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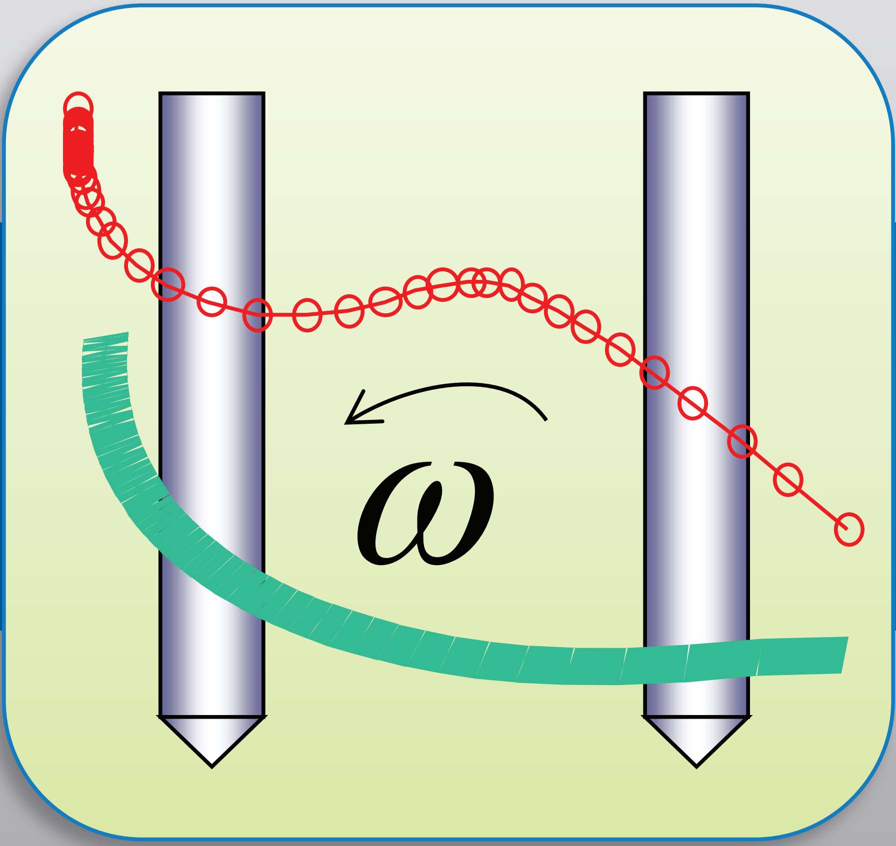

Lecture Notes on Impedance Spectroscopy

Measurement, Modeling and Applications

Editor: Olfa Kanoun

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LECTURE NOTES ON IMPEDANCE SPECTROSCOPY

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Measurement, Modeling and Applications

Editor

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Preface

Impedance Spectroscopy is a widely used and interesting measurement method applied in many fields such as electro chemistry, material science, biology and medicine. In spite of the apparently different scientific and application background in these fields, they share the same measurement method in a system identification approach and profit from the possibility to use complex impedance over a wide frequency range and giving interesting opportunities for separating effects, for accurate measurements and for simultaneous measurements of different and even non-accessible quantities.

For Electrochemical Impedance Spectroscopy (EIS) competency from several fields of science and technology is indispensable. Understanding electro chemical and physical phenomena is necessary for developing suitable models. Suitable measurement procedures should be developed taking the specific requirements of the application into account. Signal processing methods are very important for extracting target information by suitable mathematical methods and algorithms.

The scientific dialogue between specialists of Impedance Spectroscopy, dealing with different application fields, is therefore particularly important to promote the adequate use of this powerful measurement method in both laboratory and in embedded solutions.

The International Workshop on Impedance Spectroscopy (IWIS) has been established as a platform for promoting experience exchange and networking in the scientific and industrial field. It has been launched already in 2008 with the aim to serve for encouraging the sharing of experiences between scientists and to support new comers dealing with impedance spectroscopy. The workshop has been gaining increasingly more acceptance in both scientific and industrial fields and addressing not only more fundamentals, but also diverse application fields of impedance spectroscopy. By means of tutorials and special sessions, young scientist get a good overview of different fundamental sciences and technologies helping them to get expertize even in fields, which are not in the focus of their previous background.

