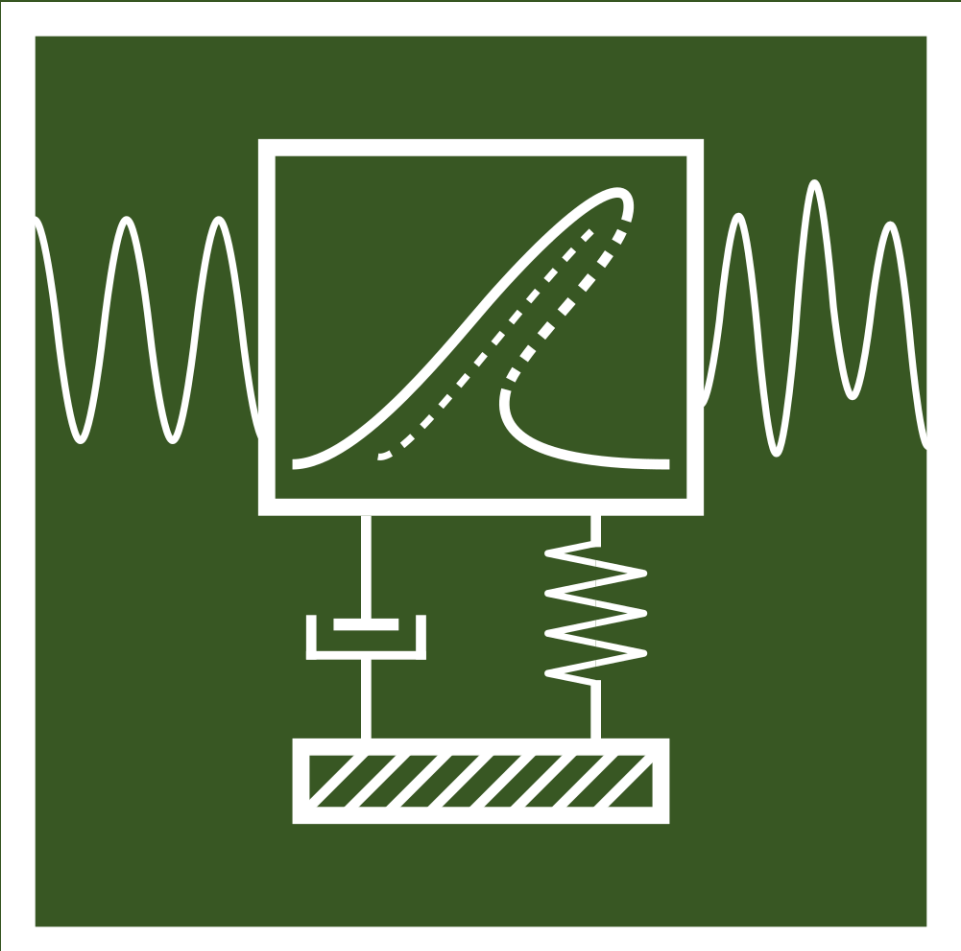


Calibrated EIS and Time-Domain Measurements of a Li-Ion Battery Module

Manuel Kasper¹, Manuel Moertelmaier¹, Mykolas Ragulskis¹, Nawfal Al-Zubaidi R-Smith¹, Johannes Angerer², Mathias Aufreiter², Alberto Romero², Jakob Krummacher², Jianjun Xu³, David E. Root³, Ferry Kienberger¹

1 Keysight Technologies Austria GmbH, Linz, Austria; 2 Kreisel Electric GmbH, Rainbach, Austria; 3 Keysight Technologies Inc., Santa Rosa, USA

Corresponding author e-mail: Ferry_kienberger@keysight.com



Abstract

A battery module of 396 interconnected cells was tested with electrochemical impedance spectroscopy (EIS) and time-domain pulsing over 260 charge-discharge cycles. An EIS calibration workflow was developed for low complex impedance values in a frequency range of 1 kHz to 50 mHz. Significant corrections on the resistance and the reactance were obtained from the calibration, particularly at frequencies above 100 Hz. Equivalent circuit parameters were extracted from the EIS spectra and the pulse response and investigated with respect to the cycle number and state-of-charge (SoC). Fit parameters were robustly extracted including R_{sol} , R_{ct} , and L from EIS, and R_0 , τ_1 and τ_2 from time-domain pulsing. The ohmic resistance decreased over the cycling number indicating an enhanced wetting of the electrodes. Charge transfer resistance R_{ct} showed a monotonic increase over the cycles related to cell ageing. From the charge and discharge pulses, the ohmic resistance R_0 was determined from the instantaneous voltage step of the recovery pulse, while the two time constants τ_1 and τ_2 correspond to the slower exponential recovery phase. R_0 from the time-domain showed a similar trend as R_{sol} plus a contribution of R_{ct} from EIS. Overall, we show that calibrated EIS and time-domain pulsing are efficient methods to gain insights into the electrochemical processes related to different SoCs and the cycling ageing of battery modules and packs.

