Electrochimica Acta 131 (2014) 20–27

Contents lists available at ScienceDirect

Electrochimica Acta

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

A Method for Improving the Robustness of linear Kramers-Kronig Validity Tests

M. Schönleber*, D. Klotz, E. Ivers-Tiffée

Institut für Werkstoffe der Elektrotechnik (IWE), Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany

ARTICLE INFO

Article history:
Received 15 September 2013
Received in revised form 5 January 2014
Accepted 7 January 2014
Available online 21 January 2014

Keywords:
EIS
Kramers-Kronig
Over-fitting
Residual
Time-variance

ABSTRACT

A method is presented of avoiding ambiguities in linear Kramers-Kronig validity tests due to under- and over-fitting. It is based on the observation that the parameters of the equivalent circuit model to be fitted start degenerating as soon as the model order chosen is too high and over-fitting is taking place. Hence, a measure of the degree of degeneration is introduced and from this a criterion is developed with which over-fitting can be easily detected. Furthermore, it is shown, how the developed criterion can be used to automatically find an appropriate model order for any given impedance spectrum. Hereby, unambiguous test results are obtained irrespective of the specific expertise of the operator. Due to its ease of use the so improved test can serve as a quick standard test revealing defectiveness of measured impedance spectra. The validity of the proposed strategy is demonstrated in simulations as well as on measurements of a commercial Lithium-Ion battery.

1. Introduction

Electrochemical Impedance Spectroscopy is a very powerful technique of analyzing the properties of electrochemical systems. From a properly measured impedance spectrum one can not only determine the overall polarization resistance of an electrochemical system but one can also separate individual loss processes and quantify their specific contributions [1–3].

The validity of all further analysis, however, requires the measured spectrum to be a representation of a linear, time-invariant and causal system.

In order to check the fulfillment of these requirements, two basic principles can be distinguished: The first is to verify them experimentally, for example by checking for harmonics in the system response or repeating the impedance measurement using different excitation signals. Also, specially designed broadband excitation signals can be used, as outlined in [4] and [5]. However, most of these approaches require insight into excitation and response signals during an impedance measurement, how it is not provided by the majority of the commonly used Frequency Response Analyzers (FRA). Other than that, the second principle is based on analyzing only the obtained impedance spectrum utilizing the Kramers-Kronig (KK) relations. The latter relate the real part of the impedance spectrum of a linear, time-invariant and causal system to its imaginary part and vice versa. The relevant equations

$$Z_{Re}(\omega) = \frac{2}{\pi} \cdot \int_0^\infty \frac{\omega' \cdot Z_{Im}(\omega')}{\omega^2 - \omega'^2}\, d\omega' \tag{1}$$

$$Z_{Im}(\omega) = \frac{-2}{\pi} \cdot \int_0^\infty \frac{\omega \cdot Z_{Re}(\omega')}{\omega^2 - \omega'^2}\, d\omega' \tag{2}$$

were, in a slightly different form, first introduced by Kramers [6] and Kronig [7]. The derivation, however, was physically motivated [8]. Nevertheless, their relation to the aforementioned properties of linearity, time-invariance and causality can be easily shown by a short derivation of KK from a system-theory point of view:

Let $z(t)$ be the impulse response of a linear and time-invariant system. The impedance spectrum of this system is then given by the Fourier-Transform of the impulse response

$$Z(\omega) = \frac{1}{\sqrt{2\pi}} \cdot \int_{-\infty}^\infty z(t) \cdot e^{-jwt} dt. \tag{3}$$

With $z(t)$ being the impulse response of an additionally causal system it is true that

$$z(t) = 0 \quad \forall \quad t < 0 \tag{4}$$

* Corresponding author. Karlsruhe Institute of Technology (KIT), 76128 Karlsruhe, Germany.
E-mail address: michael.schoenleber@kit.edu (M. Schönleber).

0013-4686/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2014.01.034

and therefore (3) can be rewritten as

$$Z(\omega) = \frac{1}{\sqrt{2\pi}} \cdot \int_0^\infty z(t) \cdot \sigma(t) \cdot e^{-j\omega t} dt \tag{5}$$

with $\sigma(t)$ denoting the Heaviside step function. By applying the convolution theorem of the Fourier-Transformation and replacing $\sigma(t)$ with its Fourier-Transform, the following requirement for the impedance spectrum of a linear, time-invariant and causal system is obtained, where $(*)$ denotes the convolution operator.

$$Z(\omega) = Z(\omega) * \left[\frac{1}{2\pi} \left(\frac{1}{j\omega} + \pi\delta(\omega) \right) \right] \tag{6}$$

Equation (6) represents a "pure" form of the KK relations. By executing the convolution an interdependence of the real- and imaginary parts of the impedance can be obtained by means of a Hilbert-transformation,

$$Z_{Re}(\omega) = \frac{1}{\pi} \cdot \int_{-\infty}^{\infty} \frac{Z_{Im}(\omega')}{\omega - \omega'} \, d\omega' \tag{7}$$

$$Z_{Im}(\omega) = \frac{1}{\pi} \cdot \int_{-\infty}^{\infty} \frac{-Z_{Re}(\omega')}{\omega - \omega'} \, d\omega' \tag{8}$$

which can be further simplified to finally obtain Equation (1) and (2).

By applying Equations (1) or (2) to either the real part or imaginary part of a measured spectrum, the remaining part can be computed. By comparing the latter to the according measured part, the spectrum's accordance to the KK relations can be judged. This concept of testing impedance spectra was first employed in [9], where an attempt was made to solve the arising problem of missing parts of the impedance when approaching frequencies of zero and infinity by using polynomial extrapolation.

