Documentation of the DRTtools

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Table of Content

1. Introduction

DRTtools is a MATLAB GUI that allows users to analyze electrochemical impedance spectroscopy (EIS) data with the distribution of relaxation time (DRT). The computation of the DRT is based on Tikhonov regularization with continuous functions discretization. The DRTtools package implements including linear and radial basis functions (RBFs). A snapshot of the DRTtools GUI is shown below:

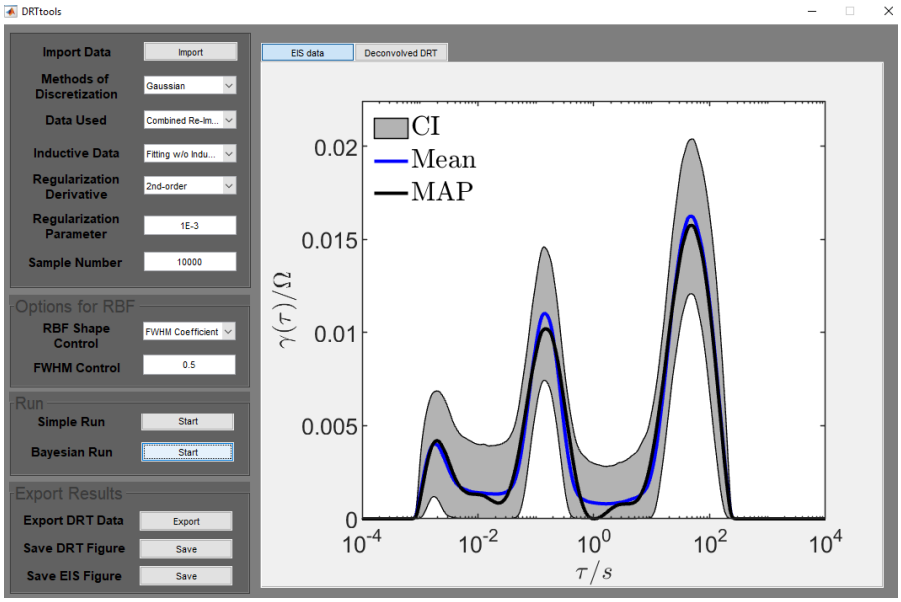


Figure 1

To launch DRTtools, the user should **run the DRTtools.m file** in MATLAB. The user should note that Optimization Toolbox is needed for executing DRTtools.

When results generated by DRTtools are used for academic purposes, the user should cite the following reference:

[1] T.H. Wan, M. Saccoccio, C. Chen, F. Ciucci, Influence of the Discretization Methods on the Distribution of Relaxation Times Deconvolution: Implementing Radial Basis Functions with DRTtools, Electrochimica Acta, 184 (2015) 483-499.

The user is encouraged to read and cite other related articles from our group. A list of related references is included in section 6 of this document. The user can also refer to the Github of our group:

https://github.com/ciuccislab

for other codes developed for analyzing data from electrochemical experiments.

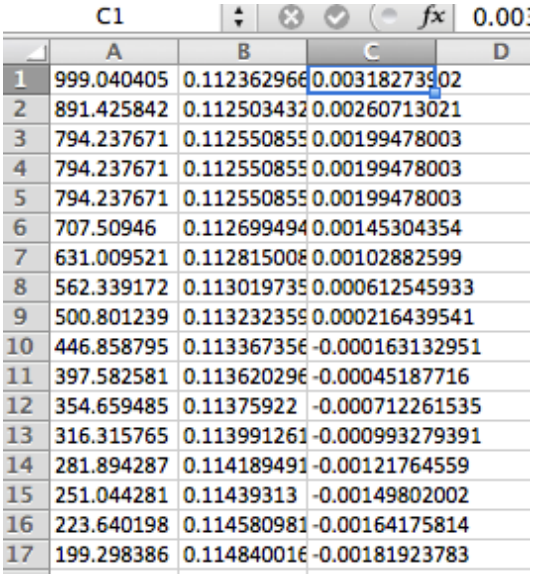
2. Basic Options

In the Basic Options panel, users can import their EIS data and select their DRT computation preferences. The basic options include the methods of discretization, part of data for computation and the regularization parameter λ.

2.1 Importing Data

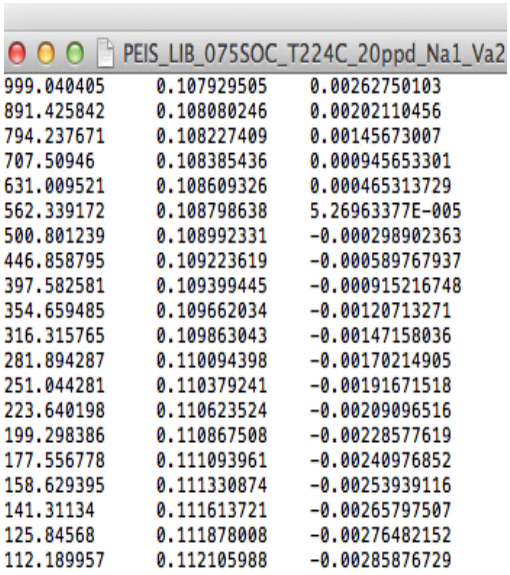
Data can be imported to DRTtools from a MATLAB file, a .csv, or a .txt file. One should click the import data button in order to import the data file. Upon clicking import button, the file management panel will open, allowing the user to find his/her file. The .csv and .txt file to be imported should have 3 columns. From left to right, the first column should correspond to the frequency data. The second column should be the real part of the EIS data. The third column should be the imaginary part of the EIS data. Here in Figure 2, you can find examples of .csv and .txt files.

