EISART User Manual

Electrochemical Impedance Spectrum Analysis and Refining Tool

By Hangyue Li

Version 2.6 on March 14th , 2023

Contents

EISART is a fast impedance spectrum analysis tool originally developed for solid oxide fuel cells.

It features one-click operations for:

- Distribution of Relaxation Time (DRT) analysis
- Auto or semi-auto Equivalent Circuit Model (ECM) fitting & ZView *.mdl model importing/exporting
- Batch processing and easy-to-use saving format

EISART is robust to noise, wiring induction, and deviated data points in EIS. It visualizes the original data and the fitting result as Nyquist and Bode plots, and shows the fitting residuals to the user in real time.

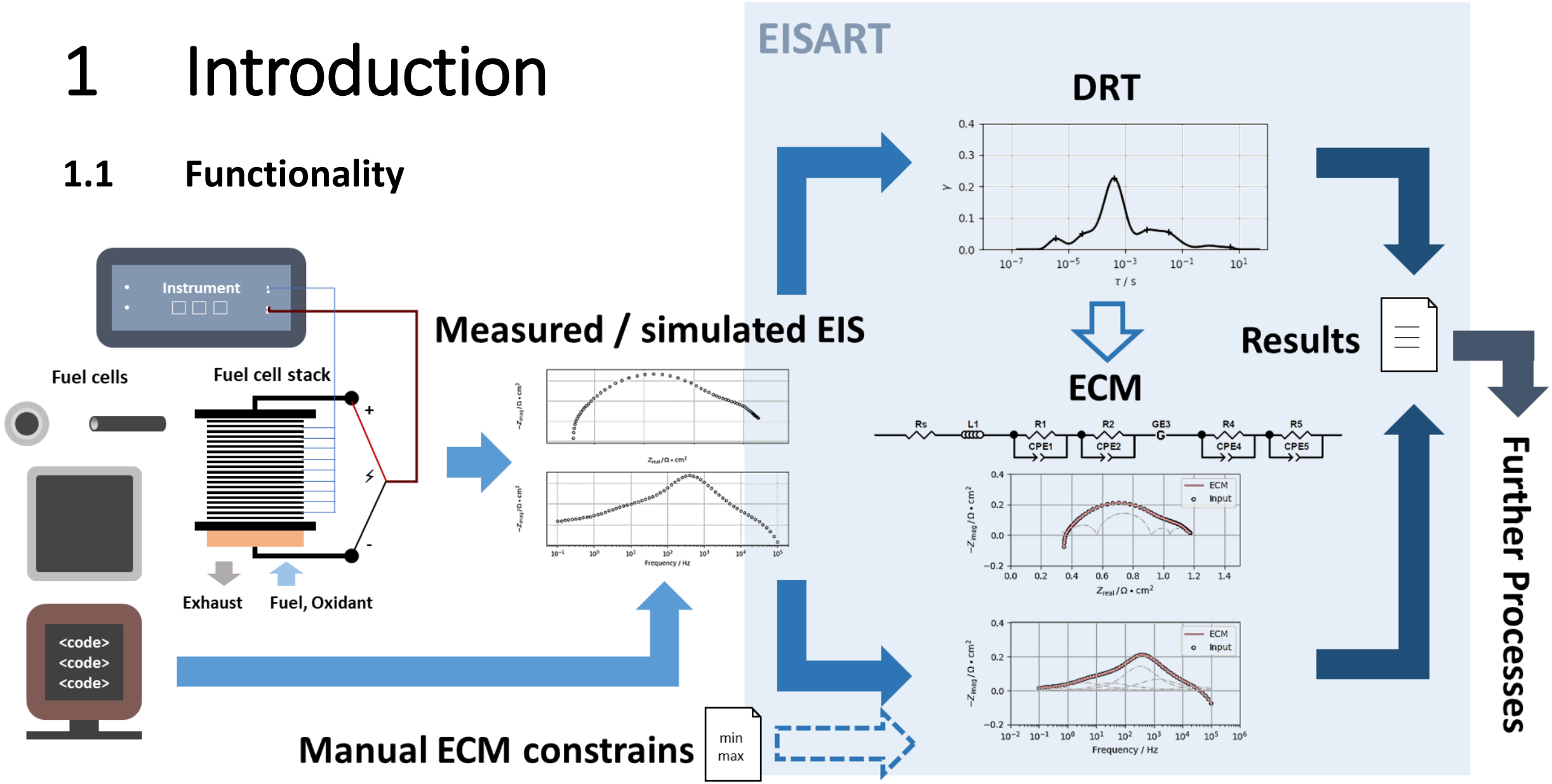
Citation

Please cite the following academic journal article if you use EISART in your work:

Li, Hangyue, Zewei Lyu, and Minfang Han. "Robust and Fast Estimation of Equivalent Circuit Model from Noisy Electrochemical Impedance Spectra." Electrochimica Acta (2022): 140474. https://doi.org/10.1016/j.electacta.2022.140474

1 Introduction

1.1 Functionality



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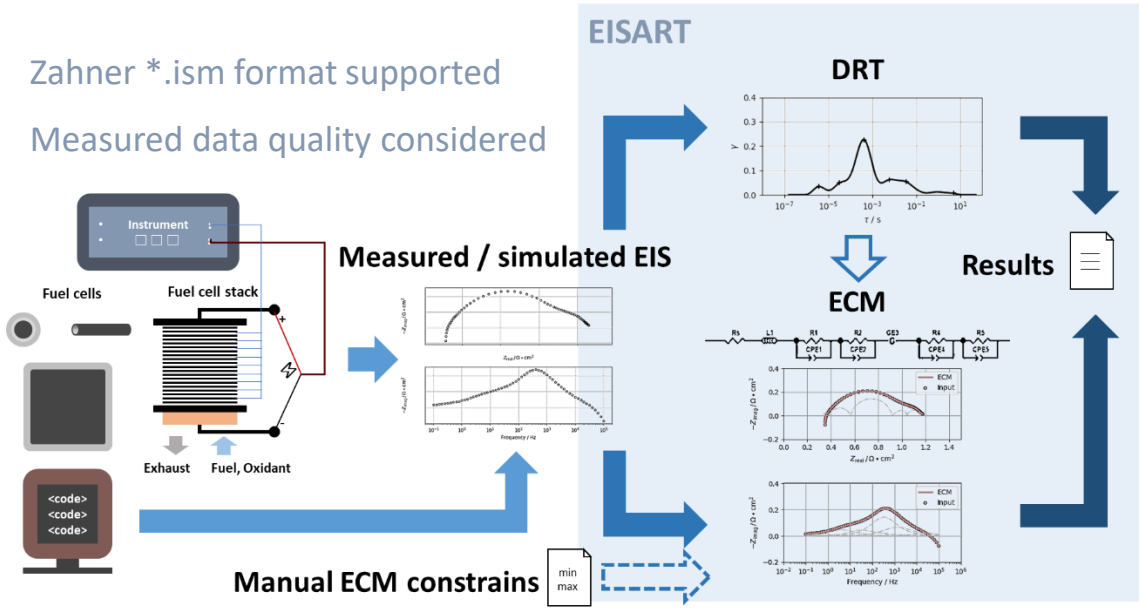

EISART is a fast impedance spectrum analysis tool originally developed for solid oxide **fuel cells**.

It features **one-click** operations for:

- Distribution of Relaxation Time (**DRT**) analysis
- Auto or semi-auto Equivalent Circuit Model (**ECM**) fitting & **ZView** *.mdl model importing/exporting
- **Batch** processing and easy-to-use saving format

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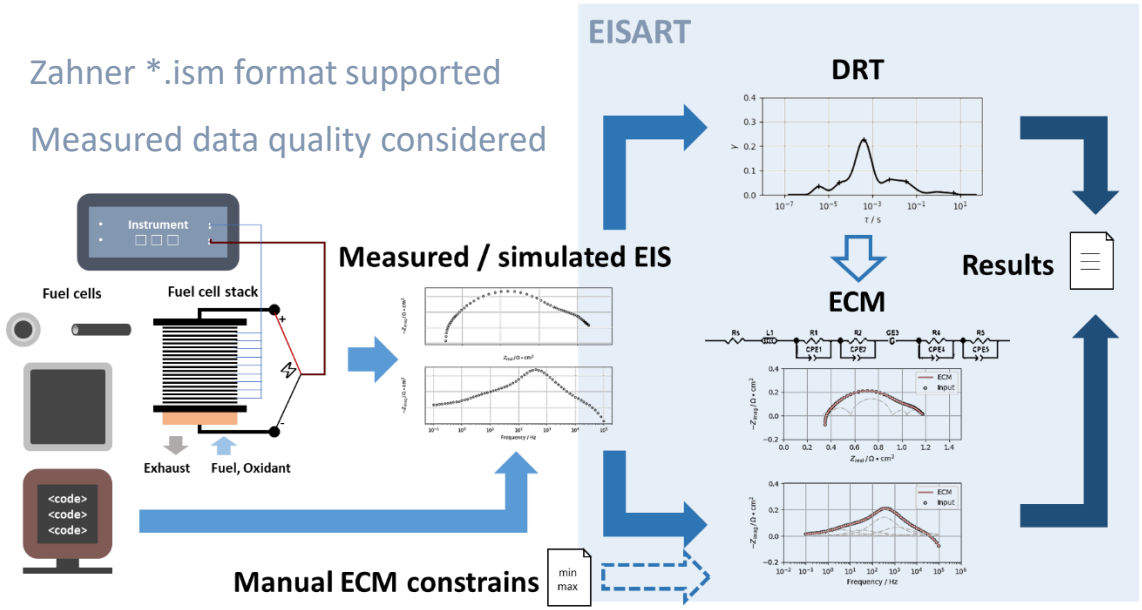
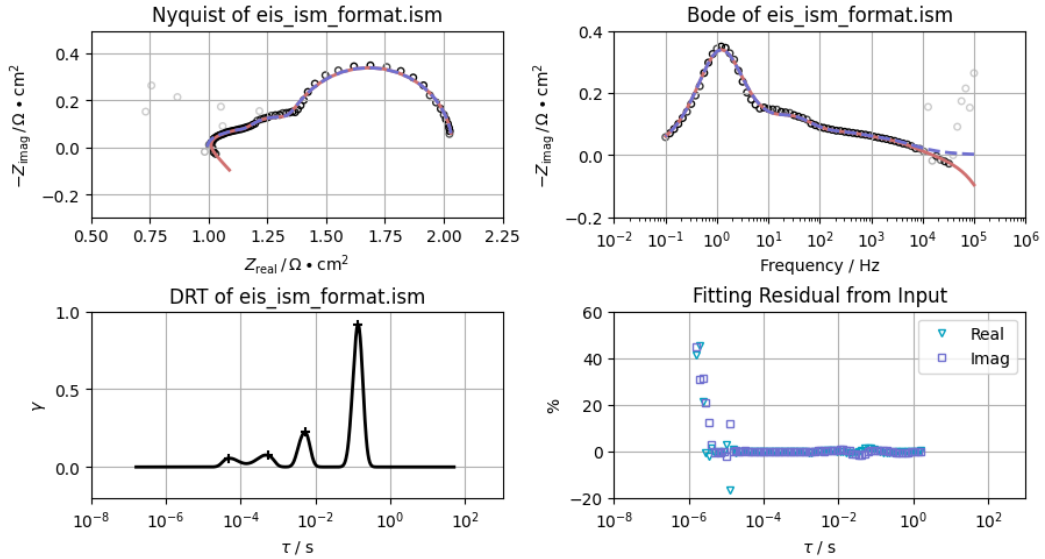


EISART may downweigh an input data point if it considers the point deviated. **The weights are shown in opacity** in the Nyquist and Bode plots.

