



Influence of measurement procedure on quality of impedance spectra on lead–acid batteries[☆]

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ABSTRACT

Many battery simulation models, but also electrochemical interpretations are based on impedance spectroscopy. However, the impedance of a battery is influenced by various factors, e.g. in the case of a lead–acid battery: state of charge (SOC), charging or discharging, superimposed dc current, short-term history or homogeneity of the electrolyte. This paper analyses the impact of those factors on impedance spectra of lead–acid batteries. The results show that very detailed information about the conditions during the measurement is crucial for the correct interpretation of a spectrum.

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1. Introduction

Dynamic battery performance in novel micro hybrid vehicles is a current topic. Simulation models are an efficient and cost saving way to predict battery behaviour. Using simulation models it is possible to increase vehicle comfort and improve fuel economy. Favourable electric power systems and strategies can be found. Suitable models with fast computing and small parameterization effort are mandatory.

There are three main types of battery simulation models. The first one is physically/chemically based, which is a precise model but needs a high numerical and high parameterization effort. Second are empirical models with a strongly limited validity range. Third are models based on an equivalent electrical circuit, with an easy implementation and parameterization.

Electrochemical impedance spectroscopy is a non-invasive measurement method for batteries. A superposition of a small ac excitation (sinusoidal) and a dc signal (working point) is applied to the battery with various frequencies and the voltage response is measured. Many battery models but also electrochemical interpretations are based on impedance spectroscopy [1,4,5,9,15,16,21,22].

An impedance spectrum can only be trusted if three conditions are observed: linearity, time invariance and causality. Causality (equal to stationary) means that a system can be built with discrete elements (capacitance, inductance, resistance) only. When time invariance is true, the condition does not change during measurement. On batteries this is never true when measuring with a superimposed dc current, as the SOC changes. Linearity is given when superposition is possible (with a linear combination of the input signal a linear combination of the output signal can be calculated). This is never true for batteries as the reaction is non-linear and follows the Butler–Volmer equation. Especially for lead–acid batteries the short-term history (charge or discharge) has an impact. In reality linearity, time invariance and causality always cannot be fulfilled during impedance spectroscopy on a battery with a superimposed current [9]. It is tried to keep deviations within a reasonable small range providing that the measurement still works.

If the deviation is within a small range, measurement can be seen as quasi-stationary. The limits to fail can be checked with Kramers–Kronig transform (calculation of real part from imaginary part) [23,24].

Schiller et al. [19,20] proposes to take care, which effects in a spectrum are artefacts due to the measurement and which ones can be interpreted. However, repeated impedance spectra of one lead–acid battery at the same state of charge, same dc current and same temperature can show deviations. The measurement of impedance spectra is very sensitive to various conditions, which need to be considered for measurement and interpretation.

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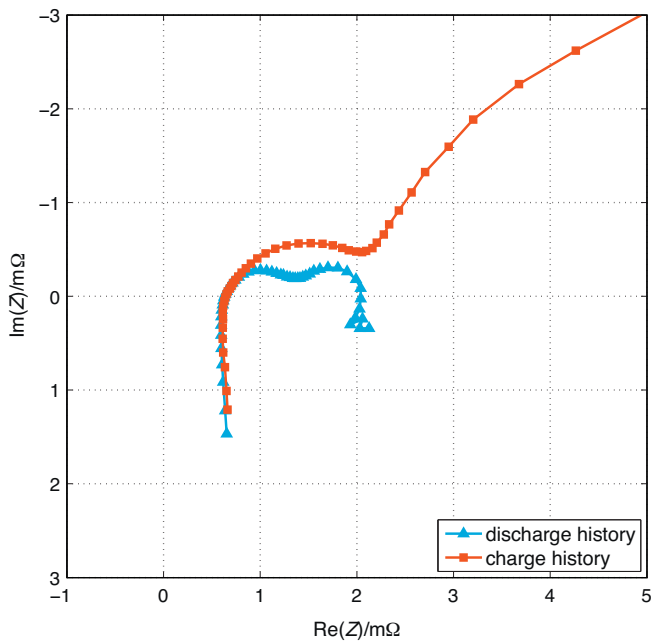


Fig. 1. Example of two spectra at the negative electrode, both at 70% SOC, 25 °C and superimposed dc charge current I_{20} , one with discharge and one with charge short-term history, frequency range: 6000–0.005 Hz, 8 frequencies per decade.

Fig. 1 gives an example of two spectra at the negative electrode, both measured at 70% SOC, 25 °C and superimposed dc charge current I_{20} ¹. The only difference between the spectra is the short-term history: the one with the smaller impedance has discharge history, the one with the higher impedance has charge history. This phenomenon is not limited to impedance spectra, it is also visible in the time domain. **Fig. 2** gives an example. Cycles were measured with 70% SOC, 25 °C and dc current I_{20} . Again, the only difference is the short-term history. During the charging pulse (700–800 s) with charging history, the voltage rises more compared to the charging pulse with discharge history.

Most batteries are charged (CHA) and discharged (DCH) unpredictably during operation. Some facts are known, e.g. that charge is easier when the battery was little discharged before [10] or that a discharge is easier when the battery was charged immediately before [22]. This can be assumed to be visible in an impedance spectrum as well because “easier” should result in a smaller impedance. The current rate, superimposed charging and discharging dc current and the state of charge all have an influence on the impedance. When measuring a spectrum, also the duration and the history of the spectrum (charging, discharging or pause) need to be considered.