This book is the fourth in the series Lecture Notes on Impedance Spectroscopy which has the aims to widen knowledge of scientists in this field and includes selected and extended contributions from the International Workshop on Impedance Spectroscopy (IWIS '12). The book reports about new advances and different approaches in dealing with impedance spectroscopy including theory, methods and applications. The book is interesting for researcher and developers in the field of impedance spectroscopy.

I thank all contributors for the interesting contributions and the reviewer who supported by the decision about publication with their valuable comments.

Prof. Dr.-Ing. Olfa Kanoun

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Modeling and parameterization

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Method for parameterization of impedance-based models with time domain data sets

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ABSTRACT: State determination of Li-ion cells is often accomplished with Electrochemical Impedance Spectroscopy (EIS). The measurement results are in frequency domain and used to describe the state of a Li-ion cell by parameterizing impedance-based models. Since EIS is a costly measurement method, an alternative method for the parameterization of impedance-based models with time-domain data easier to record is presented in this work. For this purpose the model equations from the impedance-based models are transformed from frequency domain into time domain. As an excitation signal a current step is applied. The resulting voltage step responses are the model equations in time domain. They are presented for lumped and derived for distributed electrical circuit elements, i.e. Warburg impedance, Constant Phase Element and RCPE. A resulting technique is the determination of the inner resistance from an impedance spectrum which is performed on measurement data.

Keywords: Electrochemical Impedance Spectroscopy, modeling, Li-ion cell, inner resistance, voltage step response, Constant Phase Element

1 INTRODUCTION

An emerging application for large quantities of Li-ion cells is the electrification of power trains, where Li-ion cells seem to be a proper technology which covers a broad spectrum of e-mobility applications like hybrid electric vehicles, plug-in hybrid electric vehicles and electric vehicles. For these applications a precise state determination of the Li-ion battery and its cells is mandatory to ensure a reliable operation of the vehicle.

In an laboratory environment, state determination of Li-ion cells is often accomplished with Electrochemical Impedance Spectroscopy (EIS). Using these impedance spectra, impedance-based models are parameterized in the frequency domain with well-known fitting procedures. These models are designed to reduce the dimension of the measurement data in order to describe the state of a Li-ion cell with few parameters. The parameters of these models can than be used to determine the cell's current state (SOx). There exists a variety of impedance-based models represented by electrical equivalent circuits.

Due to the high measurement and computational complexity as well as cost factors, frequency domain EIS measurements are not likely to be implemented on board in vehicles in the near future. An alternative approach is shown to parameterize impedance-based models with time domain data available on board, i.e. currents, battery or cell voltages and temperatures. Therefore, in this work, a method is proposed for the transformation of electrical circuit model equations from frequency domain into time domain model equations. Particularly for electrical circuit models containing distributed elements, e.g. Warburg impedances (WB), Constant Phase Elements (CPE), RCPE or ZARC elements, these transformations require fractional calculus methods, as will be presented in detail.

In order to prove the validity of this approach in a realistic scenario the transformation of an impedance spectrum into time domain for the determination of the conventionally defined inner resistance of a Li-ion cell will be shown. This allows for the comparison of the measurement results in frequency domain and time domain.

2 SYSTEMTHEORETICAL APPROACH

Figure 1 displays a systemtheoretical description of a Li-ion cell.

Impedance-based models are electrical equivalent circuits, containing lumped and distributed elements, e.g. resistors, capacitors, Warburg impedances. They are often used for modeling electrochemical systems like Li-ion cells [1] and describe the overvoltage η, see Figure 2. In this case, the current is the excitation and thus the input signal whereas the voltage is the response and thus the output signal of the system.

There exists a variety of impedance-based models differing in accuracy and number of model parameters, described by the parameter set $\vec{P}$. The model equation is a function of time or frequency and also a function of a parameter set $\vec{P}$.

