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Analysis of Electrochemical Impedance Spectroscopy Data Using the Distribution of Relaxation Times: A Bayesian and Hierarchical Bayesian Approach

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ABSTRACT

Electrochemical impedance spectroscopy (EIS) is one of the most important experimental techniques employed in electrochemistry because it can be used to deconvolve physico-chemical phenomena occurring at disparate timescales. Unfortunately, the analysis of EIS data is frequently challenging since it can require the selection of *ad hoc* equivalent circuits. The distribution of relaxation times (DRT) method is complementary to the approach of fitting equivalent circuits because the DRT maps the EIS data onto a function containing the timescale characteristics of the system under study. While conceptually simple, the DRT cannot be obtained by simple minimization of the least squares because the corresponding optimization problem is ill posed. Regularization methods, such as ridge/Tikhonov or Lasso regression, add a penalty term to the least squares minimization problem enabling the DRT deconvolution. In this work, we show that such regularization methods may be understood in a Bayesian context. For example, ridge/Tikhonov regression implicitly encapsulates the prior insight that the derivatives of the DRT are regular. We use this Bayesian approach as a starting point to extend the DRT regularization by considering frequency dependent oscillation levels. This approach is shown to be more robust with respect to both discontinuities and over smoothing than typical regularized DRT methods. Furthermore, the Bayesian approach is versatile and may be extended to include more informative priors.

1. Introduction

Electrochemical impedance spectroscopy (EIS) is one of the key techniques used in electrochemistry [1–5] and has been utilized in many areas including fuel cells [6–10], batteries [11–14], sensors [15–17], capacitors [18], dielectrics [19,20], electrochemical coating [21,22], imaging [23,24], and biology [25,26], just to list a few applications. The EIS is particularly useful in these fields because it is conducted over a broad range of frequencies allowing the deconvolution of physic-chemical phenomena characterized by disparate timescales [27].

The EIS data are acquired by applying small voltage (or current) perturbation to an electrochemical system so as to measure the corresponding current (or voltage) [2]. This is repeated at various frequencies to obtain the EIS spectrum. The latter is typically understood as the ratio between the voltage and the current in frequency space [5]. Namely, it is a complex-valued function defined as the Fourier transform of the potential $v(t)$ divided by the Fourier transform of the current $i(t)$

$$Z(f) = \frac{V(f)}{I(f)} \tag{1}$$

where $V(f) = \mathcal{F}[v(t)](f)$ and $I(f) = \mathcal{F}[i(t)](f)$ and where we take the unitary Fourier transform definition: $\mathcal{F}[h(t)](f) = \int_{-\infty}^{\infty} h(t)\exp(-2\pi i f t)\,dt$. The experimental impedance is then used to understand the physico-chemical properties of the system under study. For this purpose having a reliable model is critical because it aids the experimental data interpretation. Typical EIS models consist of a collection of elementary circuits, e.g., resistors, capacitors, constant phase elements, and Warburg circuits placed in series or in parallel. In spite of notable exceptions [27–38], the circuits are often selected *ad hoc* so as to follow physical intuition and the principle of parsimony [27,39,40]. Furthermore, such equivalent circuits may not be unique, in that several of them may fit the data equally well. This comes to the detriment of the physical insight that one can obtain from the EIS experiments.

One way to bypass the lack of uniqueness of problem-specific equivalent circuits (and therefore complement the analysis of the EIS) is to use the distribution of relaxation times (DRT) method

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[10,14,41–54], which models the impedance as $Z_{\mathrm{DRT}}(\boldsymbol{x}, f)$, where $\boldsymbol{x}$ is an unknown and possibly large vector. In turn $\boldsymbol{x}$ can be mapped onto the relaxation characteristics that characterize the electrochemical system under study. The entries of $\boldsymbol{x}$ are obtained by minimizing the sum of the absolute value of the residuals computed between the experimental data $Z_{\mathrm{exp}}(f)$ and $Z_{\mathrm{DRT}}(\boldsymbol{x}, f)$ at the experimental frequencies f_n

