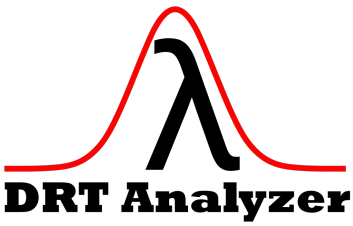
DRT Analyzer - a Toolbox for the Calculation and Evaluation of DRT Spectra



v3.0

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1 Introduction

The DRT analyzer is a toolbox devoted to the calculation and evaluation of the DRT spectra. The toolbox is developed with the MATLAB App and has a graphical user interface (GUI). Since the first release, the toolbox has undergone multiple updates and now the version v3.0 has been released. In v3.0, more new features are added and all known bugs have been fixed. Compared to v2.0, the figures displaying the separated peaks in the spectra has been added. Besides, the data export function has been implemented.

The GUI of the toolbox can be roughly separated into three sectors (see Fig. 1):

1. Calculation and validation of DRT spectra
2. Evaluation of DRT spectra
3. Data analysis and export

In the following sections, the functions embedded in each sector of the GUI will be introduced in detail.

2 Calculation and validation of DRT spectra

2.1 Load impedance data

By clicking on the menu **File**, a dialog box will appear and the file containing the impedance data can be selected and loaded. For the current version, only **.m** file can be loaded, and in the future release more options will be added. The loaded **.m** file should contain one cell array with the name **data** and each set of impedance data should be saved in the cell array as a matrix. Each matrix represents a set of impedance data and consists of three columns:

1. column 1: frequency vector in Hz
2. column 2: the real part of the impedance, namely Z'
3. column 3: negated imaginary part of the impedance, namely $-Z''$

