



An alternative approach to solve complex nonlinear least-squares problems

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ABSTRACT

In this work, a hybrid electrochemical impedance spectroscopy (EIS) strategy was developed with the aim to solve complex nonlinear least-square (CNLS) problems. For the first time the CNLS problems were solved by an alternative approach, i.e. by using Python to merge the following tactics: circuit description code (CDC), central-difference formula, Nielsen's modification of the Levenberg–Marquardt algorithm (LMA) and visual inspection of the χ^2 -function minima. It was presented that the Nielsen's damping (λ) factor updating strategy can be used to design a topical fitting engine in which the change in the λ factor is continuous. The commonly used forward-difference formula was replaced with a more accurate central-difference formula to approximate the first derivatives. It was elucidated that by combining the Nielsen's λ updating tactics and central-difference formula in the hybrid EIS strategy resulted in the design of a more robust fitting engine. The hybrid EIS strategy was enhanced by the CDC routine which allows researchers to effortlessly generate a great variety of electrical equivalent circuits (EECs). The credibility of the EEC parameters was increased by visual inspection of the χ^2 -function minima. Additionally, a novel convergence in the symmetry criterion was proposed to avoid errors during the visual inspection. The applicability of the hybrid EIS strategy was evaluated after it was integrated into a new software solution and compared to the more widely used MEISP and EQUIVCRT software packages. It was presented that the three fundamentally different software solutions yielded approximately equal EEC data. However, only EIS strategies with the similar LMA tactics produced the identical χ^2 -values in all case studies.

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1. Introduction

An increased interest in battery materials [1–3], conductive polymers [4–6] and supercapacitor [7–9] synthesis currently makes electrochemical impedance spectroscopy (EIS) a very attractive technique. To conduct the EIS study it is necessary to use various science strategies that are implemented in research software products [10,11]. Nowadays, a science strategy is straightforwardly implemented into software packages by using the, e.g. Python programming language [12–17]. Therefore, the EIS study should also be continuously integrated into research software with high reuse potential.

Impedance data can be analyzed by the application of the electrical equivalent circuit (EEC) [18,19]. However, there are many EECs that can be used to analyze the set of impedance data [20]. The usual EIS strategy to extract the EEC data is to solve the complex nonlinear least square problem (CNLS) [18,21–26] by using, e.g. the original Levenberg–Marquardt algorithm (LMA) [27,28]. In addition, LMA is also used to fit experimental data in various aspects of science [29–31].

Furthermore, the original LMA has undergone several modifications to improve its sensitivity. The earliest and most famous LMA implementation was given by Jorge Moré [32]. Interestingly, the original and Moré's LMA modification experience a discontinuous change in the

damping (λ) factor which decreases performance. In order to avoid the λ factor fluttering Nielsen et al. [33,34] offered a new λ updating strategy, which was later applied by numerous authors [35–39]. However, its benefits have not been used in the EIS strategy yet and neither analyses of the λ vs. iteration number curves (obtained by the original and Nielsen's) have been reported yet.

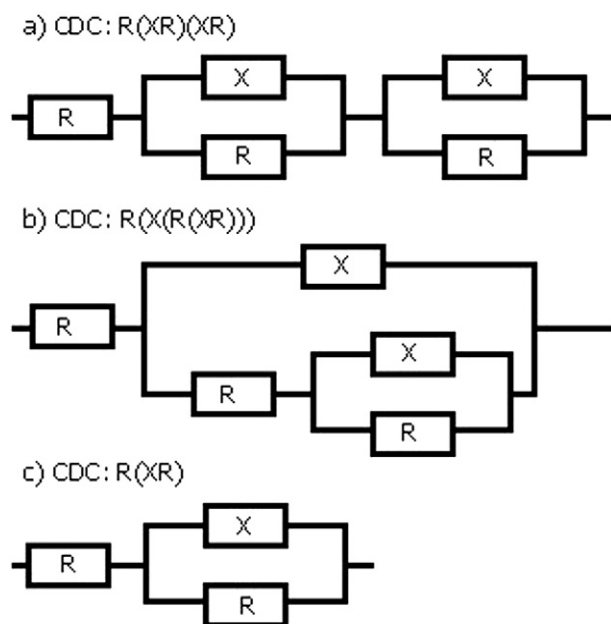
In order to apply LMA and to solve the CNLS problem, one can use EIS strategies implemented by, e.g. MacDonald [11] and Boukamp [10,23] in LEVM/MEISP¹ [40] and EQUIVCRT² [41]. Interestingly, the authors utilize different LMA modifications in which the first derivative [27,28] is numerically [42,43] or analytically [23] obtained. In addition, EEC models are imported from the software's library or designated by the Circuit Description Code (CDC) [10,23]. Therefore, the existing EIS strategies are fundamentally different, since they apply dissimilar tactics. However, a discontinuous change in λ value during the iteration process [33,34], as one of the major part of LMA, is still present in both EIS strategies.

Generally, the EEC parameters are extracted by minimizing the quadratic [43] objective χ^2 -function [18,19,23]. In order to inspect the quality of the extracted parameters, Boukamp [22,23] used the Fit

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¹ An extension of LEVM (<http://impedance0.tripod.com/MEISP3trial.zip>).

² Has also a Windows version (not a free program) (<http://www.wisseq.nl/portfolio.aspx>).



Scheme 1. Schematic presentation of the electrical equivalent circuit(s) (EEC) accompanied by circuit description code(s) (CDC) used in this work. The “X” represents capacitance (C) and constant phase element (Q).

