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Two-dimensional impedance data analysis by the distribution of relaxation times

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ABSTRACT

Electrochemical impedance spectroscopy of batteries and fuel cells suffers from ambiguity due to overlapping features of different electrochemical processes. One approach to mitigate this problem is the analysis of impedance data by the distribution of relaxation times (DRT) of the underlying physico-chemical processes. In this work an evolution of DRT analysis using generalized Tikhonov regularization with a uniform penalty and an RC kernel is discussed. By conducting the transformation without discriminating or constraining the sign of the distribution and by using both the imaginary and the real part of the RC kernel it can be distinguished between impedance contributions of RQ-like physico-chemical processes, pure ohmic resistances and inductances in the system under investigation. Furthermore, regularization can be simultaneously applied in a second, non-inverted dimension, which affords an increased resolution of the spectrum. The properties of the algorithm are demonstrated by analyzing synthetic impedance data.

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1. Introduction

The ongoing transformations of the transportation and the energy sectors demand an evolution of the state of the art batteries and fuel cells, for which a knowledge-based research and development process supported by sophisticated analytical techniques is necessary. For electrochemical research one of these techniques is the electrochemical impedance spectroscopy (EIS). It enables the unravelling of physico-chemical processes and their quantification by fitting the data with equivalent circuit models (ECM) [1,2]. In batteries, examples for such processes are the analysis of a formed solid–electrolyte interphase layer (SEI), charge-transfer processes in the active electrode material or solid-state diffusion [3–5]. In fuel cells, processes such as gas diffusion, oxygen surface-exchange kinetics as well as charge-transfer reactions can be investigated [6–9].

While the ECM fitting procedure is straightforward owing to the availability of standard software packages, it suffers from ambiguity since it requires detailed a priori knowledge of the system to obtain physically meaningful results. This problem can be mitigated by transforming frequency domain impedance data into the relaxation time domain [10,11], which does not require any assumptions about the investigated system apart from the kernel. The transformation directly provides a distribution of physical processes, which gives rise to the impedance response of a system, and it is possible to determine the number of processes that can be distinguished given the sensitivity of the data [12]. Therefore this method – the analysis of the distribution of relaxation times (DRT) – has recently become increasingly popular [13–17].

Direct inversion of impedance data to obtain the DRT is ill-posed. A variety of methods have been proposed to circumvent this problem, such as Fourier filtering (FF) [12], maximum-entropy deconvolution (MED) [18], least-squares deconvolution (LSD) [10,11,19] or regularization [20]. FF is fast and straightforward in its application but it is somewhat prone to artifacts introduced by the filter function. MED proves to be less vulnerable to artifacts but also less suitable for noisy data, since noise tends to be misinterpreted as spectral features [18]. The LSD approach starts from a generated predistributed DRT spectrum that is then optimized by complex nonlinear least squares fitting to match the original impedance spectrum [19], which requires good weighing factors and is also sensitive to noise. Regularization stabilizes the inversion and is less vulnerable to noise [21], but

incorrectly used it is prone to artifacts. In addition, regularization is often combined with the forced suppression of negative features in the DRT, which may suppress physically justified signal contributions. Hence it is necessary to carefully check the validity of the inverted data to prevent false interpretations. Taking everything into account, the regularization approach proofed to be the most suitable to stabilize the inversion and calculate the DRT [22].

In this work an evolution of the widely applied Tikhonov regularization [23] with an RC kernel is presented. Two advantages compared to the state of the art [15–17,24–26] are achieved. First, by calculating DRT on a two-dimensional (2D) data set the uncertainty of the spectrum is reduced, leading to an increased resolution – as was already successfully proven for nuclear magnetic resonance data [27]. The second dimension, which itself is not inverted, is given by varying operation conditions, such as temperature, potential or state of charge (SOC). Secondly, inductive features in the spectrum are unraveled by avoiding a non-negativity constraint, which is not generally necessary when using a uniform penalty (UP) for regularization [28]. The theoretical foundations for resolving inductances by DRT have been laid by Schönleber et al. [29]. If further stabilization of the inversion should be required, a zero-crossing penalty is applied that allows for positive as well as negative components without a bias towards one or the other [30]. By performing the transformation with both the imaginary and the real part of the RC kernel it can be clearly distinguished between impedance contributions of RQ-like physico-chemical processes, pure ohmic resistances and inductances in the system under investigation. With peak-fitting algorithms each identified process is quantified and subsequently back-transformed into the frequency domain to visualize the contributions of the different processes to the overall impedance. Major emphasis is placed on a reliable data validation.

2. Theory

DRT involves the deconvolution or inversion of impedance spectroscopy data from an electrochemical system, often using the kernel for an RC circuit element. The total system impedance is then

$$Z(\omega) = R_0 + R_{\text{pol}} \int_0^\infty \frac{g(\tau)}{1 + \mathrm{j}\omega\tau} \, \mathrm{d}\tau, \tag{1}$$

where $g(\tau)$ is the distribution of relaxation times τ with $\int_0^\infty g(\tau)\,\mathrm{d}\tau = 1$, R_0 is the ohmic resistance, R_{pol} is the polarization resistance, ω the angular frequency and $\mathrm{j} = \sqrt{-1}$ [12]. It has been shown that this kernel is capable of approximating the impedance of any non-oscillating electrochemical system, including Warburg and Gerischer elements, provided that RC elements with negative sign are permitted [29].