The intention of the description of a measurement with an impedance-based model is the dimension reduction of the measurement data. The dimension reduced measurement is expressed by the parameter set $\vec{P}$ together with the model equation, for both frequency domain and time domain. The parameterization of the impedance-based model is performed according to the modeling procedure described in Section 2.3.

This work aims to describe the impedance-based models in time domain where the voltage response $u(t)$ is the model equation. The starting point is the system description in the frequency domain using the impedances $Z(s)$ as the model equation. Time domain model equations are thus derived analytically from the frequency domain using a specific excitation signal.

2.1 *System description in frequency domain*

The impedance $Z(s)$ represents the state of a Li-ion cell in frequency domain and can be illustrated by an impedance spectrum, e.g. in a Nyquist plot in the complex plane, see Figure 3. The impedance is the system function or the frequency response locus which is in case of a Li-ion cell the complex voltage $U(s)$, i.e. the system response, divided by the complex current $I(s)$, i.e. the excitation signal. In frequency domain $s = \sigma + j\omega$ is the complex frequency with a damping term σ and the angular frequency $\omega = 2\pi f$.

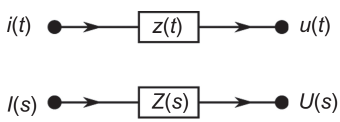

Figure 1. Description of the system of a Li-ion cell or battery, which is a two-port network. The upper graph shows the system in time domain and the lower graph shows the system in frequency domain. The input signal is the current excitation and whereasthe output signal is the voltage response.

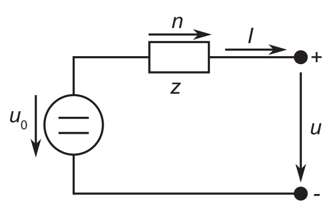

Figure 2. The graph shows the model of a Li-ion cell, with the open circuit voltage U_0, the closed circuit voltage U and the overvoltage η. The overvoltage is expressed by an impedance-based model with the impedance Z.

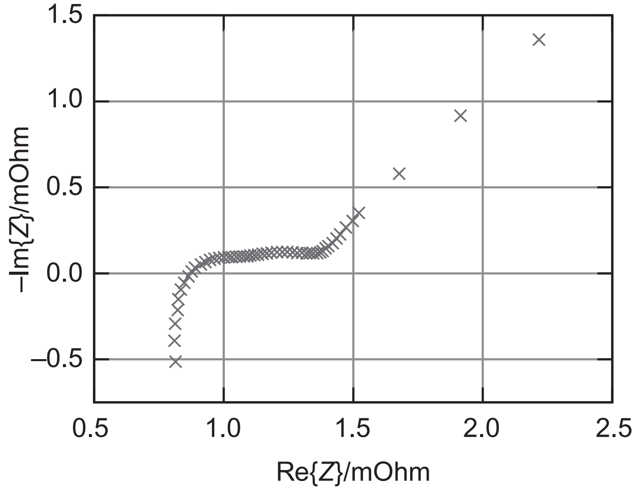

Figure 3. Example of an impedance spectrum of a Saft VL6P Li-ion cell.

A certain state of the system is described by the impedance $Z(s,\vec{P})$ as a function of a parameter set $\vec{P}$ which corresponds to the component values of the electrical equivalent circuit elements for that state, see Equation (1).

$$Z(s)=\frac{U(s)}{I(s)}\Rightarrow Z(s,\vec{P})=\frac{U(s,\vec{P})}{I(s)} \tag{1}$$

In order to determine the parameter set $\vec{P}$ for a certain state of the cell in the frequency domain, an impedance spectrum is recorded and modeled with $Z(s,\vec{P})$ according to Section 2.3.

2.2 *System description in time domain*

The model for a Li-ion cell in time domain is described by the output voltage $u(t)$ being the convolution of the input signal $i(t)$ and the system function $z(t)$. The voltage response $u(t,\vec{P})$ is a function of a certain parameter set $\vec{P}$, depending on the state of the Li-ion cell, see Equation (2).

$$u(t)=i(t)*z(t)\Rightarrow u(t,\vec{P})=i(t)*z(t,\vec{P}) \tag{2}$$

To determine the parameter set $\vec{P}$ in time domain, the voltage response $u(t,\vec{P})$ is modeled according to Section 2.3, assuming that the model equation considers the analytical description of the excitation signal $i(t)$ which is applied during the measurement.