In times of rising demands on batteries in hybrid applications, charge acceptance for regenerative braking is most interesting to know. In hybrid vehicles, the battery should be able to take as much energy as possible when it is available. Schaeck et al. [18] demonstrated that charge acceptance is highly dependent on the short-term history of the battery. It is affected by local current distribution and acid concentration [14]. During charging, Pb^{2+} ion dissolution is the rate limiting step at the negative electrode [16,17]. Kirchev et al. [11] measured spectra at the positive plate at open circuit for different SOCs (equal to different electrolyte concentration). He demonstrated that the double layer capacitance is not frequency distributed, but is related to the SOC. Charge and discharge process as not being just reverse reactions. Further,

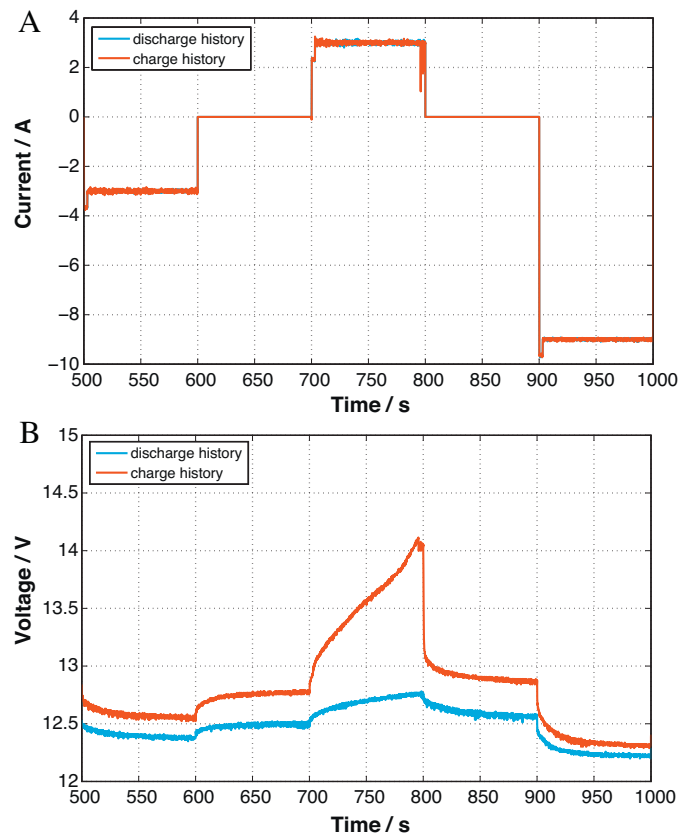


Fig. 2. Example of cycles measured in the time domain (A Current, B Voltage), both at 70% SOC, 25 °C and dc current I_{20} , one with discharge and one with charge short-term history.

Kirchev et al. [12] showed by impedance measurement with various sulphuric acid concentrations on the positive plate in completely charged state that at high acid concentration ohmic resistance and charge transfer resistance do not change. When acid concentration decreases, ohmic resistance and charge transfer resistance increase. Electrochemical double layer capacitance on the negative plate was studied by Kirchev et al. [13] with impedance spectroscopy. A characteristic frequency of the lead electrodeposition and electrodisolution on SOC was found. Pulses with the defined “electrochemical resonance” lead to maximum charge acceptance.

Various influences affect spectra, therefore it is very important that measurement of this data is done systematically and reproducibly. Before any interpretation the measurement method needs to be known very well. This paper will not give interpretations of the spectra, but it will show the difference that arises by measurement conditions.

2. Measurement of impedance spectra

The equipment used for all measurement in this paper is an EISmeter developed by ISEA, RWTH Aachen University [6]. A sinusoidal current is applied to the battery, the voltage response is measured (galvanostatic measurement). Knowing current and voltage the complex impedance for the each frequency is calculated [2].

$$Z(f, I_{dc}) = \frac{U_{ac}}{I_{ac}} \quad (3.1)$$

All spectra start at 6000 Hz continuing to lower frequencies. There are always 8 frequencies per decade measured. The lowest frequency depends on the superimposed dc current. The higher

¹ The current I_{20} is equal to $C_{20}/20$ h, where C_{20} is the nominal capacity.

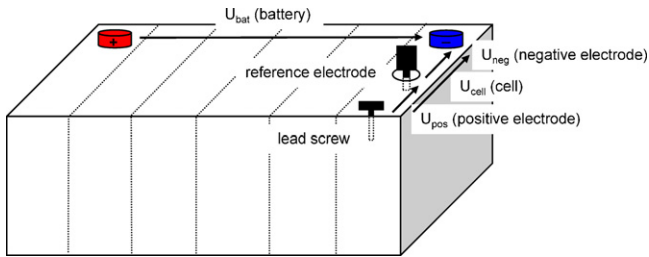


Fig. 3. Measurement setup.

the dc current is, the shorter is time of measurement as during measurement of a spectrum SOC shall not change more than 5%. One spectrum is measured during 5% charge or discharge. This method of micro-cycles was introduced by Karden et al. [8]. Measuring impedance spectra at a constant SOC makes the spectra more reproducible compared to measuring during continuous charge or discharge. The battery needs to stay in a stable state during measurement of one spectrum, which is considered to be 5% SOC change (see also Section 2.2). Always the last spectrum (with superimposed charging or discharging dc current) is analysed. Usually this is the second or third spectrum. Buller [4] showed that after the second or third spectrum it changes less. The ac amplitude is limited by a maximum voltage response interval.

In this paper, all measurement points of a spectrum are shown. There are no points cut due to Kramers–Kronig algorithm. Only few points at low frequencies might miss Kramers–Kronig check.

