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The distribution of relaxation times as basis for generalized time-domain models for Li-ion batteries

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HIGHLIGHTS

- A new method for creating automated parameterized time-domain models is introduced.
- Impedance measurements in a broad frequency range are performed.
- The Distribution of Relaxation Times (DRT) is calculated.
- The model is successfully validated with different current profiles in the time-domain.
- The advantages and limits of this modeling approach are discussed.

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ABSTRACT

A novel approach for the development of a model for Li-ion batteries with the potential for application in on-board diagnostic is introduced. This approach is not tied to a particular electrochemistry, and has the advantages of scalability and automatable parameterization as well as feasibility regarding an implementation on microcontrollers. The dynamic behavior of the cell under test, a Li-ion pouch cell with a graphite anode and a blend cathode, is characterized in an extremely broad frequency range from 100 kHz to 17 μHz. The introduced model gives predictions consistent with the experimental data, its accuracy depends on the assumed number of relaxation times respectively model order. Recommendations concerning application are given and limitations of the approach are discussed.

1. Introduction

There are special requirements for automotive application of battery systems. This has led to an increased number of publications covering methods for simulation and modeling of lithium ion batteries. The range of complexity and parameterization effort is very broad. Our approach features the distribution of relaxation times and is thereby bridging the gap between physically based mathematical models and coarse equivalent circuit models. It combines straightforward parameterization and a structure that is readily implementable on microcontrollers with a scalable degree of detail.

The application of models is always associated with constraints, i.e. accuracy, computational complexity, configuration effort or analytical insight [1]. As there is no "correct" model, the goal must be to select the model, which is optimal under given constraints. In system theory models are ranked in order of their degree of physical interpretability: white box, gray box and black box models [2].

White box models are based on physical and electrochemical partial differential equations. They describe transport processes and electrochemical processes, which can be linked. These models are often simulated applying FEM-Tools, whereby spatial resolution is variable. Calculation effort increases from 0D-models over homogenized or particle 1D models [3,4] to homogenized 2D models [5,6] up to 3D models [7]. Material constants for parameterization are either available from literature or obtained from extensive measurements.

Equivalent circuit models, for example, belong to the class of *gray box* models. They are proposed in variable degrees of detail. Physical insight can be gained by using adequate circuit elements, i.e. for electrical conductivity, charge transfer, electrochemical double layer or diffusion [8]. However, ambiguity of equivalent

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circuit models is a problem. Despite correct description of the clamp behavior, physical interpretation of circuit element values can be misleading [9]. In some cases circuit elements are of fractional nature and cannot be simulated directly in time domain. This can be solved by the implementation of a fractional integrator [10–12] or by approximating the system with a sum of RC elements [8,13]. While generally the spatial resolution of electrode processes in equivalent circuit models is lower compared to white box models, still ladder type models can be used to describe porosity [14–17]. A coarse spatial resolution is achieved via segmentation, as proposed in Refs. [18,19]. In general, equivalent circuit models are parameterized by fitting them to a measured electrochemical impedance spectrum [13,17,20–25]. Alternatively, a current or potential profile is used for parameterization [26–30].

Artificial neuronal networks [31–34], fuzzy logic [35] or NARMAX models [36] are rated among *black box models*, which are mostly used for diagnosis. Certainly their parameters do not allow for a physical interpretation, but on the other hand parameterization can be completely automated and no a priori knowledge of the processes in the batteries is needed.

The introduced model combines the advantages concerning physical insight of a gray box model with the fully automatable parameterization of a black box model. It is based on the idea, that the impedance of a capacitive electrochemical system can be interpreted as a continuous distribution of RC elements in the space of relaxation times. This is a very general assumption, which is not tied to a particular electrochemistry: Batteries and even fuel cells have proven to be well described by models based on that approach [37–40]. Its distinctive property, the ability to nicely visualize physical properties of the studied system, is based on the improved separation of physical processes like charge transfer or diffusion in the space of relaxation times [41].

There every process is represented as local maximum in a continuous distribution function. However, one does usually not operate with a continuous distribution function. Rather, a discretization of this function is used, assuming the impedance to consist not of an infinite, but only a finite number of RC elements.

Choosing this number rather small, the physical interpretability of the continuous distribution function can only be preserved by applying a priori knowledge of the time constants of the physical processes, compare Fig. 1b) and c). Without a priori knowledge, the physical interpretability of the model can only be preserved by using a sufficiently large number of evenly distributed RC elements. For the sake of a fully automated parameterization process, in this paper the latter method will be described.

