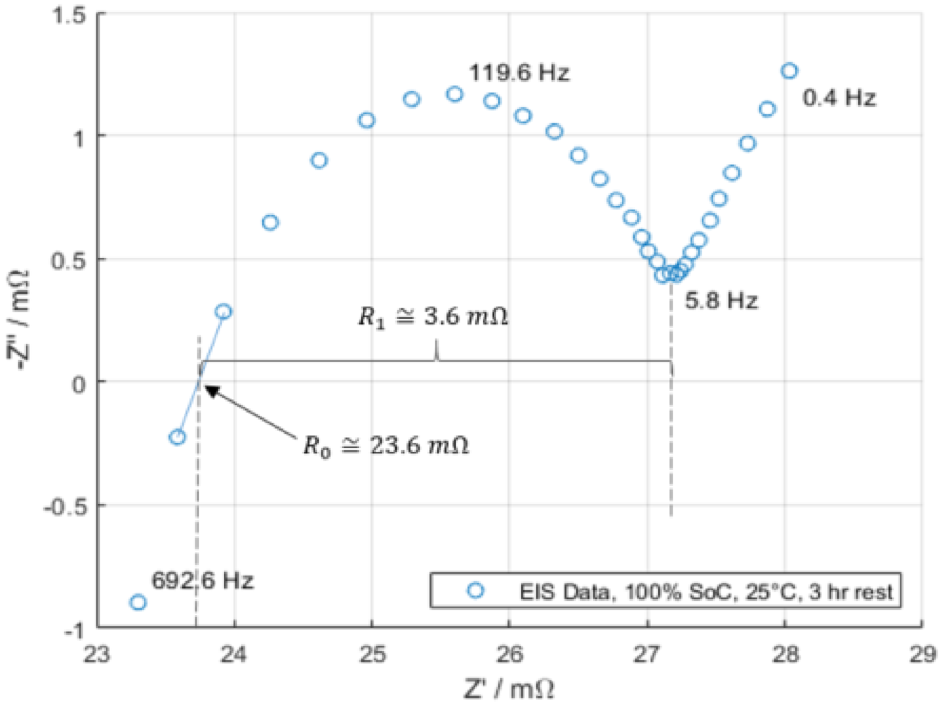
Impedance

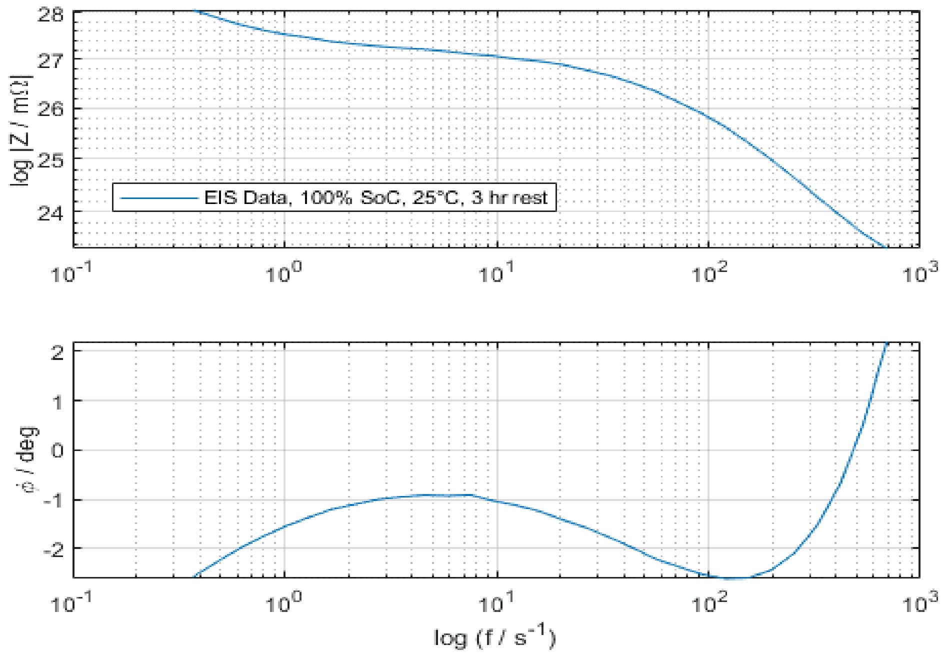
- Impedance comes from resistances and capacitances inside the battery.
  - This is caused by material properties, material interface reactions, and chemical processes.
- Impedance can be measured using electrochemical impedance spectroscopy (EIS).
  - Low amplitude voltage sine waves are applied to the battery at different frequencies and the resulting current response is measured.
  - Using fast Fourier transforms (FFT) a characteristic Nyquist plot can be obtained which can be used to parameterize battery models.