Other approaches tried to solve the missing-part-problem, using even more sophisticated methods [10], but in the end the general problem of missing information remained.

An approach that overcame this was first introduced in [11–13]: Instead of directly evaluating Equation (1) and (2), the accordance of an impedance spectrum with the KK relations is judged by its reproducibility by an appropriate KK compliant equivalent circuit model (ECM). A very general model, namely a series connection of RC-elements, is chosen, where the resistors as well as the time-constants of the ECM are fitted to a measured impedance spectrum. The benefit of this simultaneous fit is the possibility of revealing the stochastic error structure of the measurement, thereby assessing a frequency dependent confidence interval for the predicted impedance. The latter allows to define a quantitative criterion of which parts of the spectrum are to be disregarded and which parts are valid.

However, the main drawback of this method, as named in [14], is the nonlinear nature of the according fit problem. Due to fitting the time-constants of the ECM (i) good initial values have to be chosen and (ii) several solutions related to local minima of the according cost function to be minimized exist. Hence, while this approach is indispensable for a deep-level analysis of a measured impedance spectrum, if one just wants to quickly check for validity of one or several impedance spectra, the effort is quite high.

In [14] a modified version of this test was proposed, where the problems connected with the nonlinearity of the fit were solved by only fitting the ohmic resistors and pre-setting the time-constants. Thus, the fit problem became linear.

The latter concept (referenced to in the following as the "Lin-KK test") has been extensively used by the authors and experienced users can obtain valid test results quickly and easily. In contrast, inexperienced operators or operators not familiar with the field of model fitting, however often achieve ambiguous or even wrong test results. The reason for this is the user's responsibility to manually pre-set the number M of RC-elements to be fitted, thereby easily creating situations of under-fitting or over-fitting. In the following these terms, as well as their consequences, are further explained and a measure is defined by which over-fitting can be easily detected. Finally, a strategy is proposed, by which M can be automatically chosen for any given impedance spectrum. Thus, valid test results are obtained irrespective of the operator's expertise.

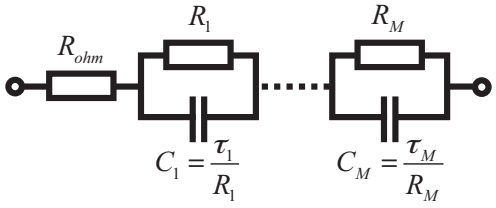

Fig. 1. Equivalent circuit model to be fitted to measured impedance spectra. The governing impedance expression is given by Equation (9).

2. The Lin-KK Test

For the reader's convenience the Lin-KK test as proposed in [14] and used in this publication is briefly summarized.

2.1. Model Type

A sufficiently general model for fitting impedance spectra is given by a series connection of an ohmic resistor and M RC-elements, see Fig. 1.

The governing impedance expression is given by

$$\hat{Z}(\omega) = \hat{R}_{Ohm} + \sum_{k=1}^{M} \frac{\hat{R}_k}{1 + j\omega\tau_k}. \tag{9}$$

Optionally, an additional capacitor or an additional inductance might be added if physically meaningful, or, as explained in [14], if the measured frequency range is small compared to the frequency range of the full impedance spectrum of the system.

2.2. Distribution of Time Constants

The M time-constants τ_k are distributed logarithmically equal over the inverse range of angular frequencies of the impedance spectrum to be tested. The smallest time-constant is therefore given by

$$\tau_{\min} = \tau_1 = \frac{1}{\omega_{\max}}, \tag{10}$$

the largest time-constant by

$$\tau_{\max} = \tau_M = \frac{1}{\omega_{\min}}, \tag{11}$$

and finally, all other time-constants by

$$\tau_k = 10^{\left[\log(\tau_{\min}) + \frac{k-1}{M-1} \cdot \log\left(\frac{\tau_{\max}}{\tau_{\min}}\right)\right]} \quad , \quad k = 2, \ldots, M-1. \tag{12}$$

2.3. Cost Function

The cost function J to be minimized can either be chosen to penalize errors between the real parts of fitted and measured

impedance, the corresponding imaginary parts or both. For fitting the real part (real-fit), the according cost function is given by

$$J = \sum_{i=1}^{N} \left[\frac{Z_{Re}(\omega_i) - \hat{Z}_{Re}(\omega_i)}{\left|Z(\omega_i)\right|} \right]^2 \tag{13}$$

with N the number of frequency points of the impedance spectrum to be tested. For fitting both, real and imaginary parts (complex-fit), it is

$$J = \sum_{i=1}^{N} \left[\frac{Z_{Re}(\omega_i) - \hat{Z}_{Re}(\omega_i)}{\left|Z(\omega_i)\right|} \right]^2 + \left[\frac{Z_{Im}(\omega_i) - \hat{Z}_{Im}(\omega_i)}{\left|Z(\omega_i)\right|} \right]^2. \tag{14}$$

If a model to be fitted does not include a capacitor, one might also consider fitting the ECM to the imaginary part of the measured impedance spectrum. Especially for spectra where the low frequent imaginary part shows no asymptotic behavior this was stated to be beneficial [13]. However, as soon as a capacitor has to be added to the ECM–as it is the case for Lithium-Ion batteries, for example–, this method needs to be discarded in the proposed test-framework. There, simultaneous fitting of the imaginary parts of RC-elements and a capacitor yields an assignment of information to different parts of the ECM which is prone to ambiguities: Parts of the low frequent imaginary part, which should be represented by RC-elements, might be assigned to the capacitor. As the impedance of the capacitor has no contribution to the real part, the misassigned portion of the imaginary part will cause an error within the real part. Hence, in this paper that method has been disregarded.