(a)



	A	B	C	D
1	999.040405	0.112362966	0.003182739	02
2	891.425842	0.112503432	0.00260713021	
3	794.237671	0.112550855	0.00199478003	
4	794.237671	0.112550855	0.00199478003	
5	794.237671	0.112550855	0.00199478003	
6	707.50946	0.112699494	0.00145304354	
7	631.009521	0.112815008	0.00102882599	
8	562.339172	0.113019735	0.000612545933	
9	500.801239	0.113232359	0.000216439541	
10	446.858795	0.113367356	-0.000163132951	
11	397.582581	0.113620296	-0.00045187716	
12	354.659485	0.11375922	-0.000712261535	
13	316.315765	0.113991261	-0.000993279391	
14	281.894287	0.114189491	-0.00121764559	
15	251.044281	0.11439313	-0.00149802002	
16	223.640198	0.114580981	-0.00164175814	
17	199.298386	0.114840016	-0.00181923783	

(b)



PEIS_LIB_075SOC_T224C_20ppd_Na1_Va2

999.040405	0.107929505	0.00262750103
891.425842	0.108080246	0.00202110456
794.237671	0.108227409	0.00145673007
707.50946	0.108385436	0.000945653301
631.009521	0.108609326	0.000465313729
562.339172	0.108798638	5.26963377E-005
500.801239	0.108992331	-0.000298902363
446.858795	0.109223619	-0.000589767937
397.582581	0.109399445	-0.000915216748
354.659485	0.109662034	-0.00120713271
316.315765	0.109863043	-0.00147158036
281.894287	0.110094398	-0.00170214905
251.044281	0.110379241	-0.00191671518
223.640198	0.110623524	-0.00209096516
199.298386	0.110867508	-0.00228577619
177.556778	0.111093961	-0.00240976852
158.629395	0.111330874	-0.00253939116
141.31134	0.111613721	-0.00265797507
125.84568	0.111878008	-0.00276482152
112.189957	0.112105988	-0.00285876729

Figure 2

The decimal mark for the imported .txt file can either be a dot or a comma. If the user wishes to import a .mat file, the data should be saved as three separate vectors, “freq” (frequency data), “Z_prime” (real part of the EIS data) and “Z_double_prime” (imaginary part of the EIS data).

Moreover, it is highly recommended that the frequency data is equally spaced in logarithm scale so as to reduce computational effort. Also, the data should be arranged in such a way that the frequencies are in descending order in order to prevent computational problems. After importing, the EIS data will be plotted in a complex plot as follow:

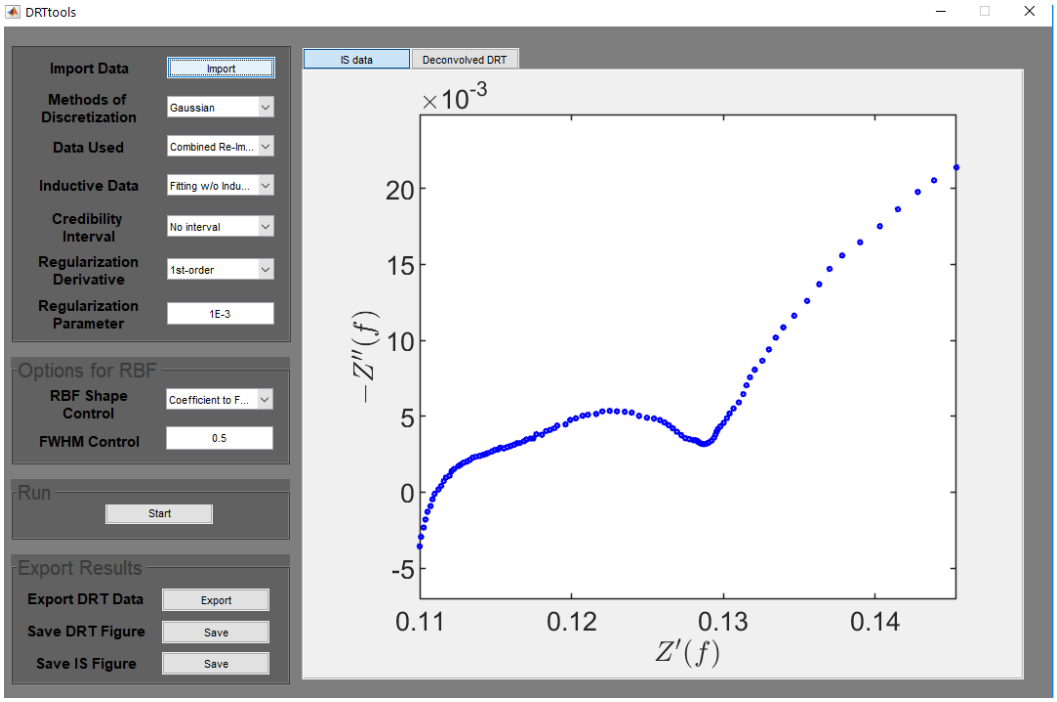


Figure 3

2.2 Discretization

Users can choose a suitable method for the discretization using the scroll down menu. The available discretization method includes piecewise linear discretization and RBF discretization. For the piecewise linear discretization,

