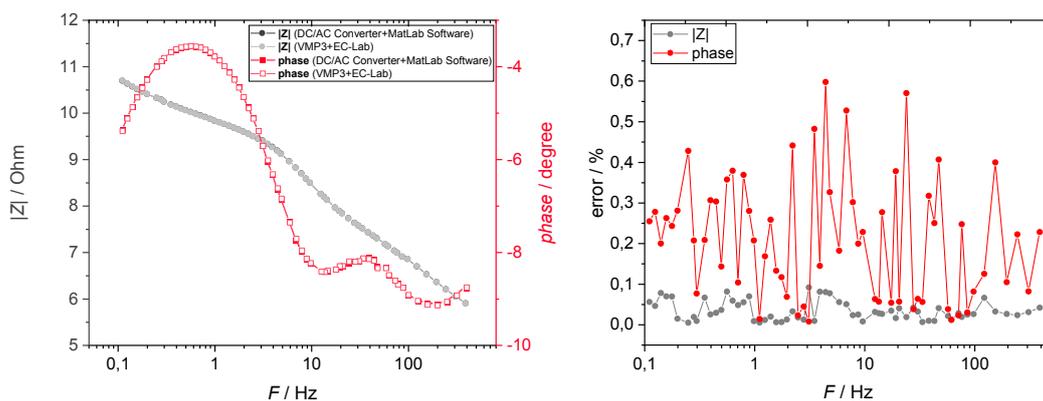


## Supplementary Material

### NLEIS method development

As it is known that lithium-ion cells can be irreversibly degraded that at high frequencies during AC/DC measurements<sup>1</sup>, an upper frequency limit of 400 Hz was selected. Thereby, however, it needs to ensure that all charge transfer processes of both electrodes are still captured. With an evaluation software (FFT) written using MatLab, the analogue output signal was decomposed into its frequency coefficients and then normalized to the fundamental frequency ( $H_1$ ). Before we used the FFT, we used a windowing function to prevent aliasing. Therefore, we chose a *Hanning* function with a window size which length is similar to the length of the digital signal.

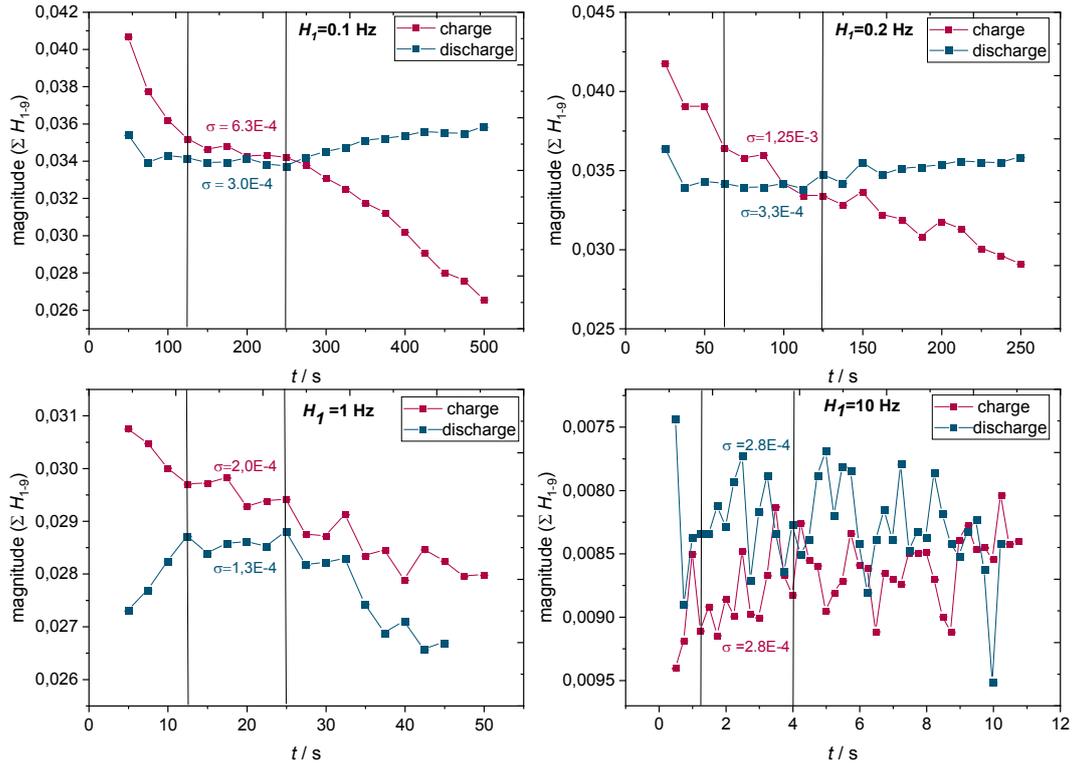
To verify that the connection of both devices does not cause any complications such as transmission delay of the signal or errors caused by the calculation of the evaluation software written with MatLab, an impedance spectrum of a Biologic dummy cell, consisting of a R-RC components, was firstly measured. The results obtained from EC-Lab+VMP3 were compared with the impedance results of the AC/DC Converter+Matlab software. Since the dummy cell exhibited much higher resistance values (app. 5000 Ohm) and lower capacitance (app. 30  $\mu$ F) than our system, the same procedure was repeated with the investigated lithium-ion cell system. The following Bode Plot from the lithium ion cell is representative of both experiments performed.



