Can The Fundamental Physical Constants Be Obtained via Fitting Temperature Dependent Nonlinear EIS Data?

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Electrochemical Impedance Spectroscopy (EIS) is a widely used technique in battery technology because it provides crucial insights about what's happening in the battery without damaging it. It can provide information about capacitance, electron transfer rate, Solid Electrolyte Interface (SEI) and other specific details independently from each other. Generally, this technique is done by applying small amplitudes of Alternating Current (AC) within a frequency range of 10 mHz to 1 MHz.

One of the topmost challenges of Electrochemical Impedance Spectroscopy (EIS) is the lack of clarity in data analysis. One of the most used analysis methods is the Equivalent Circuit model fitting which provides information that is model dependent and not unique. Further, analyzing the impact of fundamental parameters such as cathode thickness, particle size etc is almost impossible. Therefore, it is essential to offer a reliable approach to data analysis for EIS.

In 2018, Murbach and Schwartz [1] as a possible solution to the issue of data analysis in EIS, presented a physics-based simulation using a pseudo two-dimensional battery model. They prepared a database containing 38,800 EIS spectra where they used to compare experimental data and match it through a least squares matching approach. While their paper proposed a new method, it still faces challenges due to the problem of multi-matching, which can result in making wrong outputs especially in specific parameter analysis.

The ultimate goal is to develop an EIS analysis method that is grounded in the fundamental principles of electrochemistry. To obtain such an analysis method, it is necessary to get rid of the degeneracies by using temperature dependence and non-linearities as new variables. By defining parameters considering these variables, this method reduces uncertainty and minimizes the potential errors.

Instead of fitting a single impedance spectrum, we propose fitting a set of spectra taken across multiple temperatures along with the information regarding higher harmonics. This approach minimizes the multi-matching problem that Murbach and Schwartz[1] experienced.

We used a physics-based model library on Python called PyBaMM [2] to provide a new approach to EIS data analysis. We simulate voltage as a function of current within a defined frequency range. To overcome the degeneracy problem, we vary the temperature and analyze nonlinearities by looking at the second and third harmonics in frequency domain data. Obtained linear and non-linear voltage simulation data will be compared and tried to fit by using simplex fitting method.

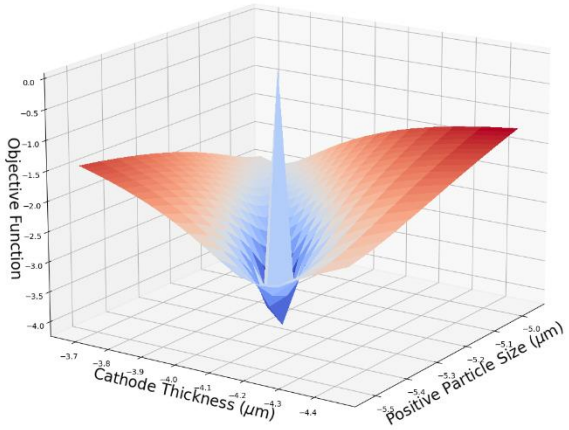

Figure 1. The objective function of Cathode Thickness and Positive Particle size ranging from 35μ to 79μ and 3μ to 11μ respectively.

$$\sum_{T=-25°C}^{65°C} \frac{1}{N} \sum_{f=100\,\mu Hz}^{10\,kHz} \frac{(z_r(f,T)-z_{0,r})^2+(z_i(f,T)-z_{0,i})^2}{(z_0)^2} + nonlinearity$$

Here we defined our objective function as where z_0 is the parameters before simulation, N is the number of frequency and z_r,z_i represent real and imaginary numbers of the impedance data. By calculating this over a frequency range and temperature range, the degeneracy will be reduced. To further increase the accuracy of simulation, we will modify and improve this function by adding a non-linearity term in order to obtain a better fitting results in our simulations.

References

[1] Matthew D. Murbach and Daniel T. Schwartz 2018 J. Electrochem. Soc. 165 A297

[2] Sulzer, Valentin, et al. "Python battery mathematical modelling (PyBaMM)." *Journal of Open Research Software* 9.1 (2021).

[3] Li, Weihan, et al. "Data-driven systematic parameter identification of an electrochemical model for lithium-ion batteries with artificial intelligence." *Energy Storage Materials* 44 (2022): 557-570

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