2.3 *Parameterization in frequency and time domain*

In principle, the parameterization can be performed on frequency or time domain data, see Figure 4. But not all physical effects are covered in both data likewise, e.g. low temperatures and high currents, see Section 4.

From a mathematical point of view, the model equations are non-linear functions with several parameters, having a bounded range. The model equations are the impedance as a function of the complex frequency $Z(s)$ in frequency domain and the voltage response to a certain current excitation signal as a function of time $u(t)$ in time domain. In principle any

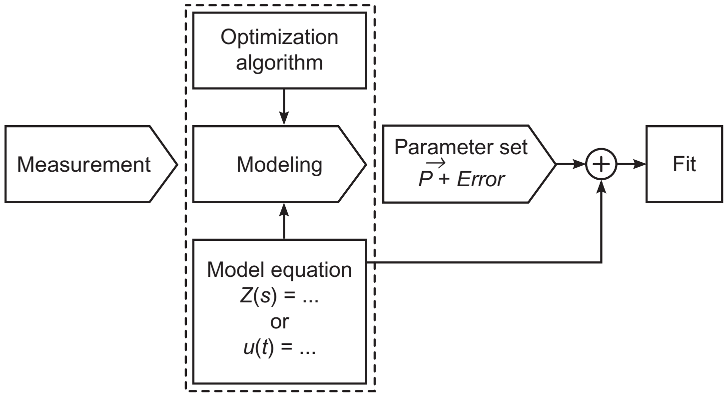

Figure 4. Process of modeling both time domain and frequency domain measurement data. The optimization process results in an adjusted parameter set $\vec{P}$ and an associated error. Together with the model equation the parameter set yields the fitting curve which is a reproduction of the measurement data.

optimization algorithm can be utilized for the modeling process, but it should be carefully selected in order to suit the mathematical problem. In this work parameterization of models is performed with the Particle Swarm Optimization (PSO) algorithm according to the modeling procedure described in [2].

The PSO is a nature inspired algorithm and allows to set boundary conditions for the model parameters and thus defines the search space, where the optimizations results are located likely. It is an iterative optimization process and during operation the search space is scanned for a minimum by a number of particles all representing possible solutions. These particles are influencing each other and share information about past and current positions in search space, i.e. the particle swarm shows intelligent behavior. The quality of an optimization result is quantified with a uniform distance measure. A detailed description of this metric can be found in [3].

The result of the modeling process is a set of parameters $\vec{P}$ that yields, together with the model equation used, a fitting curve of the measurement data together with an associated error.

3 MODEL TRANSFORMATION

If the electrical equivalent circuit model is a series connection of model elements, the overall model equation is the vector addition of the single model element equations in time domain and frequency domain, respectively. Time domain correspondences for single model elements to certain excitation signals can be calculated analytically as described in the following sections. In general these transformations can be easily computed for models consisting of lumped elements. For models containing distributed elements, fractional calculus is required.

For analytical calculations and easy metrological realization, the excitation signal should be a simple signal, e.g. Dirac delta function or the Heaviside step function. The metrological realization of the Dirac delta function is difficult, but it is easy to excite a Li-ion cell with a step-shaped current input signal. Current steps can even be found in real driving data or are easy to generate in laboratory. Furthermore, the corresponding time domain model equations can be calculated analytically.

In the following, common excitation signals are listed in time and frequency domain. Additionally the well-known voltage responses to current step excitations for single lumped elements (R, C, RC) are shown leading to the novel derivation for distributed elements

(WB, CPE, RCPE) using fractional calculus. Applying the single model element voltage step responses (VSR), the time domain model equations are set up for two common models.

3.1 *Excitation signals*

Common current excitation signals and their Laplace correspondences in frequency domain are listed in Table 1.