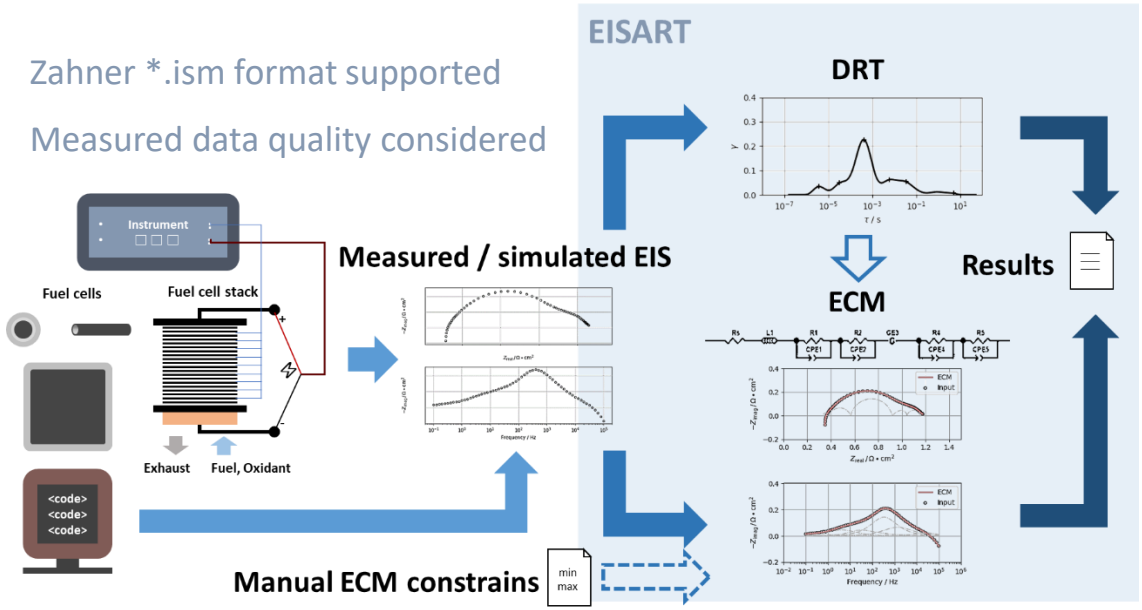
DRT analysis and ECM fitting are based on weighted input EIS data, in order to minimize the impact of noise and individual deviated points.



K-K Test Mode off, DRT plot to τ

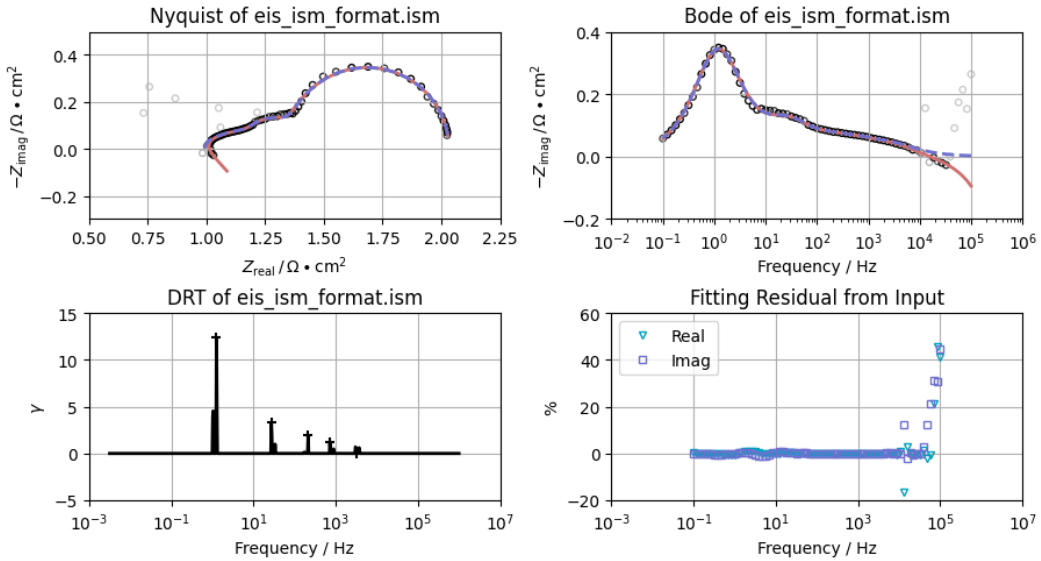
1 Introduction

1.1 Functionality



For DRT analyzing, EISART offers **K-K Test** (Krämers-Krönig Test) mode, in which the user may check the quality of input EIS data and whether the non-negative-γ DRT analysis in EISART suits the input EIS.

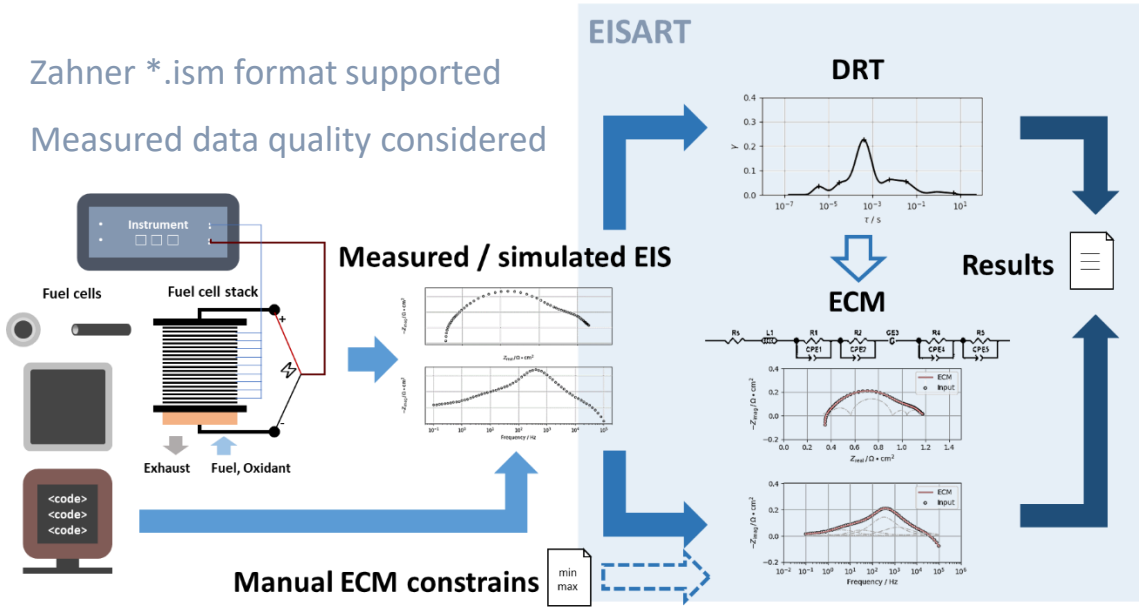
The **DRT** result may be plotted to **relaxation time** τ or **eigen frequency** $f = 1/(2\pi\tau)$.



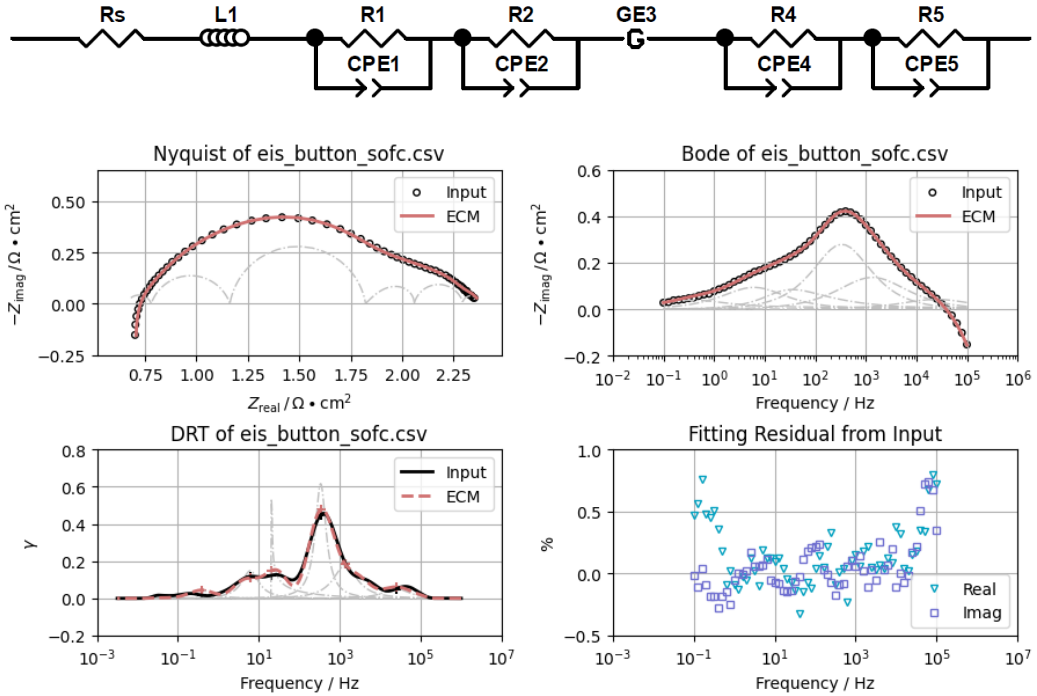
K-K Test Mode on, DRT plot to frequency

1 Introduction

1.1 Functionality



For ECM fitting, EISART supports any circuit comprising **RQ/RC elements, Gerischers, resistors, and inductors**.



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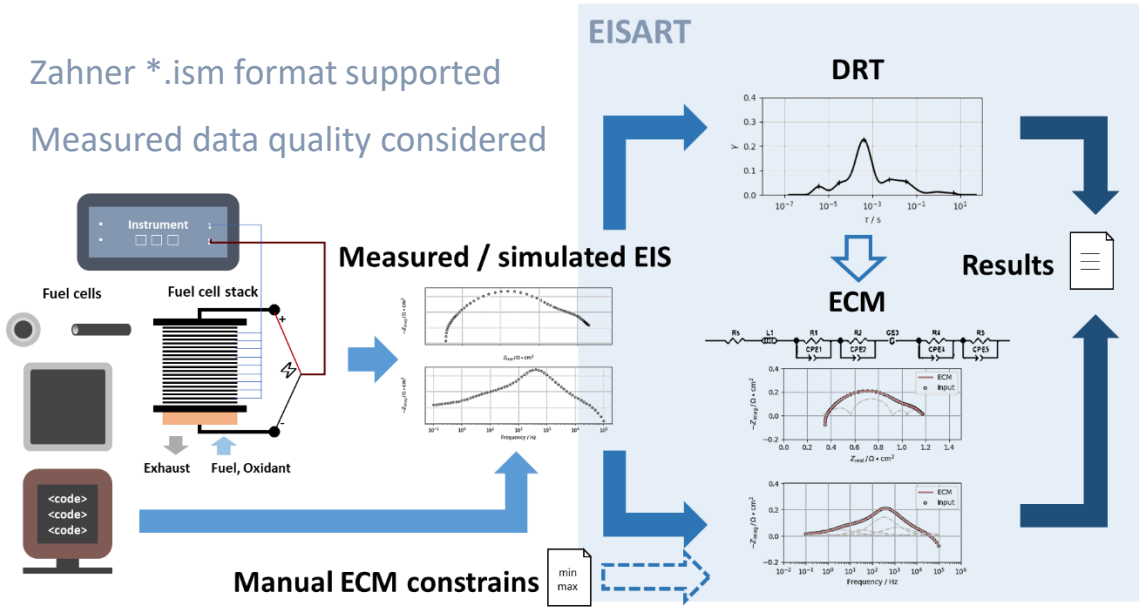
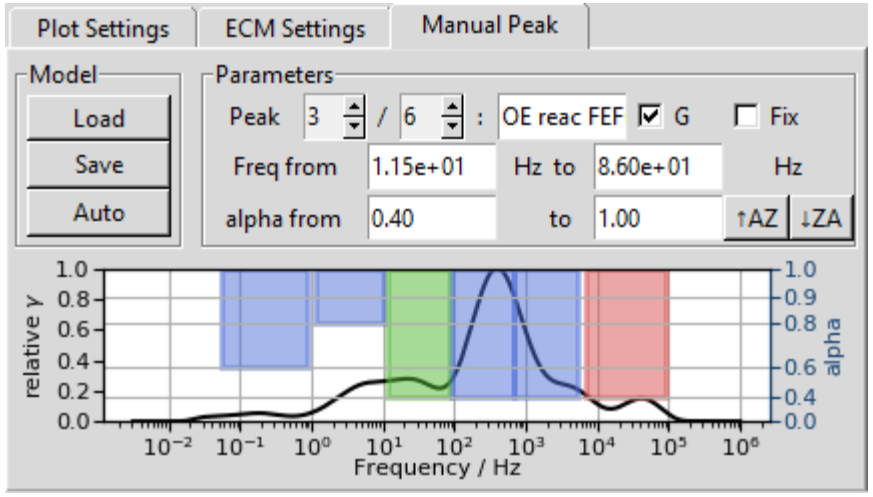