2.4. Residuals

In order to judge the reproducibility of a measured impedance spectrum by the fitted ECM, a measure describing an according deviation, the residual, is defined as

$$\Delta_{Re}(\omega) = \frac{Z_{Re}(\omega) - \hat{Z}_{Re}(\omega)}{\left|Z(\omega)\right|} \tag{15}$$

or

$$\Delta_{Im}(\omega) = \frac{Z_{Im}(\omega) - \hat{Z}_{Im}(\omega)}{\left|Z(\omega)\right|}, \tag{16}$$

respectively.

3. Experimental

In this section both the simulation and the measurement are introduced, which are later consulted in order to demonstrate the proposed method. The simulation yields synthetic impedance data that is perfectly KK compliant and is used to demonstrate a possible failing of the Lin-KK test as well as to investigate the validity of the proposed criteria to avoid over-fitting. The measurements shall demonstrate the functionality of the developed strategy for choosing an appropriate model order of the ECM at hand of realistic data. For this, two measurements were conducted, where one aimed to produce a spectrum as accurate as possible. The conditions for the second measurement were chosen so that a typical error related to time-variance of the measured object was introduced.

3.1. Simulation

All simulations were run on a standard PC using commercially available software (*MATLAB R2011b*). For reasons of simplicity and comparability, the same synthetic impedance spectrum as used in [14] is employed as an object under test (IS1). Its impedance expression is again given by

$$Z(\omega) = R_1 + \frac{R_2}{1 + j\omega R_2 C_3} + \frac{R_4 \cdot W_5(\omega)}{R_4 + W_5(\omega)}, \tag{17}$$

where

$$W_5(\omega) = \frac{1}{Y_0 \sqrt{j\omega}} \tag{18}$$

is describing a Warburg-type impedance.

The applied parameter values are given in Table 1, whereas in Fig. 2 the shape of the according impedance spectrum as well as its equivalent circuit structure is depicted. The frequency range for all simulations was chosen to be from *1 μHz* to *10 MHz*.

Table 1
Parameter values of the synthetic ECM.

Parameter	Value
R_1	100 Ω
R_2	200 Ω
C_3	0.8 μF
R_4	500 Ω
Y_0	0.4 mS·s$^{0.5}$

As explained in Section 4.1, over-fitting is closely related to measurement noise as it is naturally contained in every measured impedance spectrum. Because the data of the simulated impedance spectrum is fully synthetic, two uncorrelated white Gaussian noise processes are artificially added to its real and imaginary part.

$$\tilde{Z}(\omega) = \left[Z_{Re}(\omega) + \sigma_{\eta,Re}(\omega)\right] + j \cdot \left[Z_{Im}(\omega) + \sigma_{\eta,Im}(\omega)\right] \tag{19}$$

Thereby 3 sub-spectra are created, which differ in the standard deviation of the added measurement noise. Accordingly it is differentiated between a medium disturbed sub-spectrum IS1a, containing noise described by a standard deviation of

$$\sigma_\eta(\omega) = \frac{\left|Z(\omega)\right|}{1000}, \tag{20}$$

a strongly disturbed sub-spectrum IS1b, disturbed by noise described by a standard deviation of

$$\sigma_\eta(\omega) = \frac{\left|Z(\omega)\right|}{100}, \tag{21}$$

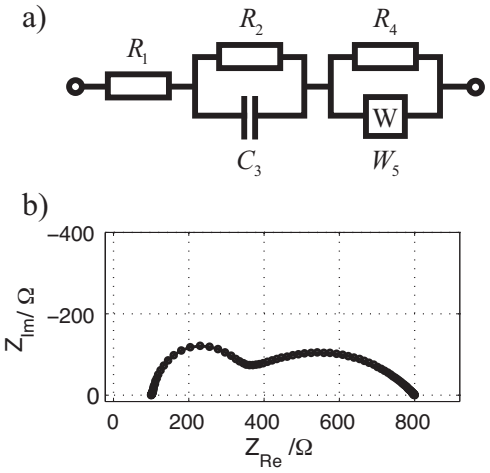

Fig. 2. (a) Equivalent circuit of the synthetic ECM. (b) Nyquist plot of the according impedance spectrum.

Table 2
Frequencies contained in the low frequency part of the measured time-variant impedance spectrum before (IS3a) and after deleting (IS3b) single frequency points.

Before Deleting (IS3a)	After Deleting (IS3b)
0.50 mHz	0.50 mHz
0.63 mHz	
0.79 mHz	0.79 mHz
1.00 mHz	
1.26 mHz	1.26 mHz
1.59 mHz	
1.99 mHz	1.99 mHz

and lastly a slightly disturbed sub-spectrum IS1c, disturbed by noise described by a standard deviation of

$$\sigma_\eta(\omega) = \frac{|Z(\omega)|}{10000}. \quad (22)$$

3.2. Measurements

All impedance measurements were performed at hand of a commercially available 2Ah Lithium-Ion pouch cell (Kokam), using an electrochemical workstation *Zennium* (Zahner). The measured frequencies ranged from *500 μHz* to *100 kHz*, whereas all frequencies larger than *3 kHz* were discarded as inductive artifacts. The density of frequency points was chosen to 10 points per decade.