All test were performed on a commercially available SLI (starting, lighting, ignition) OEM flooded lead–acid battery with 60 Ah capacity. The battery was new, but initialised with three nominal cycles before the tests. All tests were performed at 25 °C. For half cell measurement, a hydrogen reference electrode (Hydroflex by Gaskatel [7]) was used. For installation, the plug of one cell is opened and the reference electrode is inserted. As cell voltage sense, a lead screw is applied to current collectors (straps) through the battery lid. At the same time, voltages of battery, cell, negative and positive half cell are measured (Fig. 3). For the cell, the negative and the positive half cell, a defined mass and a high ohmic input resistance is needed [3].

Spectra for this paper are measured at the cell with the negative terminal. Therefore spectra from the negative half cell include the ohmic resistance between the terminal clamp and the negative terminal posts. The resistance is in the range of 0.3–0.6 mΩ.

The next sections describe the influence of current rate, superimposed charging or discharging dc current, dependency on SOC and pauses before spectra. These influences are known and usually considered when interpreting impedance spectra. The influence of starting point and duration of a spectrum is described in Section 2.2. The effect of short-term history on spectra is investigated in Section 2.3. In order to keep the electrolyte homogeneous and avoid acid stratification, nitrogen can be bubbled through a cell (Section 2.4).

2.1. Influence of current rate, superimposed charging or discharging current, state of charge (SOC) and pauses before measuring

These influences on impedance spectra are known and are presented here for completeness with few examples.

Karden et al. [8] and Buller et al. [5] analysed different dc currents (charge or discharge) which were superimposed by ac excitation. The rate of the current has a large influence on the impedance of the battery. The higher the current is, the smaller is the impedance. Spectra with a superimposed charging current have a higher impedance compared to discharging current. This aspect

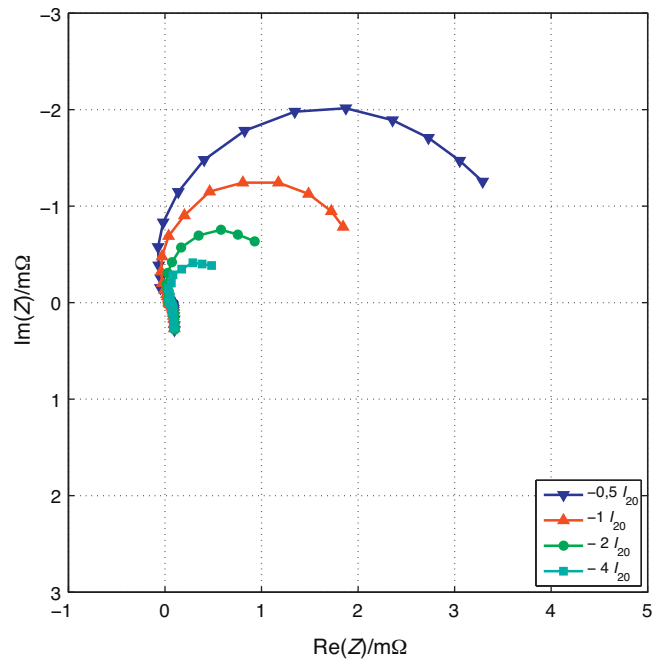


Fig. 4. Discharge spectra at the positive half cell with various superimposed dc currents, battery was discharged to 70% SOC, frequency range: 6000–0.005 Hz (for I_{20}), 8 frequencies per decade.

was tested again within this work, without new findings (Fig. 4). More details can be found at [4,9,21].

The impedance of a battery depends on the state of charge (SOC), which was investigated by Karden et al. [8]. The lower the SOC is, the higher is the impedance of a battery (Fig. 5).

The influence of various pause lengths before the measurement of a spectrum was tested. As mentioned before spectra are always measured during microcycles with 5% SOC change. Spectra after pauses of 10 s or 1 min were compared with spectra without pause. Superimposed dc current were I_{20} , $2I_{20}$ and $4I_{20}$. Tests were performed at 85% SOC (discharge history).

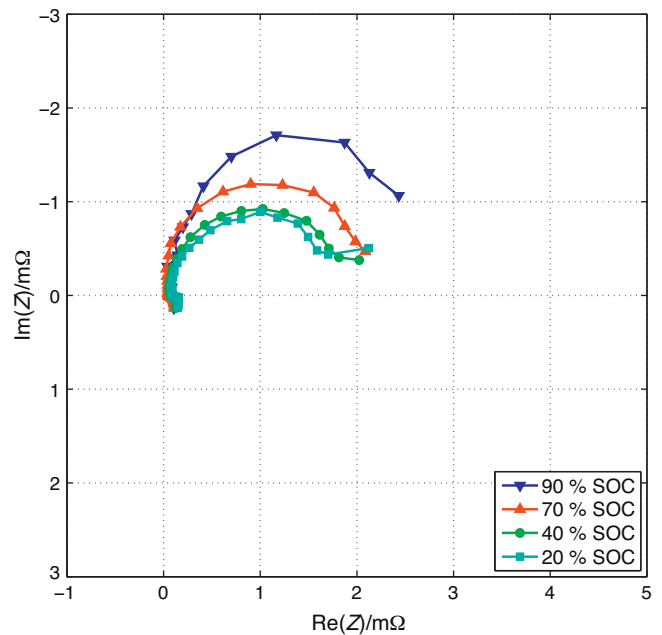


Fig. 5. Discharge spectra at the positive half cell with I_{20} superimposed current, at various SOC, battery was discharged to SOC, frequency range: 6000–0.005 Hz, 8 frequencies per decade.

