Electrochimica Acta 56 (2011) 5416–5434

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Reducing error and measurement time in impedance spectroscopy using model based optimal experimental design

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ARTICLE INFO

Article history:
Received 1 November 2010
Received in revised form 24 February 2011
Accepted 24 February 2011
Available online 25 March 2011

Keywords:
Mixed ionic and electronic conductor
Equivalent circuits
Identification of physical parameters
Frequency response analysis

ABSTRACT

In this work we introduce several novel tools for the reduction of errors in parameters estimated with electrochemical impedance spectroscopy experiments. An optimization strategy is developed that minimizes an estimate of the errors on the parameters while bounding the experimental time. The approach is also used to reduce experimental time while keeping a bound on the parameter errors. This feature is particularly critical in systems changing significantly within the experimental time. The paper uses a fuel cell electrode model to test this methodology and presents a real time algorithm for coupling experiment with the parameter estimation and experimental optimization.

1. Introduction

Electrochemical impedance spectroscopy (EIS) is a powerful technique used for more than a century [1]. It has been subject of numerous reviews and textbooks [2–4]. EIS has been used in a wide range of topics including sensors analysis and optimization [5], study of dye-sensitized solar cells [6], studies of corrosion [7], biological applications [8], characterization of novel nano materials [9], physical chemistry of solids [10,11], lithium ion batteries [12] and fuel cells [13]. Software packages for the analysis of impedance data have also emerged, see [14–16].

The typical goal of an EIS experiment is to gather significant information regarding the physico-chemical phenomena taking place in an electrochemical device. Typically, a broad frequency sweep is performed, with a linear or a logarithmic spacing between maximum and minimum frequency. The measured data is then compared with a mathematical model that describes the system. The model can be purely empirical, being composed of resistors, capacitors, and generalized electrochemical elements, or otherwise it can be based on the physics of the system. One typically compares the model and the experimental data by fitting the model against the data, i.e., by minimizing a functional that measures the distance between model and measurement via the complex nonlinear least squares (CNLS) method. It is clear that errors in the measured data propagate to the estimated parameters and the distribution of such errors can be estimated by analytical expressions under the assumption of "small" errors. We shall assume in this work, that the method used for fitting the data is (unweighted) complex nonlinear least-squares and that the design of the experiment can be optimized in such a way that increases the confidence on the parameters that define the model. Thanks to this procedure, values of the relevant physico-chemical the parameters can be obtained with greater confidence or with a faster experiment.

In an optimized EIS experiment one could aim to reduce the uncertainty of the parameters for given errors in the measurements or to decrease the experimental time without a significant increase in uncertainty. This reduction can be achieved systematically by applying optimal experimental design (OED) [17]. OED comprises of statistical and numerical methods that optimizes the design of the experiment so that the physical parameters are obtained with the greatest statistical confidence. In particular, reducing experimental time while maintaining low errors in the estimated parameters could be significant in situations where uncontrolled fluctuations of the experimental conditions, e.g., temperature, reference electrode position, occur through the experiment's duration, in cases where the systems degrades, and in non-equilibrium electrochemical systems such as batteries under bias. It is important to note that time reduction and accuracy are

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doi:10.1016/j.electacta.2011.02.098

often competing objectives. In fact, for a stable system, longer experimental time will yield more accurate results.

In this work we utilize a physics-based model as an example, however, the presented approach is general and can be easily applied to empirical models, those composed of resistors, capacitors, and generalized elements. For example the latter can be obtained by analyzing the impedance spectra with commonly used software packages [14,16].

We shall stress that the models used to interpret and identify the experiment can also be non-unique, meaning that several models can fit experimental data with comparable residuals [4,18–21], and there can be errors in some of the "known" parameters used in the model. Here we disregard those possibilities and assume that the model describes the physical system precisely. Considering possible errors in the model, the OED technique can also be used for model discrimination [22–24], i.e., for comparing different models which give similar results if tested with standard experimental procedures.

Lastly, the paper will be outlined as follows: first we introduce OED (Section 2), second we describe the model of the example system studied (Section 3), third we review the theory of experimental errors in EIS (Section 4), fourth we apply the OED method to improve impedance measurements (Section 5), and finally we present the results of computations on the given example (Section 6). To the best of our knowledge, this is the first time that OED techniques are used to optimize impedance measurements in the field of electrochemistry.

2. Optimization of model-based experiments

OED has been studied extensively in the field of statistics [17,25–27] and is frequently used in science and engineering [28–33]. OED largely relies on statistical inference [34] and on the sensitivity analysis of the estimated parameters with respect to perturbations of the data. As stated in the introduction the goal of OED is to find the experimental conditions that reduce the effects of measurement inaccuracies on the estimated parameters. In this sense OED makes the parameter identification less sensitive to sources of error in the measurements. For this purpose, the link between the variations of the data and the variations of the estimated parameters has to be determined and optimized. This link is depicted in Fig. 1. In the traditional approach model and experimental data are used to estimate parameters via CNLS. It is important to note that errors in the data and in the estimated parameters are linked. OED directly exploits this connection and "suggests" more favorable conditions for increasing the confidence on the parameters.