*Supplementary Figure 1: Quantification of the occurring measurement error as a result of the connection of both hardware systems.*

The error is less than 0.7 % over the entire frequency range. Based on these results, we can conclude that the error due to the connection of two hardware devices and the MatLab software is insignificant.

A major challenge with this method of measurement is that in order to achieve a high frequency resolution in the Fourier spectrum, the measurement signal in the time domain must have a certain length.<sup>2</sup> On the other hand, however, it must be guaranteed that the time variance of the lithium-ion battery due to the direct current does not cause any significant measurement distortions. For this reason, as part of the method development, it was first examined to what extent the frequency components of the output signal change over time. For this purpose, an evaluation method, the so-called Short Time Fourier Transform (STFT), was utilized, which is suitable for investigating time variant systems.<sup>3</sup> In doing so, four different frequencies (0.1 Hz, 0.2 Hz, 1 Hz, 10 Hz) were examined for their temporal variance with respect to their magnitudes of higher harmonics. The following figures are representative for the obtained results.

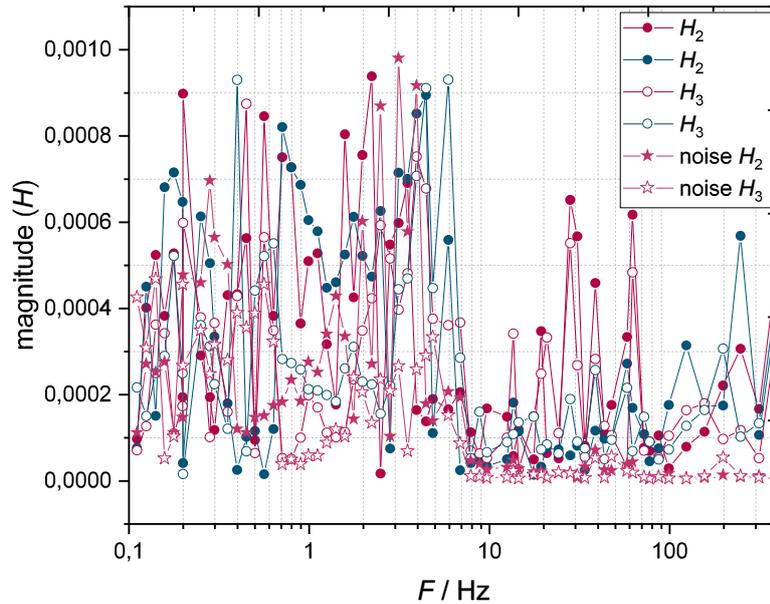


**Supplementary Figure 2:** Change of higher harmonics' magnitude ( $H_1$ - $H_9$ ) over measurement time in charge (red) and discharge (blue) direction for a measurement duration of 50 cycles per frequency at a cell temperature of  $0^\circ\text{C}$  and a cell voltage of 3.7 V.

One data point represents five cycles/measures of the corresponding frequency. All considered frequencies, except 10 Hz, show similar tendency of their higher harmonics. From a cycle count of 12, the harmonic components seem to reach a plateau. This plateau extends up to a number of about 35 cycles and afterwards undergo a strongly change. This course of the higher harmonics' magnitudes can be explained as follows. As soon as the system is excited by an oscillation, the system first enters a transient state and, after a certain time, reaches the steady state.<sup>4</sup> Since this steady state represents an equilibrium-like state (framed in black with corresponding standard deviations  $\sigma$ ), it is used for the NLEIS measurements. Here, to some extent, we can be sure that the higher harmonic magnitudes are constant over the measurement period. After this plateau, the magnitudes of the higher harmonics change significantly, which can be explained by an increasing change of the state of charge with proceeding time. At a frequency of 10 Hz, this tendency can not be clearly determined, which is probably due to the generally low magnitude of higher harmonics. In addition, such preliminary investigations were carried out at different states of charge. Based on these results, the frequency ranges for the NLEIS measurements were selected which are listed in the experimental section.

