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Analysis of the DRT as Evaluation Tool for EIS Data Analysis

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The Distribution of Relaxation Times (DRT) is an important analytical tool that is capable of giving initial information from Electrochemical Impedance Spectra (EIS) with respect to the number of relaxation processes occurring in the system and their corresponding relaxation frequencies. The DRT transformation with the Tikhonov regularization is used for analysis of EIS data obtained from the characterization Solid Oxide Fuel and Electrolysis Cells (SOFC/SOEC) operating at high temperatures. The effects of this transformation together with occurring pitfalls on the most commonly implemented circuit elements used to describe EIS data was investigated to gain a better understanding. The behavior of the DRT transformation as a function of the individual circuit elements is reported, the regularization parameter λ is taken as a sweep parameter to investigate its influence and optimal ranges for the selection of λ are presented.

Introduction

The evaluation of EIS data gives insightful information on the electrochemical system (1) but it also requires a lot of experience concerning the construction of an appropriate equivalent circuit model (ECM) describing them (2). Often the initialization of the equivalent circuit models causes difficulties regarding the number of elements to be selected (3). At this point, the DRT can make a decisive contribution. With its help, a suggestion can first be made for the possible number of elements to be selected on the basis of the raw impedance data. Since also this suggestion is not unique due to the used mathematical transformation by means of a RC kernel, which is known as an ill-posed problem (4-6), the DRT with the selected Tikhonov regularization shall be considered and evaluated more closely in here. The usage of DRT is not new (4-8) but it comes only as accompanying evaluation tool without further analysis on itself with few exceptions (6,8). This is the key point in the contribution. The behavior of the DRT analysis in the Tikhonov regularization is evaluated regarding the regularization parameter λ, a meaningful variation in the values of corresponding equivalent circuit elements and the recorded frequency range. To trace the impacts back to an ECM, artificial models are created where the true values are known. Depending on the complexity of the ECM even starting values for a complex non-linear least-square (CNLS) fit could be obtained from the DRT analysis. Not all elements of an ECM are directly recognizable from a DRT pattern which is what is tried to be formulated as well in this contribution.

Methodology

The most common used circuit elements are selected to set up a database of ECMs (resistance (R), constant phase element (CPE), inductance (L), finite Warburg-impedance (Ws) and Gerischer (G)). Most of the combinations are part of the patterns of ECMs used to evaluate impedance data for high-temperature SOFC/SOEC operation. The equivalent circuits are built and simulated by a self-written code in Python. For evaluation, the "RelaxIS" software is used to perform the DRT transformation. The transformation is conducted with the Tikhonov regularization and the peaks are forced to only Gaussian shape in order to possibly recover single peak data. The transformation operates into the time domain but the frequency is used as x-axis in the DRT data plots. The reason is a more direct association of the physical process to the Gaussian peaks. A flowchart of all processing steps is shown in Figure 1.

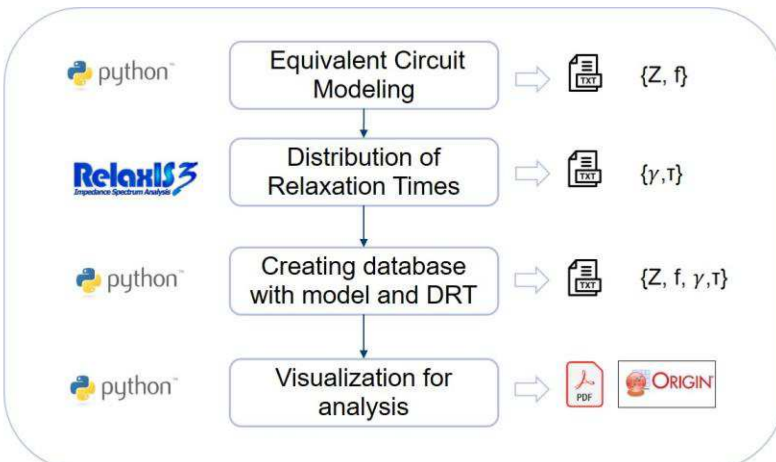

Figure 1. Workflow chart of the database creation for ECMs and their associated DRT.

With the help of a significant amount of evaluated sets of impedance data from our group a meaningful range of each individual parameter could be stated. No external data are included to ensure comparability of results in terms of setup and methodology. The database is enhanced for an extensive parameter variation within the ECM elements (see Table I).

TABLE I: Parameter ranges for the considered circuit elements and their iterative properties.