$$\phi_m(\tau) = \begin{cases} 1 - \dfrac{\ln\tau - \ln\tau_m}{\ln\tau_{m-1} - \ln\tau_m}, & \tau_{m-1} < \tau \le \tau_m \\ 1 - \dfrac{\ln\tau - \ln\tau_m}{\ln\tau_{m+1} - \ln\tau_m}, & \tau_m < \tau \le \tau_{m+1} \\ 0, & \tau_{m-1} < \tau \text{ or } \tau_{m+1} > \tau \end{cases}$$

where τ_m is the relaxation time of the m^{th} collocation point. For RBF discretization, users are allowed to choose among Gaussian, C^2 Matérn, C^4 Matérn, C^6 Matérn, Cauchy, inverse quadric, and inverse quadratic functions. The available RBFs option for discretization are listed below:

Function	$\phi_\mu(x)$
Gaussian	$\exp(-(\mu x)^2)$
C^2 Matérn	$\exp(-\lvert\mu x\rvert)\,(1+\lvert\mu x\rvert)$
C^4 Matérn	$\exp(-\lvert\mu x\rvert)\left(1+\lvert\mu x\rvert+\frac{1}{3}\lvert\mu x\rvert^2\right)$
C^6 Matérn	$\exp(-\lvert\mu x\rvert)\left(1+\lvert\mu x\rvert+\frac{2}{5}\lvert\mu x\rvert^2+\frac{1}{15}\lvert\mu x\rvert^3\right)$
Inverse Quadratic	$1/(1+(\mu x)^2)$
Inverse Quadric	$1/\sqrt{1+(\mu x)^2}$
Cauchy	$1/(1+\lvert\mu x\rvert)$

where $x = \left|\ln\tau - \ln\tau_m\right|$. Gaussian function is set as the default discretization function.

2.3 Data Used

Users can then select which part of the EIS data, either real part (Re data), imaginary part (Im data), or both real and imaginary part together (Combined Re-Im data), will be used for the computation of the DRT. The Combined Re-Im is set as the default option.

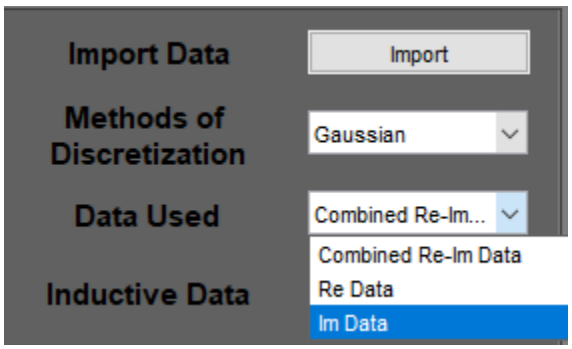


Figure 4

2.4 Inductance

There are three options for treating the inductive features: 1) fitting without inductance; 2) fitting with inductance; and 3) discarding inductive data (i.e. $\mathrm{im}\, Z > 0$).

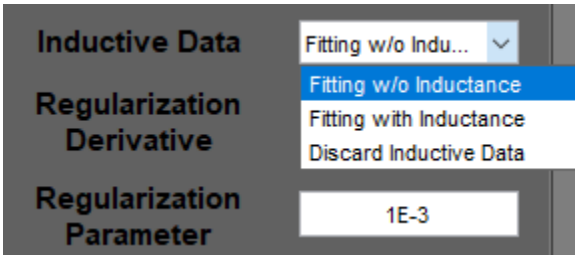


Figure 5

Option 1 corresponds to the situation of fitting the EIS data with the following DRT model:

$$Z_{\mathrm{DRT}} = R_{\infty} + \int_{-\infty}^{\infty} \frac{\gamma(\ln \tau)}{1 + i2\pi f\tau} d\ln \tau$$

where R_{∞} is the Ohmic resistance, and $\gamma(\ln \tau)$, the DRT, is a suitable function that describes the time relaxation characteristics of the electrochemical system studied.

Option 2 corresponds to fitting the EIS data with an inductive element. In other words, we fit the EIS data with the following model:

$$Z_{\mathrm{DRT}} = R_{\infty} + i2\pi fL + \int_{-\infty}^{\infty} \frac{\gamma(\ln \tau)}{1 + i2\pi f\tau} d\ln \tau$$

where the additional term, $i2\pi fL$, denotes the contribution of an inductance L.