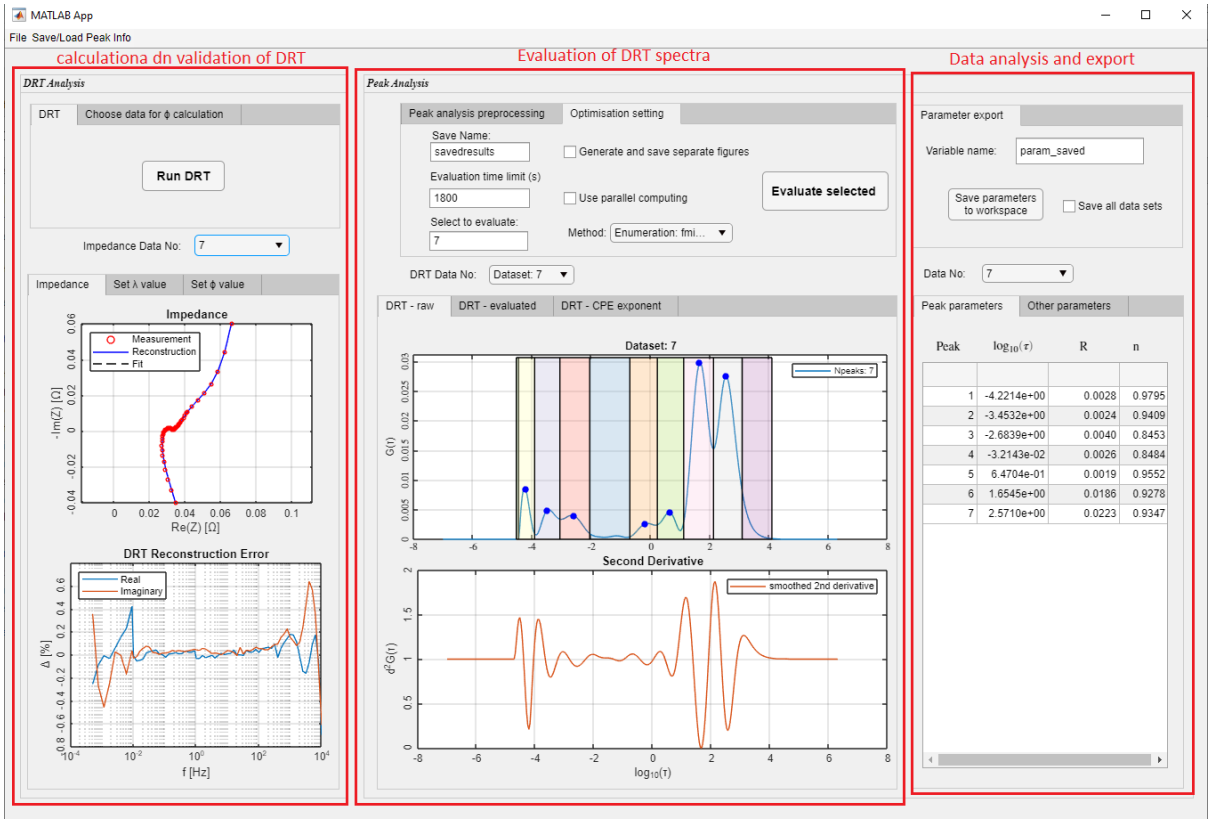

Figure 1: GUI of the DRT analyzer

After the data has been loaded into the toolbox, they will be displayed in the figure with the title **Impedance**. In case multiple data sets have been loaded into the toolbox, the drop-down menu **Impedance Data no:** can be used to switch to different data set.

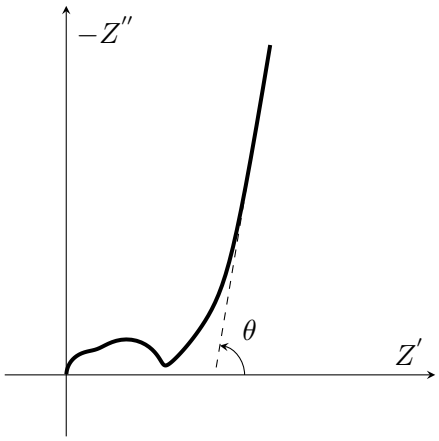

Figure 2: Schematic illustration of an impedance, where the capacitive region is represented by a CPE element

2.2 Choose ϕ value for the capacitive region

For the Lithium-ion battery, the impedance usually shows a capacitive behavior when the frequency is low. In ideal case, the impedance shows an ideal capacitive behavior and has a phase angle θ of 90°:

$$Z_{\mathrm{lf}} = \frac{1}{j\omega C} \tag{1}$$

In most of the practical applications, due to non-ideal diffusion, no ideal capacitive behavior can be observed in the low frequency range. Instead, a CPE type impedance can be observed with a phase angle θ smaller than 90° (see Fig. 2):

$$Z_{\mathrm{lf}} = \frac{1}{(j\omega C)^{\phi}} \tag{2}$$

where ϕ is the CPE exponent and $0.5 < \phi < 1$. The CPE exponent can be calculated as:

$$\phi = \frac{\theta}{\frac{\pi}{2}} \tag{3}$$

The low frequency impedance has a significant influence on the calculation of the DRT spectra and must be characterized as accurate as possible. In the present toolbox, the function for choosing data points for the calculation of the CPE exponent has been implemented (see Fig. 3):

