Institute of Engineering Thermodynamics

Electrochemical impedance spectroscopy as a non-destructive tool to investigate lithium ion battery aging

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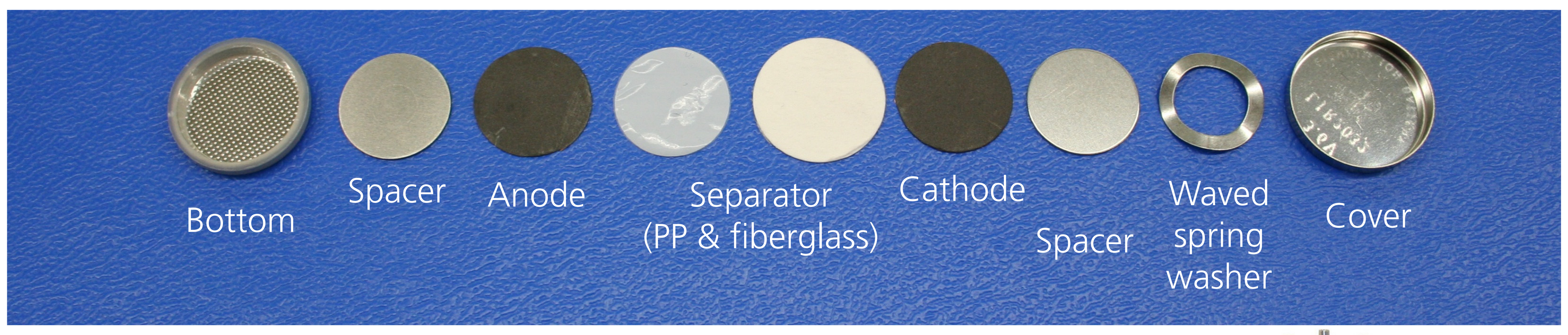
Introduction:

In order to run lithium ion batteries in a secure and lifetime optimized way, it is essential to understand the cell degradation behavior due to load cycling and calendar aging. Thereby, cell degradation is associated with an increasing cell resistance. For automotive applications battery cells will usually be replaced when the cell capacity drops under 80% or the internal ohmic resistance is doubled in comparison to the new state. A very useful and non-destructive method to detect increasing cell resistances during cell operation is electrochemical impedance spectroscopy (EIS). One main reason for increasing ohmic resistances during load cycling is attributed to a growing solid electrolyte interface (SEI) located at the phase boundary between graphite anode and electrolyte.

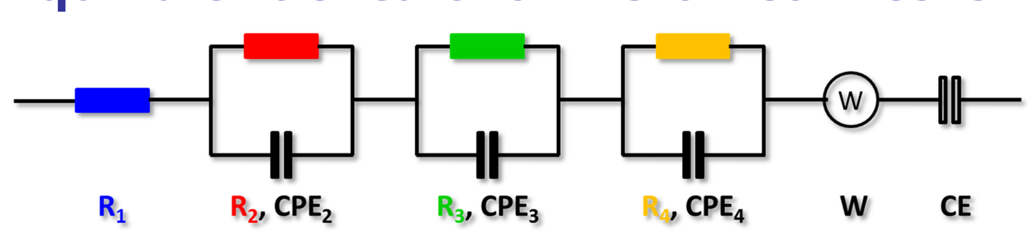
In this work we present results of EIS measurements as a function of different operating parameters. In this context, a useful tool to interpret EIS spectra is the use of suitable equivalent circuits to simulate battery components, chemical reactions and mass transfer limitations. All experiments are performed with different electrode materials assembled in self-build coin cells (LIR2032 body) or pouch cells. In general, coin cells are build with commercial electrodes while for the pouch cells self-made nanostructured lithium-nickel-cobalt-manganese oxide (NCM) electrodes are used, kindly provided through the Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-KWT).