Elements	Parameter range [min, max]	Number of variations	Type of increment
Resistance	$R = [10^{-3}, 10^{0}]\ \Omega$	4	logarithmic
Inductance	$L = [10^{-9}, 10^{-5}]$ H	5	logarithmic
Constant Phase Element	$Q = [10^{-6}, 10^{3}]$ S	10	logarithmic
	$\alpha = [0.5, 1]$	6	linear
Finite Warburg-impedance (short)	$Z_W = [10^{-3}, 10^{0}]\ \Omega$	4	logarithmic
	$\tau = [10^{-3}, 10^{1}]$ s	5	logarithmic
	$\alpha = [0.5, 1]$	6	linear
Gerischer	$Y = [10^{0}, 10^{3}]\ S \cdot s^{-0.5}$	4	logarithmic
	$k = [0, 1]\ s^{-1}$	11	linear

Results and Discussion

The result section is divided into two parts. First, some DRT plots are presented that typically result from the most common used ECMs. All patterns include a parameter variation within the usually observed range of values (see Table 1) for one of the parameters within a selected ECM. Furthermore, it is shown in what way the DRT transformation can produce artifacts. Possible solutions on how to recognize and distinguish these artifacts will follow in the subsequent discussion. In addition, the impact on the use of the regularization parameter value will be discussed using selected examples. There are certain connections between the above-mentioned topics that will be considered collectively and may provide possible avenues for further research.

Selected DRT Plots to commonly used ECMs

In the first plot in Figure 2, the code for equivalent circuit modeling should be tested for a simple ECM and hence the DRT transformation of a single (R-CPE) circuit element is displayed. The fixed parameters are R and Q while α is varied as given in Table 1.

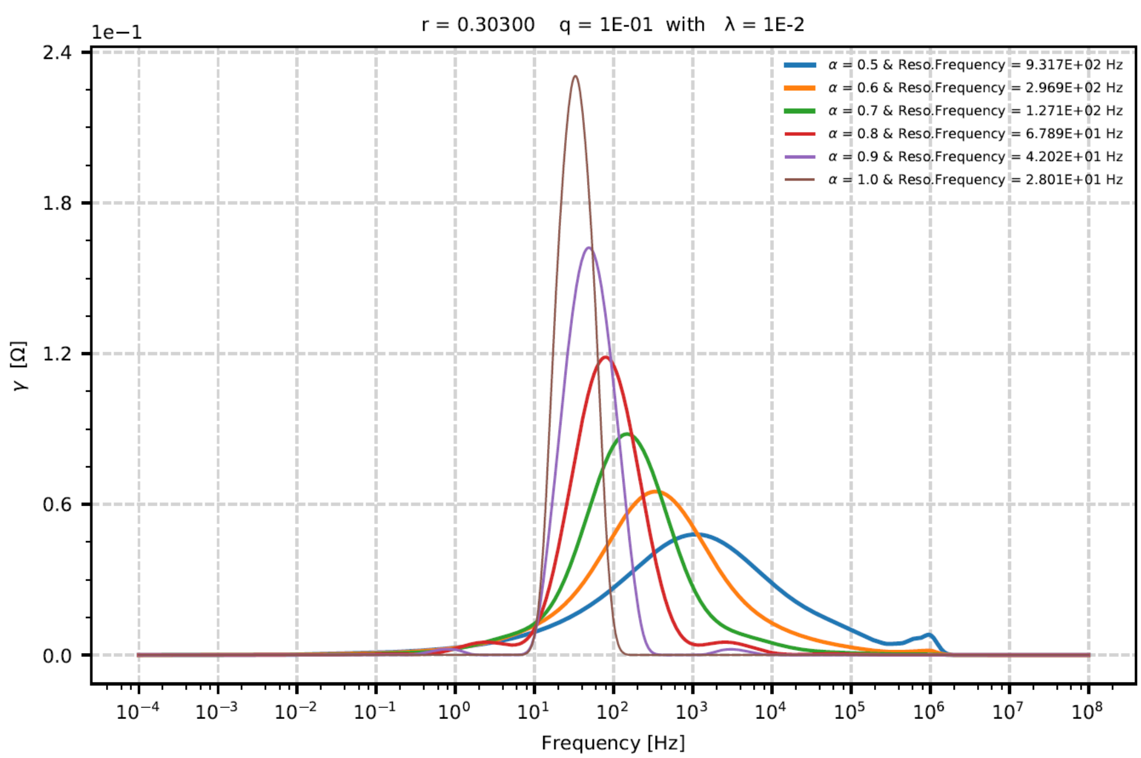

Figure 2. The DRT transformation of an (R-CPE) element in the frequency domain with the specified fixed parameters $R = 3.03 \cdot 10^{-1}$ Ω and $Q = 10^{-1}$ S while α is varied between 0.5 and 1. The regularization parameter is selected to $\lambda = 10^{-2}$.