If the current excitation signal $i(t)$ and its Laplace correspondence $I(s)$ are known, the voltage response $u(t)$ to this excitation in time domain for a model element with an impedance $Z(s)$ can be calculated by inverse Laplace transform of the product of $I(s)$ and $Z(s)$, according to Equations (3) and (4).

$$U(s) = I(s) \cdot Z(s) \tag{3}$$

$$\bullet\!-\!\circ$$

$$u(t) = \mathcal{L}^{-1}\{I(s) \cdot Z(s)\} \tag{4}$$

3.2 *Derivation of model elements time domain correspondences with a current step excitation*

In the following current step excitations are used exclusively as excitation signals, due to their simple metrological realization and since it is possible to transform VSR in frequency domain into time domain analytically.

There exist two methods for the derivation of the transient time domain voltage responses $u(t)$. One approach is to solve the differential equations of $u(t)$ in time domain for the overall model equation derived according to Kirchhoff's laws. This method is appropriate for lumped elements and simple combinations of these elements.

As an alternative the single model elements' impedances $Z(s)$ connected in series in the model, are multiplied with the Laplace transform of the excitation signal $I(s)$. These products are the voltage responses $U(s)$ in frequency domain for the single model elements and are transformed into time domain using inverse Laplace transform subsequently. The overall voltage response of the model consists of the sum of voltage responses of the single model elements. This approach is used in the following.

For lumped elements, e.g. resistors, capacitors or combinations of these elements, the differential equations, impedances and VSR are well-known [4]. Distributed elements, i.e. Warburg impedance, Constant Phase Element, or parallel connections like RCPE, also known as ZARC or Cole-Cole element, have non-integer exponents α of the complex frequency s in frequency domain. This corresponds to fractional differential equations in time domain and thus the calculation of the VSR requires fractional calculus, as can be seen in the following derivations.

Table 1. Commonly used current excitation signals in time domain and their Laplace transforms in frequency domain. $\hat{I}$ is the amplitude of the excitation siganal.

Excitation signal	Time domain		Frequency domain
Arbitrary	$i(t)$	$\circ\!-\!\bullet$	$I(s)$
Dirac delta	$\hat{I} \cdot \delta(t)$	$\circ\!-\!\bullet$	$\hat{I} \cdot 1$
Heaviside step	$\hat{I} \cdot \sigma(t) = \hat{I} \begin{cases} 0, t < 0 \\ 1, t \geq 0 \end{cases}$	$\circ\!-\!\bullet$	$\hat{I} \cdot \frac{1}{s}$
Sine	$\hat{I} \cdot \sin(\omega t)$	$\circ\!-\!\bullet$	$\hat{I} \cdot \frac{\omega}{\omega^2 + s^2}$

a) *Constant Phase Element*

The underlying differential equation of the CPE is an arbitrary fractional derivative of the order α. The model parameters of the CPE are Q and α and a CPE shows capacitive behavior for $\alpha = (0, 1]$ and inductive behavior for $\alpha = [-1, 0)$. The VSR of a CPE in frequency domain is shown in Equation (5). Performing the inverse Laplace transform of $U_{\text{step, CPE}}(s)$ using the correspondence $\frac{\alpha!}{s^{\alpha+1}} \bullet\!\!-\!\!\circ\ t^{\alpha}$ [5] leads to the VSR in time domain of a CPE which includes an arbitrary-root shaped decay, see Equation (6).

$$U_{\text{step, CPE}}(s) = I(s) \cdot Z(s) = \frac{\hat{I}}{s} \cdot \frac{1}{Q s^{\alpha}} = \frac{\hat{I}}{Q\alpha!} \cdot \frac{\alpha!}{s^{\alpha+1}} \tag{5}$$

$$\bullet\!\!-\!\!\circ$$

$$u_{step,\ CPE}(t) = \frac{\hat{I}}{Q\alpha!} t^{\alpha} = \frac{\hat{I}}{Q} \cdot \frac{t^{\alpha}}{\Gamma(\alpha+1)} \tag{6}$$

With the amplitude of the excitation signal $\hat{I}$, $\alpha! = \Gamma(\alpha+1)$ and the Gamma function $\Gamma(x)$ which is an extension of the factorial function to real and complex numbers, see [6].