Nyquist/Bode Plots

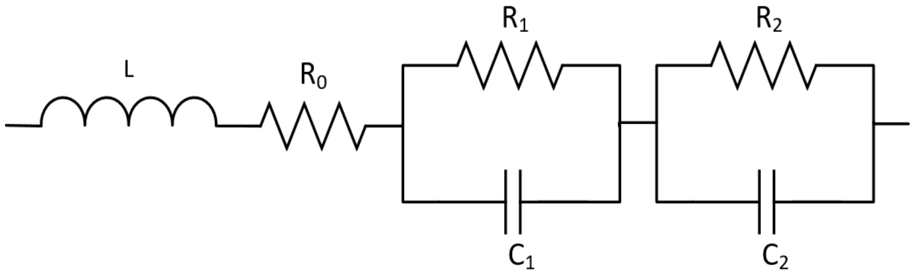
- The Nyquist plot (left) gives initial values for the model parameters R_0 and R_1 [3].
- Bode plots (right) are used to visualize the impedance with respect to frequency.
  - When impedances are very different in magnitude, information may be lost in the Nyquist plot, but not in the Bode plot [2].



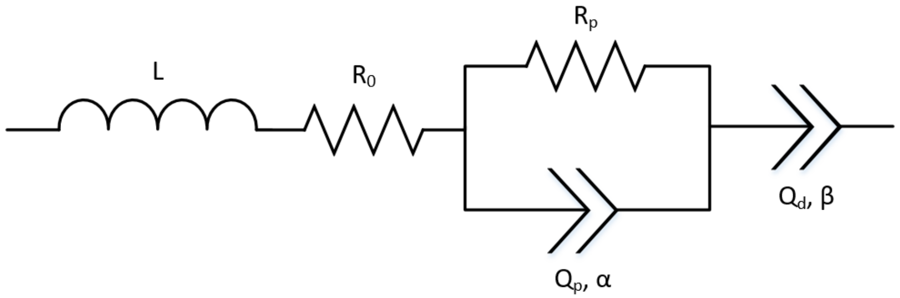


Models

- Consider two battery models:
  - A simple 2nd order RC model (R-RC-RC).
  - A more advanced model (R-ZARC-CPE) with a constant phase element (CPE) and a ZARC element (R-CPE in parallel) [1].
- Both models account for ohmic resistances, charge transfer resistance/capacitance, and diffusion effects [2].
- Both models also have an inductor (L) to model the inductive behaviour of measurement cables.