As expected, a single peak is displayed for the circuit element in each case. When the value of α is lowered, the peak width broadens because the behavior of the capacitor transforms from ideal to real. The resonance frequency of the process gets less well-defined. Nevertheless, it is clearly visible that only one circuit element (R-CPE) is involved in the transformation. This is due to the selected RC kernel which means that every transformation is trained on an (R-CPE) element to be displayed in one peak whenever possible. Before exploring difficulties with the DRT transformation, one further example of commonly used ECMs is introduced in order to recognize the pattern it produces.

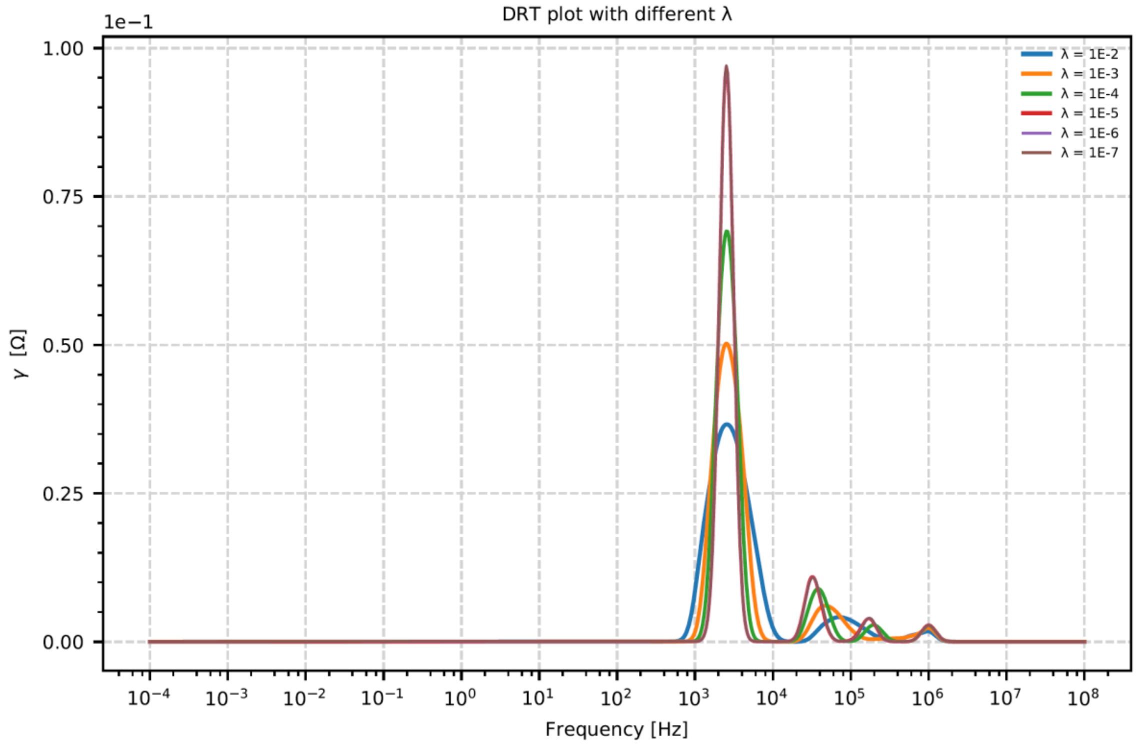

Figure 3. The DRT transformation of an (R-Ws) circuit in the frequency domain with the fixed parameters $R = 0.95\ \Omega$, $Z_W = 0.063\ \Omega$, $\tau = 10^{-3}$ s and $\alpha_W = 0.5$ while λ is varied between 10^{-2} and 10^{-7}.

Figure 3 presents the pattern that a Ws element brings about. The element does not produce a single peak and hence is asymmetric with respect to the transformation into Gaussian peaks. Even for larger values of λ (e.g. 10^{-2}), the transformation assigns multiple peaks to the element. Thus, this is an asymmetric element with respect to Gaussian peaks and is consequently approximated by several symmetric peaks. The envelope of these symmetric peak reveals the asymmetric peak of the Ws element transformation. This has consequences on the analysis of such produced patterns as will be explained in a later section. Imagine, that there is a second (R-CPE) element in series with the Ws element. Already in that more complex model various situations can happen. For example, a second peak belonging to the (R-CPE) element is not visible and may be swallowed by the peaks caused due to the Ws element. This effect can also be observed for two (R-CPE) elements in series that one peak is significantly reduced in strength of γ although the resonance frequencies of both elements are separated by some decades. This observation is plotted in Figure 4.