Self-made coin cells: type "LIR2032"



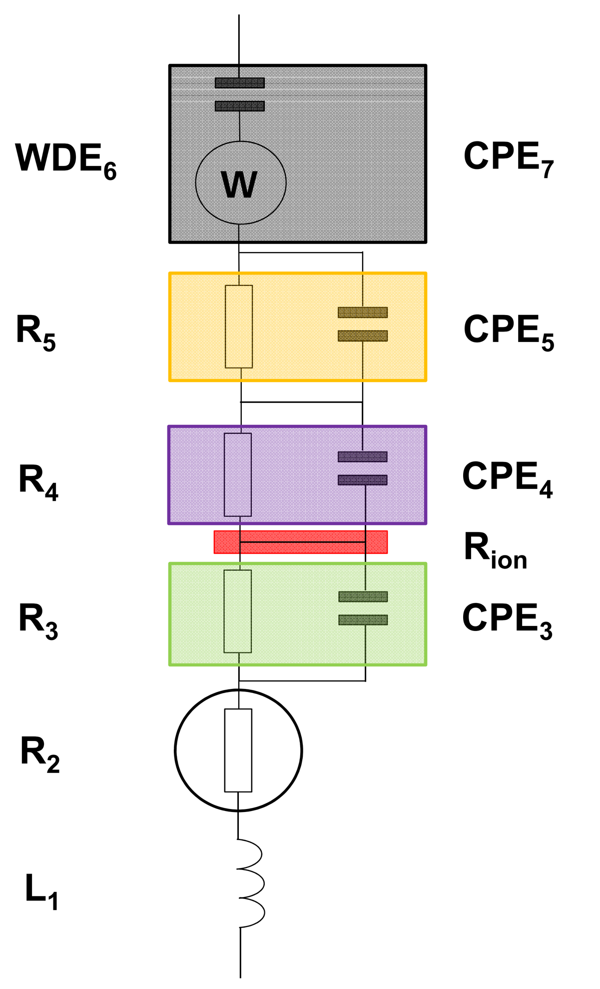
- Electrode manufacturer: Custom Cells Itzehoe GmbH
- **3 different Electrode types**: high energy, balanced, high power
- Separator: **Celgard® 2320** (Ø 16 mm) & **fiberglass** (Ø 18 mm)
- Electrolyte: **EC/DEC 3:7 (v/v)** and **1 M $LiPF_6$** conducting salt
- Sealing with polymer ring in the bottom
- Hydraulic crimper: 50 kg·cm^{-2} (MSK-110, MTI Corporation)

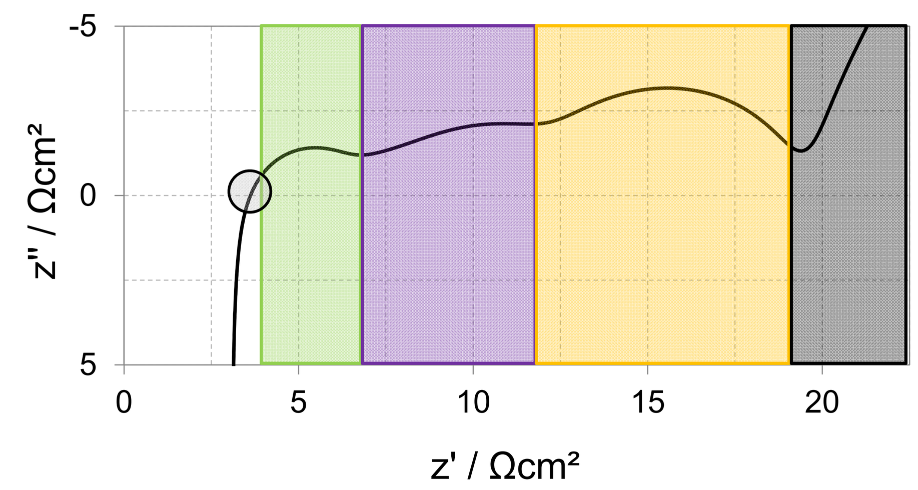
Equivalent circuit for EIS on coin cells