The first measurement (IS2) aimed at recording a valid impedance spectrum. A sufficiently small excitation amplitude of 10 mV was thus chosen to fulfill the linearity constraint. At the same time, the constraint of time-invariance was assured by placing the cell under test in a climate chamber providing a constant ambient temperature of 25°C.

The second measurement (IS3) was performed to purposely obtain an invalid impedance spectrum. For this the excitation amplitude was kept at a value of 10 mV, however time-variance was induced by linearly changing the ambient temperature of the climate chamber from 25°C to 15°C during the measurement. The measurement time for each measurement (IS2 and IS3) was 13.5 hours; the State of Charge (SOC) of the cell was 80%.

As this measurement time is quite long, in practice the density of measured frequency points in the low frequency part is often reduced. In order to isolate the impact of such a reduction of measurement points on the KK-Lin test while still keeping the same "amount" of time-variance in the spectrum, an impedance spectrum IS3b has been created from IS3 by simply deleting single frequency points: From the 6 lowest measured frequency points every second point was deleted, see also Table 2. All other frequencies remained as measured. For clarity, the originally measured spectrum is in the following named IS3a.

When testing the measured spectra IS2, IS3a and IS3b using the Lin-KK test, due to their capacitive nature an additional capacity is added to the ECM. Further, inductive effects are considered by adding an additional inductivity.

An overview of all simulated and measured impedance spectra is given in Table 3.

Table 3
Overview of simulated and measured impedance spectra.

Impedance Spectrum	Type	Validity	Added Noise	Remark
IS1a	simulation	valid	medium	-
IS1b	simulation	valid	strong	-
IS1c	simulation	valid	weak	-
IS2	measurement	valid	-	-
IS3a	measurement	invalid	-	-
IS3b	measurement	invalid	-	IS3a with less freq. points

4. Theory

4.1. The Problem of Under- and Over-Fitting

As mentioned in the introduction, a crucial shortcoming of the Lin-KK test as proposed in [14] is the necessity to set the parameter *M*, the number of RC-elements in the ECM used to fit the impedance spectrum to be tested. This has to be done by the user. If this chosen number is too small, under-fitting is taking place. This means, that the order of the ECM is too small to fit the measured impedance spectrum, even though the latter might in fact be fully compliant with the KK relations. For example, a spectrum consisting of three perfect RC circuits cannot be fitted with $M = 2$, if the time-constants are distributed to some extent. Thus large residuals are detected, thereby falsely indicating an invalid impedance spectrum.

On the other hand, if the selected *M* is too large, not only the useful information contained in the spectrum is fitted, but the measurement noise as well. A computated imaginary part from an over-fitted real part therefore contains, imprecisely speaking, KK transformed measurement noise. Therefore a comparison with the measured imaginary part of the spectrum will certainly fail, no matter if the spectrum is valid or not. Hence, the according residuals will indicate invalidity, even though the tested spectrum is fully valid.

In order to demonstrate this, the synthetic (and therefore *a priori* valid) impedance spectrum IS1a is tested by the Lin-KK test. The numbers of RC-elements connected to under- as well as over-fitting are used and a real-fit was executed. The results are shown in Fig. 3. There, the tested impedance spectrum IS1a as well as the impedance spectra computed by under- and over-fitting and the according residuals are depicted. In both cases the obtained residuals falsely indicate an invalid impedance spectrum. It is worth mentioning that in the case of over-fitting an error structure is revealed, which not only indicates invalidity, but unfortunately coincides with common measurement errors in spectra, very like those due to parasite inductivities.

An experienced user might argue that a complex-fit would have behaved much more robustly in this case of over-fitting. However when using a complex-fit, firstly small errors are less visible due to the residuals being smeared over the real and imaginary parts. Secondly, also an example can be given, where the complex-fit fails: When intending to measure impedance to low frequencies, less frequency points are usually measured in the low frequency range in order to save time. As an example, invalid impedance spectrum IS3b was chosen to be tested by the Lin-KK test. Due to the induced time-variance, large residuals are expected. However, in the case of an over-fitted complex-fit, the algorithm is able to reproduce the errors in the spectrum and thus only shows very small residuals. As small residuals are also obtained when testing the valid impedance spectrum IS2, the test which is meant to separate valid from invalid spectra here completely fails. Both cases are depicted in Fig. 4.

To summarize this section it is concluded, that due to under-fitting the Lin-KK test might falsely indicate invalidity of a spectrum. Further, when effected by over-fitting a real-fit might also falsely indicate invalidity, while a complex-fit might falsely indicate validity.

4.2. Mathematical Definition of Under- and Over-Fitting

In order to develop a strategy with which under- and over-fitting can be avoided, first a more mathematically precise definition of these terms has to be given. In the field of machine learning under-fitting is commonly defined as a situation, where by adding more complexity to a model, which is fitted to a set of training data, the capability of predicting a set of test data could be increased. Over-fitting in turn describes a situation, where by adding more

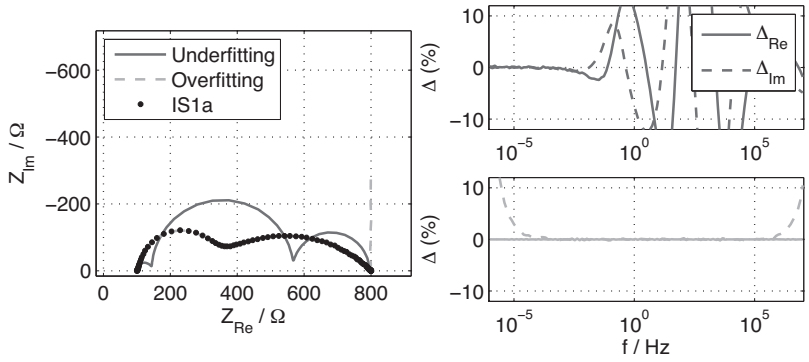

Fig. 3. (left) Valid impedance spectrum IS1a, compared to impedance spectra obtained by under-fitting and over-fitting its real part and computing an according imaginary part. (top right) Residuals in the case of under-fitting (M = 6). (bottom right) Residuals in the case of over-fitting (M = 104). Even though IS1a is fully compliant with the KK relations, seemingly non-compliance is detected.