The resonance frequencies of both processes are supposed to be situated at 10^{-3} Hz and 1 Hz, respectively, but only the second process appears at the expected frequency. The process at a lower resonance frequency is distorted by one order of magnitude and the signal is diminished in the transformation. There are two possibilities what can cause this problem: i) the Nyquist plot shows an impedance recording with a non-real valued last data point, which is a pre-requisite for a precise DRT transformation or ii) the recorded frequency range is insufficient and leads to i). In the example of Figure 4, i) is the reason. When evaluating the area under the respective peaks, the one at ω = 1 Hz integrates to 1 Ω which is the correct value. But for the second peak, the integration only yields a value of 0.1 Ω which is a tenth of the actual value. The second process is thus not properly recognizable by the DRT transformation as one of the prerequisites made for a precise transformation is not fulfilled. In experiments, the presence of an only real valued last data point might not always be easy to fulfill.

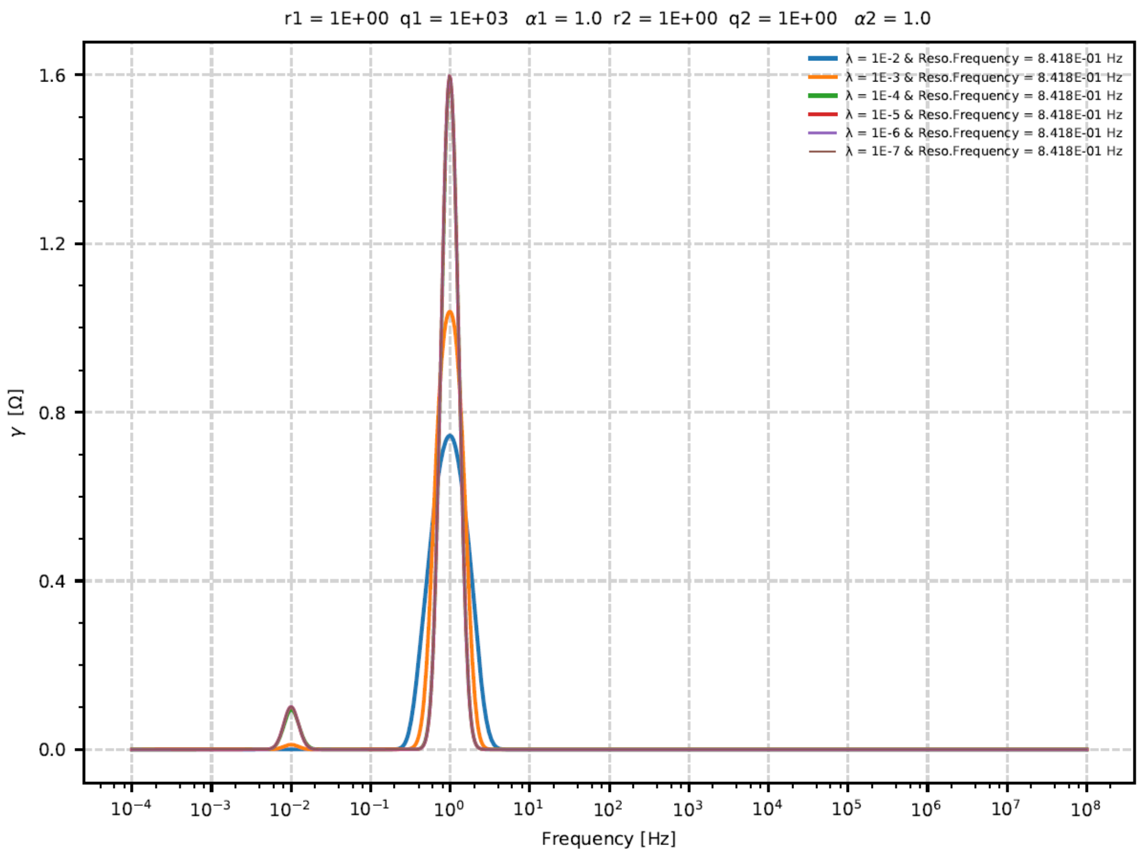

Figure 4. The DRT transformation of two (R-CPE) elements in series in the frequency domain with the specified fixed parameters $R_1 = R_2 = 1\ \Omega$, $Q_1 = 10^3$ S, $Q_2 = 1$ S and $\alpha_1 = \alpha_2 = 1$. The regularization parameter is varied between 10^{-2} and 10^{-7}. The peak for the (R-CPE) element corresponding to (R_1, Q_1, α_1) is only visible for lower values of λ at a distorted $\omega \approx 10^{-2}$ Hz.