EISART allows its user to **leave the fitting entirely to the program**, or fit **semi-automatically** by manually specify the constrains to ECM parameters. ECM constrains may be saved as file or loaded from file. Loading Zview *.mdl models supported.

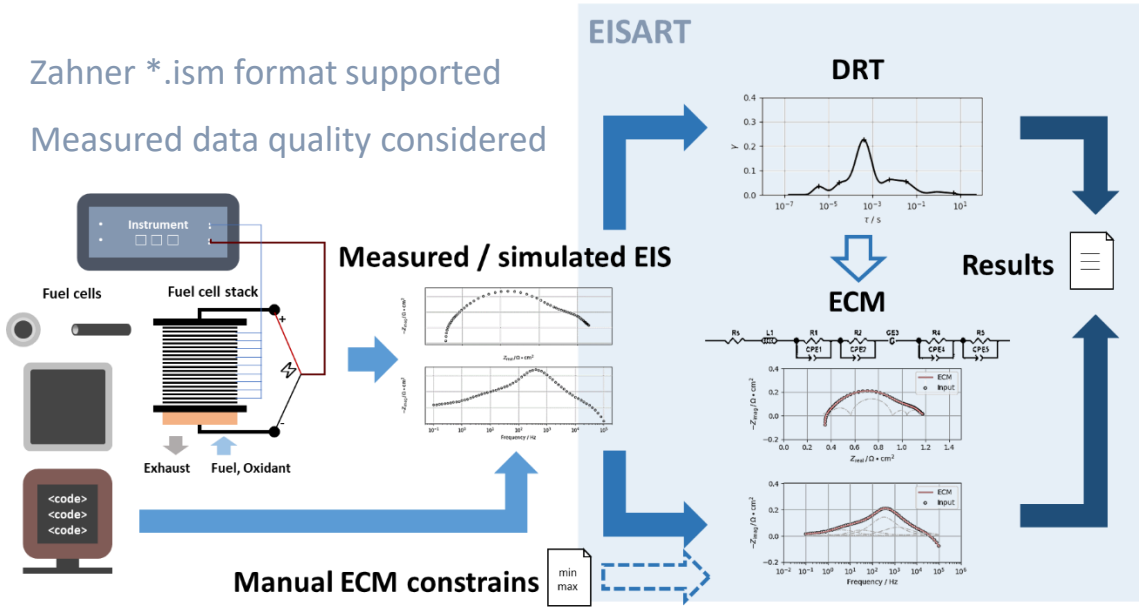
For **ECM with constrains**, the number of RQ/RC elements or Gerischers ranges from 1 to 20.

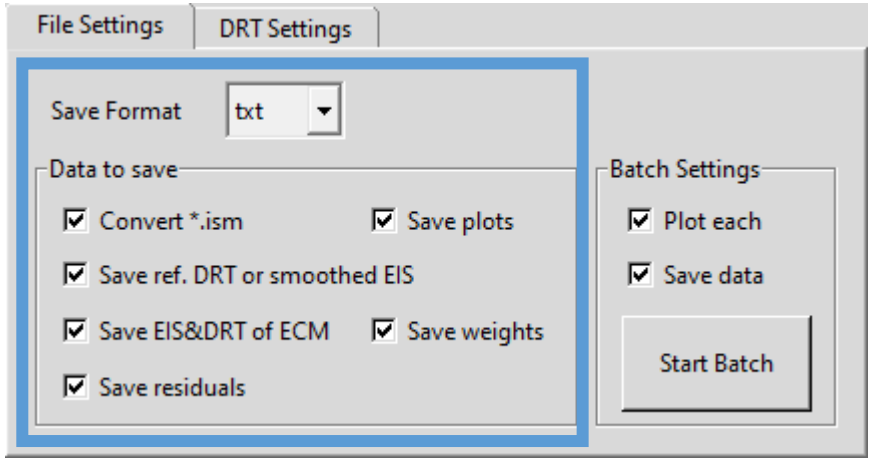


1 Introduction

1.1 Functionality

EISART offers the possibility to **save the desired part** of results as **files** in the specified format. It currently supports *.txt and *.csv. The files are saved in the same directory as the input EIS data file. The snapshot for the input file can also be automatically saved.





1 Introduction

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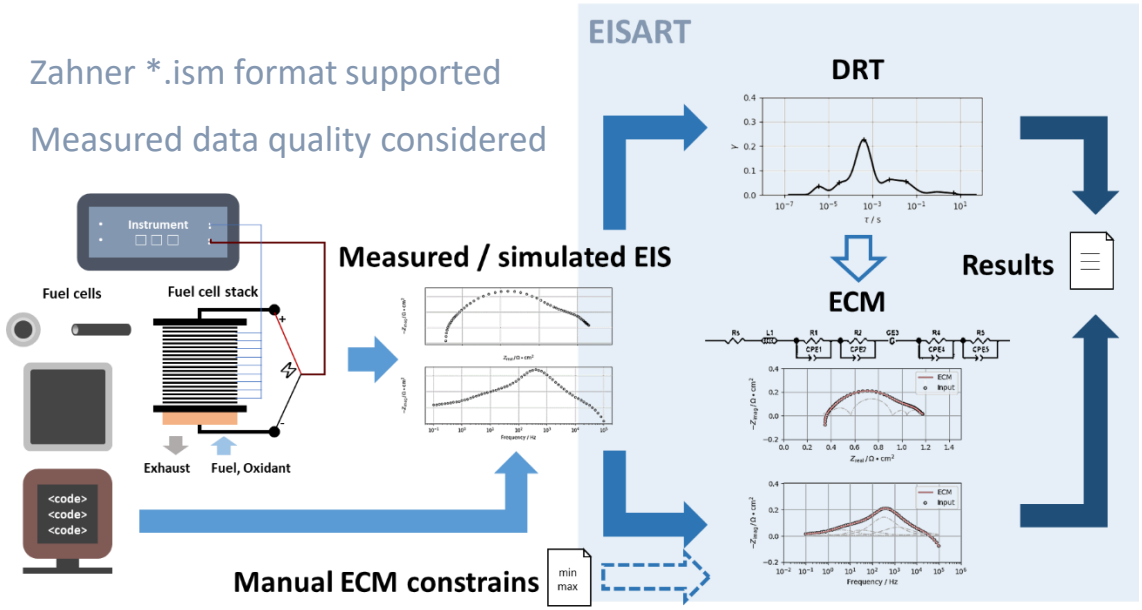
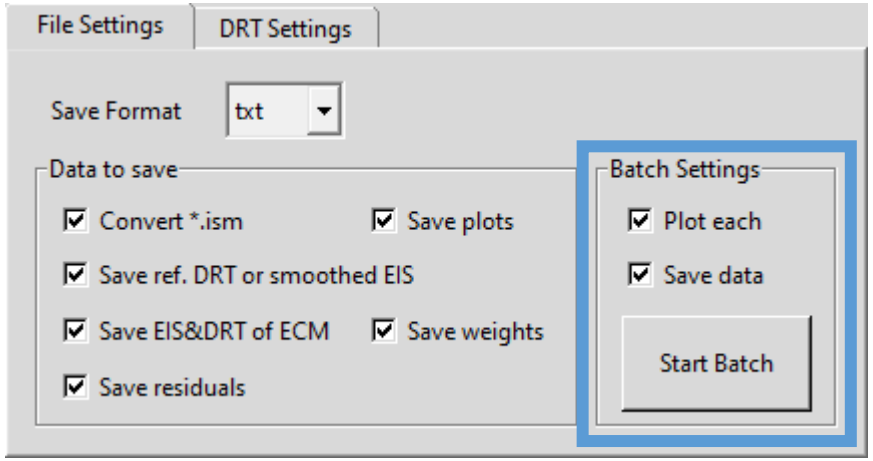


Batch processing using the same settings is possible with one click.

Results can be plotted in real time during batch processing. The snapshot for each input file can also be automatically saved during batch processing.