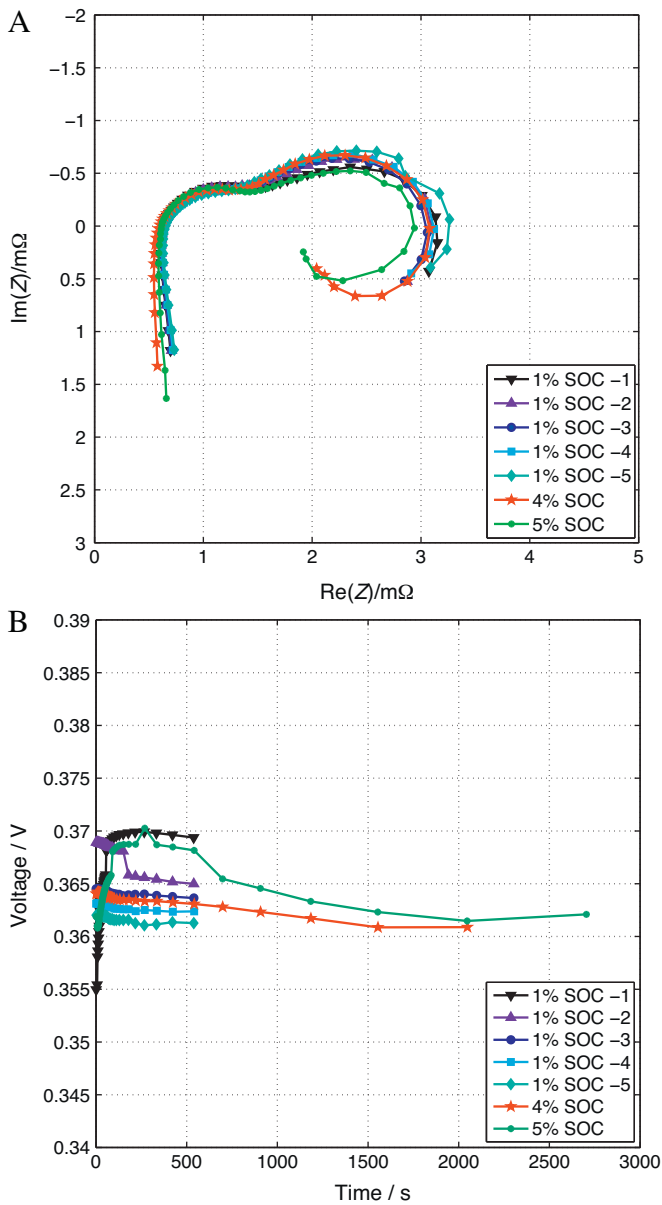


Fig. 8. Discharge spectra at the negative half cell with I_{20} superimposed current (A) and voltage at the negative half cell (B), spectrum measured 5* during 1% SOC change, 1% SOC discharged and measurement during 4% SOC change and measurement during 5% SOC change, frequency range: 6000–0.005 Hz (4% SOC change), 8 frequencies per decade.

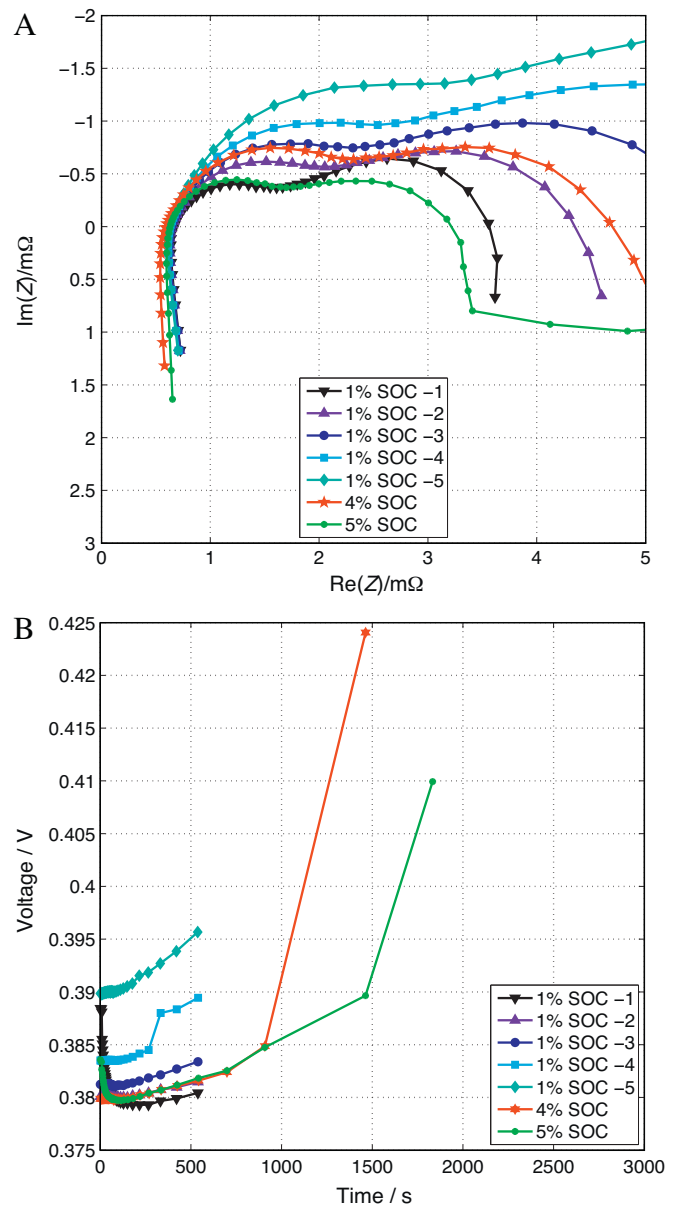


Fig. 9. Charge spectra at the negative half cell with I_{20} superimposed current (A) and voltage at the negative half cell (B), spectrum measured 5* during 1% SOC change, 1% SOC discharged and measurement during 4% SOC change and measurement during 5% SOC change, frequency range: 6000–0.005 Hz (4% SOC change), 8 frequencies per decade.