b) *Warburg impedance*

The Warburg impedance is a special case of a CPE with the constant exponent $\alpha = 0.5$, i.e. the underlying differential equation contains the half fractional derivative. Thus the VSR contains a square-root shaped decay according to Equation (7).

$$u_{\text{step, WB}}(t) = \frac{\hat{I}}{Q} \cdot \frac{\sqrt{t}}{\Gamma(1.5)} \tag{7}$$

With the amplitude of the excitation signal $\hat{I}$, the Parameter of the Warburg impedance Q and the constant value $\Gamma(1.5) \approx 0.88623$.

c) *RCPE*

The RCPE is a parallel connection of a resistor and a CPE and thus described by the model parameters R, Q and α. Its VSR in frequency domain is shown in Equation (8).

$$U_{\text{step, RCPE}}(s) = I(s) \cdot Z(s) = \frac{\hat{I}}{s} \cdot \frac{R}{1 + RQs^{\alpha}} \tag{8}$$

In order to derive the VSR of the RCPE $u_{\text{step, RCPE}}(t)$ in time domain, the inverse Laplace transform of Equation (8) has to be derived using fractional calculus, see Equations (9)–(16).

For the special case $Z(s) = \frac{1}{as^{\alpha}+b}$ the VSR $u_{\text{step}}(t)$ is shown in Equation (9) according to [7].

$$u_{\text{step}}(t) = D^{-1}z(t) = \frac{1}{a}\varepsilon_0\left(t, -\tfrac{b}{a}; \alpha, \alpha+1\right) \tag{9}$$

With the Mittag-Leffler function $E_{\alpha,\beta}(x)$ as defined in Equation (10), [7].

$$E_{\alpha,\beta}(x) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(\alpha n + \beta)} \quad (\alpha > 0, \beta > 0) \tag{10}$$

and the k-th derivative of the Mittag-Leffler function as defined in Equation (11), [7].

$$E_{\alpha,\beta}^{(k)}(x)=\sum_{n=0}^{\infty}\frac{(n+k)!\,x^n}{n!\,\Gamma(\alpha n+\alpha k+\beta)} \qquad (k=0,1,2,...) \tag{11}$$

Thus the function ε_k can be defined as in Equation (12), [7].

$$\varepsilon_k\left(t,y;\alpha,\beta\right)=t^{\alpha k+\beta-1}E_{\alpha,\beta}^{(k)}\left(yt^{\alpha}\right) \qquad (k=0,1,2,...) \tag{12}$$

And the k-th derivative $D^{\lambda}\varepsilon_k$ of the function ε_k is defined in Equation (13). With D^{λ} being the fractional differential operator to the order λ, [7].

$$D^{\lambda}\varepsilon_k\left(t,y;\alpha,\beta\right)=\varepsilon_k\left(t,y;\alpha,\beta-\lambda\right) \qquad (\lambda<\beta) \tag{13}$$

In Equation (9) D^{-1} is the first negative derivative, i.e. the first positive integral.

The VSR can thus be rewritten from Equation (9):

$$u_{step}\left(t\right)=\frac{1}{a}\varepsilon_0\left(t,-\tfrac{b}{a};\alpha,\alpha+1\right)=\frac{1}{a}t^{\alpha}E_{\alpha,\alpha+1}\left(-\tfrac{b}{a}t^{\alpha}\right) \tag{14}$$

$$=\frac{1}{a}t^{\alpha}\sum_{n=0}^{\infty}\frac{\left(-\frac{b}{a}\right)^n t^{\alpha n}}{\Gamma(\alpha n+\alpha+1)} \tag{15}$$

$$=\frac{1}{a}t^{\alpha}\sum_{n=0}^{\infty}\left(-\frac{b}{a}\right)^n\frac{t^{\alpha n}}{(\alpha n+\alpha)!} \tag{16}$$

For the case of a RCPE $a=RQ$ and $b=1$. Thus the VSR contains an $\frac{1}{\alpha}$-root-shaped voltage response and a Mittag-Leffler function shaped voltage response, according to Equation (18).