R_x: ohmic resistance
CPE_x: constant phase element
W: Warburg element
CE: capacitance element

Equivalent circuit for EIS on pouch cells

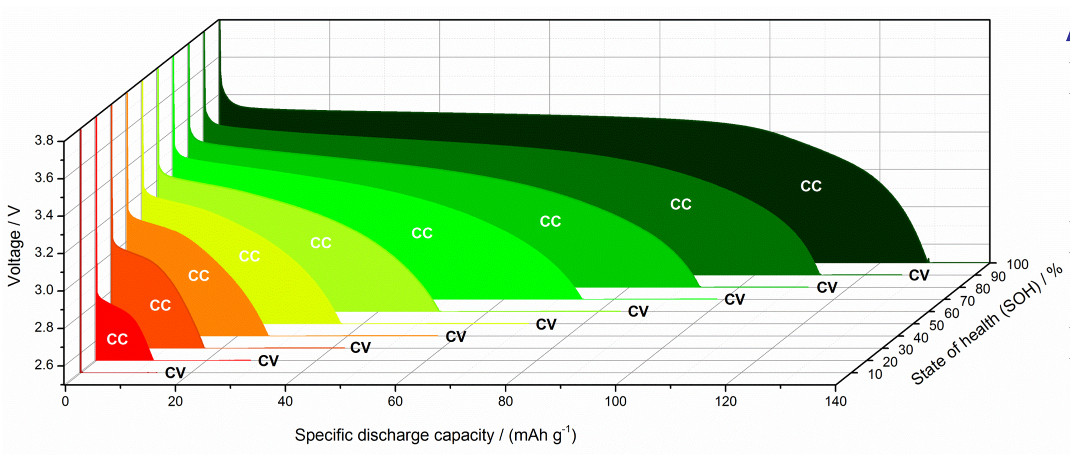




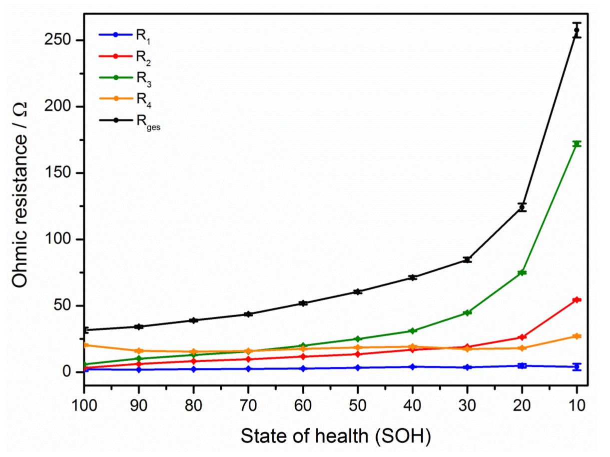
Black: **Electrolyte**
Green: **Contact resistance** between current collector and cathode/anode layer
Violet: **SEI resistance** between active material and electrolyte; **charge transfer** in the **anode**
Orange: **Charge transfer** in the **cathode**
Grey: **Diffusion** and **intercalation** of lithium
Red: Limited **ion transport** due to pore structure

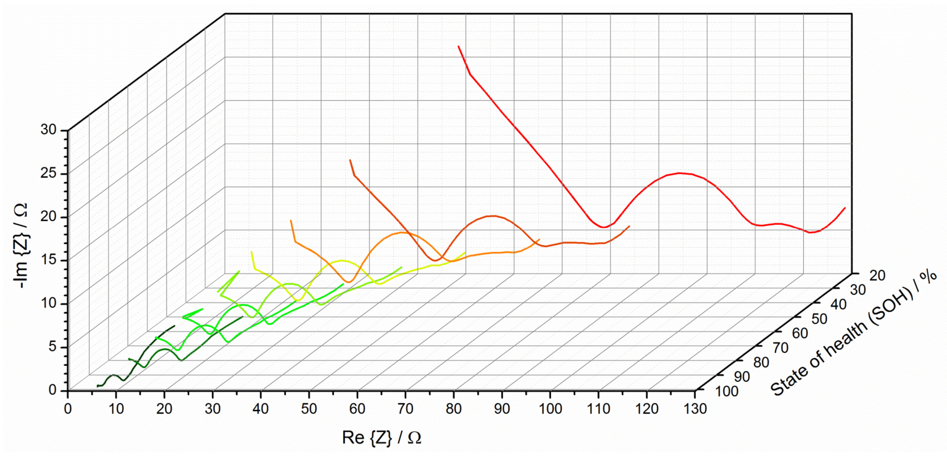
CPE: constant phase element
WDE: Warburg diffusion element