Moreover, users can also discard all the inductive data, i.e., EIS data with positive imaginary part, using option 3.

2.5 Regularization Derivative

The user can choose the order of the derivative used in the penalties. If the 1st order derivative is chosen, the norm of the first order derivative of $\gamma(\ln \tau)$, i.e. $\left\| \frac{d\gamma(\ln \tau)}{d\ln \tau} \right\|^2$ is used as a penalty. When 2nd order derivative is chosen, the norm of the second order derivative of $\gamma(\ln \tau)$, i.e. $\left\| \frac{d^2\gamma(\ln \tau)}{d\ln \tau^2} \right\|^2$ is used as a penalty.

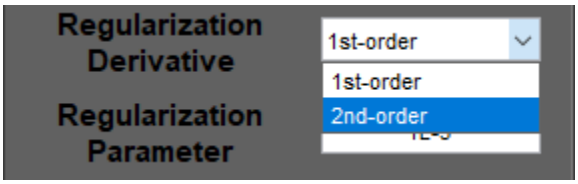


Figure 6

2.6 Regularization Parameter

This step allows the user to select the regularization parameter λ. Higher the λ value, stronger the penalty to the sum of squares for fitting, which results in smoother DRT profile. On the other hand, smaller the λ value, stronger the oscillation of the DRT profile is.

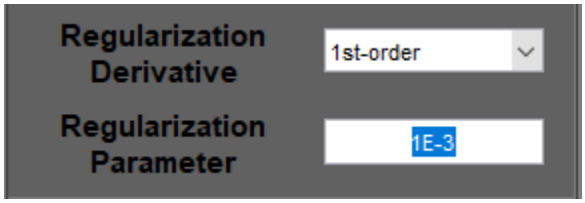


Figure 7

2.7 Sample Number

During the Bayesian run, samples are drawn from a truncated Gaussian distribution function in order to compute the credibility interval (see section 4.2). The user can choose the total number of sample drawn during the Bayesian run. The larger the sample number, the more accurate the credibility interval is at the expense of time. The sampling would not start if the total number of sample is less than 1000.

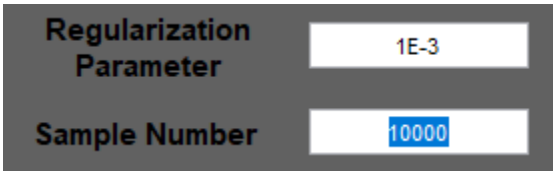


Figure 8

3. Options for Radial Basis Functions Discretization

For all RBF discretizations, the user can customize the shape of the RBF. In particular, there are two options provided for the shape control of the RBF with respect to its: 1) FWHM coefficient and 2) Shape factor. By choosing "FWHM coefficient", the full width half maximum (FWHM) of the RBF is $1/m$ times the average relaxation time spacing in logarithm scale, *i.e.,*

$$\text{FWHM} = \frac{\Delta \ln \tau}{m}$$

where m is the FWHM coefficient. The m value can be entered at the editable space next to the "FWHM control" label.

Alternatively, the user may select the "Shape Factor" option, such that he/she may specify the μ value in the discretization function directly (see the table 1). The μ value can be entered at the editable space next to the "FWHM control" label. The higher μ value, the wider the discretization functions are.

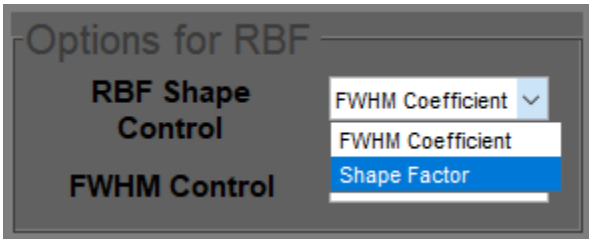


Figure 9

The shape control is set to be "FWHM coefficient" with the magnitude of 0.5 as default. In other words, the default FWHM of the discretization basis equals to two times to that of the average relaxation time spacing.

4. Run

There are two types of computation for DRTtools: 1) the Simple run and 2) Bayesian run. For simple run, the DRT is computed based on ridge regression. For the Bayesian run, in additional to the result from ridge regression, the credibility interval is also computed based on Bayesian statistics.

4.1 Simple Run

The basic DRT computation starts when the "Start" button next to the "Simple Run" label is pressed. Generally, it takes a few second for the computation complete, which depends on the number of data point of the EIS, and whether the frequency data points are equally spaced in logarithm scale.

