Supplementary Materials: Variation of Impedance in Lead-Acid Batteries in the Presence of Acid Stratification

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1. Development of spatial-resolved EEC for Stratification Modeling

In Figure S1 simulated impedance spectra with superimposed DC-current and ones with homogeneous acid and three times with stratified acid are presented.

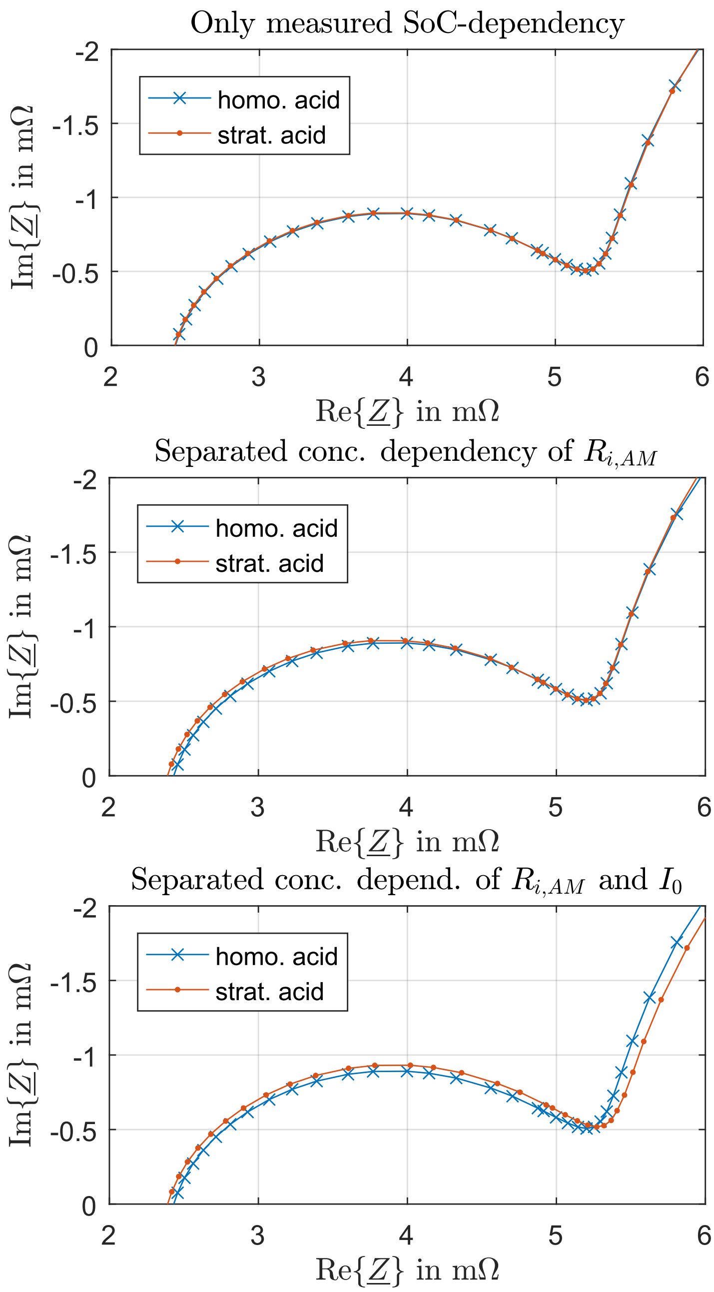

Figure S1. Simulated impedance spectra with $-4.5\,\mathrm{I}_{20}$ superimposed DC-current are presented with different features of the model.

In the upper graph the spectrum with homogeneous acid is compared with a simulation of stratified acid with a model, which contains only the measured SoC dependencies of $R_{i,AM}$ and I_0. The separation of the acid concentration dependency is not implemented, yet. The spectrum with stratified acid does not differ from the spectrum with homogeneous acid. For the spectrum in the middle graph the separated dependency of $R_{i,AM}$ on acid concentration was included in the model. The effect of this modification is an decrease of the high-frequency real part of impedance due to stratification. Because of the higher concentrated acid in the bottom, the conductivity of the electrolyte is better in the bottom, so that the over-all ohmic resistance of the cell increases. The rest of the spectrum is not affected by this modification. Last but not least the spectrum is presented in the lower graph, when the separation of acid concentration dependency is implemented for both $R_{i,AM}$ and I_0. Then the first semi-cycle is bigger with stratified acid, than with homogeneous acid.

In Figure S2 simulated impedance spectra are shown, which were generated ones with a 1D-model and ones with a spatial-resolved model. Furthermore the corresponding measured impedance spectrum from parameterization measurement is presented.