Half cell tests: e.g. lithium iron phosphate (LFP) vs. lithium (Li)



Automated test sequence:
- **Load cycling** via BaSyTec coupled with EIS measurements during long-term aging test
- **CC and CV steps** during **charging & discharging**
- SOH (based on sp. discharge capacity) is determined after each charge & discharge cycle
- **Electrochemical impedance spectroscopy (EIS)** in **10% SOH steps**.



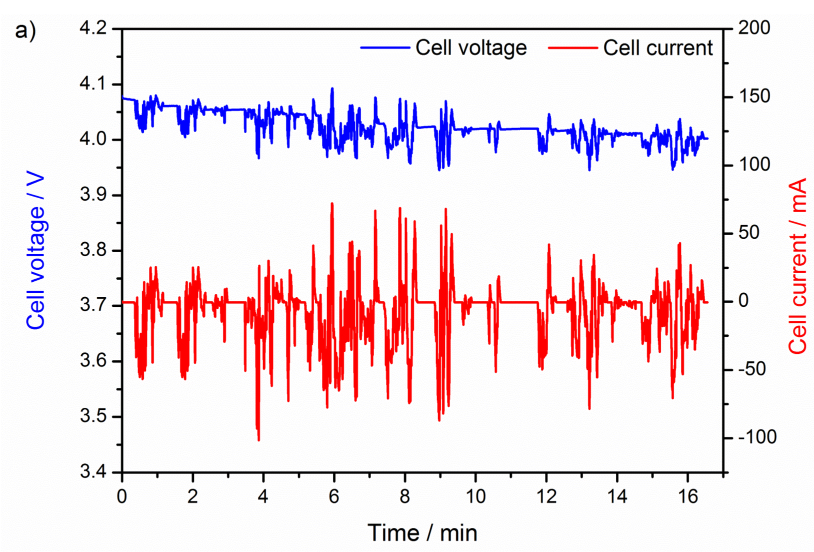


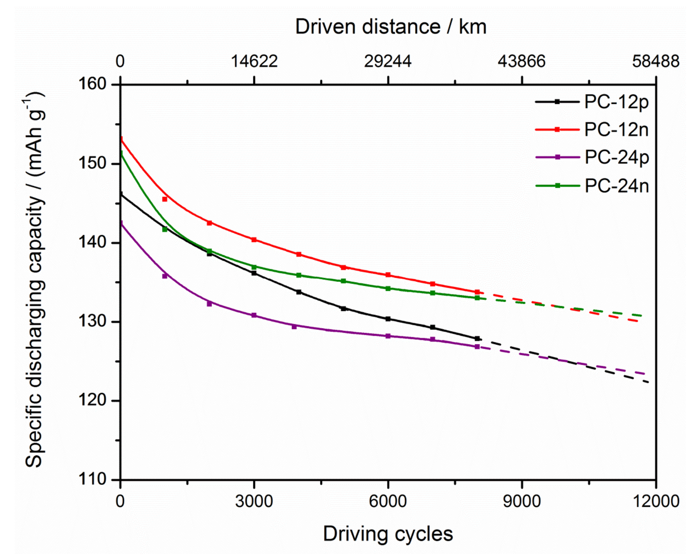
Ohmic resistances that are calculated through EIS equivalent circuit simulations:
- **R_1: Electrolyte resistance**; slightly increasing during aging process
- **R_2: Contact resistance** between current collector and cathode/anode layer
- **R_3: SEI resistance** between active material and electrolyte; **charge transfer anode**
- **R_4: Charge transfer cathode**
- **R_{ges}**: sum of all **ohmic contributions** (R_1+R_2+R_3+R_4)