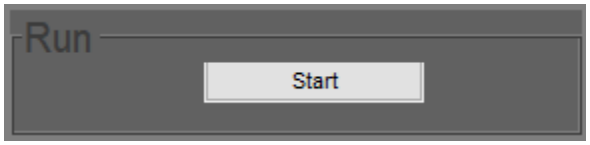


Figure 10

DRTtools provides a flag in the top right corner indicating that the computation is running:

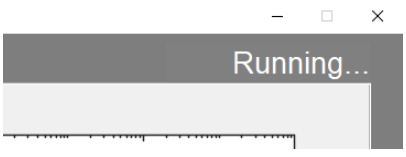


Figure 11

When the computation is finished, the graphic panel on the right of the panel will be updated as follow:

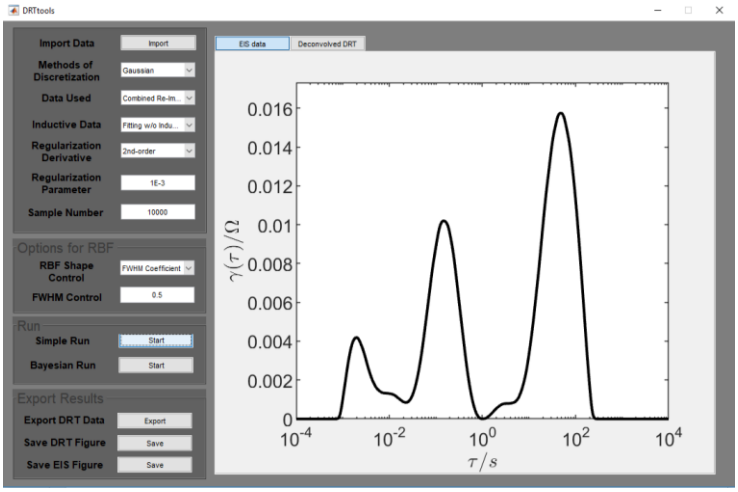


Figure 12

Due to the property of the piecewise linear discretization, the $\gamma(\tau)$ is not interpolated between the collocation points. Also, the $\gamma(\tau)$ curve is truncated at the maximum and the minimum relaxation time and will not extrapolate out of the range, as that of the radial basis function based discretization does. This is shown below:

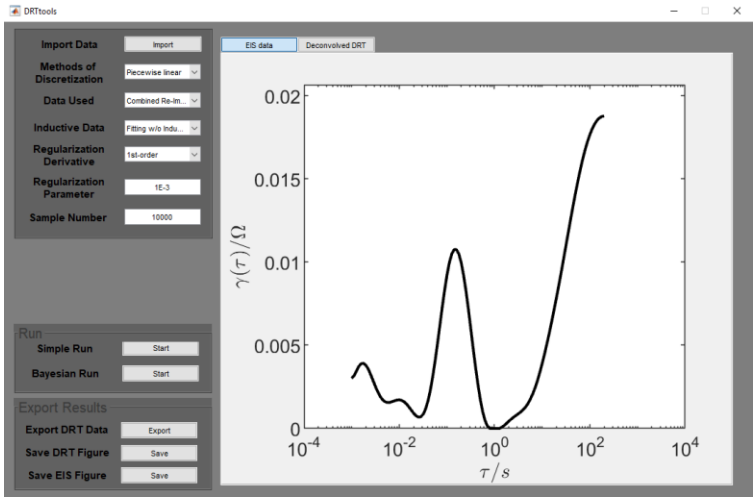


Figure 13

4.2 Bayesian Run

Alternatively, if the user would like to compute the credibility interval of the DRT, he/she may click the “Start” button next to the “Bayesian Run” label. The computation of credibility interval is based on the work of Ciucci and Chen (2015) and Effat and Ciucci (2017). The credibility

interval is computed by averaging the Bayesian DRT. Samples are drawn from a truncated Gaussian probability distribution function of the form of:

$$p(\boldsymbol{x}) \propto \mathbb{1}(\boldsymbol{x} \geq 0) \exp\left(-\frac{1}{2}(\boldsymbol{x}-\boldsymbol{\mu})^{\mathrm{T}}\boldsymbol{\Sigma}^{-1}(\boldsymbol{x}-\boldsymbol{\mu})\right)$$

where $\boldsymbol{x}$ is the vector of $\gamma(\tau)$, $\boldsymbol{\mu}$ is the mean, and $\boldsymbol{\Sigma}$ is the covariance matrix. The sampling is done with a Hamiltonian Monte Carlo sampler. For more details, interested users can refer to the work of Effat and Ciucci (2017).

If the credibility interval function is used for academic works, the user should cite the following two paper additionally:

[2] F. Ciucci, C. Chen, Analysis of Electrochemical Impedance Spectroscopy Data Using the Distribution of Relaxation Times: A Bayesian and Hierarchical Bayesian Approach, Electrochimica Acta, 167 (2015) 439-454.

[3] M.B. Effat, F. Ciucci, Bayesian and Hierarchical Bayesian Based Regularization for Deconvolving the Distribution of Relaxation Times from Electrochemical Impedance Spectroscopy Data, Electrochimica Acta, 247 (2017) 1117-1129.

