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Non-negatively constrained least squares and parameter choice by the residual periodogram for the inversion of electrochemical impedance spectroscopy data

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ABSTRACT

The inverse problem associated with electrochemical impedance spectroscopy requiring the solution of a Fredholm integral equation of the first kind is considered. If the underlying physical model is not clearly determined, the inverse problem needs to be solved using a regularized linear least squares problem that is obtained from the discretization of the integral equation. For this system, it is shown that the model error can be made negligible by a change of variables and by extending the effective range of quadrature. This change of variables serves as a right preconditioner that significantly improves the condition of the system. Still, to obtain feasible solutions the additional constraint of non-negativity is required. Simulations with artificial, but realistic, data demonstrate that the use of non-negatively constrained least squares with a smoothing norm provides higher quality solutions than those obtained without the non-negative constraint. Using higher-order smoothing norms also reduces the error in the solutions. The L-curve and residual periodogram parameter choice criteria, which are used for parameter choice with regularized linear least squares, are successfully adapted to be used for the non-negatively constrained Tikhonov least squares problem. Although these results have been verified within the context of the analysis of electrochemical impedance spectroscopy, there is no reason to suppose that they would not be relevant within the broader framework of solving Fredholm integral equations for other applications.

1. Introduction

We consider the numerical solution of ill-posed inverse problems that are motivated by measurements of electrochemical impedance spectra from which a model of the underlying physical reaction mechanisms is desired. There is extensive literature on a wide range of applications in which the same, or similar models can be applied. These include measurements for solid oxide fuel cells [1–8], microbial fuel cells [9], as well as of physiological parameters, and from a diverse range of

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dielectric models, [10–13]. In these applications the unknown distribution function of relaxation times (DRT) is related to a set of impedance measurements by the Fredholm integral equation

$$Z(\omega) = R_0 + R_{\text{pol}} \int_0^\infty \frac{g(t)}{1 + i\omega t}\, dt, \tag{1.1}$$

where ω is angular frequency, t is time, and $g(t)$ is the desired DRT with normalization $\int_0^\infty g(t)dt = 1$.

There are several models used to represent the individual processes of a DRT, many of which are mostly used for the analysis of dielectric materials and are described in [10]. Several are directly applicable to the fuel cell modeling case, where they usually take the form of theoretical circuit components used in constructing equivalent circuit models. Equivalent circuit elements used for fuel cell modeling include the Cole–Cole (also known as RQ or ZARC) element, the Generalized Finite-Length Warburg element, and the Gerischer impedance [10,14,6]. In analysis of specific fuel cell designs a log-normal form for the DRT has also been used [12,9]. Here we focus our investigations on the Cole–Cole DRT, which can be rendered temperature independent only in the limiting cases of $\beta \to 0$, 1, and the temperature independent lognormal DRT, denoted throughout by RQ and LN, respectively.

The RQ impedance is a generalization of a simple parallel RC circuit and for a single process has an impedance given by

$$Z_{\text{RQ}}(\omega) = \frac{1}{1 + (i\omega t_0)^\beta}, \tag{1.2}$$

where t_0 is the point of maximum distribution, and β is a shape parameter controlling the width of the distribution. The corresponding DRT is

$$g_{\text{RQ}}(t) = \frac{1}{2\pi t} \frac{\sin \beta\pi}{\cosh\left(\beta \ln\left(\frac{t}{t_0}\right)\right) + \cos \beta\pi}, \tag{1.3}$$

which reduces to the Dirac delta distribution when $\beta = 1$, [10]. There is, however, no analytic form for the impedance corresponding to the log-normal DRT given by

$$g_{\text{LN}}(t) = \frac{1}{t\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln(t) - \mu)^2}{2\sigma^2}\right). \tag{1.4}$$

Although a number of options have been presented in the literature for geometrically assessing the parameterization of the DRT from impedance data for a single physical process, e.g. as noted in [13], for given measured and noisy impedance data from multiple processes there are effectively only two basic approaches that may be considered to estimate the DRT. When a specific analytic but parameter dependent form for the impedance is known, as in (1.2), parametric nonlinear least squares (NLS) fitting may be used to determine the underlying parameters of the impedance and hence of the DRT, [11]. On the other hand, when no analytic representation of the impedance is available, as in (1.4), it is still possible, but more computationally expensive, to apply a parametric nonlinear fit by using direct numerical integration of (1.1). In either case, an alternative is to apply a linear least squares (LLS) fit directly to the DRT, but this is also challenging due to the general ill-posedness of the problem, e.g. [15–19]. Both approaches, as well as the geometric analyses, have been extensively considered in the literature, e.g. [10]. When the model for the DRT is not known, perhaps when the physical process is not completely understood or the number of processes has not been determined, the only option is to fit directly to the DRT, without identifying its specific parameterization.

Before further pursuing the LLS fit, we illustrate in Section 2 the use of direct NLS fitting for a simple one-process example in order to emphasize the (self-evident) significance of the prior knowledge of the model. Assuming that the wrong model leads to apparently robust data fitting, while at the same time potentially leading to incorrect conclusions about the DRT parameterization. With this conclusion we move in Section 3 to an analysis of the system describing the LLS fitting that arises when approximating (1.1) discretely. The direct discretization of (1.1) leads to two ill-conditioned systems of equations, for the real and imaginary parts separately. Most literature on the problem suggests the use of LLS for the systems obtained in this way, in conjunction with regularization to stabilize the estimation of the solution, [2,20]. In contrast, it was suggested in [6], that rather than estimating the DRT in the given t-space, a transformation to s-space via $s = \log(t)$ would be preferable and that the resulting ill-posed system be solved using a non-negative least squares (NNLS) algorithm, specifically imposing the constraint that the DRT is a positive distribution. In Section 3.2 we investigate the modeling error that arises when using the s-space transformation, leading to new results that quantify the total modeling error due to discretization and truncation in (1.1) for both real and imaginary terms. The results go beyond those presented in [9] for the t-space formulation, by providing error estimates which are primarily determined by the kernel $h(\omega, t) = (1 + i\omega t)^{-1}$, only relying on standard smoothness and decay conditions for the DRT functions.

The numerical algorithms for the estimation of the DRT are discussed in Section 4. First it is demonstrated that the s-transformation serves as a **right preconditioner**, leading to more stable estimation of the underlying basis for the solution when the time discretization is chosen appropriately in relation to the frequency measurements. Still the model remains ill-conditioned, and solution techniques using regularization are required, introducing the need for determination of a regularization parameter that weights the regularization term. Estimation of this regularization parameter for Tikhonov