By using different values of λ, it is possible to strengthen the precision of the transformation regarding the full-width half maximum of peaks as they get narrower with lower λ-values. This allows a better allocation of the process, since the frequency interval is limited. On the other hand, a too small value of λ will cause difficulties in the interpretation, as discussed in the following paragraph. Furthermore, it is important to check the impedance data on their quality before evaluating the DRT transformation. Some of the possible pitfalls are presented together with Figure 4 and in the next section.

Artifacts in the DRT Transformation

As the transformation is an ill-posed problem, there might occur artifacts in the transformed dataset. In this section, two distinct artifacts are reported and investigated in more detail. In most cases, artifacts appear only when several circuit elements are used simultaneously to describe the impedance data. In the first case, more peaks appear at the edge of the frequency data range. An example is given in Figure 5 with the simulation range between 10^{-2} Hz and 10^{6} Hz. In this data set an extra peak at 10^{6} Hz is visible, but this can only be an artifact of the transformation. The impedance data are produced with the following parameters of the ECM: $R_1 = 50\ \Omega$, $R_2 = 25\ \Omega$, $Q_1 = 10^{-3}$ S, $Q_2 = 10^{-4}$ S and $\alpha_1 = \alpha_2 = 0.7$. As the simulation data reveal, the processes are described by two (R-CPE) elements with resonance frequencies of about 70 Hz and $5.2 \cdot 10^{3}$ Hz. There should not be any further peaks involved. Comparison of the corresponding impedance data reveals, that they do not show a purely real last data point in the case of a simulated frequency interval up to 10^{6} Hz. This is a possible source of artifacts of this kind.