The user should note that sampling for the computation of the credibility interval takes extra times compared to the simple run. The time required for computation and the width of the credibility interval reduces if one chooses to use 2nd order derivatives and a larger regularization parameter for regularization. The user can also track the sampling progress on the MATLAB command window, as shown below:

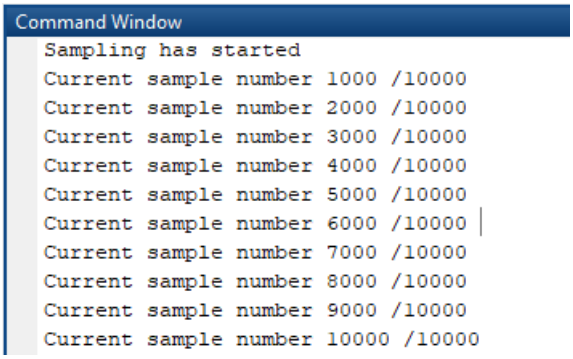


Figure 14

When the computation is finished, the graphic panel on the right of the panel will be updated as follow:

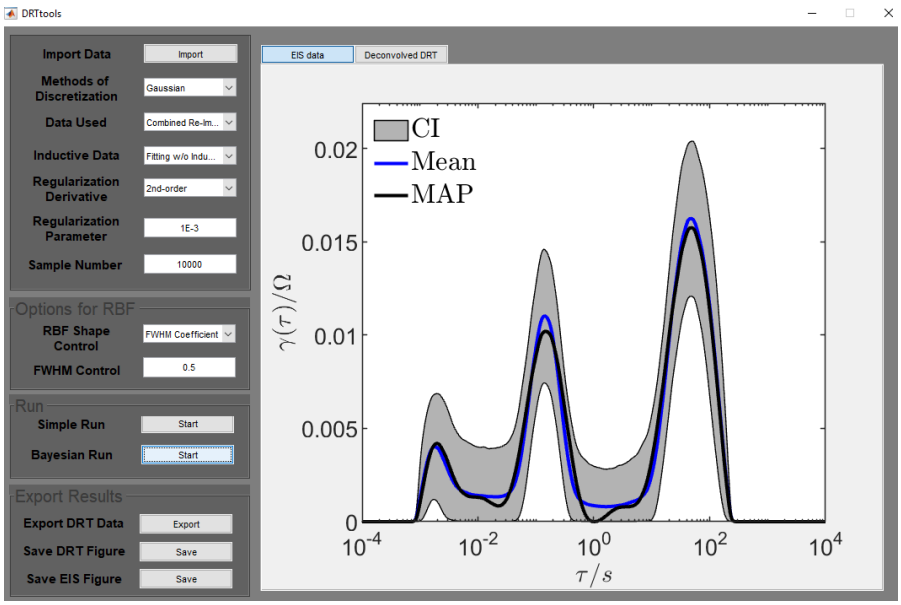


Figure 15

where the black line is the Maximum-a-Posteriori (MAP) DRT, blue line is the mean DRT and the gray region denote the 99% credibility interval.

5. Exporting the Results

5.1 Export DRT Data

The user can export the $\gamma(\tau)$ data and save the EIS and DRT figures. One may select the file type, either .csv file or .txt file.

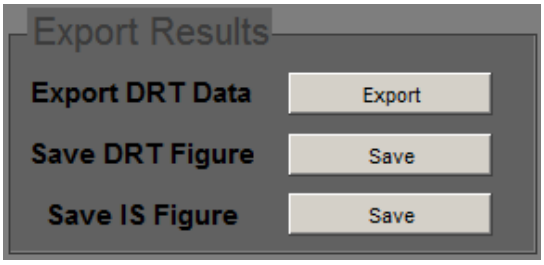


Figure 16

Upon selecting the file type, the file management panel opens. The user can find his/her preference saving directory.

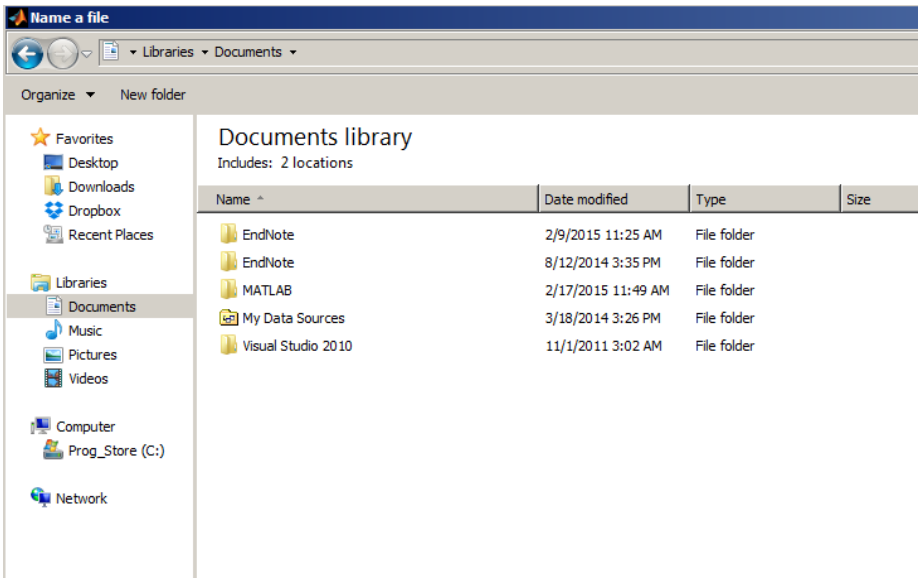
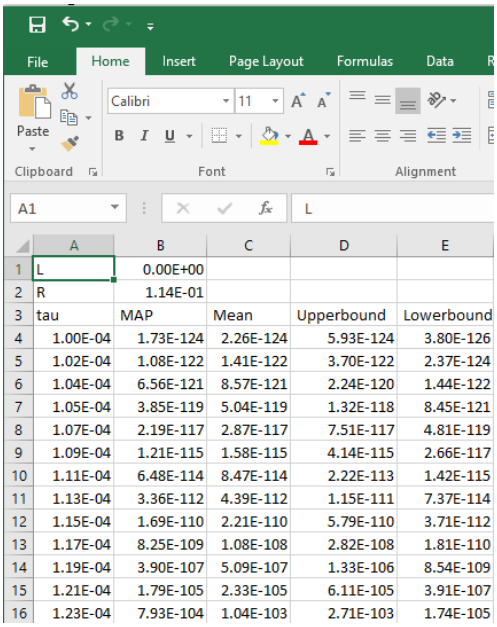