Methods

The 11S36P module of cylindrical 21700 cells having a nominal voltage of 3.7 V and a capacity of 4.9 Ah (18.1 Wh/cell). Figure 1 shows a schematic of the module test system. It includes a three-phase powered module tester (Keysight SL1001 A) with ratings of up to 100 V and 200 A. Separate force and sense connections are used to connect the module to the tester via a four-wire Kelvin connection. The sense voltage connection is terminated in a break-out box which has built-in calibration capabilities, ensuring that a defined EIS calibration plane is established. The EIS raw quantities are calibrated using a two-term correction technique.¹ The calibration is performed over a frequency range of 1 kHz to 50 mHz and uses a short standard and a coaxial shunt standard of known resistance value (100 mΩ). There are two components that contribute to the systematic error of the measured impedance (Z_m), a series impedance (Z_{ser}) and a complex gain (k). The true impedance of the module (Z_t) is obtained by the following relation: $Z_t = (Z_m - Z_{ser})/k$. Calibrated EIS is performed, with frequencies being swept from 1 kHz to 50 mHz over 50 logarithmically distributed points. The excitation current for the module is 10 A_{pk}, corresponding to 278 mA_{pk} per cell (±10 mA). Additionally, a time domain pulse test is performed at two different current amplitudes (10 A and 174 A). Each pulse is 10 seconds wide followed by a 10-minute relaxation period. Each pulse amplitude is measured at both polarities in order to keep the excitation sequence average-free and to identify if there are differences in the response based on the polarity.

Results

Figure 2c shows two EIS curves and their ECM fits are shown for different cycling numbers and SoCs. The solution resistance R_{sol} describes the ohmic resistance of the electrolyte, the ratio of the electrode surface area and the distance between the electrodes, which can be also described as the separator thickness, and the electrical connectors and is identified by the point where the impedance spectrum crosses the real axis. The charge transfer resistance R_{ct} describes the charge transfer and mass transport of Li⁺ ions in solid particles and liquid electrolyte, and it is typically observed at the end of the first semicircle. The double layer capacitance C_{dl} describes the accumulation of charge carriers of opposite signs at the electrode-electrolyte interface, as well as pseudo-capacitance due to absorption/desorption processes or fast Faradic surface reactions. The charge transfer and double layer capacitance are represented by the depressed semicircle (ZARC, a parallel connection of a constant phase element and the charge transfer resistance). Recent work has shown that at higher cycle numbers, EIS spectra start to show two distinct semicircles at intermediate frequencies. This is typically an indication of ageing, such as increased interface layer resistance, dendrite formation and electrode degradation.

Figure 3 shows the extraction of ECM parameters from the time-domain pulse response data. After each cycle, a spot measurement is done including an EIS sweep and a pulse test at specific SoC values. The R_0 data generated from both the charging pulse (Figure 3c) and the discharging pulse (Figure 3d) are in good agreement over the different SoCs and the cycle number.

