Documentation of the DRTtools

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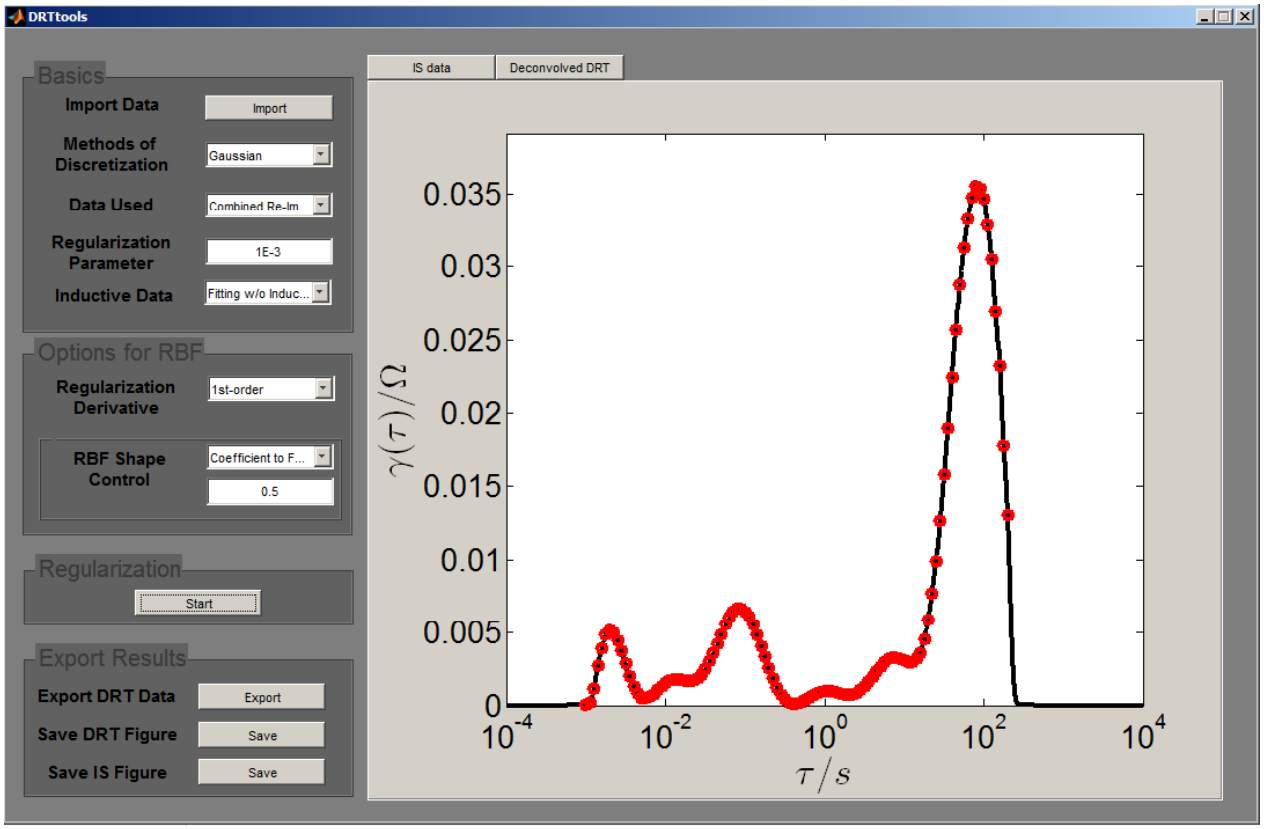
1. Introduction

DRTtools is a MATLAB GUI that allow user to interpreting the impedance spectroscopy data via distribution of relaxation time (DRT). The computation of the DRT is based on Tikhonov regularization with continuous functions discretization, including piecewise linear basis and radial basis functions basis. The outlook of the DRTtools is shown below:



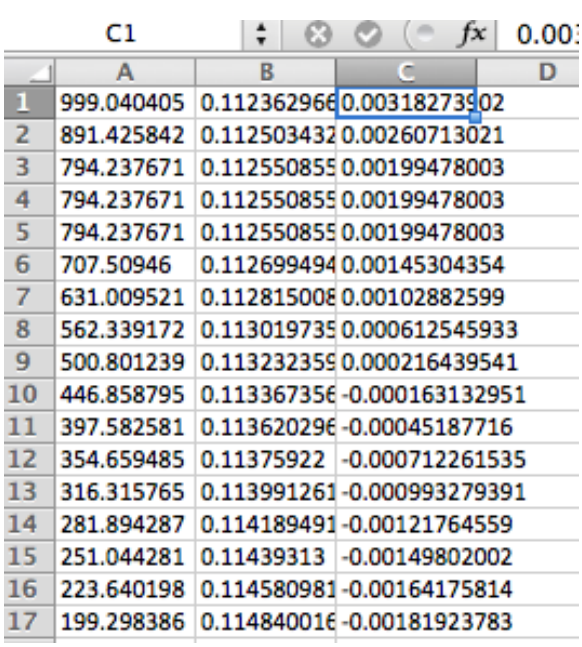
To launch the DRTtools, the user should run the DRTtools.m file in matlab. The user should notice that Optimization Toolbox is needed for the execution of DRTtools.

2. Basic Options

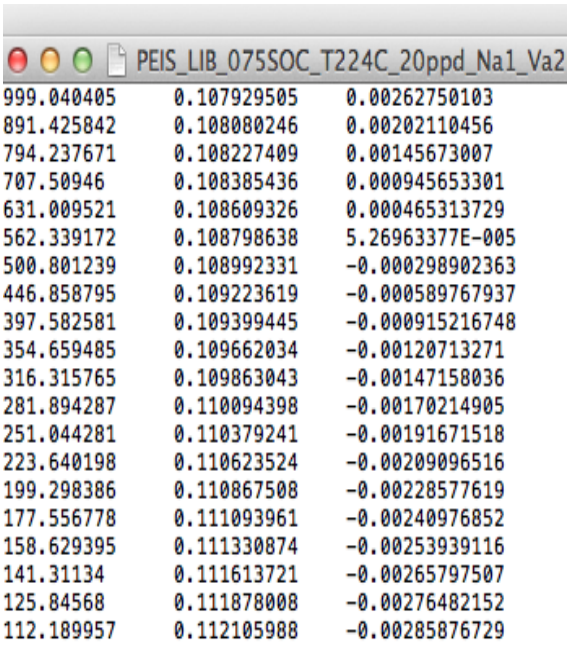
In the Basic Options panel, users are allowed to import their EIS file and select their preference for the DRT computation. The basic options include the methods of discretization, part of data for computation and the regularization parameter λ.

Importing Data

Data can be imported to DRTTOOL from a matlab file, a csv or a txt file. One should select the file type on the scroll down table. Upon selecting, the file management panel open, which allow the user to find his file. For the csv file and the txt file, the import files should have 3 columns. From left to right, the first column should consist of the frequency data. The second column consists of the real part of the impedance data. The third column consists of the imaginery part of the impedance data. Here is the example of one csv file and a text one.