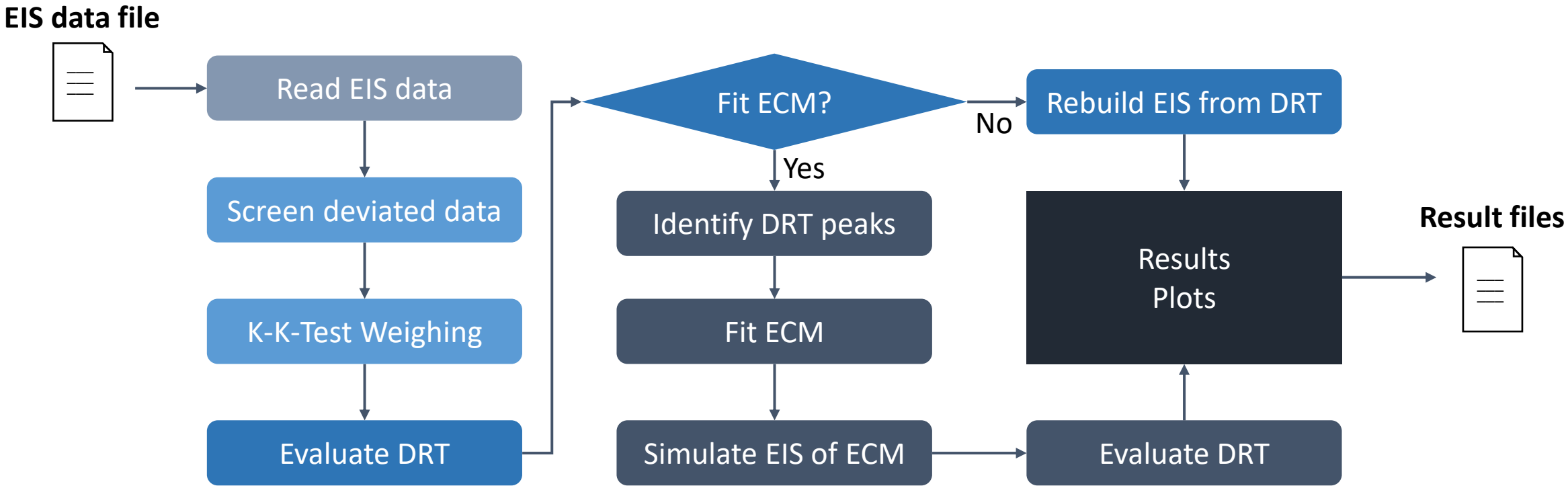


1 Introduction

1.2 Basic workflow

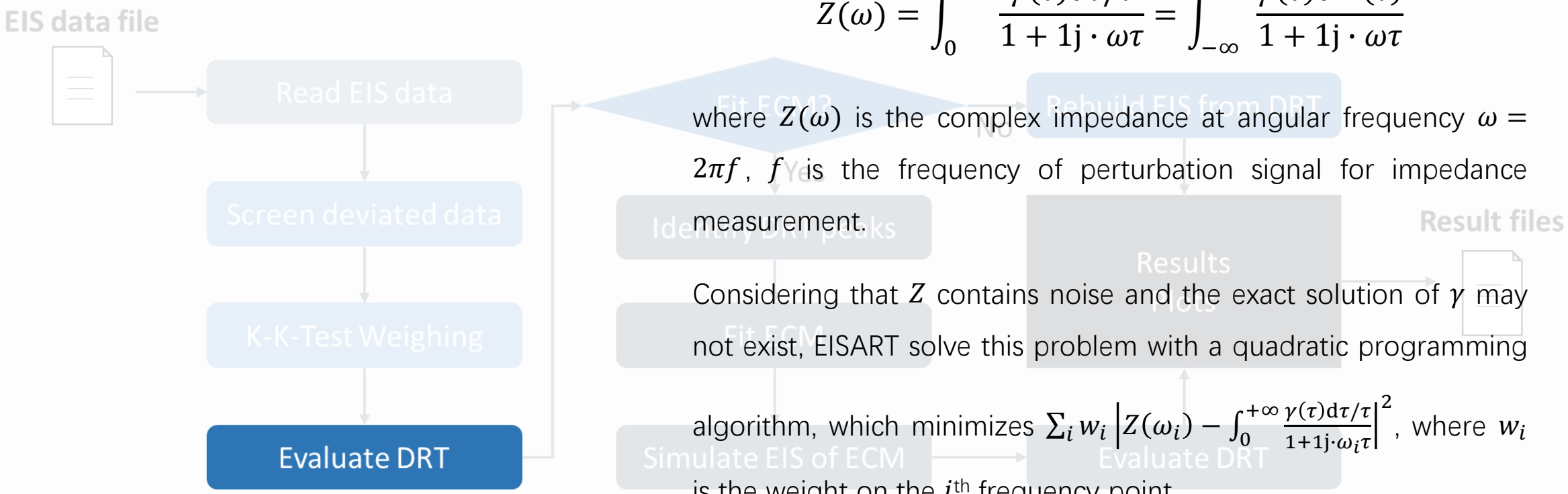
EISART process an input file in multiple steps as are shown below. The Graphical User Interface (GUI) of EISART will guide its users through these steps.

Whether or not to fit an ECM results in two different workflows.



1 Introduction

1.2 Basic workflow



The DRT result in EISART contains the **relaxation time distribution function** $\gamma(\tau)$ and its corresponding **relaxation time** τ (tau). The DRT is related to the input EIS with the following equation:

$$Z(\omega) = \int_0^{+\infty} \frac{\gamma(\tau)\mathrm{d}\tau/\tau}{1+1\mathrm{j}\cdot\omega\tau} = \int_{-\infty}^{+\infty} \frac{\gamma(\tau)\mathrm{d}\ln(\tau)}{1+1\mathrm{j}\cdot\omega\tau}$$

where $Z(\omega)$ is the complex impedance at angular frequency $\omega = 2\pi f$, f is the frequency of perturbation signal for impedance measurement.

Considering that Z contains noise and the exact solution of γ may not exist, EISART solve this problem with a quadratic programming algorithm, which minimizes $\sum_i w_i \left| Z(\omega_i) - \int_0^{+\infty} \frac{\gamma(\tau)\mathrm{d}\tau/\tau}{1+1\mathrm{j}\cdot\omega_i\tau} \right|^2$, where w_i is the weight on the i^{th} frequency point.

1 Introduction

1.2 Basic workflow

The ECM in EISART may contain series connected **resistor** R_s, **inductor**, **RQ elements** (or ZARC elements, a resistor in parallel with a constant phase element or CPE), and **Gerischers** (G elements).

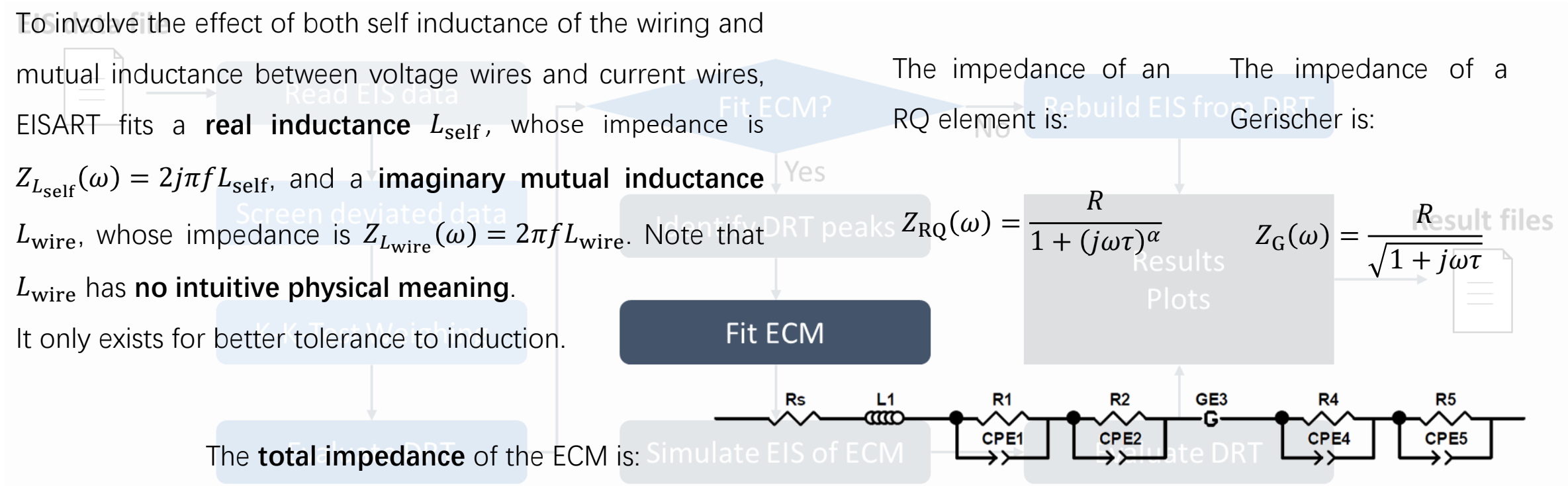
To involve the effect of both self inductance of the wiring and mutual inductance between voltage wires and current wires, EISART fits a **real inductance** L_{self}, whose impedance is $Z_{L_{\mathrm{self}}}(\omega) = 2j\pi f L_{\mathrm{self}}$, and a **imaginary mutual inductance** L_{wire}, whose impedance is $Z_{L_{\mathrm{wire}}}(\omega) = 2\pi f L_{\mathrm{wire}}$. Note that L_{wire} has **no intuitive physical meaning**.
It only exists for better tolerance to induction.

The impedance of an RQ element is:

$$Z_{\mathrm{RQ}}(\omega) = \frac{R}{1 + (j\omega\tau)^{\alpha}}$$

The impedance of a Gerischer is:

$$Z_{\mathrm{G}}(\omega) = \frac{R}{\sqrt{1 + j\omega\tau}}$$



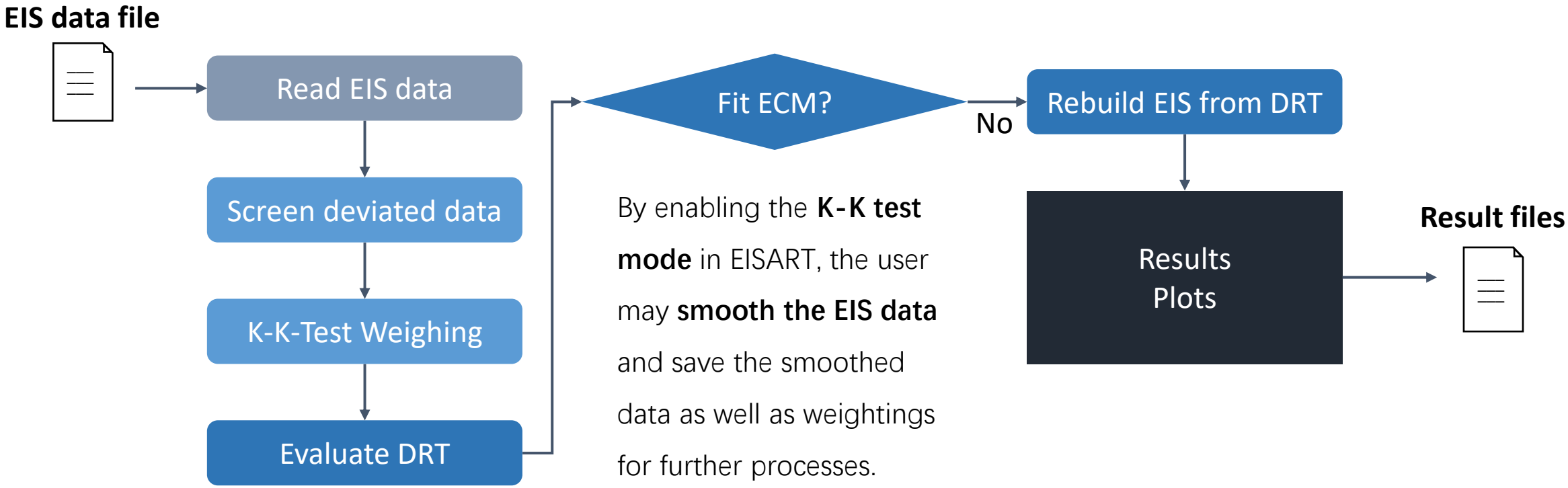
The **total impedance** of the ECM is:

$$Z_{\mathrm{total}}(\omega) = R_s + Z_{L_{\mathrm{self}}}(\omega) + Z_{L_{\mathrm{wire}}}(\omega) + \sum Z_{\mathrm{RQ}}(\omega) + \sum Z_{\mathrm{G}}(\omega)$$

1 Introduction

1.2 Basic workflow

If not to fit an ECM, EISART works as a **data inspector** and runs significantly faster (typically < 1 s). The user may check EIS data quality and the reliability of DRT analysis results.