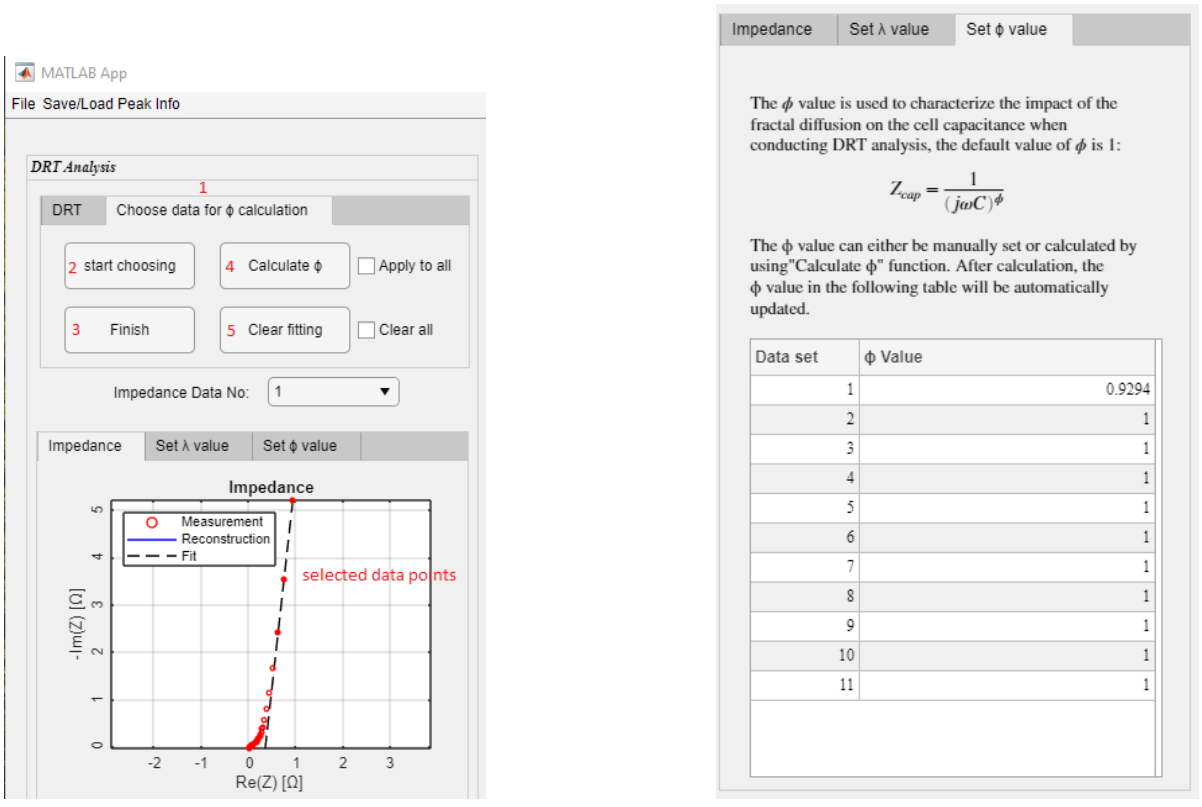

Figure 3: Calculate ϕ value for the calculation of DRT spectra. Left: calculate using linear fitting; right: input ϕ value for each data set manually

1. switch to the **Choose data for ϕ calculation** tab

2. click on the **start choosing** push-button (the mouse will be switched to the **brush data** mode in the figure) and the corresponding data points in the low frequency range can be chosen for the calculation. The chosen points should generally fulfill the following conditions: 1. all selected points should have a linear relationship (lie on the same straight line); 2. they should all be located in the capacitive region, data points in the diffusion region or close to the transition point should be avoided.

3. after the data points have been selected, click on the **Finish** push-button to end the selection process

4. next, click on the **Calculate** ϕ push-button to calculate the ϕ value. If the calculated ϕ value should be applied to all data sets, then the check-box **Apply to all** next to the push-button can be selected.

5. in case a new calculation should be conducted, the current fitting can be cleared by clicking on the push-button **Clear fitting**. Similarly, the check-box **Clear all** can be selected if all fittings should be cleared.

If necessary, the ϕ value for each data set can be input manually by switching to the **Set** ϕ **value**. The default value for ϕ is 1.

2.3 Set the regularization parameter λ

The regularization parameter λ is one of the most important parameters for the DRT calculation. λ can be set by switching to the **Set** λ **value** tab and the value for each data set can be input manually. As the optimal λ value can be determined using different methods and different results are usually obtained, the algorithm for calculating the optimal λ value is not implemented in this toolbox. The default value for λ is 0.2.

2.4 Calculation and validation

After all preparation steps introduced above have been finished, the DRT spectra can be calculated by clicking on the **Run DRT**. The calculated DRT spectra are then displayed in the figure in the **DRT-raw** tab. Besides, the impedance will be reconstructed using the calculated DRT spectra and other parameters, the reconstruction error (in %) for the real and imaginary part is displayed in the figure **DRT Reconstruction Error**. The reconstruction error plot can be also used as an implementation of the Kramers-Kronig test (KK test). An impedance can be regarded as valid if no systematic pattern can be observed in the error plot.

3 Evaluation of DRT spectra

The calculated DRT spectra always contain a series of peaks and the peaks are usually overlapping. Sometimes it's impossible to directly the useful data from the figure. To evaluate the DRT not only qualitatively but also quantitatively, a peak analysis must be conducted.