$$S(\boldsymbol{x}) = \sum_{n=1}^{N} \left[w_n' \left(Z_{\mathrm{exp}}'(f_n) - Z_{\mathrm{DRT}}'(\boldsymbol{x}, f_n) \right)^2 + w_n'' \left(Z_{\mathrm{exp}}''(f_n) - Z_{\mathrm{DRT}}''(\boldsymbol{x}, f_n) \right)^2 \right] \tag{2}$$

where Z' and Z'' indicate the real and imaginary part of the impedance respectively and w_n' and w_n'' are suitable weights. If $\boldsymbol{x}$ has size close to N, the minimization of (2) is ill posed yielding solutions highly dependent on the experimental error. There are a number of ways to circumvent this problem. Researchers have employed Fourier transformation and filtering [41,47], Monte Carlo techniques [43,44], maximum entropy methods [55–57], and advanced evolutionary programming [50–52,58]. One particularly popular method consists in minimizing the following expression [10,14,59–66]:

$$S(\boldsymbol{x}) = \sum_{n=1}^{N} \left[w_n' \left(Z_{\mathrm{exp}}'(f_n) - Z_{\mathrm{DRT}}'(\boldsymbol{x}, f_n) \right)^2 + w_n'' \left(Z_{\mathrm{exp}}''(f_n) - Z_{\mathrm{DRT}}''(\boldsymbol{x}, f_n) \right)^2 \right] + \lambda P(\boldsymbol{x}) \tag{3}$$

where the second term on the left hand side is the product of a function $P(\boldsymbol{x})$, a penalty, and a positive parameter λ. The penalty can be, as in ridge (or Tikhonov) regression, the norm of the second derivatives of the DRT obtained from $\boldsymbol{x}$.

In this article we aim at answering two open questions regarding DRT analysis:

1. Can the penalty term in the minimization problem (3) be understood using statistics?
2. Can we find a statistically motivated method to extend ridge DRT so that the level of regularization (as expressed by λ in (3)) can vary across the timescales?

We show that the regularized DRT can be derived from Bayesian statistics arguments [67]. In other words, the term $\lambda P(\boldsymbol{x})$ in (3) encapsulates the prior physical information available on the DRT. For example, ridge regression provides the (prior) information that the q$^{\mathrm{th}}$-order derivative of the DRT is distributed as a Gaussian random variable with standard deviation $\frac{1}{\sqrt{\lambda}}$. Therefore, the smaller λ is, the larger the oscillations are expected to be. Conversely, a large λ implies that one expects much smaller oscillations. This answers the first question.

The simple Bayesian approach outlined above assumes, however, that the level of regularization is uniform throughout the entire frequency spectrum. Equivalently, the prior implies that the same oscillation rates in the DRT are expected to occur across all timescales. In order to select a local λ and yet take only a limited number of tunable parameters, a hierarchy of Bayesian priors need to be used [68]. In this hierarchical approach (we have a prior of the prior itself), the DRT and the optimal penalty level are found simultaneously. This addresses the second question.

More broadly, the Bayesian framework proposed in this article serves as a starting point for extending DRT regression and for improving the interpretation of the DRT spectra.

2. Theory

2.1. The DRT Method

As outlined in the introduction, the DRT method assumes that the response of the electrochemical system under study is obtained from a distribution of relaxations (see Appendix A for details). Thus, the impedance can be written as

$$Z_{\mathrm{DRT}}(f) = R_\infty + \int_0^\infty \frac{g(\tau)}{1 + i2\pi f\tau} \mathrm{d}\tau \tag{4}$$

where R_∞ and $g(\tau)$ are both non negative and where the DRT subscript is used to emphasize that $\mathscr{F}^{-1}[Z_{\mathrm{DRT}}(f)](t)$ is a sum of decaying exponentials. Since many electrochemical experiments are conducted with a given number of points per decade, the (4) can be more conveniently rewritten as

$$Z_{\mathrm{DRT}}(f) = R_\infty + \int_{-\infty}^\infty \frac{\gamma(\ln\tau)}{1 + i2\pi f\tau} d\ln\tau \tag{5}$$

where $\gamma(\ln\tau) = \tau g(\tau) \geq 0$. We will use (5) in the remainder of the article.

