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Nonlinear Frequency Response Analysis on Lithium-Ion Batteries: A Model-Based Assessment

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ABSTRACT

The nonlinear behavior of electrochemical systems, such as batteries bears essential information on their state and processes interacting within them. A Pseudo-two-Dimensional Lithium-ion battery model is used for Nonlinear Frequency Response Analysis (NFRA). Focus is laid on identification of processes in Lithium-ion batteries. The most commonly applied dynamic electrochemical analysis method, Electrochemical Impedance Spectroscopy (EIS), is limited to linear deflections of the system. This denotes loss of information about nonlinear system behavior. In contrast, NFRA extends this approach to study the nonlinear behavior of the Lithium-ion battery. We show dependency of nonlinear responses on the input amplitude and several model parameters, such as diffusion coefficient, reaction rate constant and double layer capacitance. Parameter variation demonstrates the capability of this method for process identification by investigating the individual higher harmonics and the respective sum. Characteristic peaks can be attributed to electrode reactions and diffusion and frequency regions influenced by the signal can be identified. This work gives a deeper understanding of the nonlinear response of a Lithium-ion battery and as such of how to apply this analysis method for Lithium-ion battery state estimation. It is shown that the method NFRA is essential for reliable process identification. Battery characterization highly benefits from the combination of EIS and NFRA.

1. Introduction

Lithium-ion batteries are promising candidates to enable the change from fossil fuel driven cars to zero-emission vehicles. Deep understanding of processes occurring in the batteries is getting more important for further improvement in performance and safety. One of the most advanced and well established techniques for characterization of electrochemical cells is Electrochemical Impedance Spectroscopy (EIS). With EIS, the system is investigated under the assumption of linear behavior [1]. However, electrochemical reactions and spherical diffusion are nonlinear processes [2]. For investigations of such nonlinearities, Nonlinear Frequency Response Analysis (NFRA) is a suitable method. If a system is sinusoidally deflected using a large amplitude, not only the fundamental frequency but so called higher harmonics are excited [3]; these can be used for process identification and characterization. NFRA is used in electrical engineering where the influences of higher harmonics, treated as pollution, to power systems are investigated [4]. Another field of application is material science, where higher harmonic generation in solids is used to differentiate between interband and intraband harmonic generation and to determine the aging behavior of steel [5,6]. Additionally, electrochemical and corrosion processes are investigated by applying large AC electric signals [7]. NFRA has further been performed to study the nonlinear behavior of ferrocyanide oxidation with a mathematical model [8] and measurements [9]. M. Kiel et al. [10] applied higher harmonic analysis to access nonlinearities in impedance spectra, in general for sensing, and for determining reaction kinetics in an electrochemical cell. NFRA has also been applied to fuel cells in model based and experimental studies. Comparison of experimental spectra with modeled spectra with different

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underlying reaction kinetic models for Methanol [11] and Oxygen [12] allowed to identify suitable reaction kinetic models. Thereby, measurement of higher harmonics was not sufficient for kinetic interpretation and modeling was the essential aspect. Furthermore, NFRA was used for state estimation and methanol concentration sensing of the fuel cell [13]. Characterization of Lithium-ion batteries is a novel application for NFRA. Concerning batteries, NFRA was used by Harting et al. [14] to experimentally show the applicability of NFRA on analysis and discrimination between processes in Lithium-ion batteries. Nevertheless, research concerning dynamic analysis on Lithium-ion batteries within the last decade focusses on linear EIS. State of the art for modeling EIS for batteries are equivalent-circuit models [15–17] and electrochemical models [18–20].

Within this research, a state of the art P2D-model is used to identify processes in the battery with NFRA and to establish this new dynamic measurement method in the field of battery characterization. The output in time domain is transferred to the frequency domain with a Fast Fourier transformation (FFT) to analyze the model behavior for higher harmonics. With NFRA, we study information that is not available for small excitation amplitudes such as in EIS. This model based approach is suitable to detect the nature and sensitivity of nonlinear processes and extends the classical investigation with EIS to gain a deeper dynamic understanding. Parameter and amplitude variations are further applied to enable a reliable interpretation of NFRA measurements: Reaction rate constant, diffusion coefficient and double layer capacitance are varied to detect how nonlinear processes and the output signal are affected. A deeper insight into the cell and a more detailed dynamic analysis are the result of this research. The work demonstrates that for an understanding of the nonlinear processes in batteries not only measurement of higher harmonics but also modeling is needed.