After an EN-charge ($5I_{20}$, $U_{max} = 16$ V, 24 h) the battery was discharged to 70% SOC with I_{20} . After 30 min pause, cycles (described later) were started to see the influence of discharge history. After 10 min pause the battery was discharged to 40% SOC and then charged back to 70% SOC with I_{20} , after 30 min pause, again cycles were applied. The cycles consisted of 5% SOC change, where first 1% was charged or discharged, and then an impedance spectrum was recorded during the remaining 4% SOC change. There were first 3 cycles with I_{20} , followed by 50 cycles with $4I_{20}$, and finished with 3 cycles with I_{20} .

Short-term history test 2 (Fig. 11):

After an EN-charge ($5I_{20}$, $U_{max} = 16$ V, 24 h) the battery was discharged with I_{20} to four SOC levels (90%, 70%, 40% and 20% SOC). Afterward the battery was charged again with I_{20} to the same SOC levels. At each SOC level there was a pause of 30 min first, then spectra were measured with $0.5I_{20}$, I_{20} , $2I_{20}$ and $4I_{20}$. With $0.5I_{20}$ two

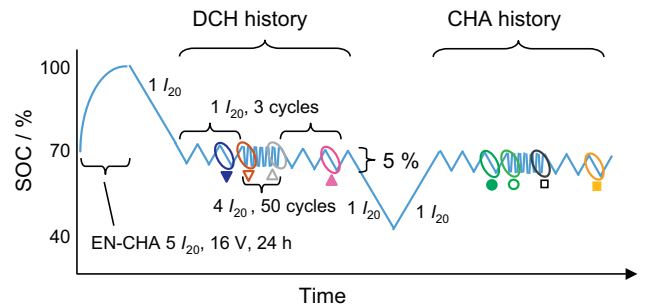


Fig. 10. Routine of test 1 for short-term history.

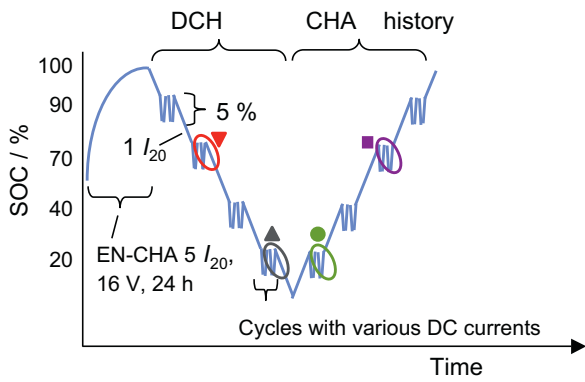


Fig. 11. Routine of test 2 for short-term history.

discharge and two charge spectra were measured, with the other currents three discharge and three charge spectra were performed at each SOC level. Always the last charge and discharge spectra are analysed [4].

2.3.2. Influence of short-term history

Fig. 12A shows discharge spectra of the negative half cell in the Nyquist plot during test 1. Shown are spectra measured during cycles with I_{20} before and after the 50 cycles with $4I_{20}$. In test 1, 50 cycles with $4I_{20}$ is equal to 2.5 times nominal capacity of the battery. Even after 2.5 capacity turnovers (“after cycles”) it is still visible if the battery was charged or discharged before the cycles. However, during the cycles, spectra become more similar, especially with charge history.