R-RC-RC



R-ZARC-CPE

Fitting

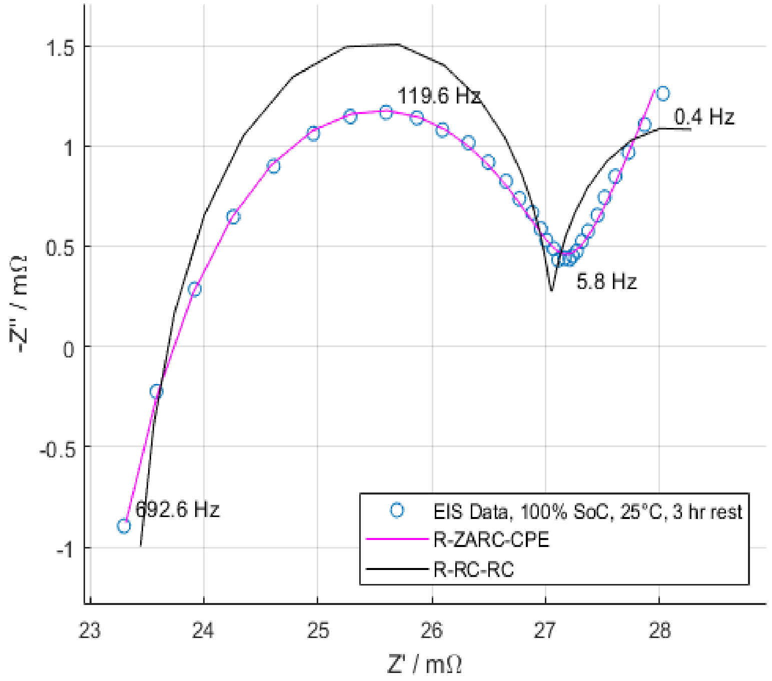
- The models are parameterized by optimizing the objective function below.
  - Z_i' is the measured real part of the impedance, $Z_{i,calc}'$ the calculated real part, and Z_i'' and $Z_{i,calc}''$ the measured and calculated imaginary parts of the impedance, respectively.
  - For some impedance spectra it is useful to implement a form of weighting [2]. In this tutorial, unity weighting is used, therefore, the weights are $w_i' = w_i'' = 1$.
- The damped non-linear least squares method or Levenberg-Marquardt (LM) is commonly used as an optimization algorithm.
- LM requires initial values close to the solution, which makes it impractical if little is known about the solution.
- Alternatively, particle swarm optimization (PSO) can be used.

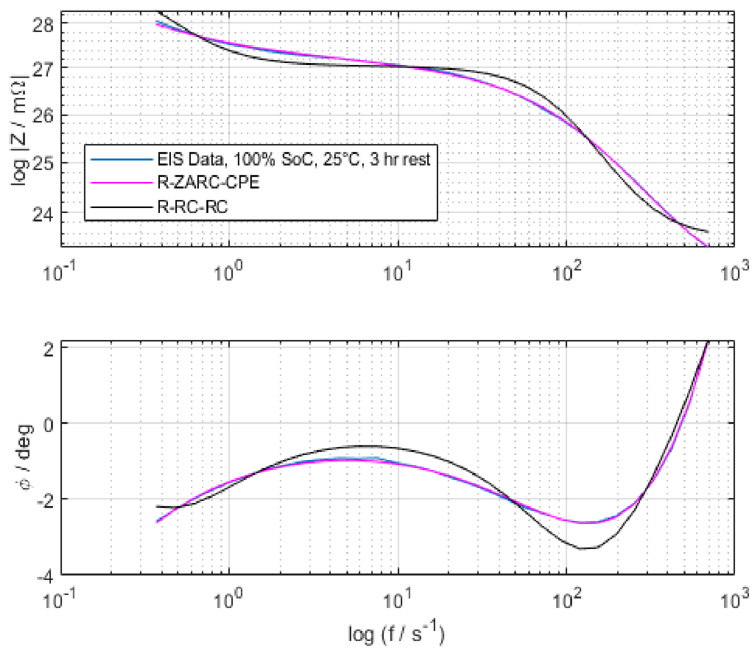
$$S = \sum_{i=1}^{N} \{ w_i' [Z_i' - Z_{i,calc}']^2 + w_i'' [Z_i'' - Z_{i,calc}'']^2 \}$$