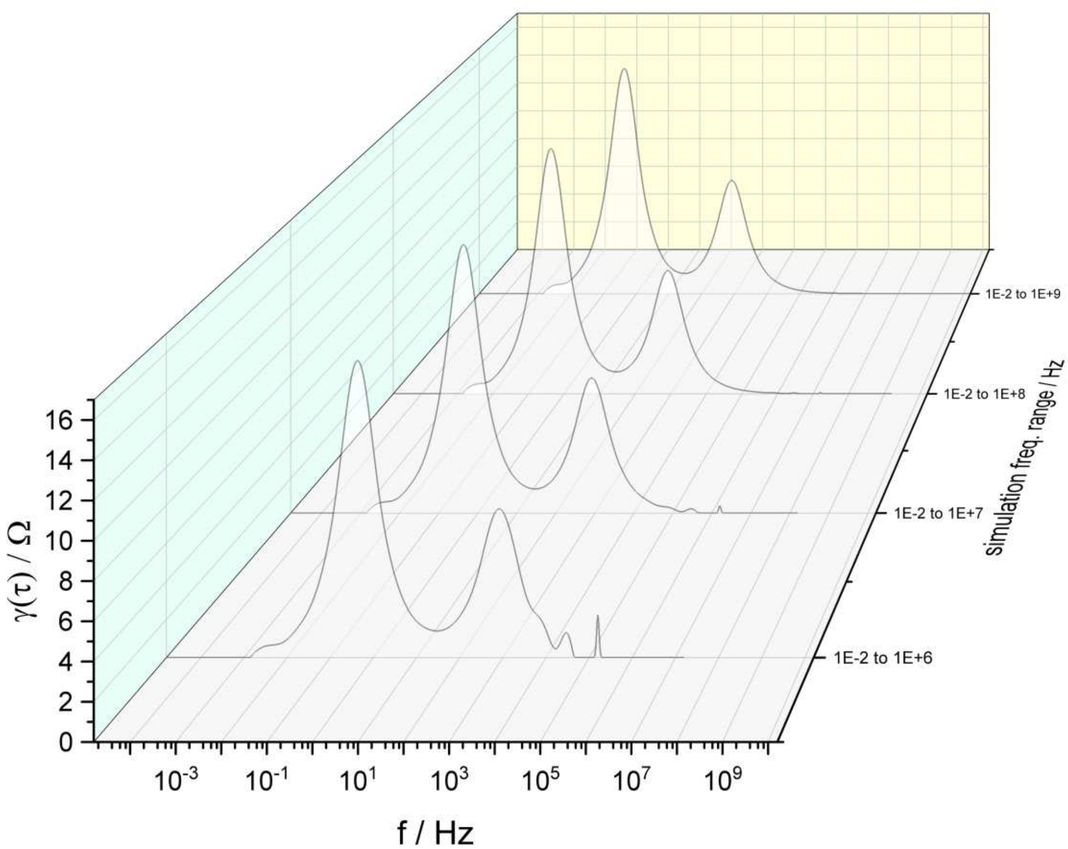

Figure 5. The DRT transformation of two (R-CPE) elements in series is plotted in the frequency domain with several simulation ranges of the frequency interval. The regularization parameter is selected to $\lambda = 10^{-5}$. The more frequency recordings are taken at the high frequency end, the better the artifacts are covered in the DRT transformation.

One possible solution to the artifact problem in this case is to extend the frequency range in order to close the gap in the impedance data to the real x-axis. If such high frequency ranges are not feasible for the measurement setup another method can be used. If the underlying process is relatively well known, an artificial real impedance data point can be inserted into the spectrum. This is done using the approximate placement of a semicircle, representative of an (R-CPE) element, in the corresponding frequency range. Where the semicircle ends on the x-axis in the high frequency range, the artificial data point as support for the DRT transformation can be included.

The second kind of artifact is due to the selected elements in the ECM. Not all elements reveal a symmetric behavior as seen in Figure 3, this also applies to the commonly used (R-CPE) element with distinct parameters in their contribution to certain frequency responses. If such an element is present in an impedance dataset, a different pattern in the DRT transformation is produced. An example is given in Figure 6 where a pattern of two (R-CPE) elements in series is shown. The important change is in the α-value of the elements. For one (R-CPE) element it is fixed to 0.5 which means that the transformation behavior is much more asymmetric than for a α-value of 1. For the other element a variation in the α-value is performed.

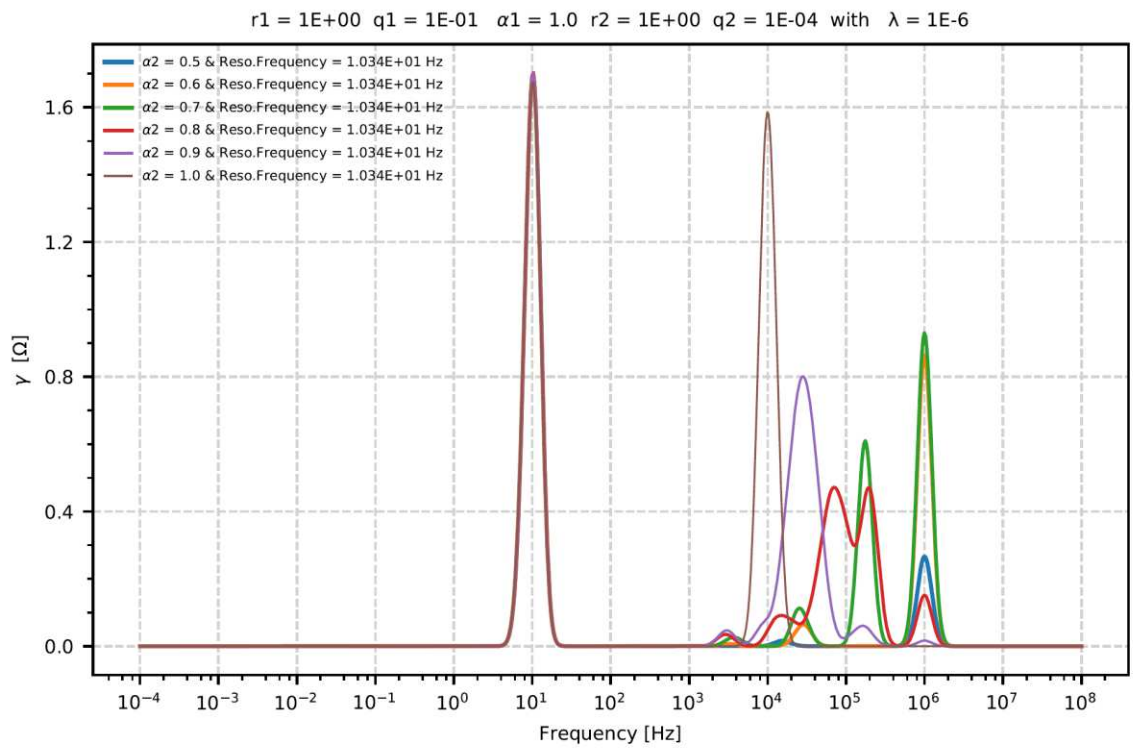

Figure 6. The DRT transformation of two (R-CPE) elements in series is plotted in the frequency domain. The fixed parameters of the elements are $R_1 = R_2 = 1\ \Omega$, $Q_1 = 10^{-1}$ S, $Q_2 = 10^{-4}$ S, $\alpha_1 = 1$ and α_2 is varied between 0.5 and 1. The regularization parameter is selected to $\lambda = 10^{-6}$.