Experimentally, only a finite number M of impedance values at frequencies ω_k can be determined. A numerical inversion of these discrete impedance data provides densities at N discrete, freely selectable relaxation times τ_l. If the polarization resistance at each RC time constant τ_l is approximated as $R_l = R_{\text{pol}} g_l$, where $\sum_{l=1}^N g_l = 1$ represents a vectorization of the continuous distribution of relaxation times [12], then Eq. (1) can be rewritten as:

$$Z(\omega_k) = \sum_{l=0}^N \frac{1}{1 + \mathrm{i}\omega_k \tau_l} R_l. \tag{2}$$

By setting $\tau_0 = 0$, the coefficient at $l = 0$ represents the frequency-independent ohmic resistance R_0.

In practice, Eq. (2) is evaluated using independent calculations for the real (rRC) and the imaginary part (iRC) of the RC kernel. The τ vector can be extended a few orders of magnitude below values

that can be faithfully resolved with a particular experimental data set. Then the R_0 component appears as a line well separated from the actual DRT components, which may be more robust than fitting R_0 with $l = 0$ in Eq. (2) for low sensitivity data or if other contributions at low values of τ are present in the DRT. Purely resistive elements only contribute to the real part of the spectrum, while inductances add an imaginary contribution with opposite sign compared to a capacitance, due to their resistive and reactive impedance, respectively. RC and RQ elements (with a constant phase element instead of a capacitor, showing a time constant distribution [2]) contribute with the same features in the real and the imaginary spectrum [12,29]. The constant phase element impedance is given by

$$Z_Q = \frac{1}{Q\omega^n} \, \mathrm{e}^{-\mathrm{j}\frac{\pi}{2}n}, \tag{3}$$

where Q is the pseudo-capacity of a charge double layer with the unit $[\Omega^{-1}\,\mathrm{s}^n]$ and $n \in [0,1]$. The RC and RQ element's distribution of relaxation times are given by

$$g_{RC}(\tau) = \delta(\tau - \tau_{RC}) \quad \text{with} \quad \tau_{RC} = RC, \tag{4}$$

$$g_{RQ}(\tilde{\tau}) = \frac{1}{2\pi} \frac{\sin((1-n)\pi)}{\cosh(n\tilde{\tau}) - \cos((1-n)\pi)} \quad \text{with} \quad \tilde{\tau} = RQ, \tag{5}$$

respectively, with resistance R, capacitance C of a particular ECM element [12].

Usually a vector τ of logarithmically spaced values (plus possibly τ_0) is chosen. Using τ and the vector ω containing all the experimental frequency values, a discretized kernel $\mathbf{K}$ can be constructed to express the impedance in matrix form as

$$\mathbf{Z} = \mathbf{KR} + \mathbf{e}, \tag{6}$$

where $\mathbf{Z}$ is a vector containing all M experimental data points of the impedance spectrum, $\mathbf{R}$ is the vector of the true underlying distribution of polarization resistances and $\mathbf{e}$ is a vector containing the unknown random noise values inherent in any experiment.

Inversion of noisy impedance data using kernel $\mathbf{K}$ is ill-posed. A direct inversion is numerically unstable due to noise enhancement, *i.e.* the amplification of experimental errors [12]. To facilitate a stable inversion, regularization is used. Thereby a penalty matrix is added that is small enough such that the result of the regularized inversion cannot be conclusively distinguished from the true DRT within the sensitivity limits of the experimental data. To obtain an estimate $\hat{\mathbf{R}}$ of the true DRT vector $\mathbf{R}$, the functional that must be minimized is

$$\hat{\mathbf{R}} = \underset{\mathbf{R}}{\text{argmin}} \left\{ \|\mathbf{KR} - \mathbf{Z}\|_2^2 + \lambda^2 \|\mathbf{\Lambda R}\|_2^2 \right\}, \tag{7}$$

where $\mathbf{\Lambda}$ is the regularization matrix and λ is a global scaling factor. Tikhonov regularization in generalized form using a UP [28] employs curvature regularization, where

$$\mathbf{\Lambda}_{\text{UP}} = \mathbf{CL}_2, \tag{8}$$

represents the UP contribution to the regularization matrix, $\mathbf{L}_2$ is the second derivative operator, and $\mathbf{C}$ is a variable coefficient matrix whose elements are iteratively adjusted to keep the regularization term nearly uniform in regions with a significant spectral density of $\hat{\mathbf{R}}$ [28,30]. While curvature regularization with a constant coefficient has been suggested in combination with a non-negativity constraint to analyze impedance spectra of batteries for systems where sign changes of the spectrum can be ruled out [31], UP regularization generally does not show non-physical oscillating features when used with an RC kernel, hence a non-negativity constraint is not necessary. In addition, compared