Equation 1

Results

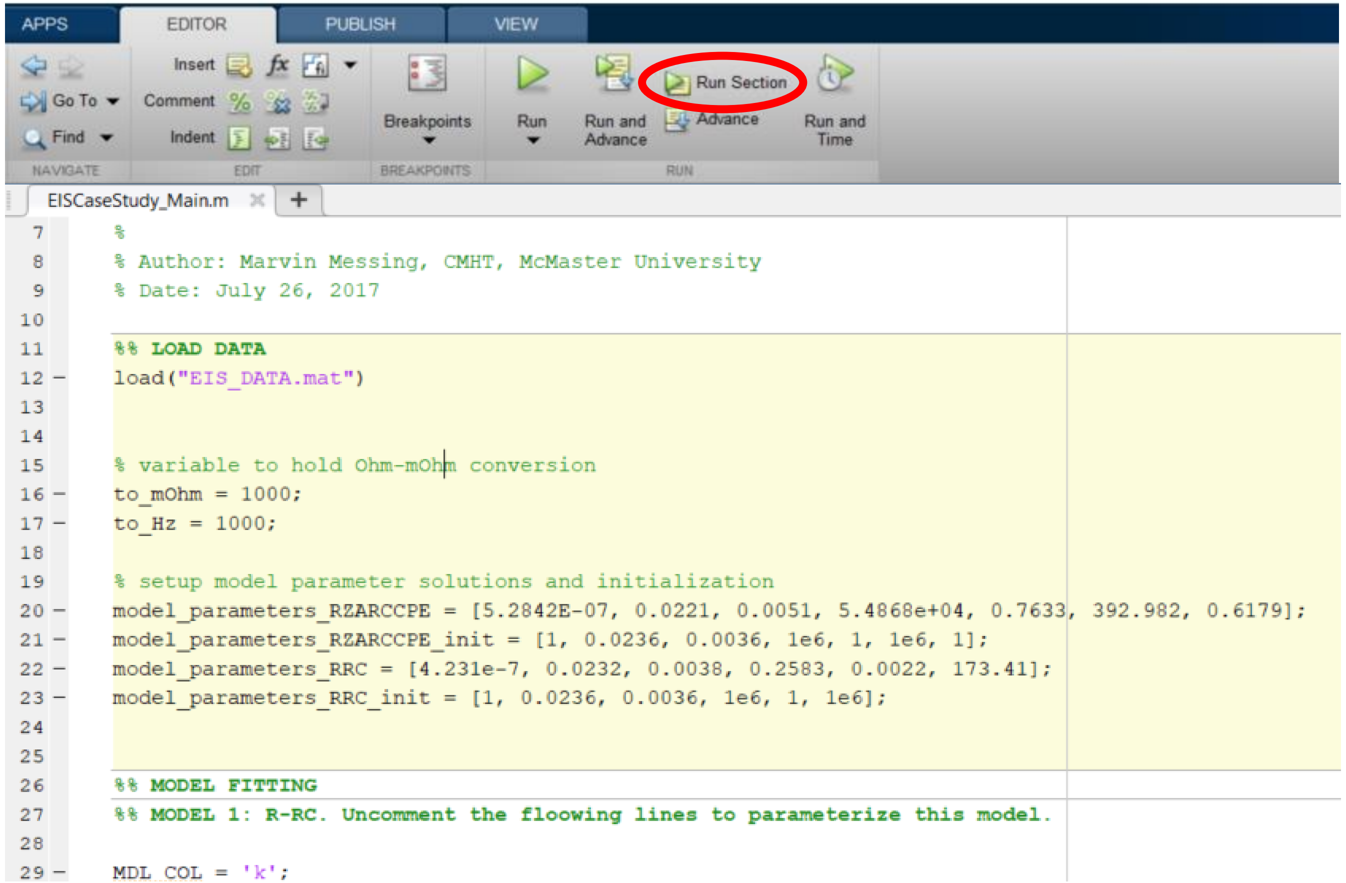
- The R-RC-RC model produces ideal semi-circles.
- The R-ZARC-CPE model accounts for non-ideal behaviour of the battery.
- The R-ZARC-CPE model results in a much better fit.





Matlab Companion Code

- To run the different parts of the companion code in Matlab, use the “Run Selection” button.



References

- Matlab companion code required files:

#	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 1) 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.

- References for further reading on EIS fitting:

[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.