In the case of symmetric elements in the ECM ($\alpha_1 = \alpha_2 = 1$), the contribution of both can be clearly separated due to the strong peak at their respective resonance frequencies. The pattern of the second (R-CPE) element for $\alpha_2 < 1$ is distributed over a broader range of frequencies and produces several additional peaks as seen in case of the Ws element. The DRT transformation tries to mimic the asymmetrically distributed peak again by several symmetric Gaussian peaks. Following the local maxima of each peak and connecting them with a line reveals the envelope of the asymmetric process. First of all, it is not that clear anymore which element may be responsible for an asymmetric pattern. Second, in cases where the resonance frequencies are even closer of two distinct processes, especially in the cases of $\alpha \leq 0.9$, the peaks of the DRT transformation might overlap in such a way that a simple separation by eye is not possible anymore. Another difficulty is then the fact that the multiple peaks cannot be clearly assigned to each of the processes. It would not be correct to assign a separate (R-CPE) element to each of the peaks, since otherwise the model would be overdetermined and the results would not be interpretable.

An Optimality Criterion for Impedance Experiments

The advantage in DRT should be to be able to separate and classify appropriately recorded processes in the impedance spectrum. Therefore, the number of recorded data points per decade of the frequency range plays an important role. Figure 7 shows which number of frequency points per decade should be optimally selected in order to still be able to distinguish between two closely situated processes. The specifications of the underlying ECM are: $R_1 = 100\ \Omega$, $R_2 = 50\ \Omega$, $Q_1 = 10^{-4}$ S, $Q_2 = 10^{-3}$ S and $\alpha_1 = \alpha_2 = 0.9$. Simulated impedance data on the model are taken for 10, 20, 30, 40 and 50 points per decade of frequency. To couple this result to an optimality criterion on the λ that has to be selected every time a DRT transformation is performed Figure 8 has to be considered simultaneously. There is a trade-off in the selection of λ. A lower value of λ brings about a sharpening of the peak, when the element already behaves symmetrical. A larger value of λ allows for a more reliable result in the potential number of elements expected to be selected for the ECM as non-symmetric elements are not split into multiple peaks. In the beginning of evaluating impedance data with the help of DRT it is thus necessary to test for several λ-values. Only then it is possible to get a feeling how the dataset behaves and what kinds of possible implications there can be in it. A useful starting value for λ can be stated between 10^{-3} and 10^{-5} since neither of these values exhibit the impacts that the extreme lower or upper values do on the impedance data transformation.

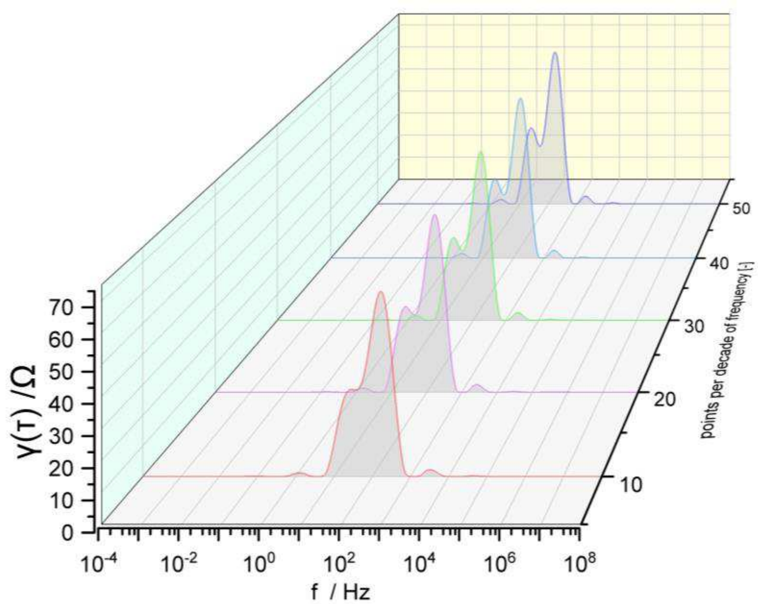

Figure 7. The DRT transformation of two (R-CPE) elements in series plotted in the frequency domain. The transformation is conducted separately for impedance data containing between 10 and 50 points per decade of frequency. The shoulder in the main peak for the recording of 10 points per decade is resolved when the number of recorded data points is increased. The selected regularization parameter is $\lambda = 10^{-3}$.