In the following sections (i) scalability and (ii) automatable parameterization will be discussed. After the experimental chapter the model is validated with different current profiles and limitations of the model are discussed.

2. Theory

The method of the distribution of relaxation times has been successfully applied for years for the analysis of impedance spectra of solid oxide fuel cells (SOFC) [41,42] and has recently been applied for the analysis of lithium ion cells [43,44]. Its major benefit is the better separation of processes with different time constants compared to the Nyquist or Bode plot [41]. An impedance spectrum can be written as integral equation, where $g(\tau)$ represents the distribution of relaxation times:

$$Z(\omega) = R_0 + R_{\text{pol}} \int_0^\infty \frac{g(\tau)}{1 + j\omega\tau} \mathrm{d}\tau. \quad (1)$$

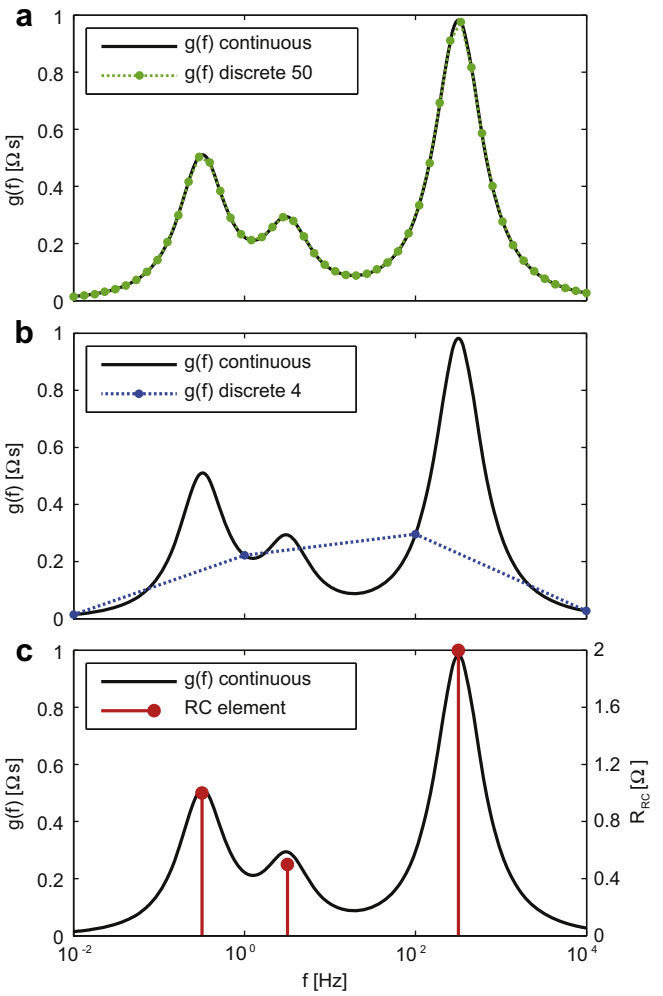

Fig. 1. a) Continuous distribution of relaxation time for an exemplary system exhibiting three different time constants and an approximation with a numerical calculated discrete distribution with an evenly resolution of 50 time constants. b) The continuous distribution in comparison with a discrete distribution comprising only four evenly distributed time constants. c) The continuous distribution function approximated with three RC-elements whose time constants were selected using a priori knowledge.

Since the inversion is performed numerically, the distribution itself is not obtained as an analytical function but as discrete values. Therefore the integral equation becomes a sum:

$$Z(\omega) = R_0 + R_{\text{pol}} \sum_{n=1}^{N} \frac{g_n}{1 + j\omega\tau_n} \delta_{\tau,\log}. \quad (2)$$

Here $\delta_{\tau,\log}$ is the difference between the logarithmically equidistant distributed time constants τ. From this equation it can be deduced, that the measured impedance $Z(\omega)$ can be represented by a serial connection of N RC elements and an ohmic resistance R_0. With an increasing number of relaxation times N, the number of RC elements as well as the computational effort increase.

The according equivalent circuit is depicted in Fig. 2. From equation (2), the calculation of the parameters of the nth RC element can be derived. The resistance of the RC element is calculated as

$$R_n = g_n \cdot \delta_{\tau,\log} \cdot R_{\text{pol}} \quad (3)$$

and the capacitance as

$$C_n = \tau_n / R_n. \quad (4)$$