Figure 17

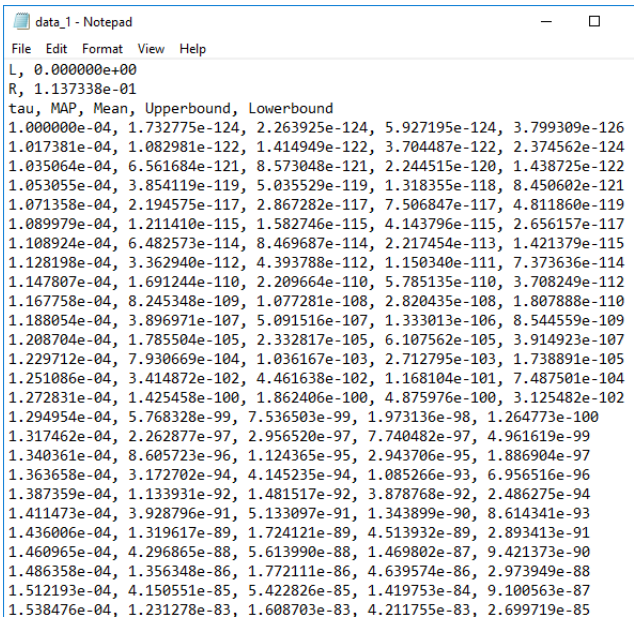
The first two rows of the saved set correspond to the fitted value of Ohmic resistance R_∞ and inductance L. The rows under the resistance and inductance are the DRT results. The first column has the obtained τ values and the second column corresponds to the computed $\gamma(\tau)$. If the credibility interval is computed, the second column has the MAP DRT result, the third column has the mean DRT, the third and fourth columns corresponds to the upper bound and the lower bound of the 99% credibility interval.

(a)



	A	B	C	D	E
1	L	0.00E+00			
2	R	1.14E-01			
3	tau	MAP	Mean	Upperbound	Lowerbound
4	1.00E-04	1.73E-124	2.26E-124	5.93E-124	3.80E-126
5	1.02E-04	1.08E-122	1.41E-122	3.70E-122	2.37E-124
6	1.04E-04	6.56E-121	8.57E-121	2.24E-120	1.44E-122
7	1.05E-04	3.85E-119	5.04E-119	1.32E-118	8.45E-121
8	1.07E-04	2.19E-117	2.87E-117	7.51E-117	4.81E-119
9	1.09E-04	1.21E-115	1.58E-115	4.14E-115	2.66E-117
10	1.11E-04	6.48E-114	8.47E-114	2.22E-113	1.42E-115
11	1.13E-04	3.36E-112	4.39E-112	1.15E-111	7.37E-114
12	1.15E-04	1.69E-110	2.21E-110	5.79E-110	3.71E-112
13	1.17E-04	8.25E-109	1.08E-108	2.82E-108	1.81E-110
14	1.19E-04	3.90E-107	5.09E-107	1.33E-106	8.54E-109
15	1.21E-04	1.79E-105	2.33E-105	6.11E-105	3.91E-107
16	1.23E-04	7.93E-104	1.04E-103	2.71E-103	1.74E-105