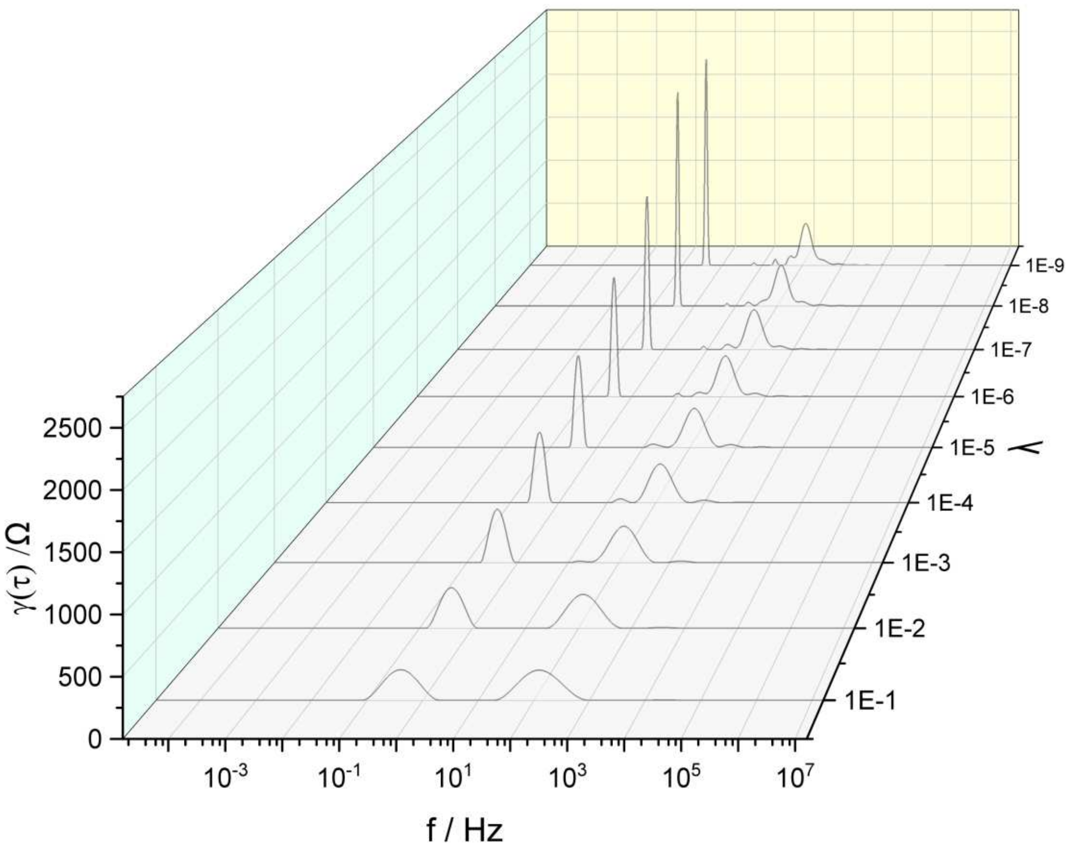

Figure 8. The DRT transformation of two (R-CPE) elements in series plotted in the frequency range is performed for nine different values of λ. Symmetric elements are sharpened in their position of the resonance frequency for lower values of λ. Even slightly non-symmetrical elements exhibit additional satellite peaks at low λ-values.

Conclusion

In this paper, the DRT transformation with the Tikhonov regularization itself is investigated in detail. Patterns to recognize different elements frequently used in ECMs are presented together with artifacts that appear during the transformation. Solutions to prevent artifacts are sketched. A sensitivity analysis on the regularization parameter λ is performed to judge its influence on the transformation especially for the most common used (R-CPE) element.

When using this kind of DRT transformation, it is not possible to directly associate an (R-CPE) process with each appearing peak. Rather, the pattern of the transformation must be analyzed in more detail to determine if multiple peaks belong to an asymmetrically distributed element. The regularization parameter λ plays an important role for forming the pattern and the same data should be plotted for at least several selected values of λ in order to get a feeling for the transformation behavior of the dataset. A good starting value of λ independent of knowing how the investigated system behaves under an impedance measurement is between 10^{-3} and 10^{-5}.

Acknowledgments

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