3.1 Define peaks

To conduct the peak analysis, first the possible/guessed peak locations should be defined. To define the possible locations of peaks, first switch to the **Peak analysis preprocessing** tab and then click on the push-button **Switch to peak view**. By switching to the **peak view**,

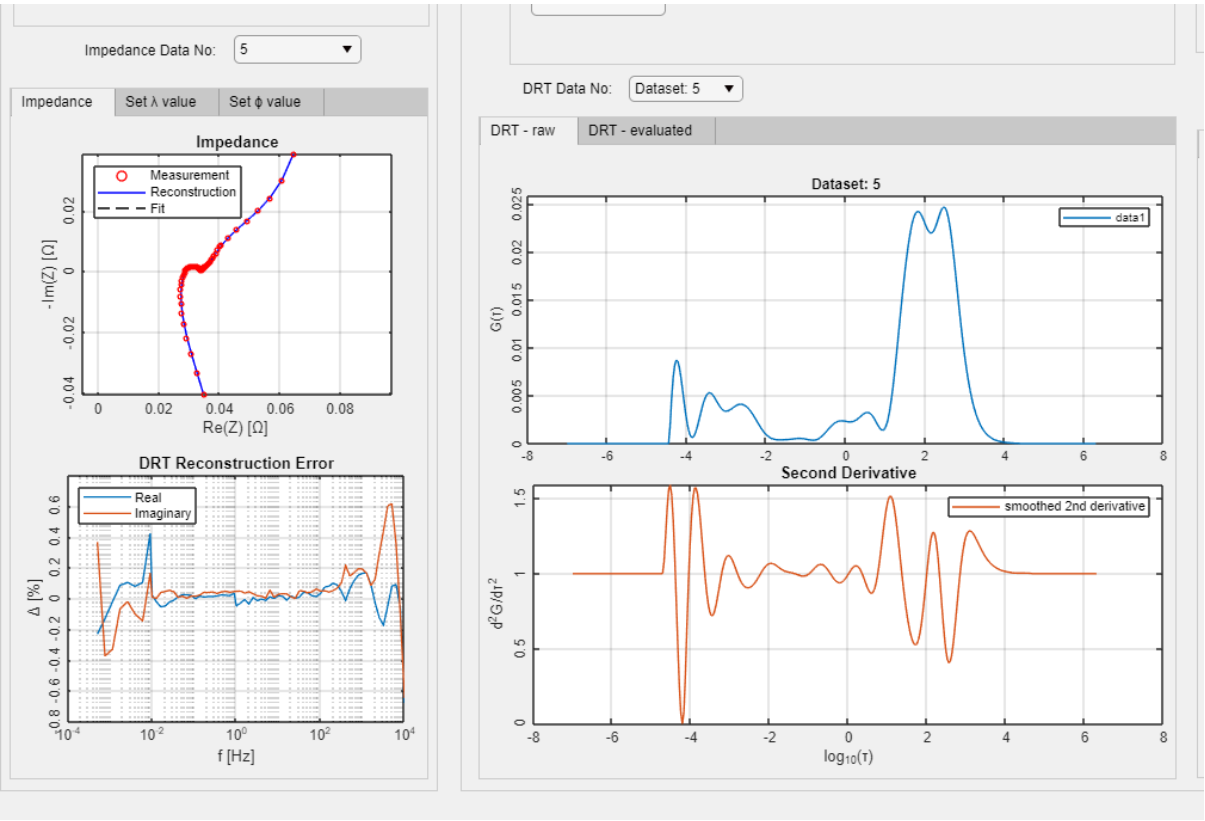

Figure 4: Calculated DRT spectra and the corresponding error plot

the algorithms implemented in the toolbox will first automatically detect the possible locations of the peaks (marked by blue dot).

Though all possible peaks have been detected by the algorithm implemented in the toolbox, sometimes a few peaks may be missed or the operator would like to add more peaks based on additional information or knowledge. A additional peak can be defined by first clicking on the push-button **Add peaks** and then directly clicking on the plot where a peak possibly exists. A defined peak location is marked again by a blue dot. A peak can be deleted by using the **Delete peaks** push-button and clicking on the corresponding blue dot. The add/delete peak function can be deactivated by clicking on the corresponding button again.

To simplify the calculation, the upper and lower bound for each peak should be defined. After switching to the **peak view**, the algorithm implemented in the toolbox will automatically determine the bounds for each detected peak and the range for each peak will be marked with different colors. If the operator intends to add additional bounds in order to reduce the margin and accelerate the optimization, an additional bound can be defined by first clicking on the **Add bounds** and then click on anywhere where a bound should be defined. Similarly, the bound can be deleted by using **Delete bounds**.