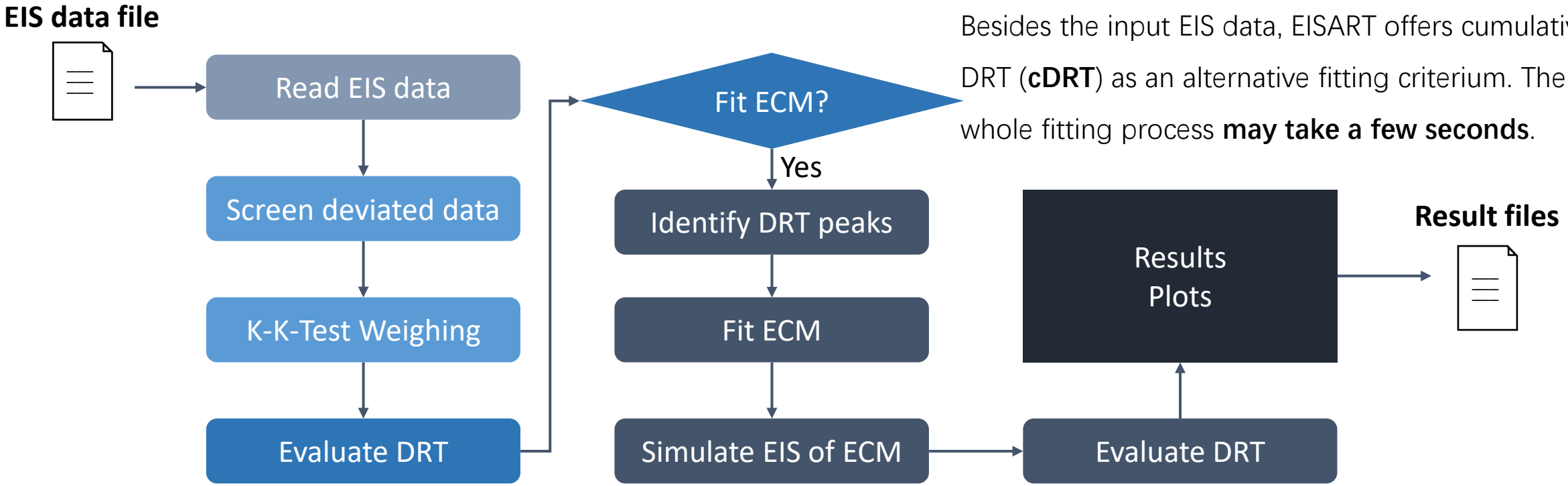
By enabling the **K-K test mode** in EISART, the user may **smooth the EIS data** and save the smoothed data as well as weightings for further processes.

1 Introduction

1.2 Basic workflow

If to fit an ECM, EISART can **automatically identify DRT peaks** as indicators of ECM parameters. The user may also **manually specify constrains to ECM parameters**. EISART fit an ECM with the Complex Nonlinear Least Squares (**CNLS**) algorithm.

Besides the input EIS data, EISART offers cumulative DRT (**cDRT**) as an alternative fitting criterium. The whole fitting process **may take a few seconds**.



1 Introduction

1.3 Using the GUI

Active cell area

Enter active cell area in cm^2 so that EISART gives the right results in $\Omega \cdot \mathrm{cm}^2$

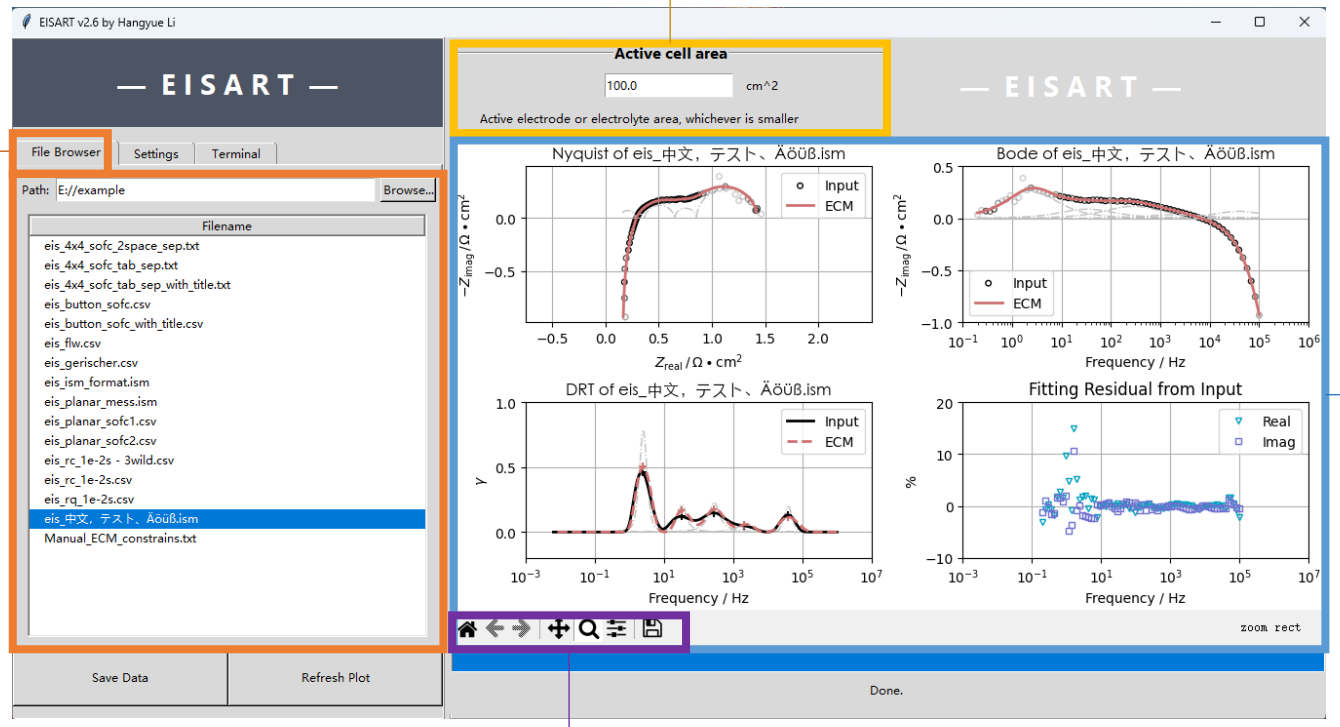
You may **double-click** a file in File browsing panel or **press Enter** in the Active cell area entry box to refresh **the plot**.

File browsing panel

Select an EIS data file

You may click the “Browse” button to choose a file, or enter/paste a path to the file, and then press “Enter” on your keyboard.

You may try the EIS files in the “**samples**” folder that is in the EISART package.



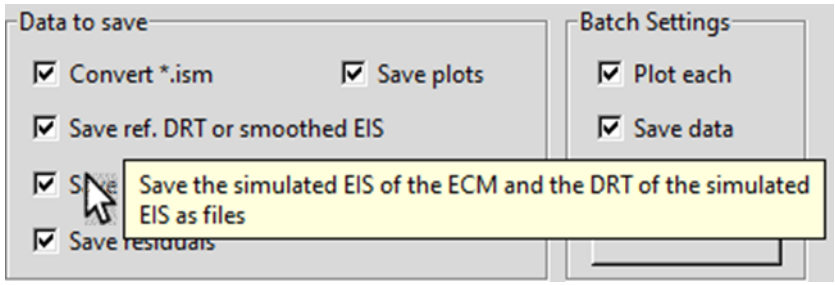
You may use the plot controller buttons to pan, zoom or save the plot.

Plot region

The input and output data is visualized in the plot region with a Nyquist plot, a Bode plot, a DRT plot, and a residual plot.

1 Introduction

1.3 Using the GUI

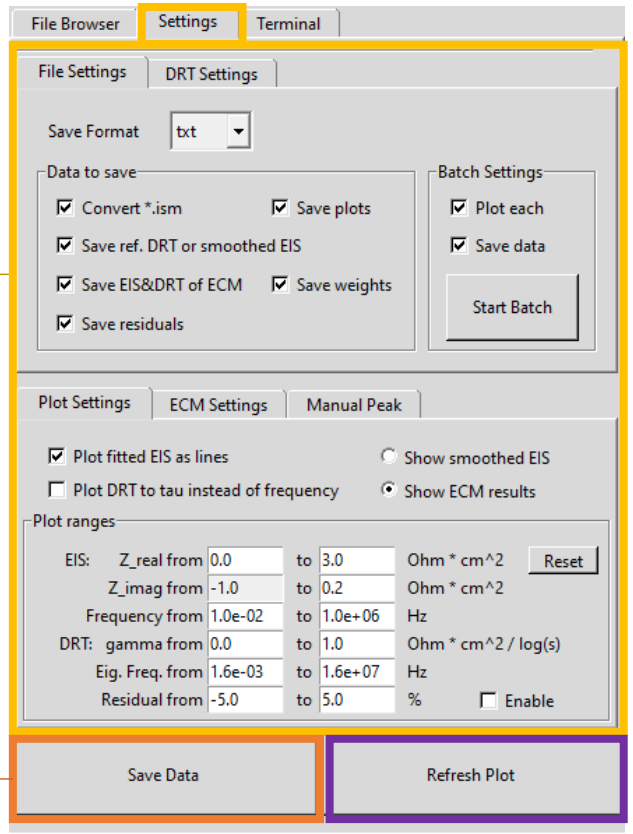


Hints

Place the mouse over text widgets and the hints will show.

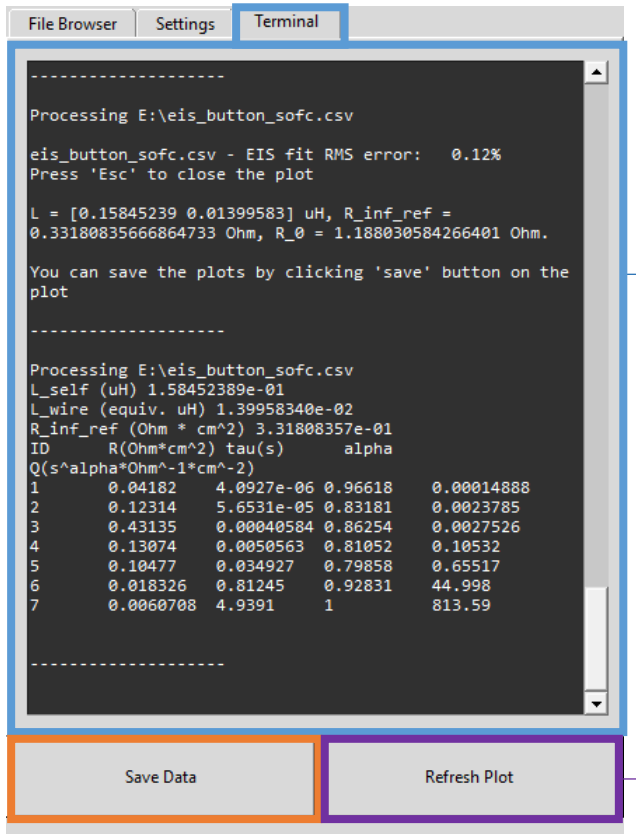
Settings

Control options for the data processing workflow, parameters etc.



Terminal

The text output portal of EISART, shows the results in text.



Save Data

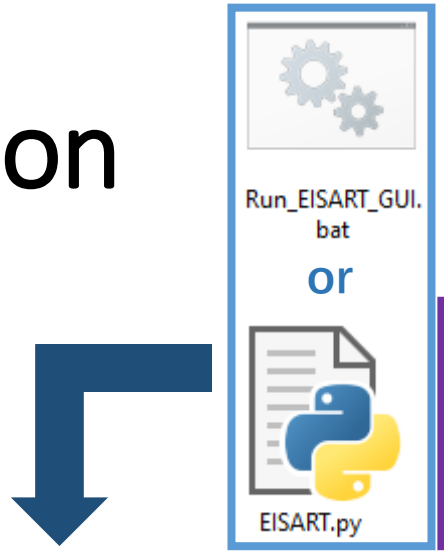
Re-calculate, plot, and save the results.

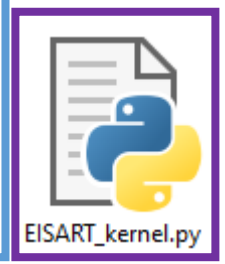
Refresh Plot

Re-calculate, plot, but not save the results.