2. Mathematical modeling

The battery model used for the simulation of NFRA is described within this chapter. First, model equations are stated. Subsequentially, the evaluation methods are explained. A model based on state of the art P2D-models is used, as described in Refs. [21–23]. Within the P2D model we assume porous, structured electrodes consisting of active material, binder, conducting additives and electrolyte. Two intercalation electrodes with graphite (C_6)as active material in the anode, Lithium Cobalt Oxide ($LiCoO_2$) in the cathode and a separator are considered. Detailed derivation of model equations are not given within this work but can be found elsewhere [21–23]. The model considers the following processes: Solid diffusion, Equation (1), diffusion and migration in the electrolyte, Equation (3), potential distribution in the electrodes and electrolyte, Equations (2) And (4), charge accumulation at double layers, Equation (6), Butler-Volmer kinetics, Equation (7), concentration dependent exchange current density i_0, Equation (8), Nernst approach for the open circuit potential, Equation (9) and a Nernst-Einstein approach for the electrolyte conductivity, Equation (10). The model equations are summarized in Table 1. The model uses spatial discretization by application of a finite volume method. Through a highly resolved uni-volume mesh it is made sure that the solution is mesh independent. Time derivatives are solved by an adaptive solver in MATLAB.

The working principle of NFRA is schematically shown in Fig. 1. NFRA is based on a nonlinear excitation of the system, generated by a sinusoidal input with a high AC amplitude. The output signal in the time domain is transferred to the frequency domain using a Fast Fourier Transformation (FFT), included in Matlab, to display voltage responses decomposed in higher frequency responses as a function of the input frequency. These higher frequency responses are so called higher harmonics Y_i. Due to their different parities, odd (Y_{2i+1}) and even (Y_{2i}), higher harmonics can show different sensitivities and therefore a different progression [14]. Within this research, individual higher harmonics Y_i as well as their sum ($i = 1:9$) are analyzed and interpreted.

Once a system is excited with a sinusoidal input, it will reach a (dynamic) steady state after a certain time [24]. Therefore, one can distinguish between the initial time dependent response and the periodic, i. e steady state response of the system. Within the experimental investigation, the first four output oscillations are analyzed. Therefore, the response contains the steady state and transient part. Because of this, our simulated investigation focuses on the initial response by analyzing the response to the first sinusoidal oscillation only. A systematic analysis of the contribution of the transient part to the overall response, i.e. the homogeneous part of the solution of the differential equation system, is focus of ongoing work and out of scope of this research. In this case, NFRA is an instationary investigation method. Further, the aspect of a possible discharge of the battery due to a high AC amplitude is neglected for this research.

For presented simulations, if not declared otherwise, parameters from Table 2 are taken. The electrolyte diffusion coefficient D_e is thereby decreased compared to the literature [22] to demonstrate the influence of a limiting electrolyte. Further, reaction rate constants of the anode k_a and cathode k_c are self-chosen and differ by one order of magnitude to distinguish between the reaction processes in the NFRA and EIS spectrum. All simulations are performed at a state of charge (SOC) of 60%.

3. Experimental

Measurements were performed at a constant environmental temperature of 25 °C in a climate chamber. The frequency range is set between 10^{-2} Hz and 10^{6} Hz. All measurements were conducted with a Zahner Electrochemical Workstation (Zennium E) in galvanostatic modus. Three cells in total with two different cell designs were investigated, a commercial 18650 cell with a capacity of 800 mAh and two hand-made pouch cells from the Battery LabFactory Braunschweig with a capacity of $\approx$ 35 mAh. The pouch cells differ concerning the cathode active material: Lithium Manganese Oxide ($LiMn_2O_4$) for pouch cell A and Nickel Manganese Cobalt ($Ni_{1/3}Mn_{1/3}Co_{1/3}$) for pouch cell B. The excitation AC amplitude is set to 2.9 C for the 18650 cell and 1.6 C for the pouch cells. The Measurement device can not guarantee a precise sinusoidal input prior to the second oscillation. Therefore, the first output oscillation is discarded. The presented experiments use the first real output oscillation and the four further waves to calculate an average signal with minimum random measurement error.

4. Results and discussion

In this section, higher harmonic measurements and simulations are discussed. Concerning simulations, at first, amplitude dependency of NFRA is investigated and then, parameters are varied. This variation covers diffusion coefficient, double layer capacitance, particle radius and electrolyte properties. We aim to show influences of individual processes on the spectrum to enable process identification with NFRA.

4.1. Experimental analysis

In Fig. 2a–f), measurements of higher harmonics at Lithium-ion batteries with different cell designs, e.g. 18650 cell and pouch cells, are shown as an example for nonlinear voltage responses of such