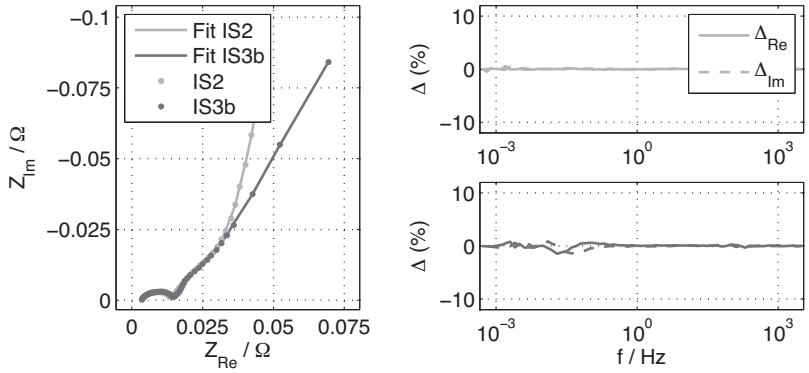

Fig. 4. (left) Valid impedance spectrum IS2 compared to the invalid impedance spectrum IS3b. Further shown are the fit results from the Lin-KK test. (top right) Residuals in the case of testing IS2 using a complex-fit. Compliance with the KK relations is correctly indicated. (bottom right) Residuals in the case of testing IS3b using a complex-fit. Non-compliance with the KK relations is hardly detected.

complexity to a model the capability of predicting a set of test data decreases [15]. For the problem at hand adding complexity is equivalent to increase M, the number of RC-elements. Training data is the real part of the spectrum the applied model is fitted to. Finally, test data is the according imaginary part, which we try to predict from the real part fit. In other words: A valid spectrum is under-fitted if, by adding more RC-elements to the ECM, the error between given and predicted imaginary part decreases. On the other hand, a spectrum is over-fitted, if by adding more RC-elements to the ECM, the error between the given and predicted imaginary parts increases. For further clarification, Fig. 5 shows an easy example: A situation is depicted, where the real part of IS1a is fitted by a varying number M of RC-elements. The according cumulated error between actual and predicted imaginary part,

$$\chi^2_{Im} = \frac{1}{N}\sum_{i=1}^{N}\left[\frac{Z_{Im}(\omega_i) - \hat{Z}_{Im}(\omega_i)}{\left|Z(\omega_i)\right|}\right]^2, \tag{20}$$

is plotted for each fit.

The minimum of the cumulated prediction error indicates the optimum number of RC-elements to fit the given impedance spectrum with its given noise disturbance. Fewer RC-elements again lead to a poor fit (under-fitting), with more RC-elements the fit becomes increasingly tuned to measurement noise or other errors (over-fitting). While this minimum and, by extension, the optimal number of RC-elements can easily be determined within a simulation, for a real impedance spectrum this is not possible. In this case the ideal imaginary part is not known and therefore neither the cumulated prediction error nor its trajectory can be computed.

4.3. A Criterion for Detecting Over-Fitting

Although the optimal number of RC-elements for a real measurement cannot be determined by a cumulated prediction error, finding this number is still possible. Aiming to only fit the valid information contained in a measured spectrum (and not the superposed noise) some *a priori* knowledge has to be used. An easy

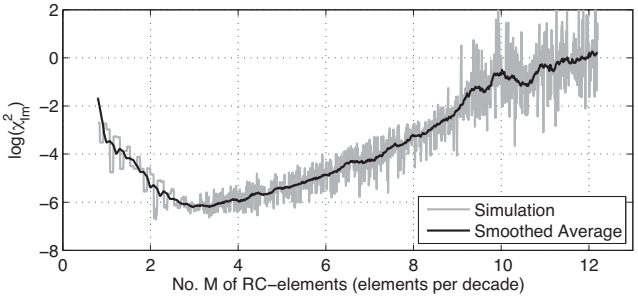

Fig. 5. Trajectory of the cumulated prediction error $\chi_{Im}{}^2$ between actual and predicted imaginary part of IS1a. For the prediction a varying number M of RC-elements are fitted to the real part of IS1a. Using a number of RC-elements left of the minimum is equivalent to under-fitting, using a number of elements right of the minimum coincides with over-fitting. To clarify the illustration, additionally a smoothed average is shown.

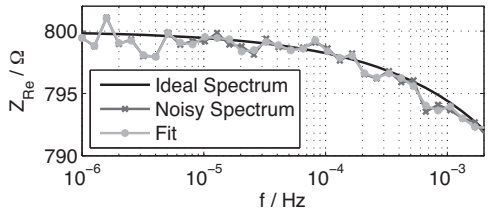

Fig. 6. An enlargement of the real parts of the impedance spectra IS1a shown in Fig. 3. Comparison with the ideal spectrum reveals the appearing oscillations in the noisy spectrum. The fit reproduces this behavior because of over-fitting.

way to distinguish between the noise part and the information part of an impedance spectrum is the fact that neither the real part nor the imaginary part of an ideal spectrum show oscillatory behavior when plotted over the frequency. Therefore, all oscillations contained in a measured impedance spectrum are caused by noise or measurement errors. On the other hand, a fitted spectrum that oscillates cannot be physically valid and must have been tuned to noise or other errors, which is again precisely the definition of over-fitting. Looking closely at the real parts of the over-fitted spectrum given in Fig. 3 easily reveals this fact, as Fig. 6 demonstrates.