To ease the **Add peaks** process, the 2^{nd} order derivative of the DRT spectra has been calculated and plotted in the figure **Second Derivative**, each valley in the derivative curve should indicate that there may exixt a peak at this location. A peak can be also added by clicking on the valley location in the derivative curve.

3.2 Selecting candidate fitting functions

Depending on the nature of the processes, usually different fitting functions should be selected for each peak. For example, an RC element usually corresponds to a peak in the DRT spectra with a "gaussian-bell" like form, an RQ (ZARC) element corresponds to the following DRT function:

$$g_{\mathrm{ZARC}}(\tau) = \frac{1}{2\pi\tau} \frac{\sin(\phi\pi)}{\cosh[\phi \ln(\tau/\tau_0)] + \cos(\phi\pi)} \tag{4}$$

which has different form other than the gaussian function. For some peaks near the upper/lower bound of the time constants, the peaks may have skewed form [1]. As a result, the skewed gaussian function has been selected as the third candidate function for the fitting. If the operator is unsure about the functional form of the fitting function, multiple candidate functions can be selected for the same peak and the implemented algorithm will try to find the best candidate function combination. The candidate fitting function can be selected for each peak respectively by clicking on the **Select Candidates**. Generally using the **Select Candidates (all)** is not recommended unless all DRT spectra have the same number of peaks.

3.3 Define optimization parameters

After the data preprocessing is finished, the parameters for the optimization should be defined by switching to the **Optimisation setting** tab. The following parameters should be defined:

- Save Name: with this defined name, the evaluation results for each data set will be saved in the **results** folder.
- Evaluation time limit (s): in certain cases the program may run for a long time. A defined maximum running time can be defined to limit the running time of the program. This option is only valid for the GlobalSearch algorithm.
- Select to evaluate: define the data sets to be evaluated, e.g. 1-5 or 2-5, 7-9.
- Generate and save separate figures: when selected, two separate figures of the peak analysis will be generated and saved in the results folder
- Use Parallel computing: when selected, the parallel computing will be activated to speed-up the optimization
- Method: select optimization method, usually **Enumeration: fmincon** should produce satisfactory results. Other algorithms can be selected if the default algorithm doesn't produce good results or takes a too long time

3.4 Display results

After all the preparation steps introduced above have been conducted, the **Evaluate selected** button can be pushed to start the peak analysis. After the peak analysis is finished, the results can be inspected by switching to the **DRT - evaluated** tab. In the **DRT-Fitted** figure, the calculated DRT spectrum and the fitted curve using candidate functions are shown so that the fitting quality can be assessed. In the **DRT-Separated peaks** figure, the separated peaks are plotted.

Another powerful function of the DRT_analyzer toolbox is that after the peak analysis is done and all peaks are separated, a more detailed analysis can be conducted with each separated

peak. With the DRT spectrum for each peak, the impedance corresponding to each peak can be reconstructed using the DRT spectra. The reconstructed impedance corresponding to each peak can be calculated as follows:

$$Z_{\text{peak}} = \int_0^{\infty} \frac{g(\tau)}{1 + j\omega\tau} d\tau \tag{5}$$

The calculated impedance can be used to analyze the process represented by the peak. The impedance corresponding to each peak can be inspected by switching to the **DRT - CPE exponent** tab, by clicking on the **Peak no** drop-down menu, each peak can be inspected (see Fig. 5).