	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	

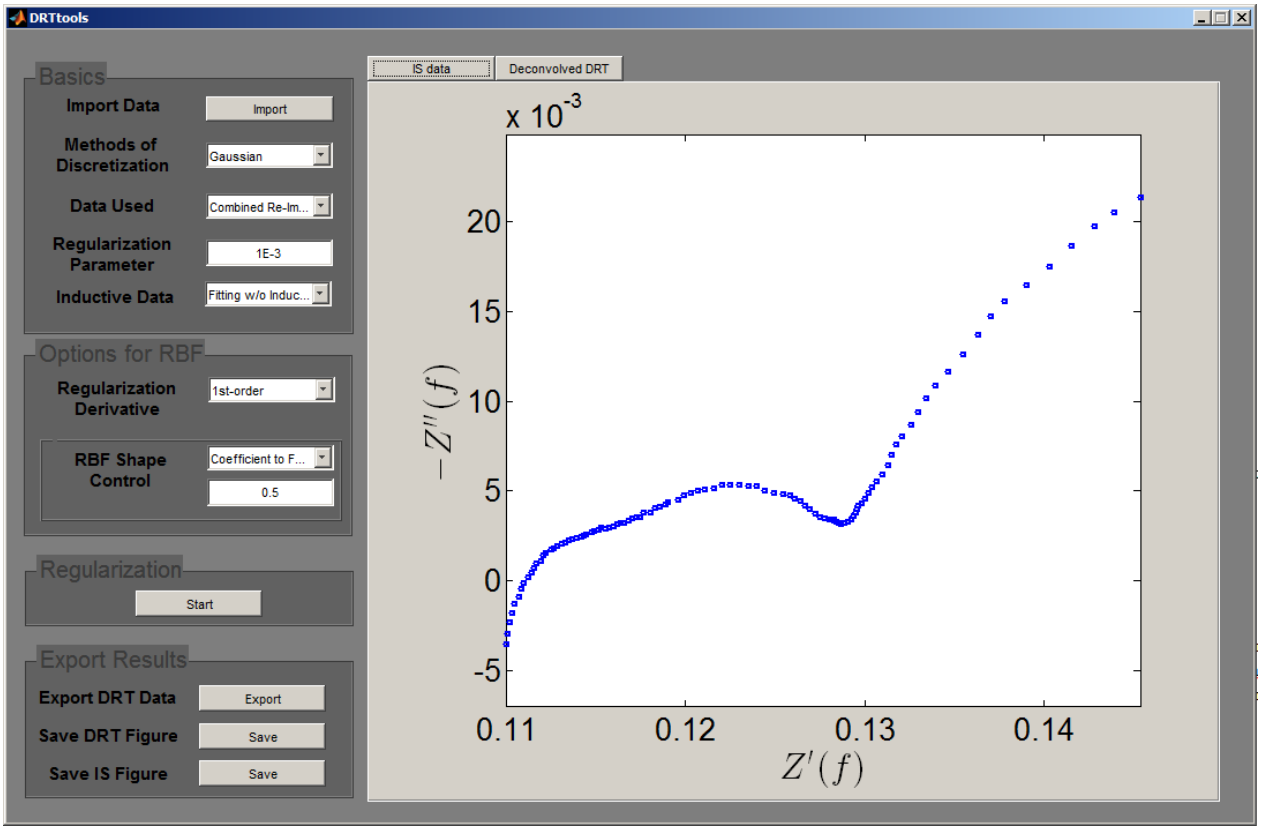


PEIS_LIB_075SOC_T224C_20ppd_Na1_Va2

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

One should notice that the decimal mark for the imported txt file can either be a dot or a comma. If user would like to import a mat file, the data should be saved in three vectors, "freq", "Z_prime" and "Z_double_prime", each of the vectors possess frequency data, real part of the impedance data and imaginary part of the impedance data respectively.

Nonetheless, it is highly recommend that the frequency data is equally spaced in logarithm scale so as to reduce computational effort. Also, the data should be arranged in a way such that frequency is in descending order in order to prevent any computational problems. Upon importing, the IS data will be plotted in a complex plot as follow:


DRTtools
Basics
Import Data
Import
Methods of Discretization
Gaussian
Data Used
Combined Re-Im...
Regularization Parameter
1E-3
Inductive Data
Fitting w/o Induc...
Options for RBF
Regularization Derivative
1st-order
RBF Shape Control
Coefficient to F...
0.5
Regularization
Start
Export Results
Export DRT Data
Export
Save DRT Figure
Save
Save IS Figure
Save
IS data
Deconvolved DRT
x 10^-3
20
15
10
5
0
-5
0.11
0.12
0.13
0.14
$-Z''(f)$
$Z'(f)$

Discretization Methods

Users can choose a suitable method of discretization using the scroll down menu. The available discretization method includes piecewise linear discretization and radial basis function discretization. For the piecewise linear discretization:

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

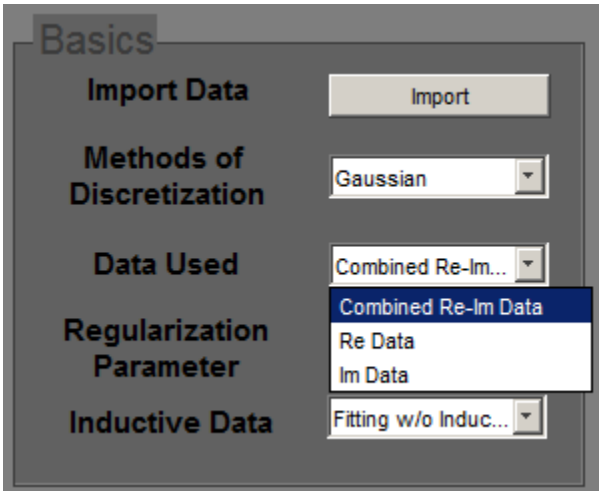
where $\tau_m$is relaxation time of the m^{th} collocation points. For radial basis function discretization, users are allowed to choose among Gaussian function, C2_Matern function, C4_Matern function, C6_Matern function, Cauchy function, inverse quadric function and inverse quadratic function. The radial basis functions for the discretization are shown below:

	$\phi_\mu(x)$
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.