Hence, over-fitting can be avoided by choosing the number of RC-elements in such a way as that no oscillations occur. Due to the structure of the ECM this doesn't need to be done *a posteriori*, e.g. by analyzing the shape of the fitted spectrum for oscillations. Rather, a specific property of RC-elements and the Lin-KK Test can be exploited: Consider that (i) within the Lin-KK test only values of the ohmic parts of the RC-elements are determined and (ii) for a series connection of RC-elements, oscillations can only occur if some of the ohmic parts have a negative sign. The occurrence of alternating signs in the fit values of the Lin-KK Test has already been discussed in [14]. In order to prevent the fit from oscillating the influence of negatively signed ohmic elements has to be limited. To quantify the latter we propose to use a measure relating the mass of negatively signed elements to the mass of the positively signed elements.

$$\mu = 1 - \frac{\sum_{R_k<0} |R_k|}{\sum_{R_k\geq 0} |R_k|}, \tag{21}$$

The suggested measure μ has a value of 1 as long as the mass of negatively signed elements is small compared to the mass of positively signed elements. In this case there is no danger of over-fitting. As soon as over-fitting starts, the mass of negative elements increases and μ monotonously goes to zero, see Fig. 7.

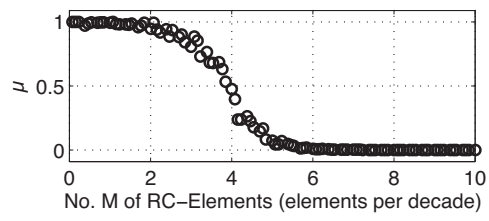

Fig. 7. Development of the measure μ computed for spectrum IS1a. It describes the influence of negatively signed elements on the fit. A monotonous decrease is observed as soon as a certain number of RC-elements are exceeded. Choosing a number of RC-elements during or after the decrease provokes over-fitting.

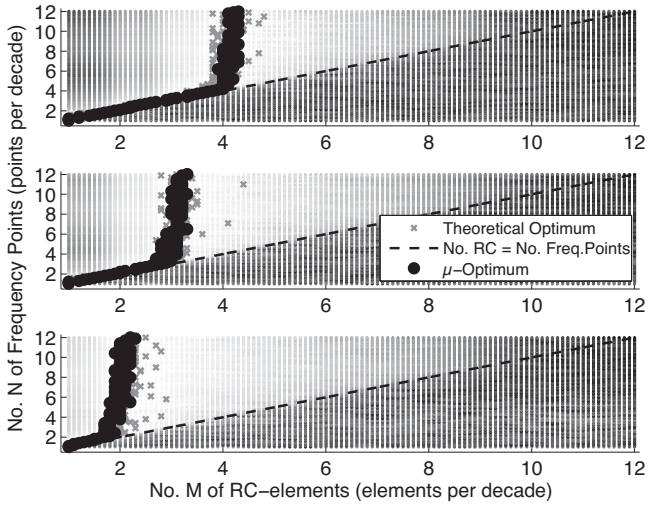

Fig. 8. The color coded values for the cumulated prediction error χ_{Im}^2 (see Equation (20)) for different combinations of numbers of frequency points for the tested spectrum and numbers of RC-elements used for the fit are depicted. A black dot coincides with a large value of χ_{Im}^2, whereas a bright dot coincides with a small value. Additionally, minimal values of χ_{Im}^2 (theoretical optimum) are marked by a cross, the according μ-optimum is marked by black dots. The latter perfectly coincides with the theoretical optimum. (top) Result for impedance spectrum IS1c (weak noise). (middle) Result for impedance spectrum IS1a (medium noise). (bottom) Result for impedance spectrum IS1b (strong noise).

4.4. Validity of the Introduced Criterion

The measure μ, as introduced in Equation (21), describes the influence of negatively signed RC-elements on the fit. Fig. 7 shows an exemplary trajectory of spectrum IS1a, where the Lin-KK test was evaluated using a different number of RC-elements. For every evaluation result μ is computed and plotted. It is argued in Section 4.3, that μ has a value of almost 1 in the area of under-fitting and rapidly decreases towards zero as soon as too many RC-elements are chosen and over-fitting starts. At the same time Fig. 5 shows, that the optimal number of RC-elements coincides with the minimal prediction error, which is achieved just before over-fitting starts. It is therefore expected, that the number of RC-elements just before the rapid decrease of μ is the most appropriate number to fit the given impedance spectrum. To ascertain if this number does indeed coincide with the theoretical optimum determined by evaluating the cumulated prediction error in Section 4.2, the impedance spectra IS1a (medium noise), IS1b (strong noise) and IS1c (weak noise) are investigated. Firstly, to capture a potential dependency of the optimal number of RC-elements, M_{opt}, from the number of measured frequencies, N, various combinations of these parameters are analyzed. For every combination the Lin-KK test is executed by fitting the spectra's real part and computing the according imaginary part. From this the cumulated prediction error χ_{Im}^2 was computed for all combinations (see also Section 4.2, Equation (20)). The result of this computation is depicted in Fig. 8, where the gray-scaling decodes the size of the according cumulated prediction error, e.g. a black dot coincides with a very large error, whereas a bright dot coincides with a small error. Additionally, the combinations for which χ_{Im}^2 has a minimal value (which coincides with the number of elements corresponding to the theoretical optimum) are marked by crosses. Finally, the numbers of RC-elements where μ first crosses a threshold of c = 0.85 (μ-criterion), are plotted. In the following section the hereby predicted optimal number of elements is referenced to as the μ-optimum. It is shown in Fig. 8 that for all tested spectra theoretical optimum and μ-optimum coincide perfectly.