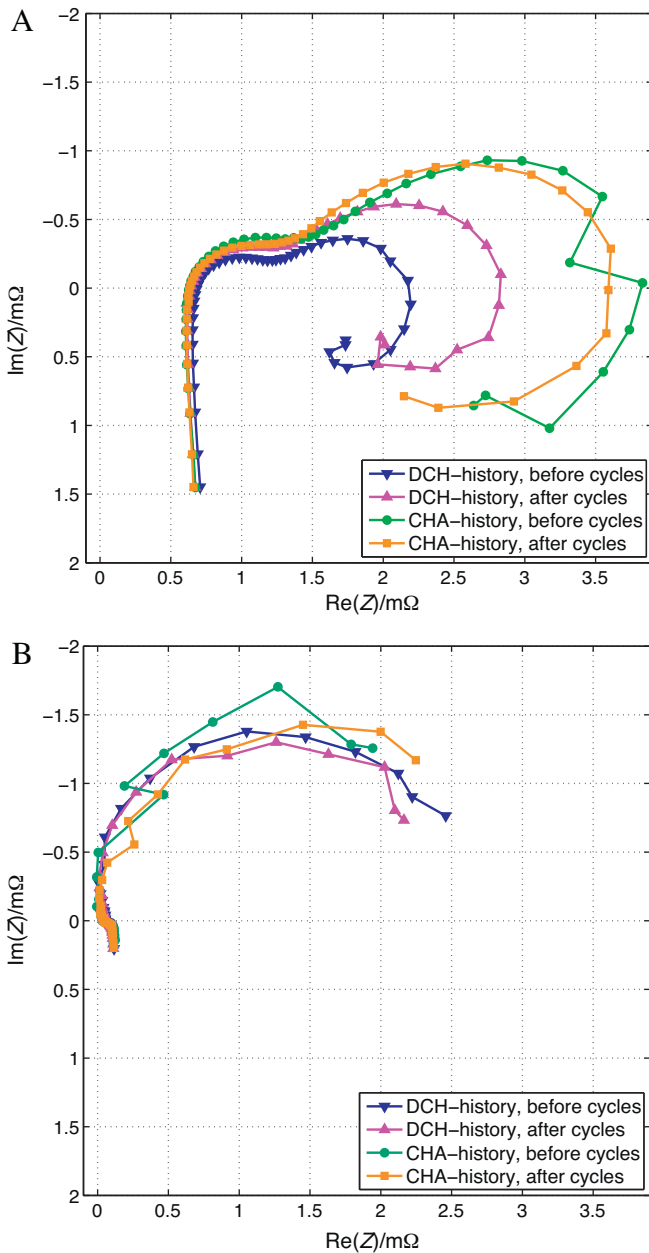


Fig. 12. Test 1 of short-term history → Discharge spectra at the negative (A) and positive (B) half cell with I_{20} superimposed current, before and after cycles, with discharge and charge short-term history, at 70% SOC, frequency range: 6000–0.005 Hz, 8 frequencies per decade.

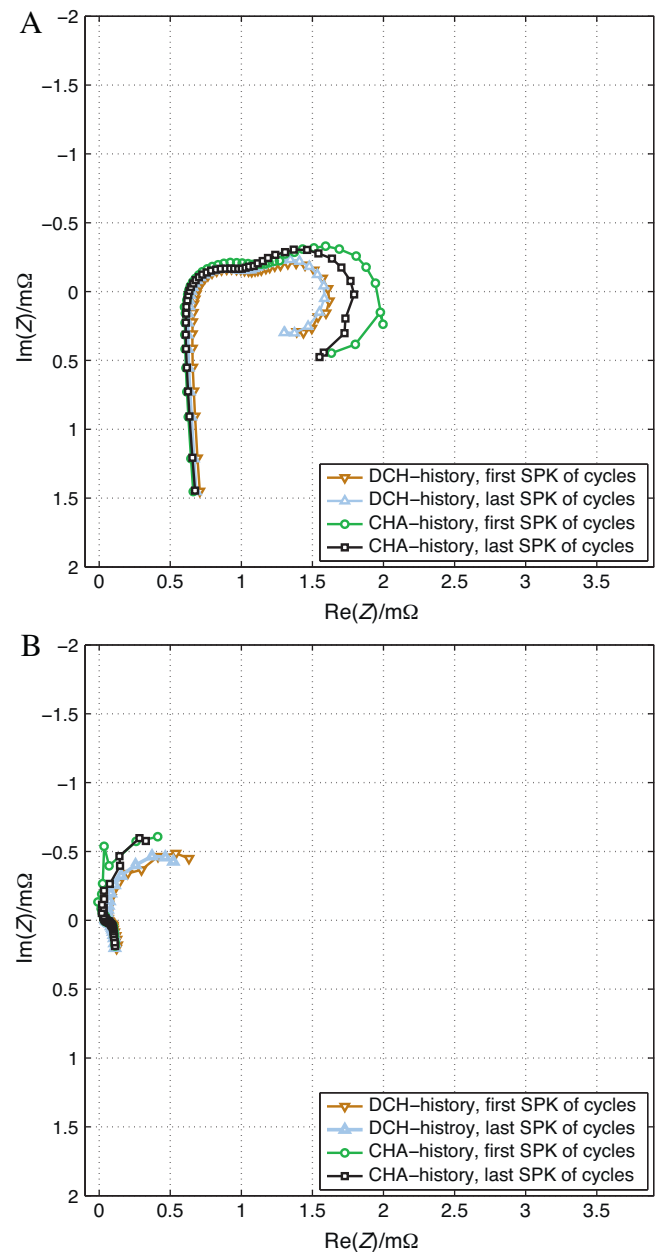


Fig. 13. Test 1 of short-term history → Discharge spectra at the negative (A) and positive (B) half cell with $4I_{20}$ superimposed current, first and last spectrum of cycles, with discharge and charge short-term history, at 70% SOC, frequency range: 6000–0.02 Hz, 8 frequencies per decade.