One of the key ideas of OED is to use asymptotic nonlinear estimation to approximate the covariance matrix of the estimated parameters. In order to do that one needs to either assume or measure the error structure of the experimental data. In our case relative errors in the amplitude and in the argument of the measured impedance (see Section 4.2) are considered. The uncertainty in the measured data induces uncertainty in the estimated parameters, i.e., after a fit one should give a mean value for each estimated parameter and an estimation of the variances. The latter are usually represented by error bars. A more complete way to describe the uncertainty is the calculation of the covariance matrix, which gives not only error bars (the diagonal terms of the matrix) but also the correlations between the parameters. A large correlation between two parameters means, that if one of them is known with a large uncertainty, then the other could be affected as well. The covariance matrix, as explained in Appendix B.3, defines the so-called confidence region, which under the assumption of "small" normally distributed errors is depicted by an ellipse (in the case there are only two parameters) or an ellipsoid (in the case the parameters are more than two). The region inside the ellipse defines the range of values that the parameters could have due to measurement errors. To have a pictorial view of the ellipsoidal area we refer back to elementary statistics [35], and for completeness we depict in Fig. 2 two Gaussian probability density functions (p.d.f.s) centered around 0 with covariance matrix $\mathbf{V}$ whose analytical expression is p.d.f. $(\boldsymbol{\theta}) = 1/(2\pi\sqrt{\det(\mathbf{V})})\exp\left(-(1/2)\boldsymbol{\theta}^{\mathrm{T}}\mathbf{V}^{-1}\boldsymbol{\theta}\right)$ and where the parameter vector is $\boldsymbol{\theta} = \begin{bmatrix}\theta_1\\ \theta_2\end{bmatrix}$. In the top row we show the p.d.f. with $\mathbf{V} = \begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$, in the bottom panels we depict instead the p.d.f. with $\mathbf{V} = \begin{bmatrix}0.505 & 0.495\\ 0.495 & 0.505\end{bmatrix}$. While the former distribution is circularly symmetric, the latter is elongated and preferentially oriented in the direction $[1, 1]^{\mathrm{T}}$. By drawing points from each of the distributions one obtains that most points lie inside the circle in the first case and an elongated ellipse in the second case. Both curves are defined as the points $\boldsymbol{\theta}$ for which $\boldsymbol{\theta}^{\mathrm{T}}\mathbf{V}^{-1}\boldsymbol{\theta} = K$ where $K = 9$.[1] One typical goal of OED is to modify the confidence region. Fig. 3 shows schematically the effect of applying OED in case of two parameters (θ_1, θ_2), where $\hat{\theta} = (\hat{\theta}_1, \hat{\theta}_2)$ is the vector of the parameters estimated via CNLS.

In optimizing EIS, one could use OED to select the frequencies that lead to greater parameter confidence (see Section 6.1). Another strategy could determine the "best" sample geometry for the identification of the parameters in the system under study (see Section 6.2). This is achieved by connecting the error in the measurements with the error on the parameters Fig. 1 and subsequently by modifying the experimental design $\boldsymbol{\xi}$ so that the confidence on the estimated parameters in increased, Fig. 3. Depending on the experiment, OED can improve in different ways the results of the nonlinear estimation procedure. Specifically OED can

- decrease the volume of the confidence region;
- decrease the correlation between the parameters;
- optimize the experimental conditions, for example, by decreasing the overall time of the experiment or allowing to take measurements at more convenient conditions.

The use of the covariance matrix $\mathbf{V}$ of the parameters estimates to define the confidence region has been proven useful in many applications that use nonlinear models [31,36,37]. However, the direct determination of $\mathbf{V}$, for example via a Monte Carlo method, would be computationally taxing even for a small number of parameters. An asymptotic estimate $\mathbf{V}_{\mathrm{asympt}}$ of matrix $\mathbf{V}$, see Appendix C, has a clear computation advantage over Monte Carlo strategies because the number of computations necessary to achieve an informative result regarding the covariance matrix is greatly reduced. In addition, the derivatives of functions of $\mathbf{V}_{\mathrm{asympt}}$ can be easily computed numerically, for example via finite differencing or automatic differentiation [38], and can be used in existing optimization algorithms to solve an OED problem. We note that this optimization is rather complex since $\mathbf{V}_{\mathrm{asympt}}$ is a nonlinear function of $\boldsymbol{\theta}$, of the measurement error structure, and it depends on the method used for fitting the data, for details see Appendix C.15 in Appendix C.

The design of an optimal experiment for improving parameter precision reduces then to minimizing a functional of the asymptotic

[1] $K = 9$ corresponds to assuming that the data will likely fall within 3 standard deviations of the average value.