The dependency of theoretical optimum and μ-optimum on the standard deviation of the added measurement noise perfectly matches the expectation that: The more noise a spectrum contains, the more this noise tends to get fitted, so to avoid this fewer elements have to be chosen.

Further, the depicted line describing equal numbers of frequency points and RC-elements per decade delimits the area, where more model parameters than frequency points are used for the fit. This obvious case of over-fitting is consistently accompanied by very large values of χ_{Im}^2. As long as there are too few RC-elements to fit the measurement noise, the μ-criterion correctly detects this line as border to over-fitting.

4.5. Strategy to Avoid Under- and Over-Fitting

Summarizing the results of Sections 4.1 to 4.4, the following strategy of avoiding under- and over-fitting for any given impedance spectrum is proposed.

1) Execute the Lin-KK test with a sufficiently small number of RC-elements, e.g. $M = 1$.
2) Take the resulting parameters and compute μ (Equation (21)).
3) Check if μ is smaller than a threshold c, e.g. $c = 0.85$. (μ-criterion)
4) If μ is larger than c, increase M by 1. Then repeat the Lin-KK test and go back to 2.).
   If μ is smaller than c, the μ-optimum is found.
5) End procedure and evaluate test result.

The value of c is a design parameter, however from the author's experience $c = 0.85$ has proven to be an excellent choice.

For clarity, the proposed strategy is also given in the flow chart in Fig. 9. Results using this procedure will be demonstrated for IS1a and IS3b in the following section.

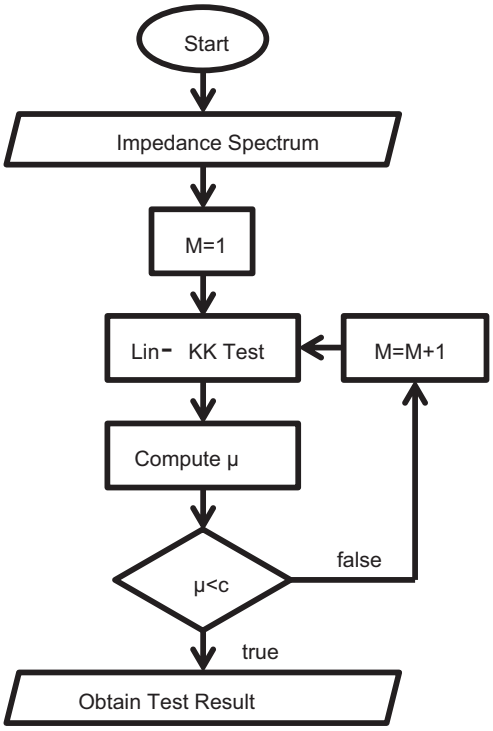

Fig. 9. Flow chart of the proposed strategy to avoid under- and over-fitting for any given impedance spectrum.

5. Results and Discussion

The functionality of the proposed strategy is demonstrated by repeating the failed Lin-KK tests shown in Fig. 3 and Fig. 4. Therefore, the impedance spectra IS1a and IS3b are evaluated according to steps 1 to 5, as mentioned in Section 4.5 (compare Fig. 9). The obtained residuals as well as the trajectory of μ and the chosen number of RC-elements according to the μ-criterion are depicted in Fig. 10.

The valid impedance spectrum IS1a is correctly identified as being valid, while the invalid impedance spectrum IS3b is correctly identified as invalid.

It is worth mentioning that the detected μ-optimum of 16 RC-elements for IS3b coincides with 2.4 RC-elements per decade. The distribution of frequency points for IS3b as given in Table 2 results in 6.7 equivalent frequency points per decade for the sparsely occupied low frequency part. In order to emphasize the benefit of the proposed strategy, we compare the obtained results with another intuitive approach: The idea is to select the number of RC-elements per decade to be just a bit lower than the number of frequencies in the most sparsely occupied frequency range, e.g. for 6.7 frequency points per decade choosing 6 RC-elements per decade (40 RC-elements total). It might be argued that this approach avoids over-fitting, as it locally prevents the number of RC-elements from being greater than the number of frequency points. At the same time the model contains a sufficiently large number of RC-elements; it follows that under-fitting is also not to be expected. However, it can be seen from Fig. 11 that this approach results in a less clear detection of invalidity than when using the strategy based on the μ-criterion. Considering an according value for μ of 0.02, this is expected.