1 Introduction

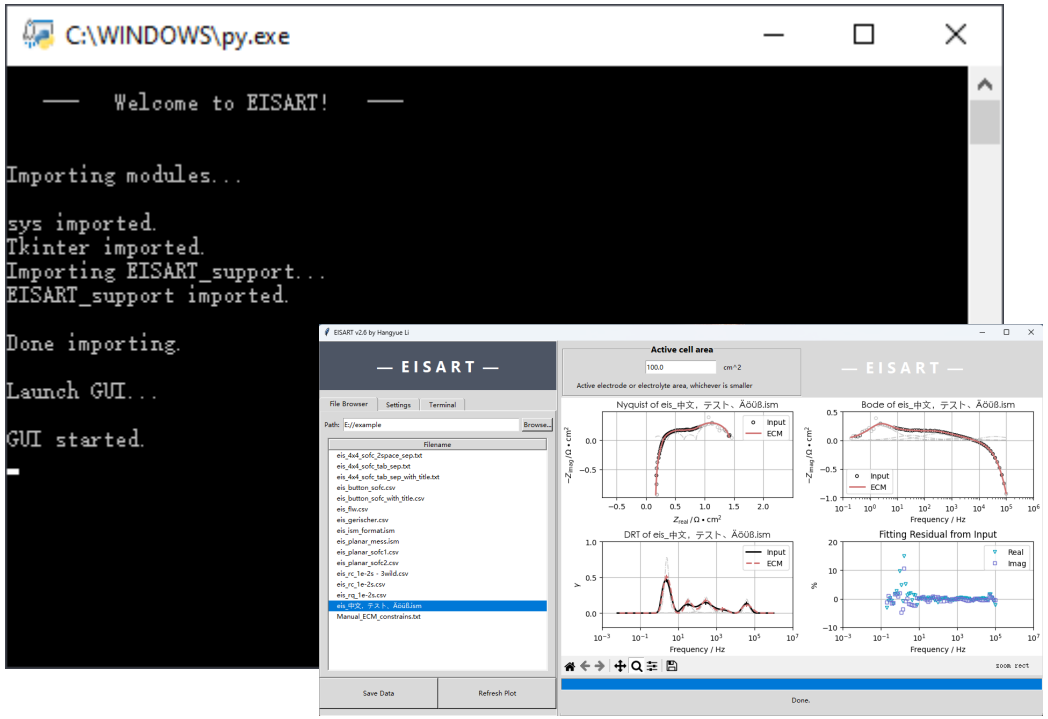
1.3 Using the GUI

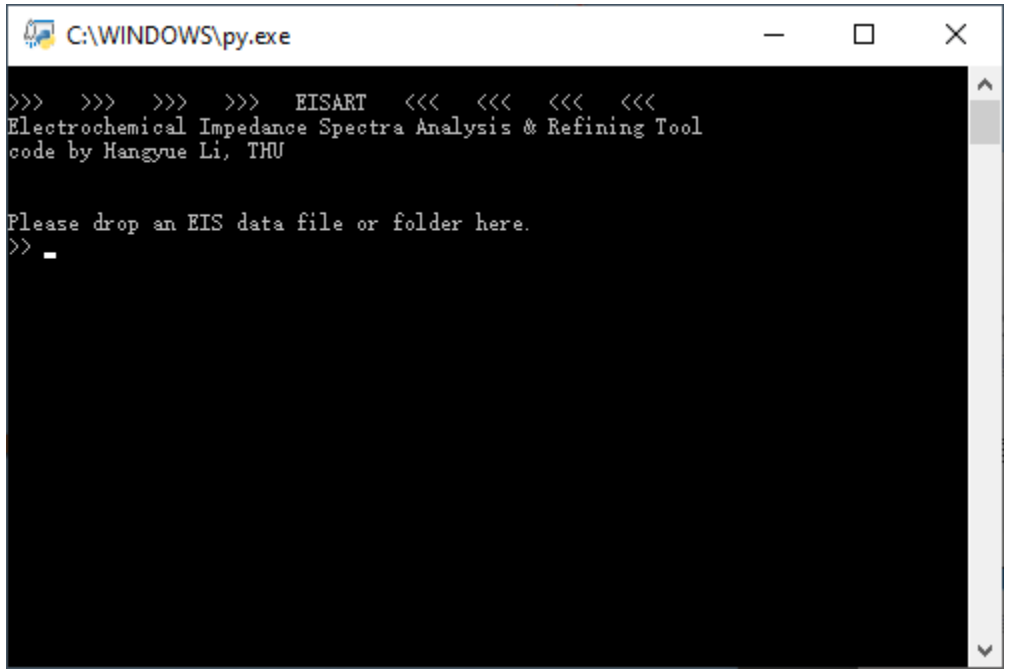




Besides the GUI, EISART has a Text User Interface (TUI) when the GUI is running. It may show valuable information for debugging.

The kernel of EISART can be launched without GUI.



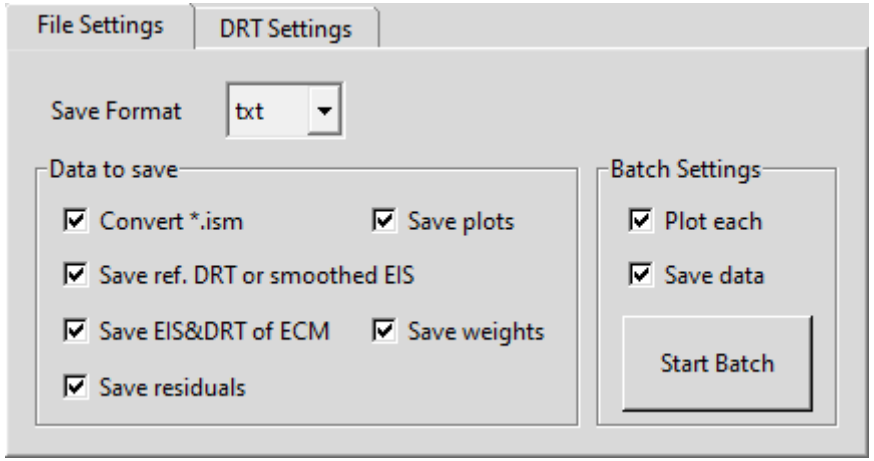


2 Settings

2.1 File and DRT Settings

File Settings:

controls visual and file output



Save Format: controls extension of the saved files, **txt** (tab separated) or **csv** (comma separated).

Data to save: controls which part of the result to save, if applicable.

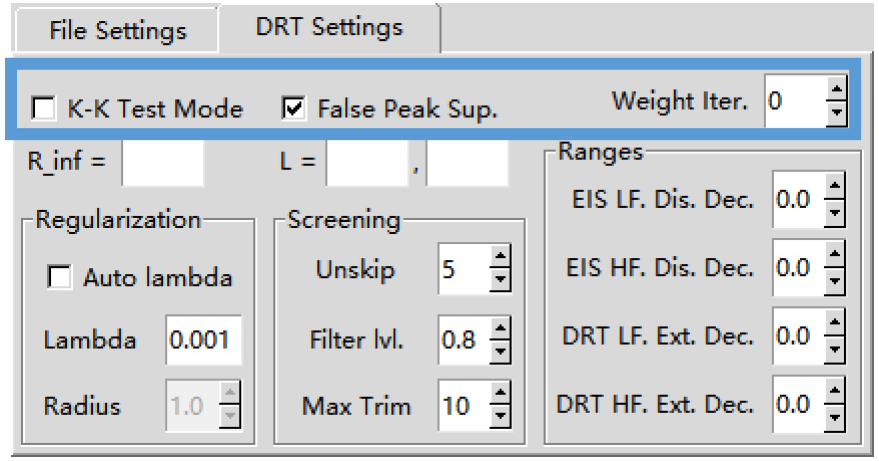
For more information, please see Output.

Batch Settings: controls visual and data output when running a batch.

2 Settings

2.1 File and DRT Settings

DRT Settings: controls how DRT is evaluated. This also affects ECM fitting



K-K Test Mode: display K-K test results. Only applicable when ECM is not fitted (otherwise K-K tests would be done but not shown). The unweighted algorithm is proposed by Schönleber et al.

False Peak Sup.: suppress possibly false peaks in DRT at the very edge of the range of relaxation time.

Weight Iter.: re-weighting iteration count. Weights are updated according to the error in weighted K-K tests.

Regularization: control options for Tikhonov regularization in DRT evaluation.

Screening: control options for EIS data screening (downweighing “bad” data points).

Ranges: ranges for evaluated frequencies in EIS data and relaxation time in DRT.

2 Settings

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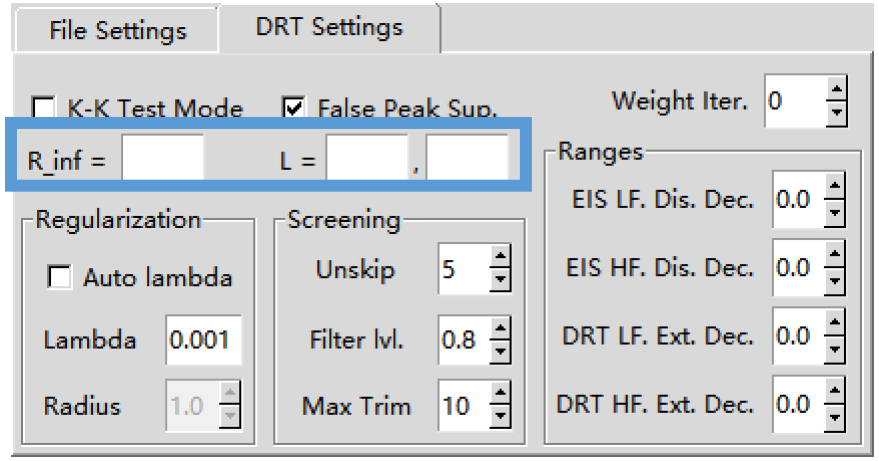
DRT Settings: controls how DRT is evaluated. This also affects ECM fitting



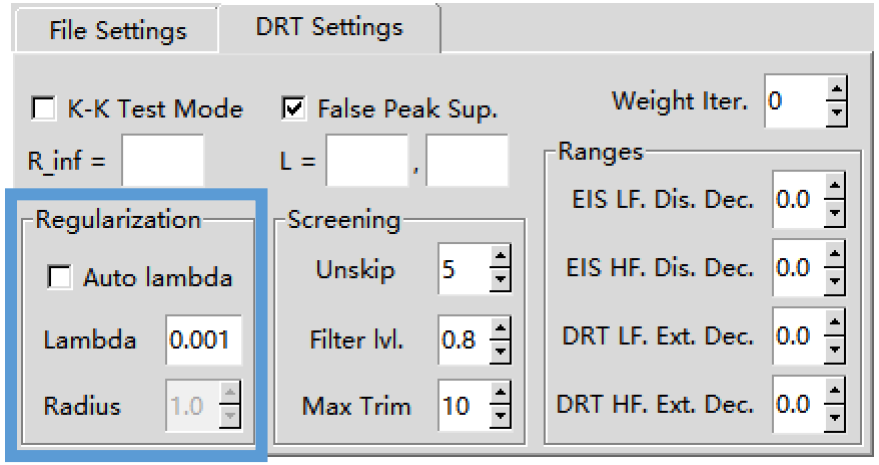
R_inf = : user-specified R_inf or ohmic resistance in $\Omega \cdot \mathrm{cm}^2$. The value you specified in this entry box will remain unchanged throughout the analysis. Leave this entry box blank if you want EISART to find R_inf for you.