(b)



```
data_1 - Notepad
File  Edit  Format  View  Help
L, 0.000000e+00
R, 1.137338e-01
tau, MAP, Mean, Upperbound, Lowerbound
1.000000e-04, 1.732775e-124, 2.263925e-124, 5.927195e-124, 3.799309e-126
1.017381e-04, 1.082981e-122, 1.414949e-122, 3.704487e-122, 2.374562e-124
1.035064e-04, 6.561684e-121, 8.573048e-121, 2.244515e-120, 1.438725e-122
1.053055e-04, 3.854119e-119, 5.035529e-119, 1.318355e-118, 8.450602e-121
1.071358e-04, 2.194575e-117, 2.867282e-117, 7.506847e-117, 4.811860e-119
1.089979e-04, 1.211410e-115, 1.582746e-115, 4.143796e-115, 2.656157e-117
1.108924e-04, 6.482573e-114, 8.469687e-114, 2.217454e-113, 1.421379e-115
1.128198e-04, 3.362940e-112, 4.393788e-112, 1.150340e-111, 7.373636e-114
1.147807e-04, 1.691244e-110, 2.209664e-110, 5.785135e-110, 3.708249e-112
1.167758e-04, 8.245348e-109, 1.077281e-108, 2.820435e-108, 1.807888e-110
1.188054e-04, 3.896971e-107, 5.091516e-107, 1.333013e-106, 8.544559e-109
1.208704e-04, 1.785504e-105, 2.332817e-105, 6.107562e-105, 3.914923e-107
1.229712e-04, 7.930669e-104, 1.036167e-103, 2.712795e-103, 1.738891e-105
1.251086e-04, 3.414872e-102, 4.461638e-102, 1.168104e-101, 7.487501e-104
1.272831e-04, 1.425458e-100, 1.862406e-100, 4.875976e-100, 3.125482e-102
1.294954e-04, 5.768328e-99, 7.536503e-99, 1.973136e-98, 1.264773e-100
1.317462e-04, 2.262877e-97, 2.956520e-97, 7.740482e-97, 4.961619e-99
1.340361e-04, 8.605723e-96, 1.124365e-95, 2.943706e-95, 1.886904e-97
1.363658e-04, 3.172702e-94, 4.145235e-94, 1.085266e-93, 6.956516e-96
1.387359e-04, 1.133931e-92, 1.481517e-92, 3.878768e-92, 2.486275e-94
1.411473e-04, 3.928796e-91, 5.133097e-91, 1.343899e-90, 8.614341e-93
1.436006e-04, 1.319617e-89, 1.724121e-89, 4.513932e-89, 2.893413e-91
1.460965e-04, 4.296865e-88, 5.613990e-88, 1.469802e-87, 9.421373e-90
1.486358e-04, 1.356348e-86, 1.772111e-86, 4.639574e-86, 2.973949e-88
1.512193e-04, 4.150551e-85, 5.422826e-85, 1.419753e-84, 9.100563e-87
1.538476e-04, 1.231278e-83, 1.608703e-83, 4.211755e-83, 2.699719e-85
```

Figure 18

One should note that when the piecewise linear discretization is used, the total number of computed $\gamma(\tau)$ data points is equal to the number of EIS frequencies. On the other hand, when the radial basis function discretization is used, the total number of computed $\gamma(\tau)$ data points is 10 times the number of EIS data points used, with τ_{max} being one order of magnitude larger than that of $1/f_{min}$; τ_{min} being one order of magnitude smaller than that of $1/f_{max}$.

5.2 Save Figure

The user can also save the as-computed result by pressing the "Save" button. Upon pressing the button, the file management panel will open, which allows the user to select his/her preferred directory.

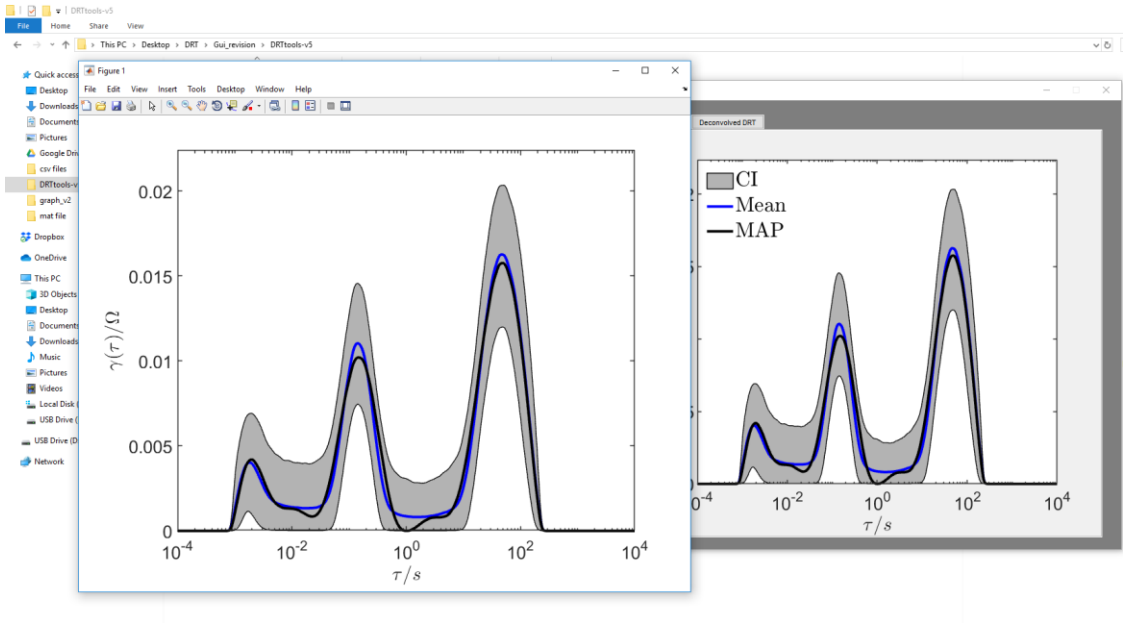


Figure 19

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