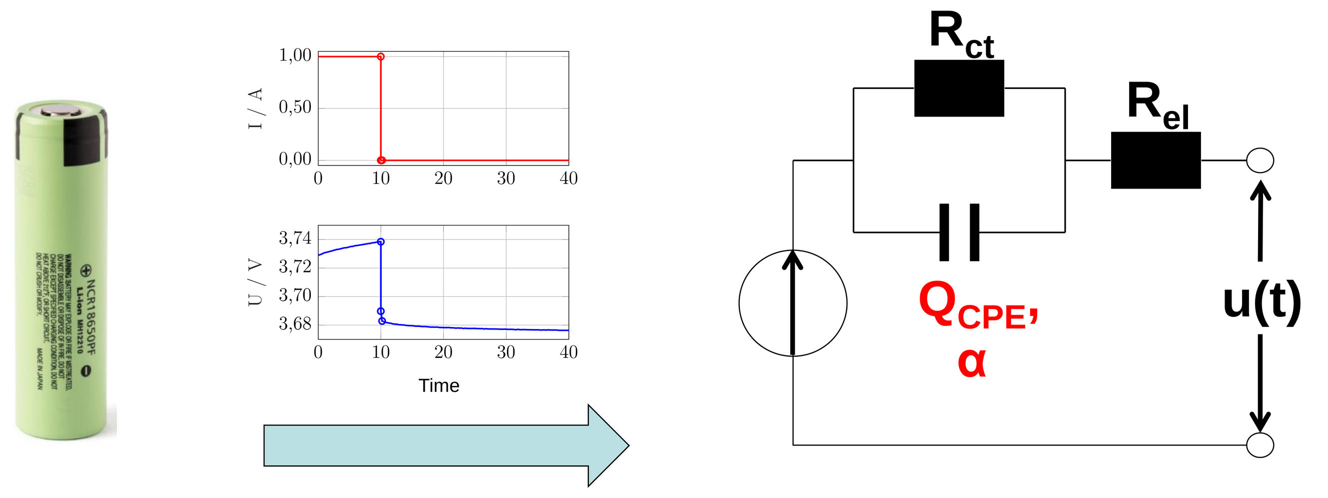
German Aerospace Center (DLR)

Institute of Engineering Thermodynamics

Extraction of the parameters of a fractional order equivalent circuit model based on time-domain relaxation measurements

C. Heim[1], W. Strunz[2], N. Wagner[1], K. A. Friedrich[1,3]
[1]German Aerospace Center (DLR), Pfaffenwaldring 38-40, 70569 Stuttgart, Germany
[2]Zahner-elektrik GmbH & Co. KG, Thüringer Straße 12, 96317 Kronach-Gundelsdorf, Germany
[3]Institute for Energy Storage, Pfaffenwaldring 31, University of Stuttgart, Germany
Corresponding author: christopher.heim@dlr.de

Introduction



Equivalent circuit models are a common way to describe the electrochemical behavior of batteries and other electrochemical devices. Usually equivalent circuit parameters are obtained by fitting impedance spectra with a suitable model circuit. This work explores a method to fit fractional order equivalent circuits from time-domain relaxation measurements after current excitation of a battery.

Theory

For a current step excitation we can find for an equivalent circuit (EC) consisting of a parallel RQ element and a resistor R_{el} in series:

$$U(t) = U_{t=0} - I_{t=0} \cdot \mathcal{L}^{-1}\left\{\frac{1}{s} \cdot Z_{EC}\right\} \quad with \quad Z_{EC} = R_{el} + R \cdot \frac{1}{RQ \cdot s^{\alpha} + 1}$$

Expanding the expression for the inverse Laplacetransform in a geometric series and performing the transform, one obtains:

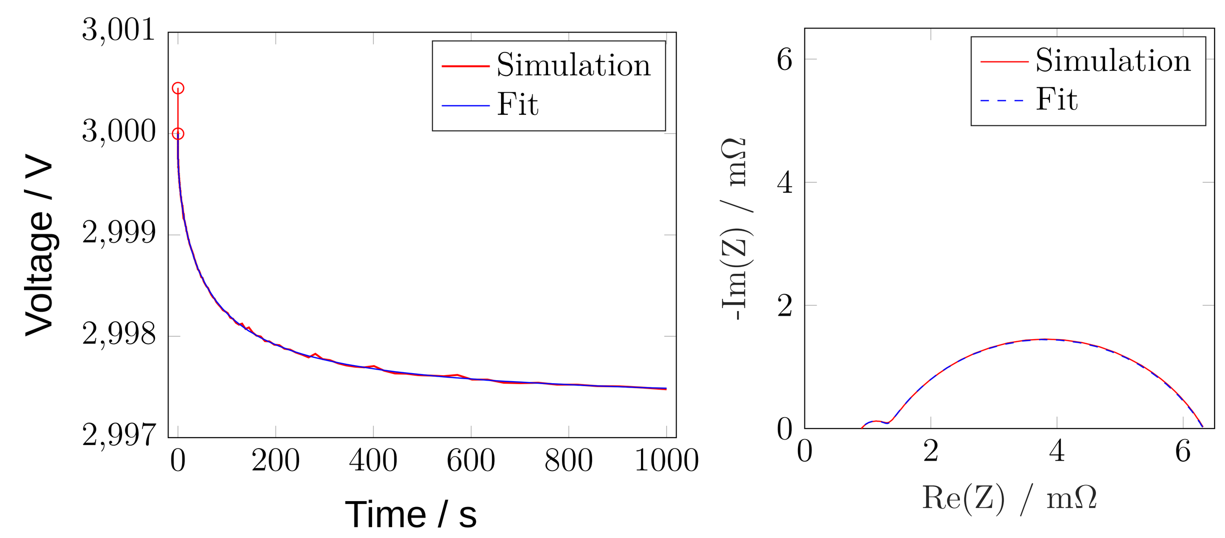
$$U(t) = U_{t=0} - I_{t=0} \cdot \left[R_{el} + R \cdot \sum_{n=0}^{\infty} \frac{1}{\Gamma(n \cdot \alpha + 1)} \cdot \left(-\frac{t^{\alpha}}{RQ}\right)^{n}\right]$$

Finally, introducing the Mittag Leffler function $E_{\alpha}(z)$ results in,

$$U(t) = U_{t=0} - I_{t=0} \cdot \left[R_{el} + R \cdot E_{\alpha}\left[\left(-\frac{t^{\alpha}}{RQ}\right)\right]\right] = U_{t=0} - I_{t=0} \cdot [R_{el} + R \cdot E_{\alpha}(z)]$$

which can easily be expanded to contain a serial connection of further parallel RQ elements.

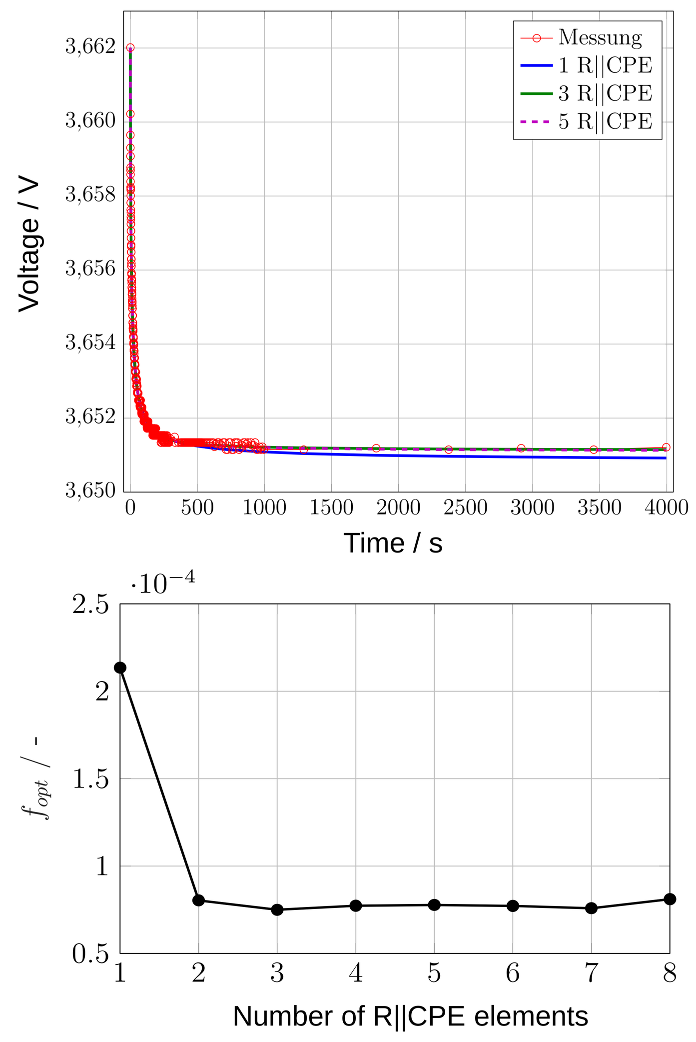
Validation on noised synthetic data (simulation)