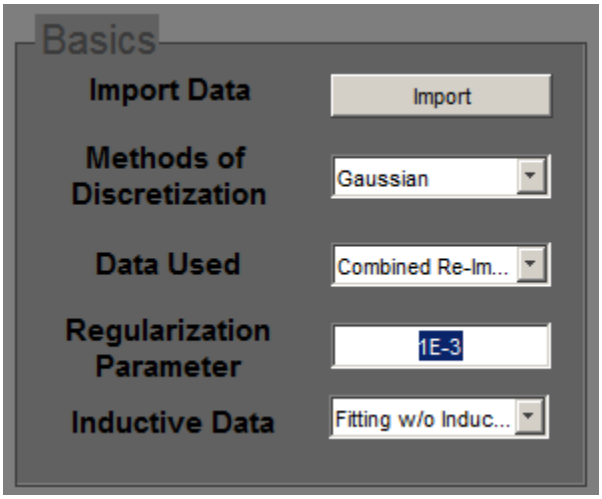
Data Applied

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



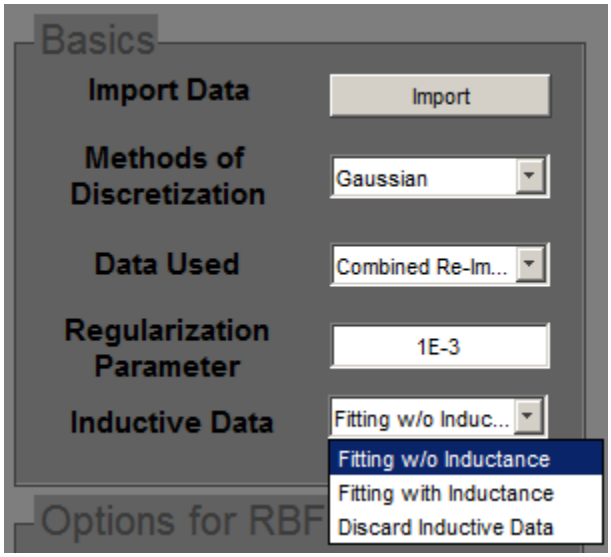
Regularization Parameter

This step allows the user 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.



Inductive Data Treatment

There are three options for the inductive data treatment: 1) fitting without inductance, 2) fitting with inductance and 3) discard inductive data.



Option 1 corresponds to the typical situation of fitting the impedance 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 $\gamma(\ln \tau)$ is a suitable function that describes the time relaxation characteristics of the electrochemical system studied.

Option 2 corresponds to fitting the impedance data with the inductance effect being considered. In other word, we fit the impedance 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, $i2\pi fL$, denote the contribution of inductance L to the impedance.

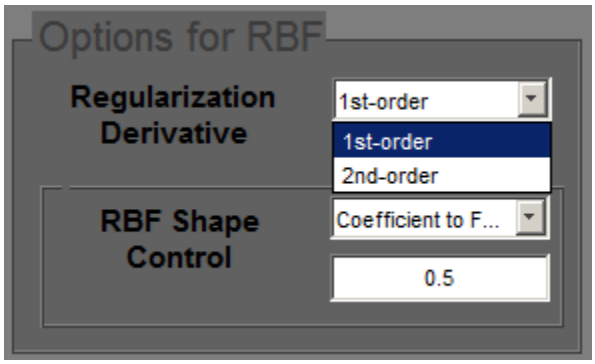
Moreover, user can also discard all the inductive data, i.e. impedance data points with positive imaginary part, by option 3.

3. Options for radial basis functions basis discretization:

For all types of discretization except the piecewise linear discretization, user are allowed to have two extra options: the regularization derivative and the shape of the radial basis function.