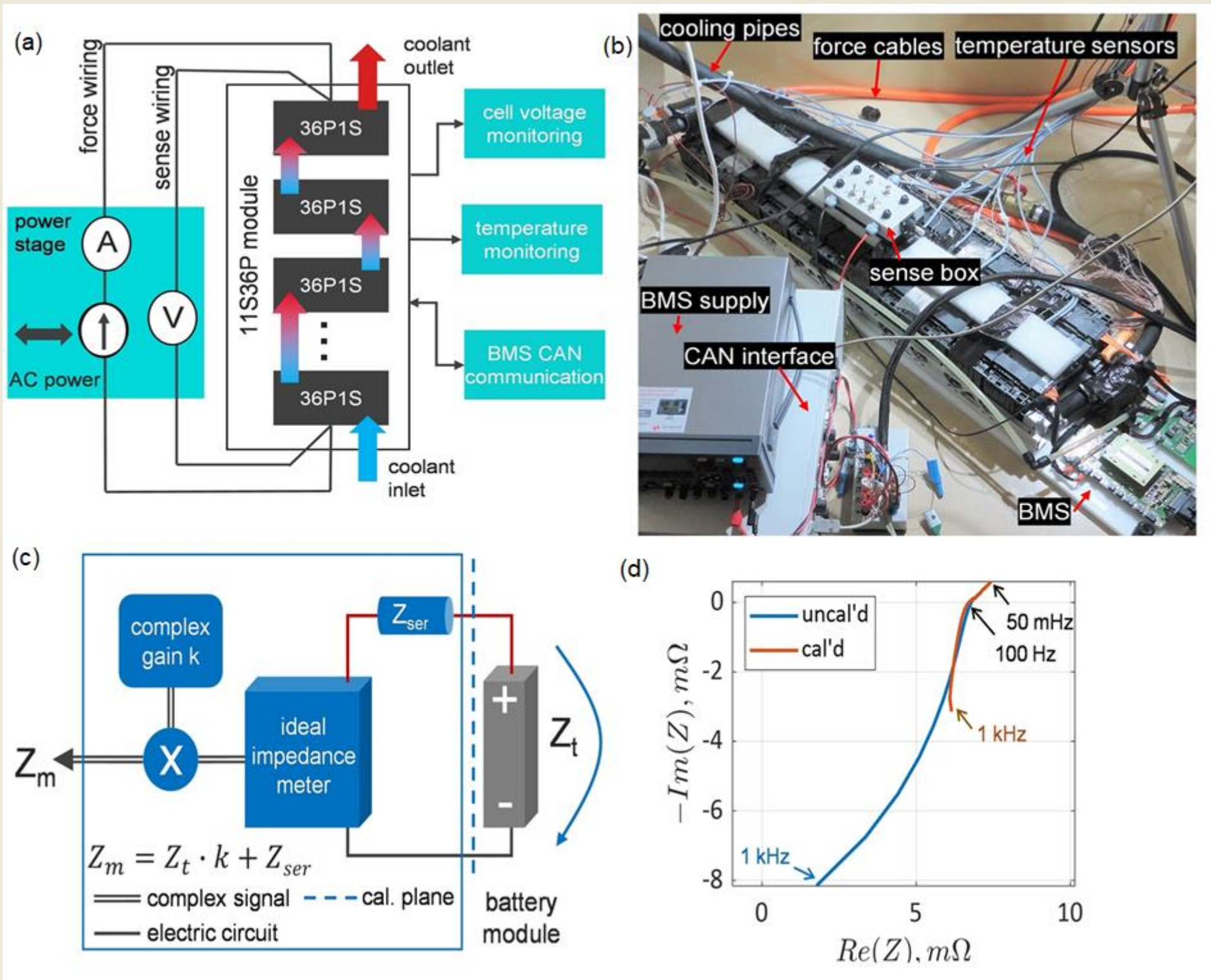


Fig 1. a) Conceptual overview of the test setup with a 4-wire connection to the module. The liquid cooling flow is indicated by colored arrows. b) Photograph of the test setup, cooling pipes, temperature sensors, BMS, and interface to the BMS control. c) Error model and workflow for the module test system. The EIS measurement is described by combining an ideal impedance meter with a series error impedance Z_{ser} and a gain error term k . The measured impedance Z_m is related to the true impedance Z_t via the complex gain factor k and the offset Z_{ser} . d) Comparison of raw and calibrated EIS across the frequency range of 1 kHz to 50 mHz. The raw data (blue) and the corrected data (red) are shown for the 7 kWh module measured at room temperature and approximately 50 % SoC. Characteristic frequency points are indicated by arrows.

Discussion

Significant corrections on the resistance and the reactance were obtained from the calibration, particularly at high frequencies above 100 Hz. In this work, a certain tradeoff between the overall sampling time and the number of cycles was considered, as well as the time constraints required for upcoming implementation in EV battery management systems. It is notable that we fit the EIS model with a single ZARC and the pulse data with two RC elements. The first RC element corresponds to the main EIS ZARC, while the second RC element, at a time constant of about 20 seconds, corresponds well to the linear EIS Warburg tail which is around 50 mHz. Future studies will focus on advanced time-domain pulsing with longer pulse rest durations and electrochemical model interpretation and battery ageing, including also defined automotive test profiles following protocols like WLTP.

Conclusions

R_{sol} showed a decrease over the cycle numbers which is explained by the enhanced wetting of the electrodes due to new cells used in the module. R_{ct} showed a monotonic increase over the 260 cycles related to the module ageing, and the inductance L was constant at about 170 nH, as it is related to the module geometry, fixture and cables. From the pulse response the main time-domain parameters R_0 , τ_1 , and τ_2 were robustly extracted. R_0 showed a similar trend as $R_{sol}+R_{ct}$ over SoC and the cycle number.