Table 2. The table shows for often used elements for impedance based models the differential equations in time domain, the impedances and the VSR. The overall impedance of a model containing these elements can be set up by summing up the equations of the single model elements. $\Gamma(x)$ denotes the Gamma function and $E_{\alpha,\beta}(x)$ denotes the Mittag-Leffer function.

Model element	Differential equation $i(t)$ =	Impedance $Z(s)$ =	Voltage step response $u_{\mathrm{step}}(\mathrm{t})$ =
R	$\frac{u(t)}{R}$	R	$\hat{I}R$
C	$C\frac{\mathrm{d}}{\mathrm{d}t}u(t)$	$\frac{1}{Cs}$	$\frac{\hat{I}}{C}t$
RC	$\frac{u(t)}{R}+C\frac{\mathrm{d}}{\mathrm{d}t}u(t)$	$\frac{R}{1+RCs}$	$\hat{I}R\left(1-\exp\left(-\frac{t}{RC}\right)\right)$
WB	$Q\frac{\mathrm{d}^{0.5}}{\mathrm{d}t^{0.5}}u(t)$	$\frac{1}{Qs^{0.5}}$	$\frac{\hat{I}}{Q}\frac{t^{0.5}}{\Gamma(1.5)}$
CPE	$Q\frac{\mathrm{d}^{\alpha}}{\mathrm{d}t^{\alpha}}u(t)$	$\frac{1}{Qs^{\alpha}}$	$\frac{\hat{I}}{Q}\frac{t^{\alpha}}{\Gamma(\alpha+1)}$
RCPE	$\frac{u(t)}{R}+Q\frac{\mathrm{d}^{\alpha}}{\mathrm{d}t^{\alpha}}u(t)$	$\frac{R}{1+RQs^{\alpha}}$	$\frac{\hat{I}}{Q}t^{\alpha}E_{\alpha,\alpha+1}\left(-\frac{1}{RQ}t^{\alpha}\right)$

$$U_{step,\,\mathrm{RCPE}}(s) = \hat{I}\,R\frac{1}{s}\frac{1}{1+RQs^{\alpha}} \tag{17}$$

$$\bullet\!\!-\!\!\circ$$

$$u_{setp,\,RCPE}(t) = \frac{\hat{I}}{Q}t^{\alpha}\sum_{n=0}^{\infty}\left(-\frac{1}{RQ}\right)^{n}\frac{t^{\alpha n}}{(\alpha n+\alpha)!} \tag{18}$$

This result conforms with the VSR of a RCPE presented in [8].

For commonly used lumped and distributed elements, the differential equations, impedances and VSR are summarized in Table 2.

3.3 *Examples for models*

Many impedance-based models have been proposed in the past [9–13]. It turned out that the models depicted in Figure 5 and 6 are able to match the measured impedance spectra to a high degree [2]. In the following, both models are presented with their characteristic properties, their impedances and VSR, which are derived according to the method proposed in the previous sections.

a) *R-RC-RC-WB model*

This model contains lumped circuit elements and one Warburg impedance, and its parameter set has six elements $\vec{P} = \left[R_2, R_3, R_4, C_3, C_4, Q_5\right]$. In the Nyquist plot this model results in two symmetric semicircles and a –45° diffusion branch shifted on real axis with the value of the series resistance R_2. Figure 5 shows the electrical equivalent circuit and the impedance is given by Equation (19).

$$Z(s) = R_2 + \frac{R_3}{1+R_3C_3s} + \frac{R_4}{1+R_4C_4s} + \frac{1}{Q_5s^{0.5}} \tag{19}$$

The VSR in time domain includes exponential function decays and a square root decay caused by the Warburg impedance, see Equation (21). This model is a good compromise between fitting accuracy and computational effort.

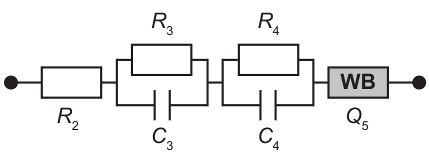

Figure 5. The figure shows the R-RC-RC-WB model. Besides the Warburg impedance, this model contains only lumped elements. Its impedance is shown in Equation (19), the VSR in frequency domain is shown in Equation (20) and the VSR in time domain is shown in Equation (21).