## Harmonic Spectrum of the Supercapacitor

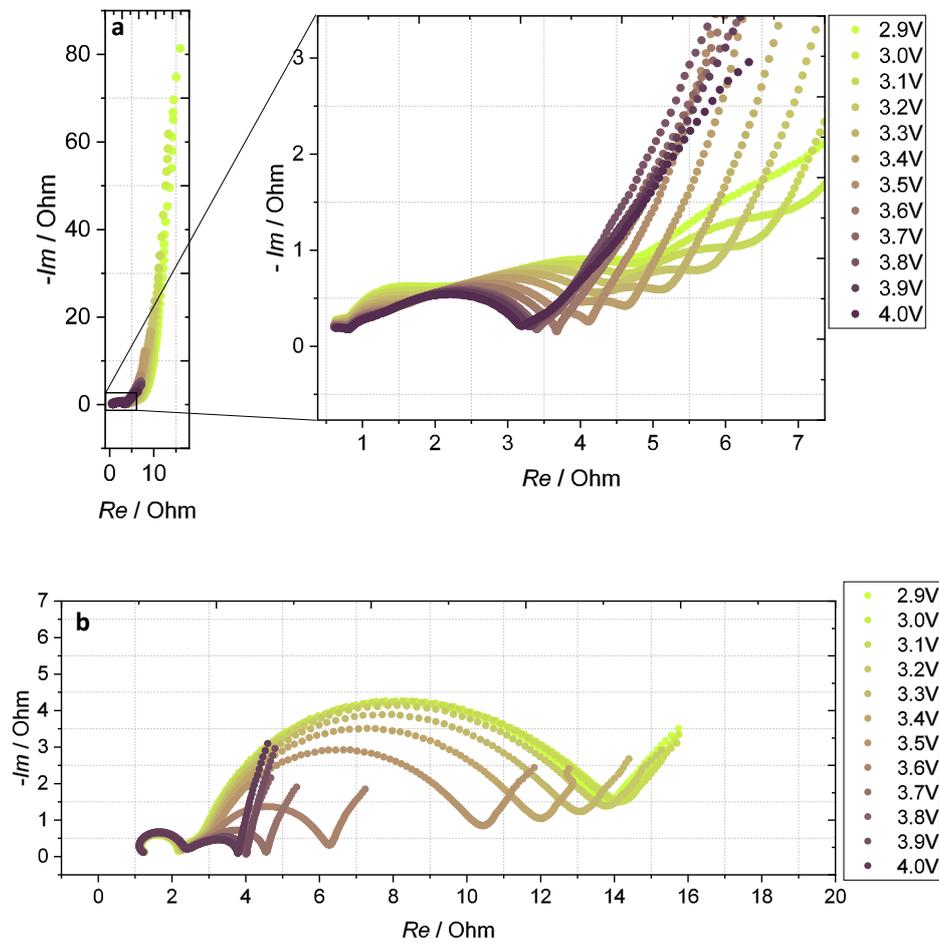
The following graph depicts the higher harmonic spectrum of a supercapacitor (KEMET, 10 V, 22 mF). Only the 2<sup>nd</sup> and 3<sup>rd</sup> harmonic are shown, since these two are considered in this work. The magnitudes of the 2<sup>nd</sup> and 3<sup>rd</sup> harmonic are representative for the magnitudes of all higher harmonics (2<sup>nd</sup>- 9<sup>th</sup> Harmonic). The applied DC bias was 1 mA and the AC was 0.5 mA. Note that it was not possible to choose a DC bias of 5 mA (as in the case of the lithium-ion battery), since the rated voltage was reached before the measurement was completed.