Regularization Derivative

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



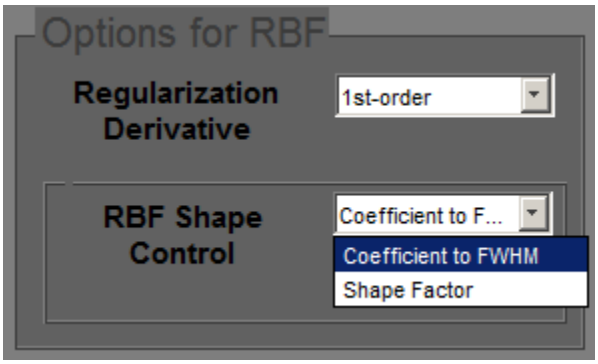
RBF shape control

To utilize the application of radial basis functions, user can adjust the shape of the radial basis function applied as discretization basis. User can adjust the full width half difference (FWHM) of the radial basis function by selecting the option, "coefficient to FWHM", and enter the magnitude m at the editable space below the scroll down table. By choosing "coefficient to FWHM", the FWHM of the radial basis function discretization basis hold the following relationship with the average relaxation time spacing in logarithm scale:

$$m(\text{FWHM}) = \Delta \ln \tau$$

If $m = 0.5$, it means that the FWHM of the discretization basis is equal to two times the average relaxation time spacing, $\Delta \ln \tau$.

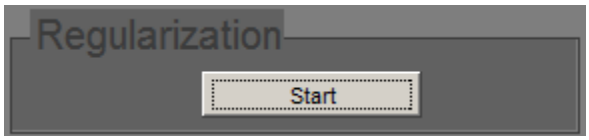
Alternatively, user may select the "Shape Factor" option, such that user may specify the magnitude of the shape factor of the radial basis function, i.e., μ in the discretization function directly. The value of μ can be entered at the editable space under the scroll down table. The higher the value of μ, the greater the (FWHM) of the discretization function is.



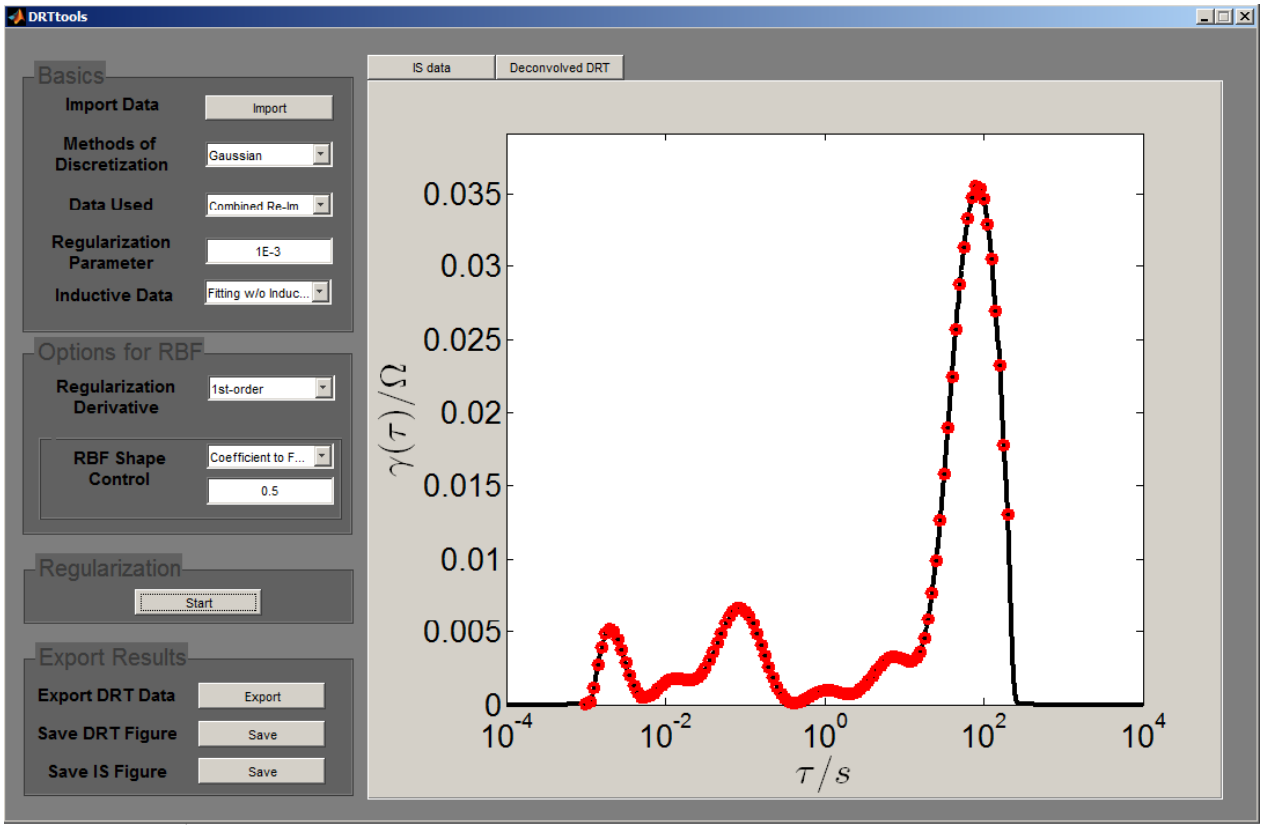
The shape control is set to be "coefficient to FWHM" with magnitude of 0.5 as default.