L = : user-specified inductance in equivalent $\mu\mathrm{H}$. The value you specified in these two entry boxes will remain unchanged throughout the analysis. The entry box on the left stands for the self inductance of the test object and affects only the imaginary part of impedance. The entry box on the right stands for the estimated mutual induction effect between current cables and voltage wires, and affects only the real part of impedance. Leave any of or both the entry boxes if you want EISART to find L for you.

2 Settings

2.1 File and DRT Settings

DRT Settings: controls how DRT is evaluated. This also affects ECM fitting



Regularization: control options for Tikhonov regularization in DRT evaluation. Lambda (λ) is the **regularization parameter** for all frequencies in the input EIS.

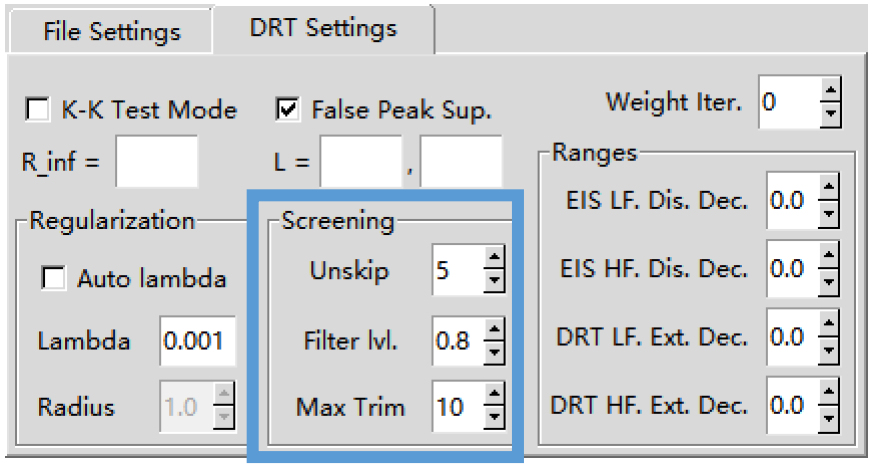
If **Auto lambda** is enabled, lambda may increase for frequencies in the input EIS data with lower weights. This option may **reduce the resolution** of DRT, but increase the **robustness** of DRT result **to disturbances** in the input EIS data.

If auto lambda is NOT enabled, the recommended value for **lambda** is 0.001, for a balance of DRT resolution and variance for input EIS noise level of ±0.5%. If the **noise level is higher**, larger lambda is recommended.

2 Settings

2.1 File and DRT Settings

DRT Settings: controls how DRT is evaluated. This also affects ECM fitting



Screening: control options for EIS data screening (downweighing "bad" data points).

The input EIS data is examined **point-wise** by the screener. The screener checks for the "worst" data point, downweigh it if it meets the screening rules, and then move to the next point. The screener terminate screening if the next data point is "good enough".

Unskip defines the minimum number of points to be examined by the screener. This may cause the screener to ignore terminating signals and examining more points, but not necessarily trim more.

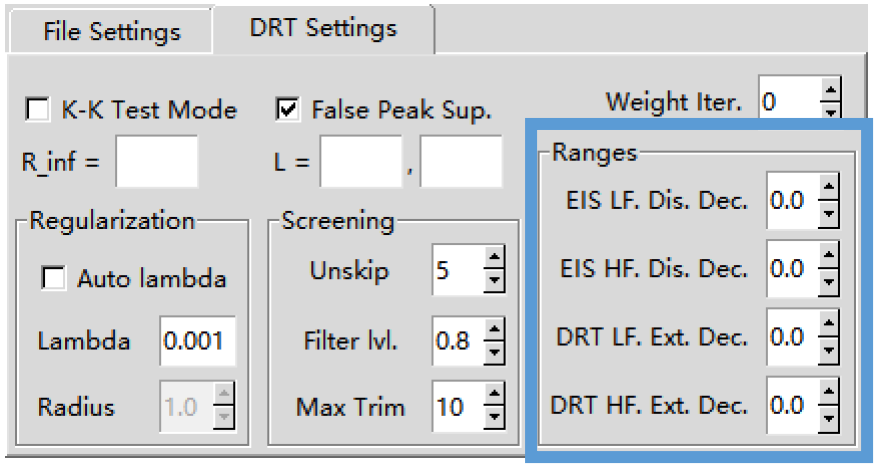
Filter level (**Filter lvl**.) defines the screening rules that tells the screener whether to move to the next data point or terminate. The higher this value, the more likely data points are treated as bad points.

Max Trim defines the maximum number of EIS data points to be trimmed by the data quality filter. This may override Unskip.

2 Settings

2.1 File and DRT Settings

DRT Settings: controls how DRT is evaluated. This also affects ECM fitting



Ranges: ranges for evaluated frequencies in EIS data and relaxation time in DRT.

EIS LF. Dis. Dec.: number of decades to be discarded in the low-frequency end of the input EIS data. Use this when the low-frequency end of EIS data is of poor quality.

EIS HF. Dis. Dec.: number of decades to be discarded in the high-frequency end of the input EIS data. Use this when the high-frequency end of EIS data is of poor quality.

DRT LF. Ext. Dec.: number of decades of the lowest frequencies / longest taus in DRT extended beyond the analyzed EIS frequency range. Recommended values are below 1.0

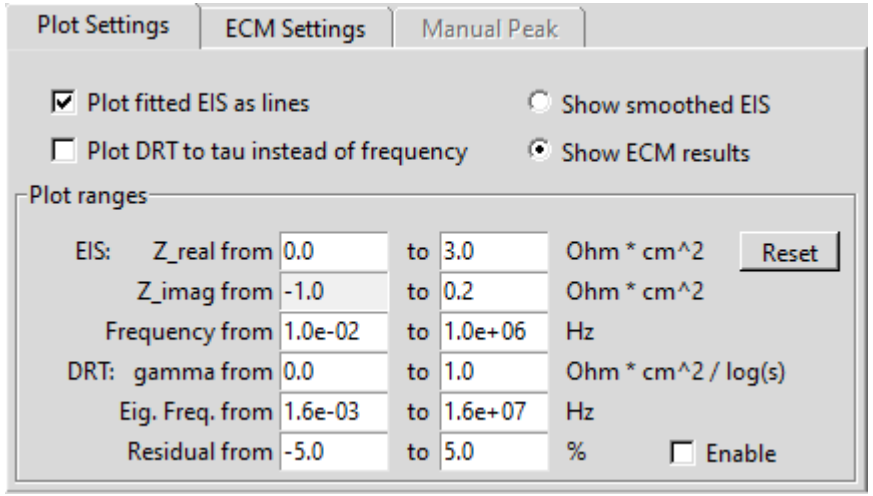
DRT HF. Ext. Dec.: number of decades of the highest frequencies / shortest taus in DRT extended beyond the analyzed EIS frequency range. Recommended values are below 1.0

2 Settings

2.2 Plot and ECM Settings

Plot Settings:

Controls the workflow and plot options



Plot ranges controls the range to show in the plots. If not enabled, the ranges are automatically determined.

Plot settings

Plot fitted EIS as lines:

(Fig. 1)

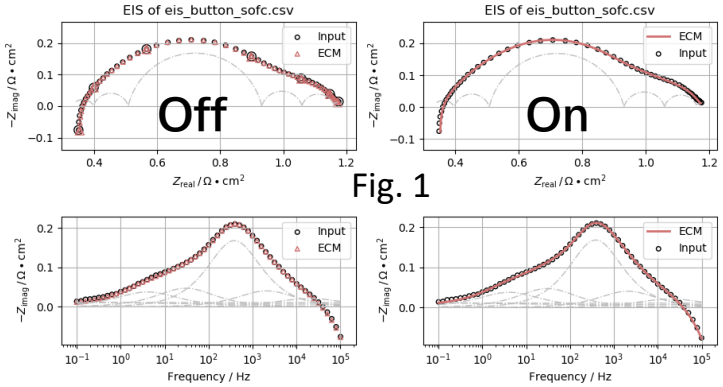


Fig. 1

Plot DRT to tau instead of frequency: this also updates the GUI

(Fig. 2)

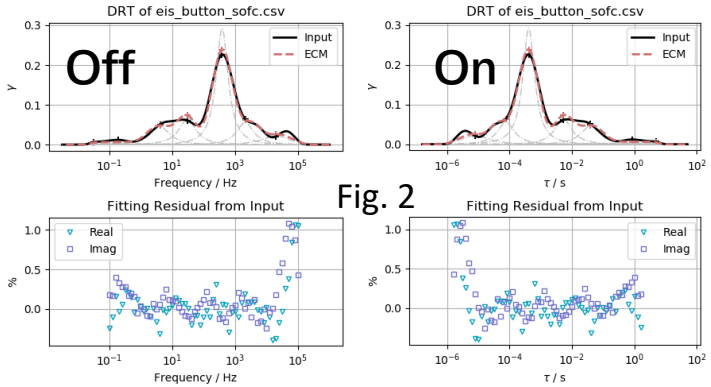


Fig. 2

Show smoothed EIS:

(Fig. 3)

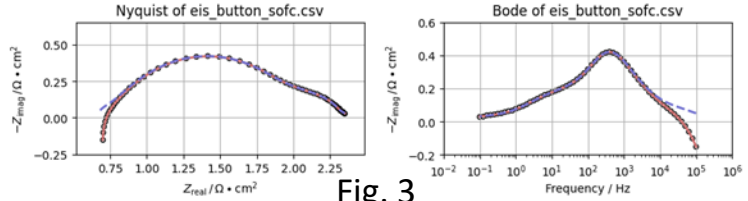
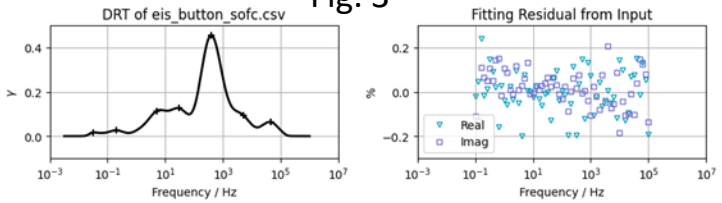


Fig. 3

Show ECM results ↓

(as is shown in Fig. 1 and Fig. 2)

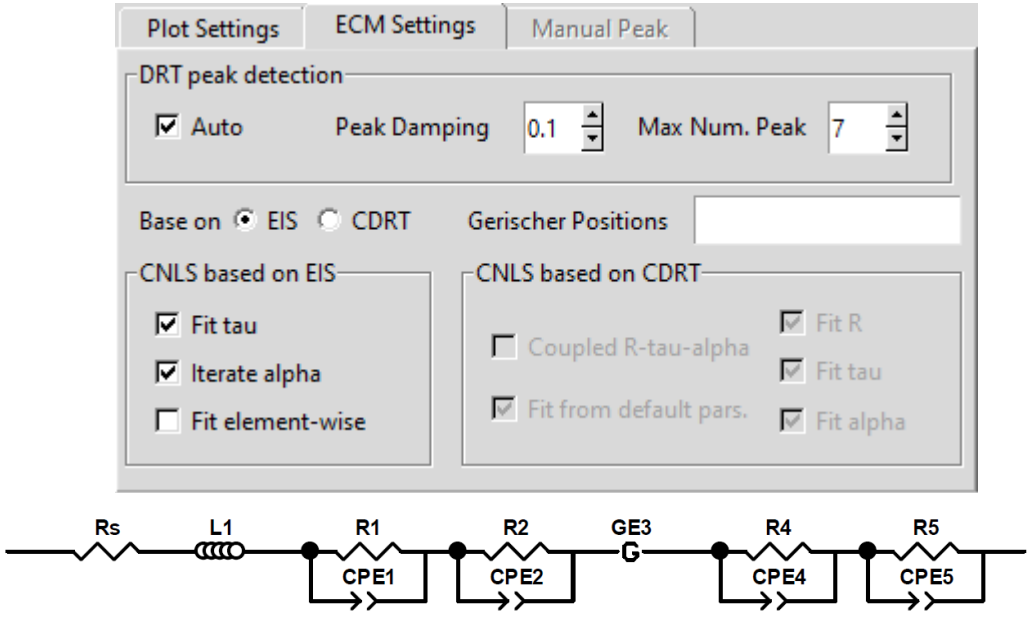


2 Settings

2.2 Plot and ECM Settings

ECM Settings:

Controls ECM fitting process



ECM Settings: settings for fitting an ECM, only usable when "Show ECM results" in Plot Settings is selected.