*Supplementary Figure 3: 2<sup>nd</sup> and 3<sup>rd</sup> harmonic of the supercapacitor in charge (red) und discharge (blue) direction with random noises of 2<sup>nd</sup> and 3<sup>rd</sup> harmonic quantified by an ohmic resistance (10 Ohm).*

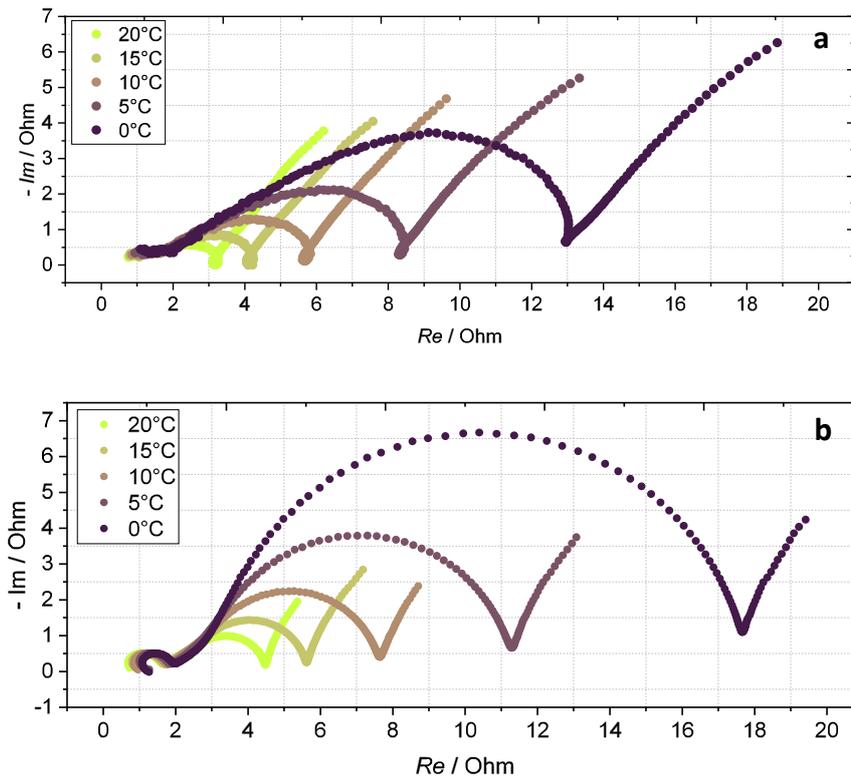
## EIS Spectra

### EIS Spectra in dependence of the state of charge



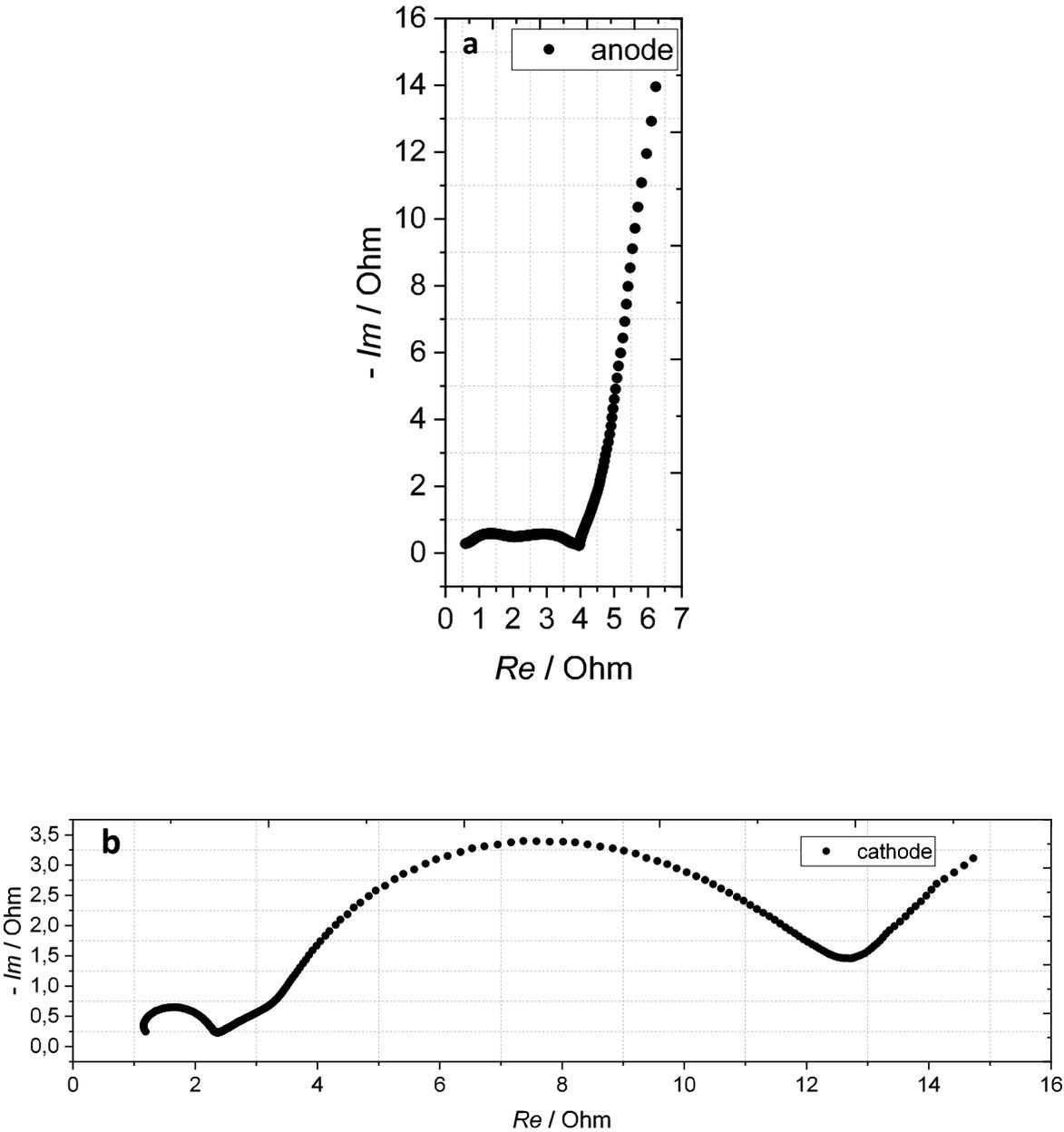
*Supplementary Figure 4: EIS spectra of anode (a) and cathode (b) in dependence of the cell voltage at a temperature of 20 °C.*