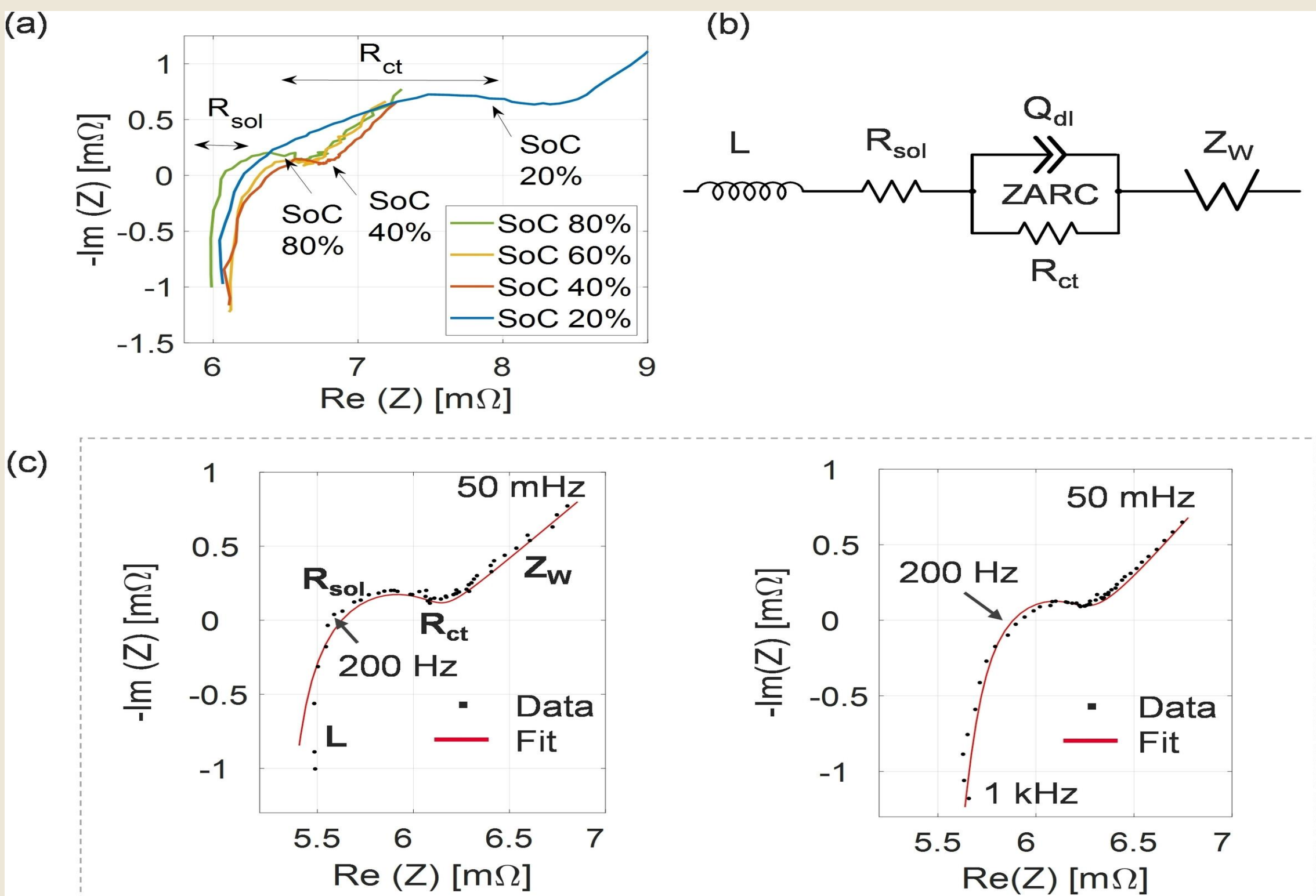


Fig 2. EIS module data and equivalent electric circuit model (ECM). a) EIS spectra superposition at cycle # 99 and varying SoC from 80 % to 20 %, in a discharge direction. The arrows indicate the ohmic resistance values to the end of the Nyquist semicircle for 20 % SoC (blue curve). b) The ECM used to fit the module EIS data. c) Two different EIS spectra fitted with the ECM (left: 80 % SoC and cycle # 99; right: 40 % SoC and cycle # 69). The minimum and maximum frequency points are labelled (c, right), as well as the point of intersection with the real axis at 200 Hz.