DRT peak detection: how the peaks in DRT are detected for ECM.

Auto: automatically detect the peaks.

Peak Damping: how sensitive the detector to peaks is.

Max Num. Peak: the maximum number of peaks to be detected.

Based on: whether to minimize the fitting results according to EIS or cumulative DRT (cDRT or CDRT). Fitting to CDRT is only recommended if all peaks are blurred (short and wide).

Gerischer Positions: the positions of RQ elements to be replaced with Gerischers.

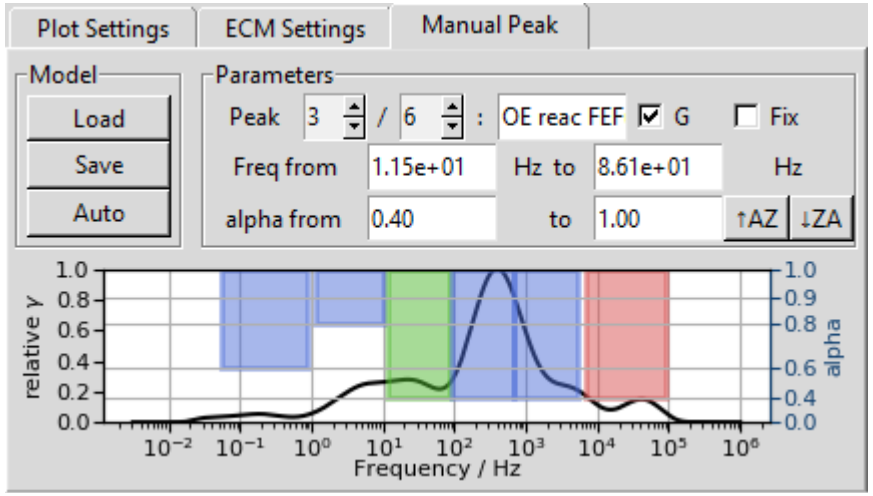
CNLS based on EIS / CDRT: options for complex nonlinear least squares (CNLS) fitting. Please see the hints in the GUI.

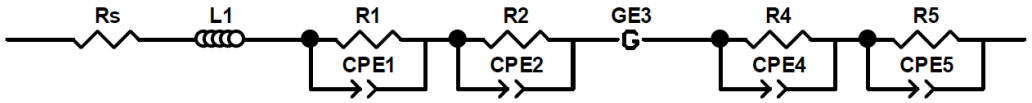
2 Settings

2.2 Plot and ECM Settings

Manual Peak:

Controls manual peak / ECM constrains.





Manual Peak: manual peak / ECM constrain settings. This tab is only usable when **Auto** peak detection in ECM Settings is **NOT** enabled.

You may **load** ECM constrains from a file or **save** them as a file. ZView *.mdl model can be loaded here if its circuit model is compatible with EISART.

You may also let EISART **automatically** generate ECM constrains as a starting point for you.

You may **select** the peak (ECM element) you wish to view or modify, or **add** / **remove** / **sort** elements as you wish.

The constrains on peak parameters are plotted as **rectangles** on the tab in real time as you edit them.

The fitting does not adjust tau and alpha of a peak if it is **fixed** (in red), while its R may still be adjusted.

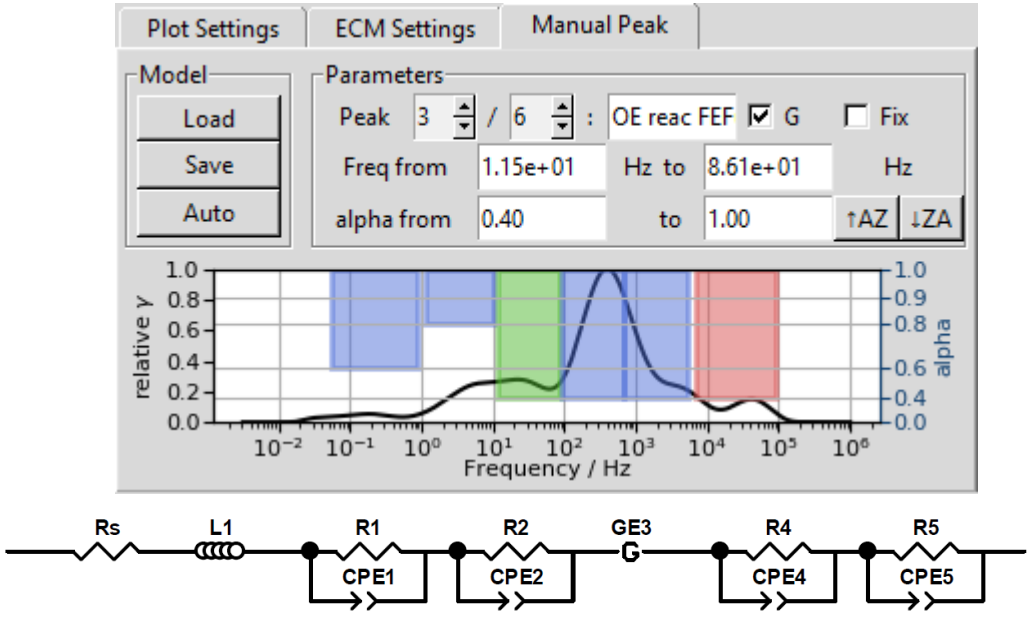
Unfixed Gerischers are plotted green, RQ elements are plotted blue.

2 Settings

2.2 Plot and ECM Settings

Manual Peak:

Controls manual peak / ECM constrains.



About the elements in ECM:

An RQ element has 3 parameters: R, tau (τ) and alpha (α)

A Gerischer has 2 parameters: R and tau (τ)

For mathematical definitions, see workflow.

R is the DC resistance of an RQ element or a Gerischer. A larger R corresponds to a larger arc in Nyquist plot and larger area below a peak in DRT.

tau is the time constant of an RQ element or a Gerischer. Varying tau corresponds to a horizontally translating peak in DRT.

alpha is the dispersion exponent of an RQ element. It ranges from 0 to 1. A smaller alpha corresponds to a flatter arc in Nyquist plot and a flatter, wider peak in DRT.

3 Input/Output File Format

3.1 Input file format

f (Hz)	real(Z)	imag(Z) (Ω)
54463	0.011942	0.002333
44954	0.012158	0.0016927
37105	0.012288	0.0010789
30627	0.012461	0.00057649
25279	0.012694	0.00012743
20866	0.012906	-0.0002106
17223	0.013127	-0.0005367
14216	0.013385	-0.00078684
11734	0.0137	-0.00094189
9685	0.013932	-0.0010762
7994	0.014161	-0.0011479
6598	0.014415	-0.0011877

For ∗.txt and ∗.csv format:

Input EIS data file should contain 3 columns with or without title:

Frequency, the real and the imaginary part of impedance.

For **∗.txt** format, columns can be separated by arbitrary many **tabs** or **white spaces**.

For **∗.csv** format, columns are separated by **commas**.

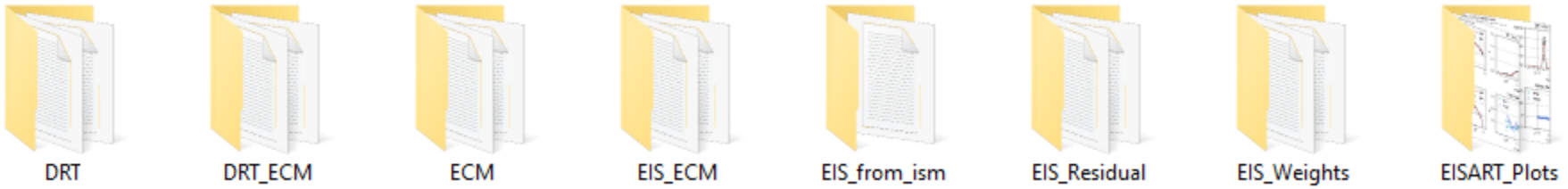
Decimal points should be **dots**.

If the unit of impedance is $\Omega \cdot \mathrm{cm}^2$, the active cell area in EISART should be $1.0\ \mathrm{cm}^2$.

∗.ism formatted binary files saved by Thales software using Zahner instruments can be directly loaded into EISART.

3 Input/Output File Format

3.2 Output: folders created by EISART



DRT: DRT results of the input EIS data — Data is marked with text

DRT_ECM: DRT results of EIS_ECM — Data is marked with text

ECM: the parameters of each element in ECM — Data is marked with text, parameter Q included, G stands for Gerischer and ∗.mdl models for ZView

EIS_ECM: the simulated EIS of ECM — Frequency, the real and the imaginary part of impedance

EIS_from_ism: original EIS data from ∗.ism files — Frequency, the real and the imaginary part of impedance

EIS_Residual: relative residual to the input data — Frequency, relative residuals of the real and the imaginary part of impedance

EIS_Weights: weights applied on the EIS data — Frequency, weights on the real and the imaginary part of impedance

EISART_Plots: plots/snapshots from EISART — As the plot displayed in the plot region in GUI, ∗.png format

Default units are: Hz for frequency, second for tau, $\Omega \cdot \mathrm{cm}^2$ for impedance, $\Omega \cdot \mathrm{cm}^2/\ln(\mathrm{second})$ for γ in DRT.

4 About

固体氧化物燃料电池实验室
Solid Oxide Fuel Cell Laboratory

EISART is developed by Hangyue Li in the research group of Prof. Minfang Han in the Department of Energy and Power Engineering, Tsinghua University, Beijing, China.

https://scholar.google.com/citations?user=p0S-PukAAAAJ&hl=zh-CN

http://www.depe.tsinghua.edu.cn/depeen/info/1035/1131.htm

https://www.researchgate.net/profile/Hangyue_Li

Algorithm & Cases: Li, Hangyue, Zewei Lyu, and Minfang Han. "Robust and Fast Estimation of Equivalent Circuit Model from Noisy Electrochemical Impedance Spectra." Electrochimica Acta (2022): 140474.

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5 References

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  https://orbit.dtu.dk/files/2369271/Electrochemical%20characterisation%20and%20performance%20evaluation.pdf
- K-K Test: M. Schönleber et al. (2014), Electrochimica Acta vol.131, pages20-27
- DRT: https://ciucci.org/project/drt/

  DRTtools: T. Wan et al. (2015), Electrochimica Acta, vol.184, pages483-499

  Hyper λ: Effat et al. (2017), Electrochimica Acta, vol.247, pages1117-1129
- ECM:

  RQ element (http://www.consultrsr.net/resources/eis/zarc.htm) Gerischer (http://www.consultrsr.net/resources/eis/gerischer.htm)