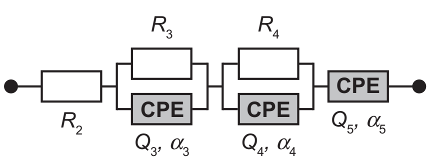

Figure 6. The figure shows the R-RCPE-RCPE-CPE model. This model contains only distributed elements besides the series resistance R_2. Its impedance is shown in Equation (22), the VSR in frequency domain is shown in Equation (23) and the VSR in time domain is shown in Equation (24).

$$U_{\text{step}}(s) = \hat{I}\left[\frac{R_2}{s} + \frac{R_3}{s + R_3C_3s^2} + \frac{R_4}{s + R_4C_4s^2} + \frac{1}{Q_5s^{1.5}}\right] \tag{20}$$

$$\bullet\!\!-\!\!\circ$$

$$u_{\text{step}}(t) = \hat{I}\left[R_2 + R_3\left(1 - e^{-\frac{t}{R_3C_3}}\right) + R_4\left(1 - e^{-\frac{t}{R_4C_4}}\right) + \frac{\sqrt{t}}{Q_5\Gamma(1.5)}\right] \tag{21}$$

b) *R-RCPE-RCPE-CPE model*

This model contains two RCPE and one CPE and therefore has nine parameters $\vec{P} = [R_2, R_3, R_4, Q_3, Q_4, Q_5, \alpha_3, \alpha_4, \alpha_5]$. In the Nyquist plot this model corresponds to two depressed semicircles and an arbitrary angled diffusion branch shifted on the real axis with the value of the series resistance R_2. Figure 6 shows the electrical equivalent circuit and the impedance is given by Equation (22).

$$Z(s) = R_2 + \frac{R_3}{1 + R_3Q_3s^{\alpha_3}} + \frac{R_4}{1 + R_4Q_4s^{\alpha_4}} + \frac{1}{Q_5s^{\alpha_5}} \tag{22}$$

The VSR in time domain includes Mittag-Leffler function decays and an arbitrary root-shaped decay caused by the single CPE element, see Equation (24). For the calculation of the Mittag-Leffler functions, there exist toolboxes for MATLAB. This model provides an excellent fitting accuracy of the impedance spectra, but the parameterization in time domain requires more computational effort due to the number of parameters and the complexity of the Mittag-Leffler functions.

$$U_{\text{step}}(s) = \hat{I}\left[\frac{R_2}{s} + \frac{R_3}{s + R_3Q_3s^{\alpha_3+1}} + \frac{R_4}{s + R_4Q_4s^{\alpha_4+1}} + \frac{1}{Q_5s^{\alpha_5+1}}\right] \tag{23}$$

$$\bullet\!\!-\!\!\circ$$

$$u_{\text{step}}(t) = \hat{I}\left[R_2 + \frac{1}{Q_3}t^{\alpha_3}E_{\alpha_3,\,\alpha_3+1}\left(-\tfrac{1}{R_3Q_3}t^{\alpha_3}\right) + \frac{1}{Q_4}t^{\alpha_4}E_{\alpha_4,\alpha_4+1}\left(-\tfrac{1}{R_4Q_4}t^{\alpha_4}\right) + \frac{1}{Q_5}\frac{t^{\alpha_5}}{\Gamma(\alpha_5+1)}\right] \tag{24}$$

4 EXPERIMENTAL

A proof and a possible application for this method is the determination of the inner resistance R_i from an impedance spectrum. This technique enables comparisons between measured impedance spectra and conventionally determined inner resistances.

The inner resistance of a Li-ion cell is defined as the voltage drop after a certain time t_x due to a current step excitation $i(t) = \hat{I} \cdot \sigma(t)$ with the amplitude $\hat{I}$. Thus the inner resistance is a time-dependent value, see Equation (25).

$$R_i(t_x) = \frac{u(t_x) - u(t_0)}{\hat{I}} \tag{25}$$

To determine the inner resistance from an impedance spectrum, the EIS measurement is carried out and parameterized in frequency domain with an impedance-based model, leading to the parameter set $\vec{P}$. The model is transformed analytically from frequency