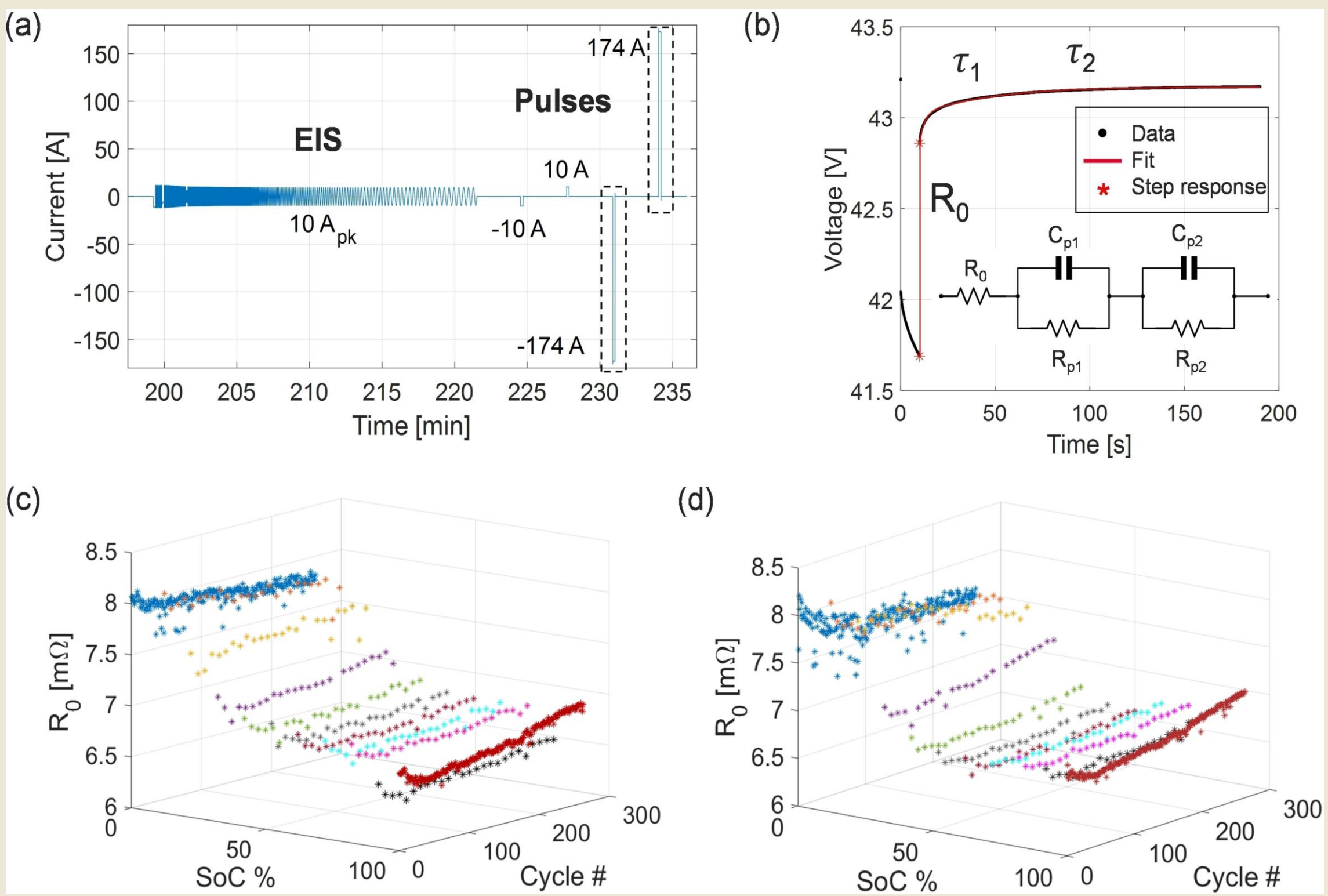


Fig 3. Extraction of ECM parameters from pulse response data. a) Current profile as a function of time for the EIS and pulse spot excitation tests at an SoC of 80 %. The left dashed box shows the discharge pulse selected in panel (b). The duration of the pulses was t=10 s. b) The voltage recovery phase (black, starting at t=10 s) and the ECM fit (red), including the step response R_0 at t=10 s and two RC elements ($R_{p1}||C_{p1}$; $R_{p2}||C_{p2}$) in series. c, d) The ECM fit parameter R_0 (ohmic resistance) shown in a 3D plot with respect to SoC and the cycle number, extracted from the -174 A discharge pulse (c), and from the 174 A charge pulse (d).

Acknowledgements

This work was funded in part by the European Union's Horizon 2020 research and innovation program NMBP 'NanoBat' under grant agreement no. 861962.

References

[1] M. Kasper, A. Leike, J. Thielmann, C. Winkler, N. Al-Zubaidi R-Smith, F. Kienberger, J. Power Sources 2022, 536, 231407.