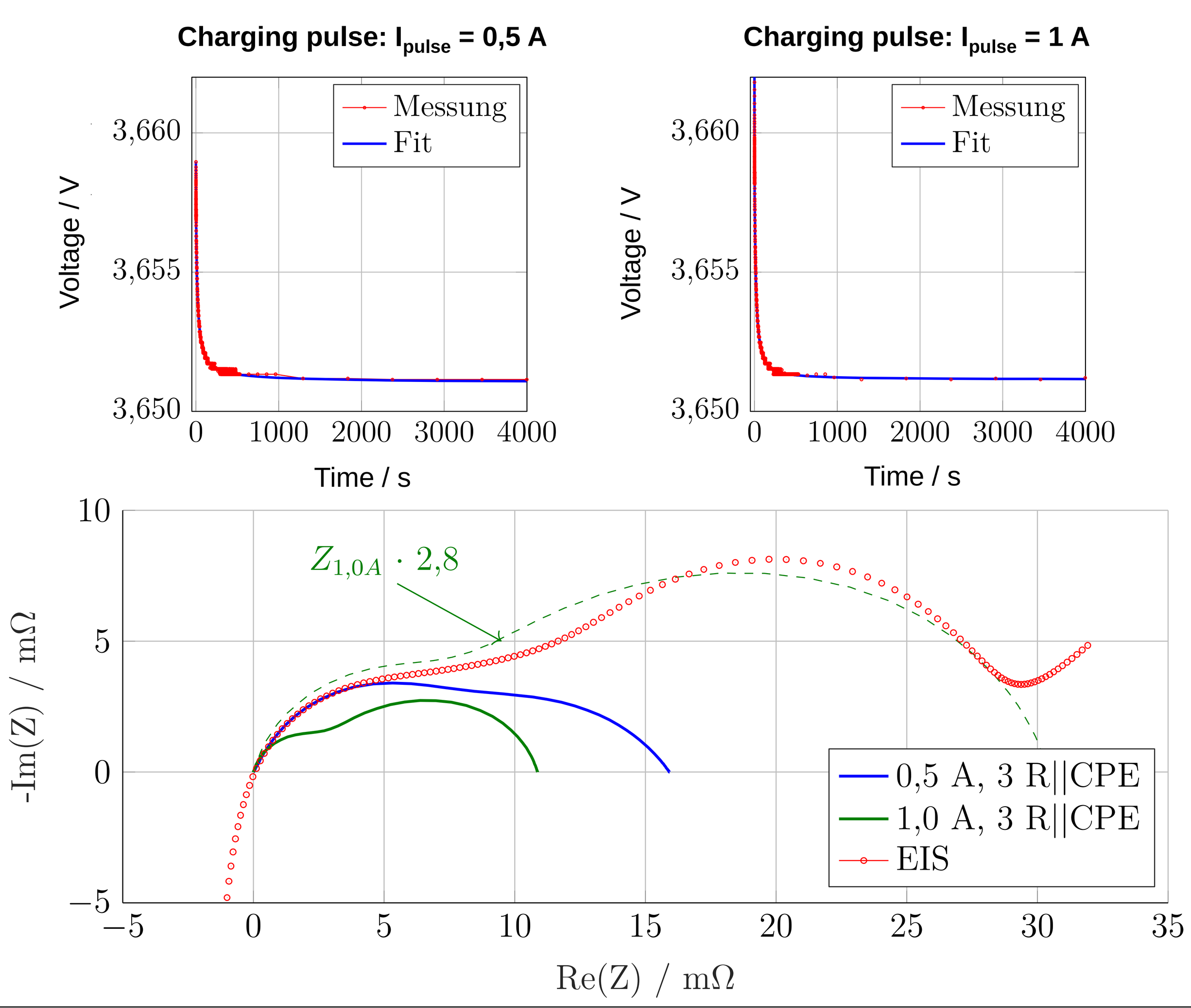
Experimental Results

Experimental investigations were performed with a commercial 18650 cell:

Error vs. number of R||CPE



Comparison with Electrochemical Impedance Spectroscopy (EIS)



Time-domain fitting:

- Time-domain fit with very good accuracy possible
- Charging & discharging pulses of different magnitude and length tested
- Sampling-rate and measurement noise have a big influence on resolution and fit-quality

Nyquist diagram of circuit with parameters obtained from fit of EIS versus circuit with parameters from time-domain fit:

- Both, EIS & time-domain fit, were performed with the same equivalent circuit
- Big discrepancy between EIS & time-domain spectra visible
- Most likely cause: Parameters from the time-domain fit depend on pulse current versus currentless parameters from the EIS fit

Conclusions

- A theoretical approach to extract fractional order equivalent parameters from time-domain data has been succesfully developed
- Approach was validated with synthetic data
- Good accuracy in time-domain can be achieved with fits of real battery data
- Comparison to parameters from EIS shows big discrepancy that needs to be resolved

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