One last possible point of criticism might be the supposedly high computational cost of repeating the Lin-KK test till the μ-criterion is fulfilled. However, owing to the enormous computational power

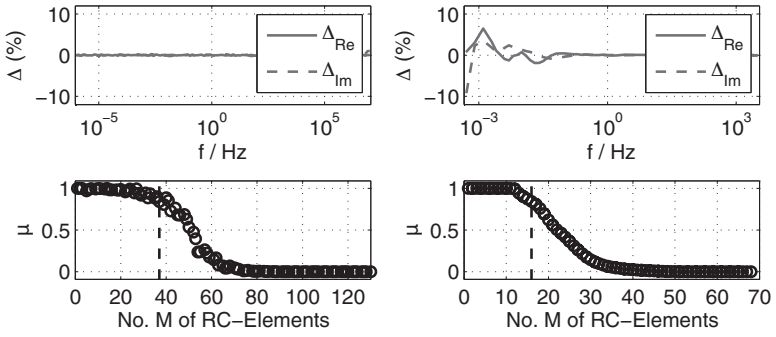

Fig. 10. Residuals and trajectories of μ. The number of RC-elements chosen by the proposed strategy is marked by a straight line. (left) Result for impedance spectrum IS1a. Using the μ-criterion the Lin-KK test now delivers the correct result that the spectrum is valid (compare Fig. 3). (right) Result for impedance spectrum IS3b. Using the μ-criterion the Lin-KK test now delivers the correct result that the spectrum is invalid (compare Fig. 4).

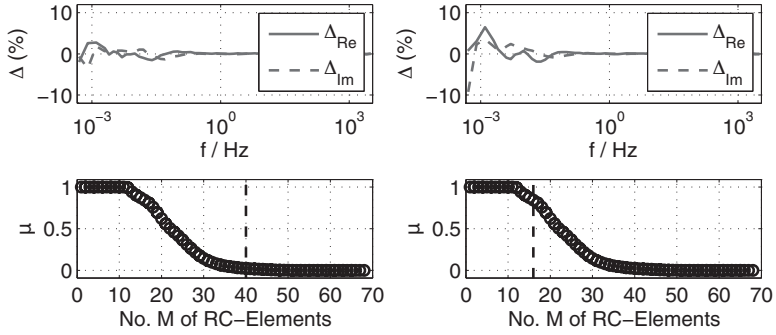

Fig. 11. Residuals and trajectories of μ. The number M of RC-elements chosen by the according strategy is marked by a straight line. (left) Result for impedance spectrum IS3b using an intuitive strategy of choosing *M*. (right) Result for impedance spectrum IS3b using the proposed strategy. Using the intuitive strategy the obtained residuals are much less pronounced than for the μ-strategy. Considering an according value of μ of 0.02, this is expected.

of a modern standard PC, the evaluations showed in Fig. 10 each took less than 1 second.

6. Conclusion

A strategy to avoid ambiguous results of the popular Kramers-Kronig test from [14] (Lin-KK test) is presented. It is based on an automated procedure to determine the optimum value of the number of RC-elements for the corresponding fit model.

It was shown with the help of simulations that the Lin-KK test can fail for some examples by choosing a wrong number of RC-elements. Further, impedance spectra of a commercial Lithium-Ion battery were measured under temperature variation. For the same reason the obvious invalidity of these spectra was hardly detected. Both cases were related to under-fitting and over-fitting.

As a solution, the so dubbed μ-criterion was introduced and employed to determine an optimum number of RC-elements. It was thereby shown that the obtained μ-optimum perfectly coincides with the theoretical optimum for several cases of disturbances.

Finally, the proposed criterion was embedded in a general strategy to find an appropriate number of RC-elements for any given impedance spectrum, thereby avoiding under-fitting as well as over-fitting. The strategy was tested by simulations and measurements and in both cases its functionality could be confirmed.

By using the Lin-KK test in combination with the proposed strategy unambiguous test results can be obtained irrespective of the experience of the operator. Due to its ease of use the so improved test can serve as a quick standard test revealing defectiveness of measured impedance spectra.

References

[1] A. Leonide, V. Sonn, A. Weber, E. Ivers-Tiffée, J. Electrochem. Soc. 155 (2008) B36.
[2] J. Illig, M. Ender, T. Chrobak, J.P. Schmidt, D. Klotz, E. Ivers-Tiffée, J. Electrochem. Soc. 159 (2012) A952–A960.
[3] J.P. Schmidt, T. Chrobak, M. Ender, J. Illig, D. Klotz, E. Ivers-Tiffée, J. Power Sources 196 (2011) 5342.
[4] E.v. Gheem, R. Pintelon, J. Vereecken, J. Schoukens, A. Hubin, P. Verboven, O. Blajiev, Electrochim. Acta 49 (2004) 4753–4762.
[5] E.v. Gheem, R. Pintelon, A. Hubin, J. Schoukens, P. Verboven, O. Blajiev, J. Vereecken, Electrochim. Acta 51 (2006) 1443–1452.
[6] H.A. Kramers, Transactions of Volta Centenary Congress 2 (1927) 545.
[7] R. de, L. Kronig, Journal of the Optical Society of America. 12 6 (1926) 547–556.
[8] C. Bohren, Eur. J. Phys. 31 (2010) 573–577.
[9] M. Urquidi-Macdonald, S. Real, D. Macdonald, Electrochim. Acta 35 (10) (1990) 1559–1566.
[10] J. Esteban, M.E. Orazem, J. Electrochem. Soc. 138 (1) (1991) 67–76.
[11] P. Agarwal, M.E. Orazem, L.H. Garcia-Rubio, J. Electrochem. Soc. 139 (1992) 1917.
[12] P. Agarwal, O.D. Crisalle, M.E. Orazem, L.H. Garcia-Rubio, J. Electrochem. Soc. 142 (1995) 4149.
[13] P. Agarwal, M.E. Orazem, L.H. Garcia-Rubio, J. Electrochem. Soc. 142 (1995) 4159.
[14] B.A. Boukamp, J. Electrochem. Soc. 142 (1995) 1885.
[15] C. Bishop, Pattern Recognition and Machine Learning, Springer, New York, USA, 2006.