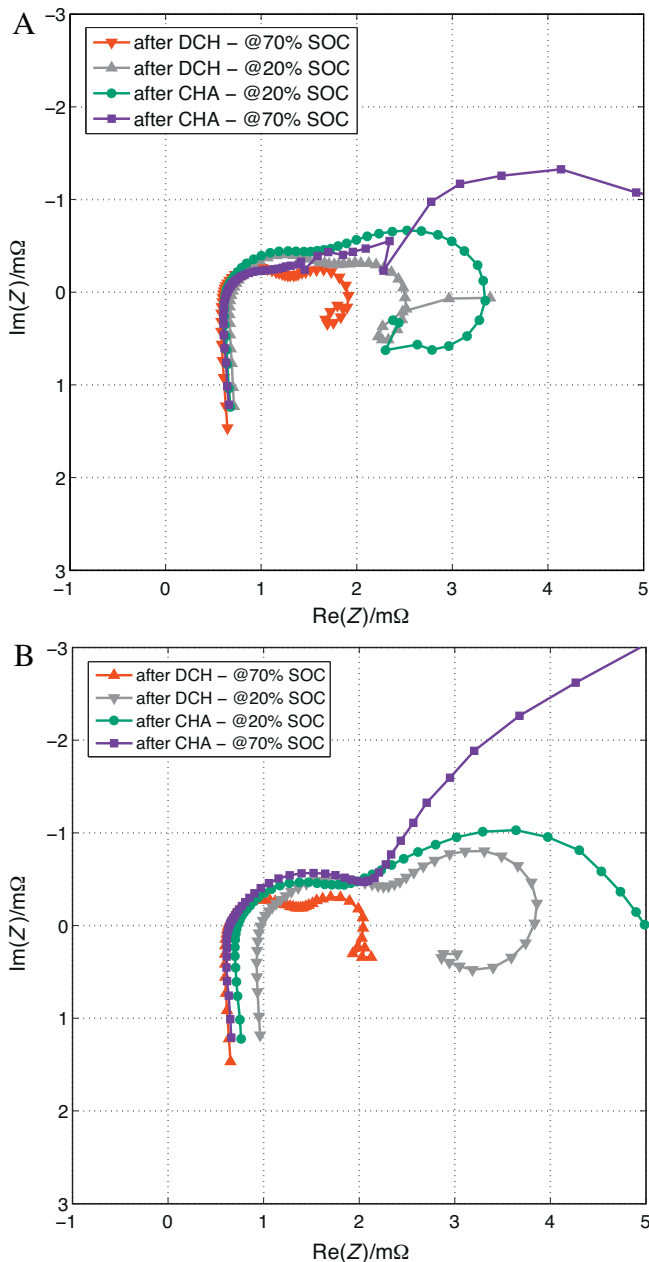


Fig. 14. Test 2 of short-term history → Discharge (A) and charge (B) spectra at the negative half cell with I_{20} superimposed current, charge or discharge current to the SOC is I_{20} , frequency range: 6000–0.005 Hz, 8 frequencies per decade.

The short-term history influences mainly the 2nd semicircle at the negative half cell, the impedance with charge history is larger compared to discharge history. This is valid for charge and discharge spectra. The inductive branch and the 1st semicircle of the spectra show no visible impact (until the frequency of ~ 8.14 Hz). For the positive half cell the differences are less pronounced (Fig. 12B). Observations for charge spectra are similar to the ones for discharge spectra.

Fig. 13 shows spectra at the beginning and at the end of the cycles, with charge and discharge short-term history, with $4I_{20}$, for negative and positive half cell. When the superimposed current is higher, the positive half cell is more dominant. The influence of the short-term history is higher with smaller currents (compare Fig. 13A and Fig. 14A). Further differences between spectra with charge or discharge history can be found, e.g. charge short-term history has a higher influence on the spectra than discharge history.

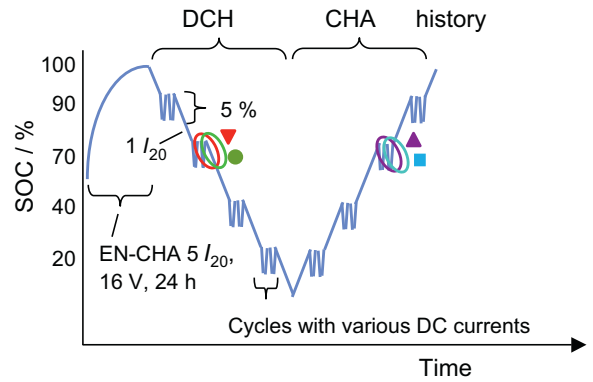


Fig. 15. Routine of test 2 for short-term history, performed twice, once with and once without mixed electrolyte.

It seems that spectra with charge history converge towards the spectra with discharge history after some time or some cycles. This is negligible for high frequencies (>2 Hz, until the end of the first semicircle at the negative half cell).

Fig. 14 shows spectra with charge and discharge history (test 2). The spectra are measured at 20 and 70% SOC. With charge history, the 2nd semicircle is larger as well in this measurement. The higher impedances of spectra with charge history might be caused by Pb^{2+} dissolution limitation.

In general, the difference between spectra with charge and discharge history can be assumed to be highest at low frequencies (visible in the 2nd semicircle). The second semicircle (low frequency) is either due to the porous surface and surface coverage by lead sulphate or to the charge transfer reaction [16]. Hence, one of these reactions is probably influenced by the short-term history.

The effect of short-term history in the frequency domain (impedance spectrum) reflect similar dependencies that have been frequently observed in the time domain, e.g. during stop/start validation testing in cars [14].

2.4. Mixing electrolyte

Short-term history is related to acid stratification. During EN-charge, acid stratification is built up. Whether the influence of short-term history can be reduced if there is no acid stratification is analysed next.

When a car is driving, the electrolyte is mixed slightly by the movement. When the electrolyte is mixed, acid stratification may be reduced. In a laboratory environment, one way of reproducing this is mixing the electrolyte in the battery with nitrogen. A thin glass tube is set to the bottom of a cell, which allows nitrogen to bubble through the battery. The injected nitrogen causes equal distribution of electrolyte convection in the cell.

The throughput of humidified nitrogen during measurement of the spectra shown in this section is approximately 10 ml min^{-1} . Current was applied to the complete battery. As nitrogen only flew through one cell, regulation of current by voltage was controlled to this cell.

Test routine 2 for short-term history was repeated with a mixed electrolyte (Fig. 15). Then the electrolyte was mixed at all times during the test. When there is minimum acid stratification (nitrogen is bubbled through the cell), semicircles in the spectra are smaller and less depressed (Fig. 16A). This is especially the case for the second semicircle at the negative half cell. With a homogeneous electrolyte the impedance is smaller. It is assumed that bubbled nitrogen leads to a more homogeneous electrolyte and therefore to a more homogeneous current distribution in the cell.