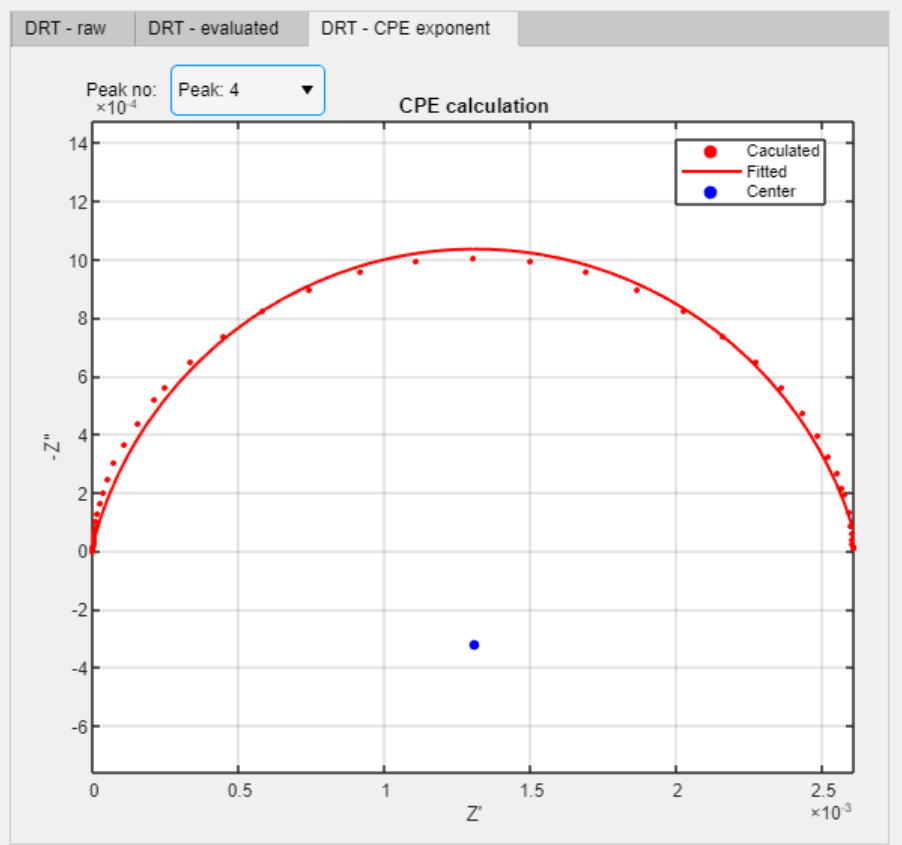

Figure 5: Figure showing the reconstructed impedance corresponding to the peak 4

The calculated impedance is then fitted using a circle to analyze its properties. The CPE exponent is calculated and listed in the table on the rightmost side of the GUI.

For the detailed explanation of the peak analysis, please refer to [2, 3].

4 Data analysis and export

After the peak analysis is done, the parameters for each peak of each impedance is shown in the table on the rightmost side of the GUI. The **Data No:** can be used to choose different data sets. The table has three columns: the first column is the number of the peak, the second column is the corresponding time constants in logarithmic scale, the third column is the polarization resistance of each peak, i.e., the area under each separated peak and the fourth column indicates the CPE exponent of each process.

Under the tab **Other parameters**, the capacitance and the ohmic resistance of the impedance data are listed. All results can be exported to the MATLAB workspace by clicking on the **Save parameters to workspace** button. The exported results will be saved in a cell array, each data set corresponds to an element in the cell array. For each data set, the results are saved in a structure array with the following elements:

- t_DRT: time constant vector of the original calculated DRT spectra in logarithmic scale
- DRT: the calculated DRT spectra, which should be combined with the t_DRT to produce the DRT spectra
- t_DRT_Separated_peak: the time constants corresponding to each separated peak in the DRT spectra
- DRT_Separated_peak: the DRT spectra of all separated peaks, each column in the matrix corresponds to one peak
- CPE_exponent: the CPE exponent corresponding to each peak
- parameters.RC: the parameters of all peaks are saved in the matrix. The first column corresponds to the logarithmic time constants, the second column indicates the height of the peaks, the third column represents the polarization resistance of the peaks.
- parameters.R_ohm: ohmic resistance of the impedance
- parameters.capacitance: capacitance of the impedance, if can be calculated

References

[1] Xin Li, Mahshid Ahmadi, Liam Collins, and Sergei V. Kalinin. Deconvolving distribution of relaxation times, resistances and inductance from electrochemical impedance spectroscopy via statistical model selection: Exploiting structural-sparsity regularization and data-driven parameter tuning. 313(2):570–583, 2019.

[2] Yulong Zhao, Volkan Kumtepeli, Sebastian Ludwig, and Andreas Jossen. Investigation of the distribution of relaxation times of a porous electrode using a physics-based impedance model. *Journal of Power Sources*, 530:231250, 2022.

[3] Yulong Zhao, Simon Kücher, and Andreas Jossen. Investigation of the diffusion phenomena in lithium-ion batteries with distribution of relaxation times. *Electrochimica Acta*, page 141174, 2022.