The main goal of the DRT analysis is to obtain an estimate of $\gamma(\ln\tau)$. In order to do that, we first need to approximate $\gamma(\ln\tau)$ and $Z_{\mathrm{DRT}}(f)$ using a suitable discretization. Subsequently, we estimate the discrete approximation using regression. The discretization of $\gamma(\ln\tau)$ can be obtained by expanding the DRT over a given finite basis $\mathscr{B} = \{\psi_1(\ln\tau), \psi_2(\ln\tau), \ldots, \psi_M(\ln\tau)\}$ as [69]

$$\gamma(\ln\tau) = \sum_{m=1}^{M} x_m \psi_m(\ln\tau) + e^{\mathrm{discr}}(\ln\tau) \tag{6}$$

where the x_m's are scalars and where $e^{\mathrm{discr}}(\ln\tau)$ is the discretization error. The latter depends on the basis $\mathscr{B}$ chosen and on the particular function $\gamma(\ln\tau)$. By plugging (6) into (5), we can write the following vector equation

$$\boldsymbol{Z}_{\mathrm{DRT}} = R_\infty 1 + \boldsymbol{A}'\boldsymbol{x} + i\boldsymbol{A}''\boldsymbol{x} + \boldsymbol{e}^{\mathrm{approx}} \tag{7}$$

where $(\boldsymbol{Z}_{\mathrm{DRT}})_n = Z_{\mathrm{DRT}}(f_n)$ with $1 \leq n \leq N$, $\mathbf{1}$ is a vector with N entries all equal to 1, $\boldsymbol{x} = (x_1, x_2, \ldots, x_M)^T$, $\boldsymbol{A}'$ and $\boldsymbol{A}''$ are real $N \times M$ matrices, and $(\boldsymbol{e}^{\mathrm{approx}})_n$ is the error made in approximating (at the frequency f_n) the DRT (5) using the first 3 terms on the right hand side of equation (7). We emphasize that M, the dimension of the basis, and N, the total number of experimental points, need not be identical. Further, we will consider that our model is simply $\boldsymbol{Z}_{\mathrm{DRT}} = R_\infty \mathbf{1} + \boldsymbol{A}'\boldsymbol{x} + i\boldsymbol{A}''\boldsymbol{x}$. The $\boldsymbol{x}$ of the expansion (6) can then be obtained via regularized regression by solving the following problem with respect to $\boldsymbol{x}$ [53]

$$\boldsymbol{x} = \underset{\boldsymbol{x}\geq 0}{\mathrm{argmin}} \left[\left\| \boldsymbol{\Omega}' \left(R_\infty 1 + \boldsymbol{A}'\boldsymbol{x} - \boldsymbol{Z}_{\mathrm{exp}}' \right) \right\|^2 + \left\| \boldsymbol{\Omega}'' \left(\boldsymbol{A}''\boldsymbol{x} - \boldsymbol{Z}_{\mathrm{exp}}'' \right) \right\|^2 + \lambda P(\boldsymbol{x}) \right] \tag{8}$$

The first two terms are the sum of the residuals (the measure of the distance between the data and the model) weighted in accordance to the matrices $\boldsymbol{\Omega}'$ and $\boldsymbol{\Omega}''$[i]. If we set $P(\boldsymbol{x}) = \|\boldsymbol{L}\boldsymbol{x}\|^2$, where $\boldsymbol{L}$ is a suitable q$^{\mathrm{th}}$ order differentiation matrix, we obtain the ridge DRT.

[i] In reference to (2), $\boldsymbol{\Omega}' = \mathrm{diag}\left(\frac{1}{\sqrt{w_1'}}, \frac{1}{\sqrt{w_2'}}, \ldots, \frac{1}{\sqrt{w_N'}} \right)$ $\boldsymbol{\Omega}'' = \mathrm{diag}\left(\frac{1}{\sqrt{w_1''}}, \frac{1}{\sqrt{w_2''}}, \ldots, \frac{1}{\sqrt{w_N''}} \right)$.