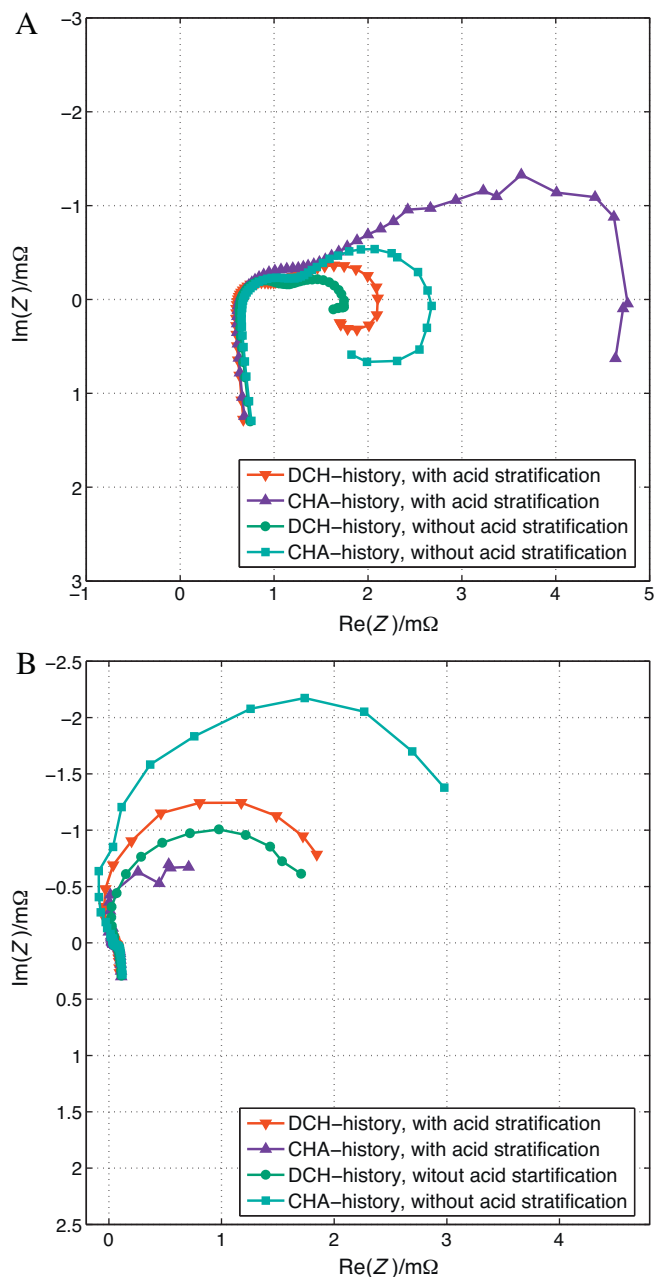


Fig. 16. Discharge spectra at the negative (A) and positive (B) half cell with I_{20} superimposed current, with discharge and charge short-term history, at 70% SOC, with and without nitrogen bubbling, frequency range: 6000–0.005 Hz, 8 frequencies per decade.

For some spectra with charge history it can occur, that the impedance with minimum stratification (with N_2 bubbling) is larger than the ones with stratification (Fig. 16B). So far there is no explanation for this.

The effects of acid stratification are more pronounced in the spectra of the negative half cell, compared to the positive half cell. In the tested battery, the positive plates are in envelopes. Nitrogen bubbling has stronger influence on the electrode without separator envelopes. Acid and nitrogen bubbling can hardly pass envelopes. Thus, the nitrogen bubbling has hardly any influence on the acid inside the envelopes.

It is also visible, that minimization of acid stratification does not fully suppress the short-term history (charge or discharge). Espe-

cially the 2nd semicircle in the spectra with discharge history is smaller compared to the ones with charge history (Fig. 16A).

3. Summary

When measuring impedance spectra, various influences need to be considered. They need to be decided before measuring, recorded in detail and taken into account for interpretation of spectra.

The higher the superimposed dc current is, the smaller is the impedance of a battery. The impedance is higher when the battery is charged compared to discharge. The lower the SOC is, the higher is the impedance of a battery. These effects are well known and usually considered.

Pauses in the range of 10 s–1 min have no significant influence on a spectrum compared to no pause. This was measured for charge and discharge spectra as well as for current rates from $0.5I_{20}$ to $4I_{20}$ and can be assumed to be valid for higher currents as well. Hence, when several spectra are measured one after the other, e.g. with various currents, no pause is needed in between.

Spectra were measured during 5% SOC change, which is considered to be quasi-steady state for the battery. As dc voltage changes most at the beginning of charge or discharge, now, first 1% SOC is charged or discharged and the spectrum is measured during the remaining 4% SOC change. This way voltage drift is minimized during measurement of a single spectrum.

The short-term history is often not considered. The influence whether a battery was charged or discharged before measuring a spectrum is longer lasting than expected. Even after 2.5 capacity turnovers with 5% DOD cycles (current $4I_{20}$), preceding charge or discharge affects the spectrum. Overall, the investigation shows a high dependency of the behaviour of lead–acid starter batteries from the preceding charge or discharge. This needs to be taken into account for comparison and interpretation of measurement results. In particular, interpretation of spectra does not make sense when history and test setup are not documented precisely.

By bubbling nitrogen through a cell, the electrolyte becomes more homogeneous, acid stratification is minimized. Then the capacitive semicircles are smaller in the impedance spectrum. Avoiding acid stratification does not fully extinguish the short-term history (charge or discharge), though.

Many apparent and controversial discussed phenomena on impedance spectra may be due to the measurement procedure and do not reflect any real effects. Already one mOhm of difference in the impedance can cause up to 0.5 V in the voltage prediction during cranking. Therefore measurement method needs to be well known to gain reproducible spectra for interpretation.

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