## EIS Spectra in dependence of the temperature

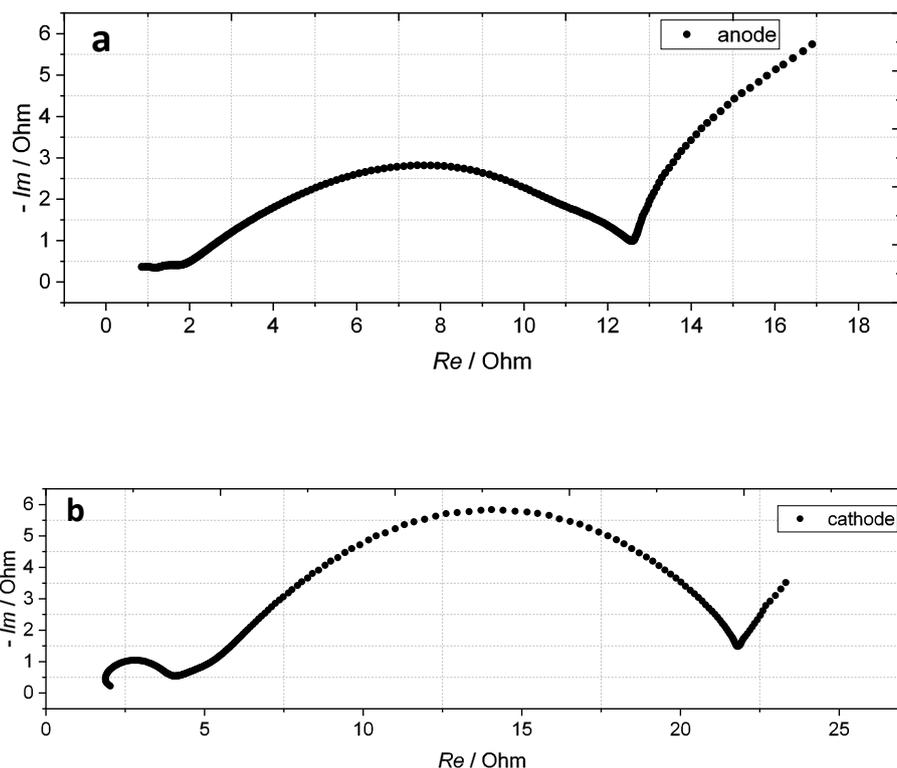


*Supplementary Figure 5: EIS spectra of anode (a) and cathode (b) in dependence of temperature at a cell voltage of 3.7 V.*

### EIS Spectra of the DRT plots



*Supplementary Figure 6: EIS spectra of anode(a) and cathode (b) at a cell voltage of 3.3 V and a temperature of 20 °C.*



**Supplementary Figure 7:** EIS spectra of anode (a) and cathode (b) at a cell voltage of 3.7 V and a temperature of 0 °C.

## References

1. Uddin, K. *et al.* The impact of high-frequency-high-current perturbations on film formation at the negative electrode-electrolyte interface. *Electrochim. Acta* **233**, 1–12 (2017).
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