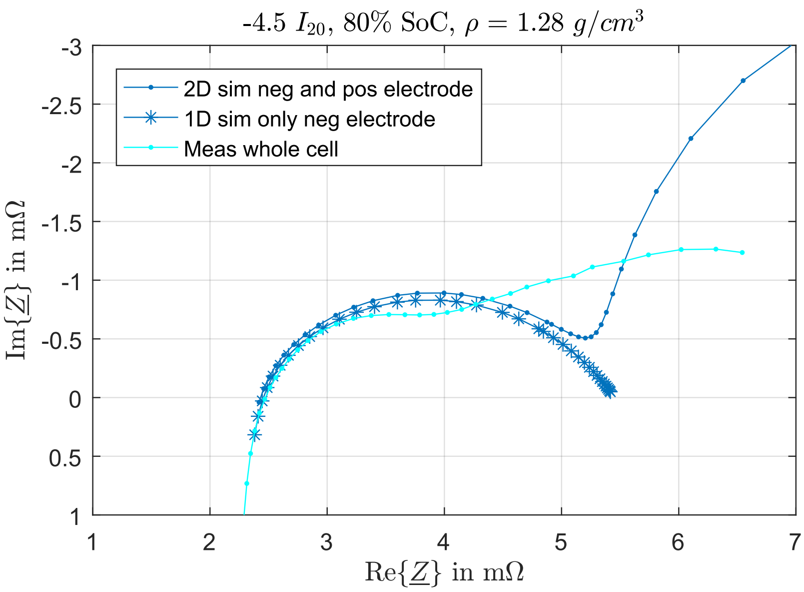

Figure S2. Simulated impedance spectra with $-4.5\,I_{20}$ superimposed DC-current at 80 % using an 1D- and the spatial-resolved model with the same set of parameters, only that the parameters were adapted to spatial-resolved model. Also the measured impedance spectrum for the same DC-current and SoC is shown as well.

With the 1D-model the positive electrode was not modeled, as the spectrum parts of the negative electrode generated by 1D and spatial-resolved models are already equal. The visible difference is generated by the superimposed impedance of the positive electrode. The spectrum of the spatial-resolved model spectrum was fitted to an 1D-model containing also an RC-element for the positive electrode and the determined value for $R_{ct,neg}$ is equal to the value used for the 1D-model spectrum (3.2 mΩ).
In comparison to the corresponding measured spectrum from parameterization differences are visible. The $R_{ct,neg}$ of this spectrum is 2.9 mΩ. While at high frequencies the spectra are all equal, the first semi-circle of measured spectrum is more depressed towards lower frequencies. This and the difference between the $R_{ct,neg}$ values comes from the polynomial description of the SoC dependency of I_0, which is not exact. Furthermore the second electro-chemical process of negative electrode is visible in the measured spectrum, which changes the shape on the right side.

2. Description to the provided Measurement Data

Impedance spectra together with the voltage and current profiles measured during the parameterization and the stratification test procedure are provided with this publication.
The dataset contains data recorded with a *Digatron* test rig (*MCT 10-06-12 ME*), named here *Digatron-data* and the data recorded with an*EISmeter* from *Digatron*, named here*EIS-data*. All data are provided in Matlab file format. Furthermore, Matlab scripts are provided to plot the single Matlab-files.

2.1. Information to the Folder Structure

The data set contains folders with the names "Ref1", "Strat1", "Ref2" and "Strat2" , "Ref3" and "Ref4". These folders have all data recorded on the test cell during the stratification tests. The folder "Parameterization" contains the spectra from parameterization.
In such a folder following data can be found:

- EISData: containing all EIS measurements performed during the EIS set. The name of every EIS-data provide information at which SoC in % the EIS measurement was performed and with which DC-current (XI20)
- Pdf-files: containing the test procedures, which was programed for the Digatron and EISmeter test rig
- For the EISmeter only the program EISslave was required
- All other files contain programs for Digatron test rig
- The date in the name of the files is the starting date of the test
- Matlab-file: this file contain the Digatron-data and its name consists of the name of the test and the starting date

2.2. Information to the Digatron-Data

The Digatron-data contain the measured voltage, current and temperature data of the tests. Every file corresponds to one EIS set.

2.3. Information to the EIS-Data

The EIS-data were recorded by the *EISmeter* and one file contains one impedance spectrum. The information at which condition the EIS was performed can be found in the name of the file. "XXper" at the end of the name specifies the SoC. The DC-currents are given relative to the I20 current rate. This current discharges the nominal capacity within 20 hours. Here 1I20 corresponds to 0.5 A. The "+" sign before the current indicates a charging current and the "-" sign a discharging current. The number in the name after the DC-current rate (either 1 or 2) indicates the number of cycle during EIS.

2.4. Usage of the Matlab-Scripts

To the data set three Matlab-files can be found:

- *plotDigatron.m*: After a file with Digatron-data is loaded to workspace the script can be started to plot the current, voltage and temperature data over time.
- *PlotEIS.m*: After a file with EIS-data is loaded to workspace the script can be started to plot the spectrum as Nyquist diagram. Additionally the data are verified using zHit and the verification results are plotted in the diagram, too.
- *zHit.m*: This is a function to do the zHit verification of the impedance spectrum. The function is used in the plotEIS script.

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Abbreviations

The following abbreviations are used in this manuscript:

EIS	Electro-chemical Impedance Spectroscopy
SoC	State-of-Charge
EEC	Equivalent Electrical Circuit
CPE	Constant-Phase Element
srEEC	spatially-resolved equivalent electrical circuit
OCV	Open Circuit Voltage