Quality Plot (FQ-plot). However, the existing EIS strategies do not have additional tactics (included in software) to verify that the EEC parameters are properly collected from the χ^2 -function minima. Therefore, the credibility of the EEC parameters will be additionally increased if the quadratic shape (i.e. U-shape) of the χ^2 -function is confirmed visually and/or by a novel stopping criterion. Thus, the visual inspection of the χ^2 -function at the iteration's end should be a novel tactic embedded in the EIS strategy.

Nowadays, the Nielsen's λ updating strategy [34] and the central-difference formula [42,43] can be used to design a modern EIS fitting engine in which the λ factor value exhibits a continuous change. Furthermore, CDC can be applied to straightforwardly prepare the EEC. Finally, the inspection of the χ^2 -function shape will increase the credibility of the final parameters. Therefore, merging the above novel-noted and existing tactics into a hybrid EIS strategy (by using Python) would represent an alternative approach to solve the CNLS problems.

In this work the hybrid EIS study strategy was developed by merging a novel tactic with the existing tactics. Hence, it was necessary i) to design the EIS fitting engine based on the Nielsen's LMA modification and central-difference formula, ii) to develop a CDC routine for EEC production and iii) to enable the visual inspection of the χ^2 -function minima. Overall, it was necessary to develop a new software solution to test the hybrid EIS strategy.

The aim of this work is to use the alternative approach i) to design a hybrid EIS study strategy, ii) to implement it into a new software tool (EisPy), iii) to develop a more robust EIS fitting engine in which the fluttering of the λ factor is omitted and iv) to investigate the effect of the different tactics by the utilization of EisPy, EQUIVCRT and MEISP in solving diverse CNLS problems.

2. Experimental

2.1. The process of integrating the hybrid EIS strategy into the software solution

In order to promote the wider use of the hybrid EIS strategy, it was implemented into a new program solution, i.e. Electrochemical Impedance Spectroscopy in Python (EisPy) [44]. EisPy is a free

stand-alone executable software designed in Python (v.2.7.5.), which is free and it can be used to continuously develop and extend various research software products. The following free modules³ were applied to develop EisPy:

- NumPy v1.7.1: a fundamental package for computing,
- Matplotlib v1.2.1: a Python 2D graphic library,
- wxPython v2.9.4.0: a GUI framework (or toolkit) and
- PyInstaller⁴ v1.5.1: a Python programs converter into stand-alone executables.

2.2. The existing software packages used in the present study

The tactics used in this work have not been reported as a part of one EIS strategy yet. Therefore, it was essential to determine the effect of different tactics by applying EisPy, EQUIVCRT [41] and MEIPS [40] to solve the CNLS problems. MEISP v3.0 (trial version) is a software which solves the CNLS problems by using the LEVM fitting engine and adds to it an additional functionality [11]. The MEISP/LEVM fitting engine is based on the Moré's LMA [32,45] in which the first derivative is numerically approximated. On the other hand, EQUIVCRT applies the Circuit Description Code⁵ (CDC) to prepare the EEC model, whereas the fitting engine is designed by means of the original LMA [27,28] and an analytical derivatives routine [23]. It should be emphasized that LMA is extremely sensitive to initial values particularly if they are far from the optimal one [23], so the starting parameter values must be carefully chosen.

2.3. EEC models used in this study

CDCs used in this work were: “R(QR)(QR)”, “R(CR)(CR)”, “R(CR(CR))” and “R(CR)”, whereas associated EEC models (Scheme 1) were designated as: $EEC_{R(QR)(QR)}$, $EEC_{R(CR)(CR)}$, $EEC_{R(CR(CR))}$ and $EEC_{R(CR)}$. The hybrid EIS strategy applies a Circuit Description Code (CDC) routine to produce EEC model(s). The details related to the application of CDC, the list of elements (Table 1), as well as guidelines how to prepare the CDC routine to generate/interpret the EEC model were given by Boukamp [24].

The components abbreviations that are available to create CDC are: R (resistor), C (capacitor), Q (constant phase element), L (inductance), W (Warburg), T (Finite Space Warburg), O (Finite Length Warburg) and G (Gerischer). The proposed software solution has an ability to fit EEC model consisted of maximal 30 parameters.

2.4. The synthetic and non-synthetic (experimental) data

In order to investigate the ability of the hybrid EIS strategy to resolve diverse EIS problems, the set of the synthetic and non-synthetic (experimental) data were analyzed by EisPy. The synthetic impedance data were also used by Boukamp [23,46] and Macdonald [25,47] to approve the conducted analyses. In addition, Boukamp [46] even polluted the synthetic data with noise to conduct more comprehensive analyses. Therefore, the synthetic impedance response of polyaniline was computed in this work by $EEC_{R(QR)(QR)}$ and the parameters presented in Table 2.

The details related to the utilized $EEC_{R(QR)(QR)}$ were previously reported [48,49]. $EEC_{R(QR)(QR)}$ parameters values were chosen to imitate PANI impedance data in the potential region of the PANI capacitive current plateau, whereas the frequency range was from 0.01 Hz–100 kHz taking five points per decade, which presents a sufficient number of points to obtain optimal fitting results [23].

³ <https://wiki.python.org/moin/NumericAndScientific>.

⁴ <https://pypi.python.org/pypi/PyInstaller/1.5.1>.

⁵ See: http://www.utwente.nl/tnw/ims/publication/downloads/CDC_Explained.pdf.

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