EIS spectra of LFP vs. C half cell:
- **Impedances** are continuously **increasing** → direct correlation with battery cell aging
- **Capacity loss** (decreasing SOH) can be **non-destructively monitored by EIS** data

Acknowledgments:
We thank the **German Federal Ministry of Education and Research (BMBF)** for funding work on coin cells (Li-EcoSafe; FKZ: 03X4636B). The presented pouch cell experiments were carried out in the frame of the theme "Elektrochemische Speicher im System – Zuverlässigkeit und Integration" within the research portfolio of the **Helmholtz Association of German Research Centers (HGF)**.

Pouch cell aging with Common Artemis Driving Cycle (CADC)

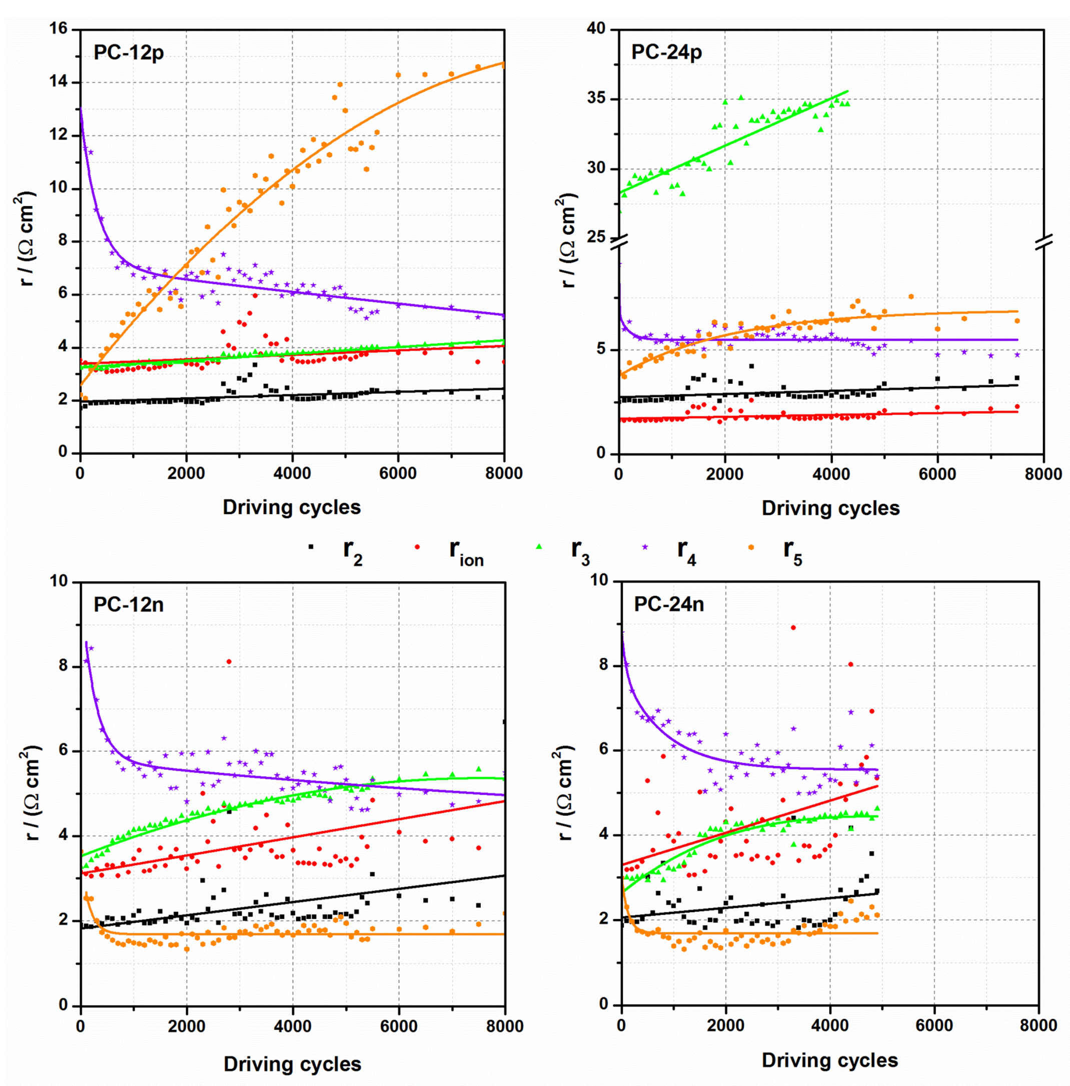




Long-term test with CADC urban profile:
- Battery charging and discharging
- Cell operation: **3.0–4.2 V; SOC 10–90%**

Capacity decrease as aging indicator:
- **Nanostructured electrodes** at the cathode exhibit **long-term advantages**

Determination of specific resistances with in-situ EIS



Increasing specific resistances due to cell degradation caused by long-term cycling:
- **Different degradation mechanisms** for pristine and nanostructured NCM electrodes
- **Pristine material: crack formation** leads to capacity loss
- **Nanostructured material: delamination** between **active material** and **current collector** is the weak point

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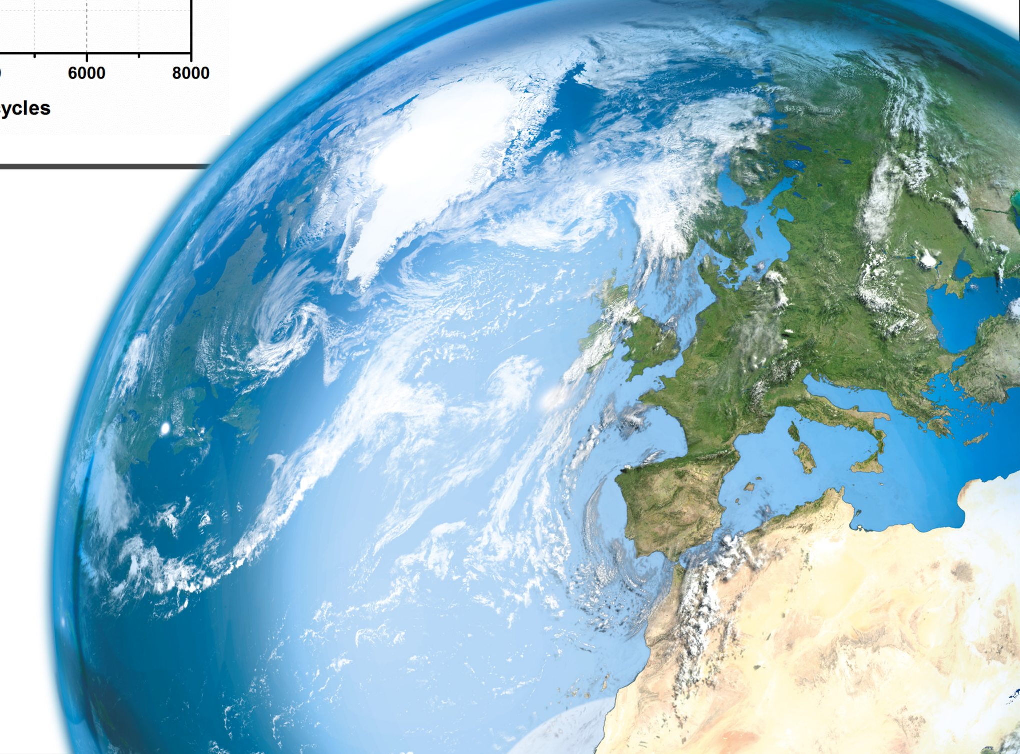
Wissen für Morgen



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