4. Regularizations

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

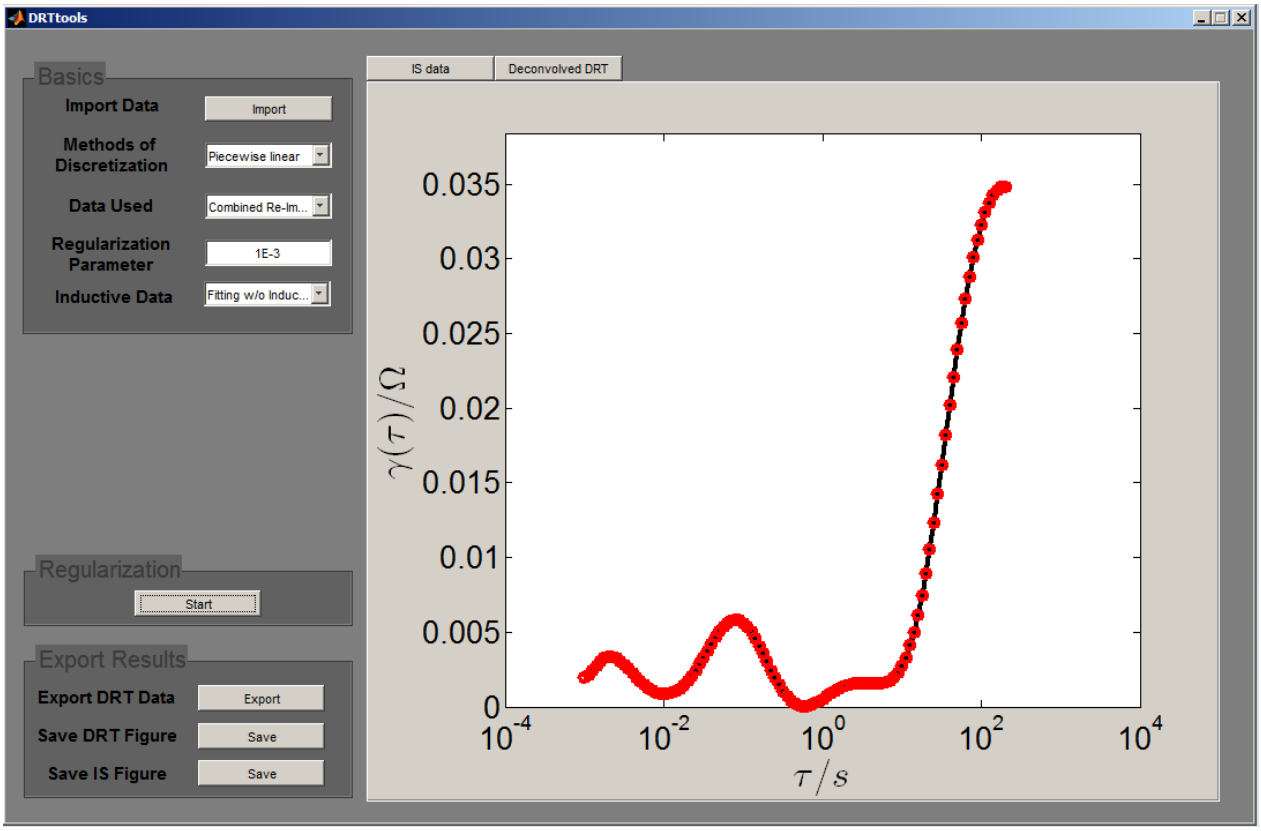


When the computation is finished, the graphic panel on the right of the panel will be updated as follow:



where the red dots denote the computed $\gamma(\tau)$ value at the collocation points (i.e. the data point of the impedance spectroscopy). The red dots appear only when radial basis function based discretization is chosen. When user chooses the piecewise linear discretization is chosen, the computed $\gamma(\tau)$ is presented with only one black line:

Due to the property of the piecewise linear discretization, the $\gamma(\tau)$ curve is truncated at the maximum and the minimum relaxation time and will not extrapolating out of the range, as that of the radial basis function based discretization does.

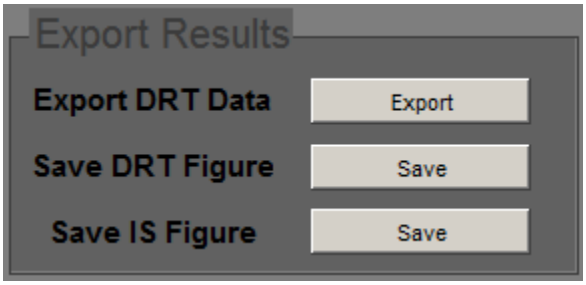


One can input another set of data or adjust the computation options, and then conduct new computation by pressing the "Start" button again.

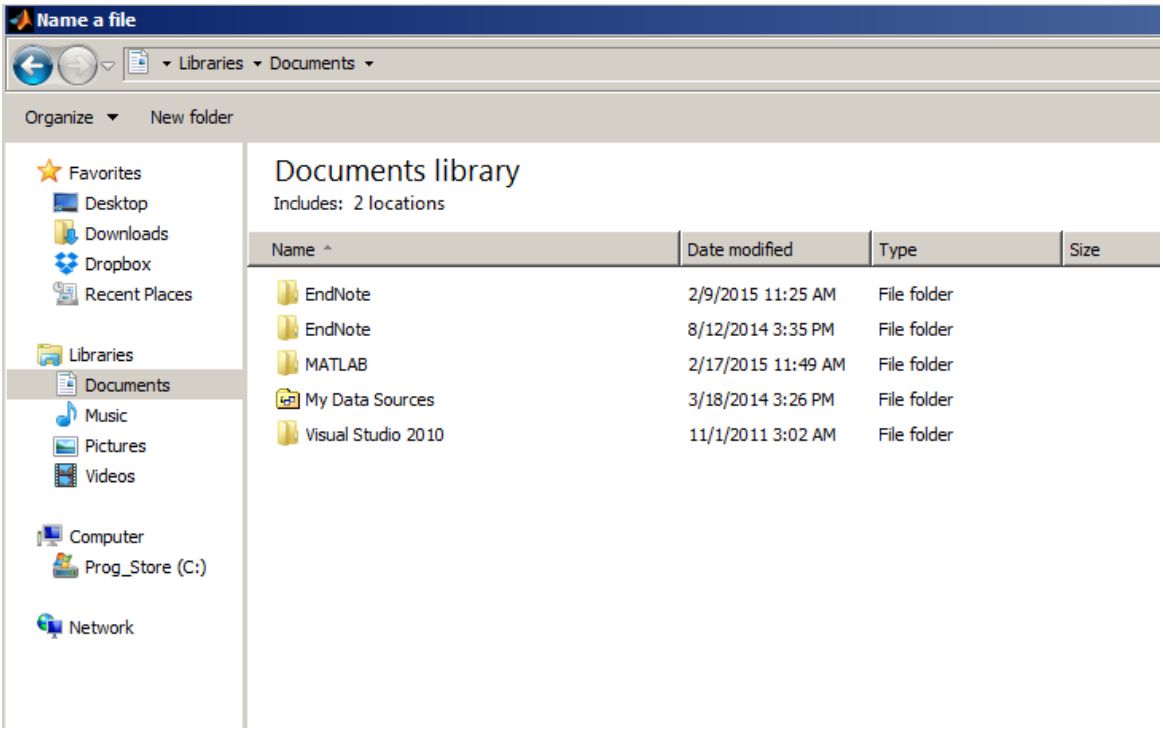
5. Export Results

Save Data

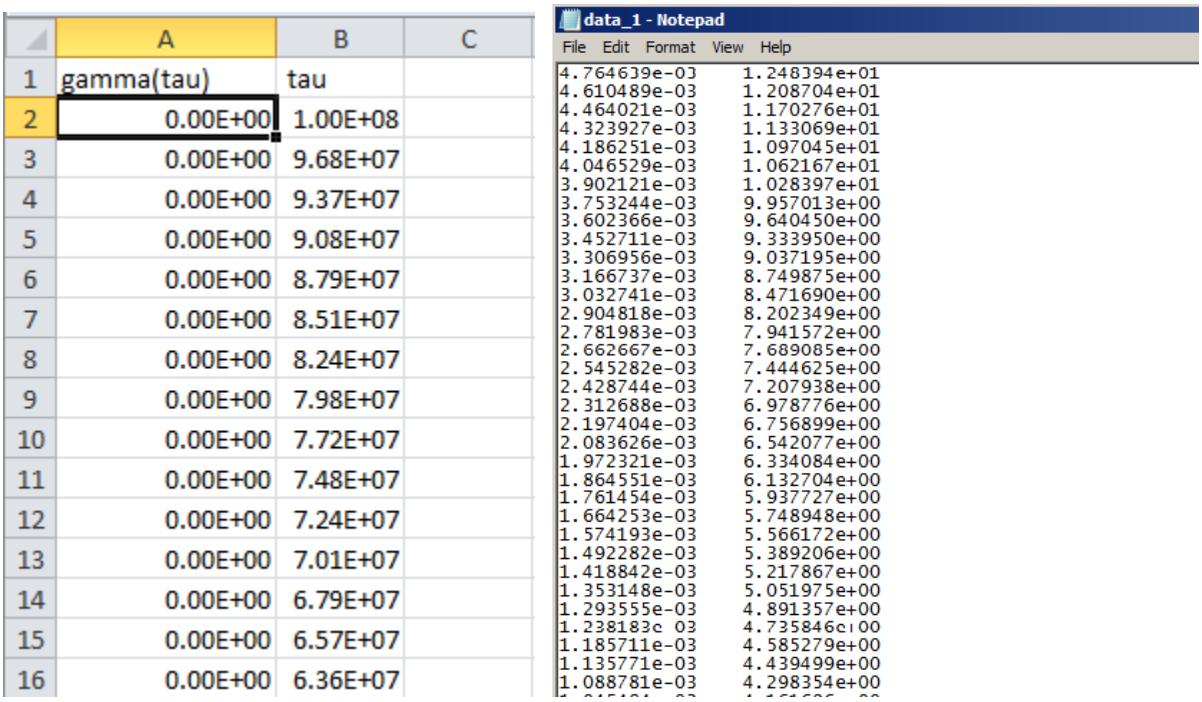
The user may export the $\gamma(\tau)$ data and save the figure for both impedance and DRT result. One may select the file type, either csv file or txt file, for saving.



Upon selecting the file type, the file management panel will open, which allows the user to find his preference directory for saving.



The saved data consist of two columns. The first two rows correspond to the fitted value of Ohmic resistance R_∞ and inductance L. The rows under the resistance and inductance are the DRT results with the first column consists of the computed $\gamma(\tau)$ and the second column is corresponding τ value.



	A	B	C
1	gamma(tau)	tau	
2	0.00E+00	1.00E+08	
3	0.00E+00	9.68E+07	
4	0.00E+00	9.37E+07	
5	0.00E+00	9.08E+07	
6	0.00E+00	8.79E+07	
7	0.00E+00	8.51E+07	
8	0.00E+00	8.24E+07	
9	0.00E+00	7.98E+07	
10	0.00E+00	7.72E+07	
11	0.00E+00	7.48E+07	
12	0.00E+00	7.24E+07	
13	0.00E+00	7.01E+07	
14	0.00E+00	6.79E+07	
15	0.00E+00	6.57E+07	
16	0.00E+00	6.36E+07	

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

Save Figure

In addition, user can save the as computed result figure by pressing the "Save" button. Upon pressing the button, the file management panel will open, which allows the user to find his preference directory for saving. The figure being saved is in the MATLAB figure as show