Institute of Engineering Thermodynamics

Development of operational strategies for lithium ion batteries to guarantee a safe and lifetime optimized performance

Andreas M. Dreizler, Oliver S. Fitz, Norbert Wagner, K. Andreas Friedrich

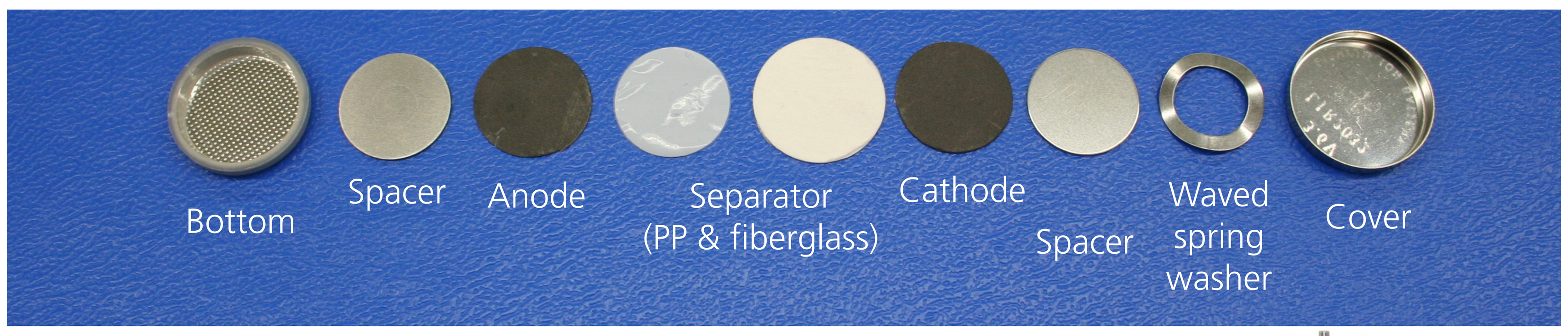
Deutsches Zentrum für Luft- und Raumfahrt (DLR), Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany; andreas.dreizler@dlr.de

Introduction:

Important hurdles for the market launch of different types of lithium ion batteries are operation security, long calendar life, cycle durability and fast-charging capability. The main focus of this work is to identify unfavorable operation and environmental conditions which generally accelerate cell degradation such as c-rates during cycling, load profiles and temperature. All experiments are performed with different electrode materials assembled in self-built coin cells (LIR2032 body).

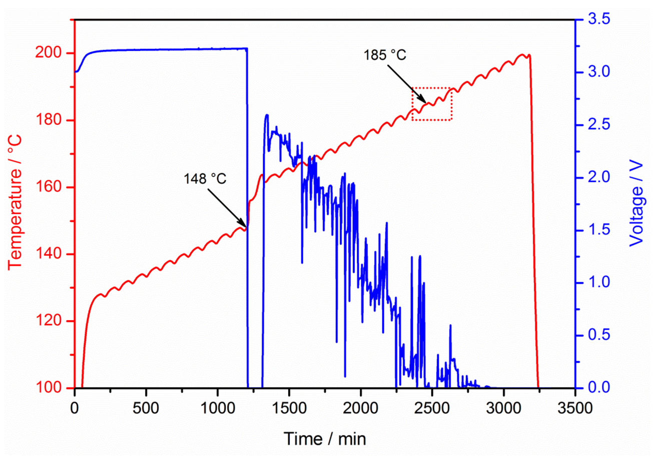
In order to run batteries in a secure and lifetime optimized way, it is essential to determine the state of charge (SOC) and the state of health (SOH) accurately. A useful method to detect increasing cell resistances during cell operation is electrochemical impedance spectroscopy (EIS). One main reason 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 first results of EIS measurements as a function of different operating parameters. Thereby, a useful tool to interpret EIS spectra is to use suitable equivalent circuits to simulate battery components, chemical reactions and mass transfer limitations. In addition, accelerating rate calorimetry (ARC) and thermogravimetric analysis (TGA) are supplementary methods to identify relevant cell and component aging mechanisms in order to improve lifetime and performance.

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)

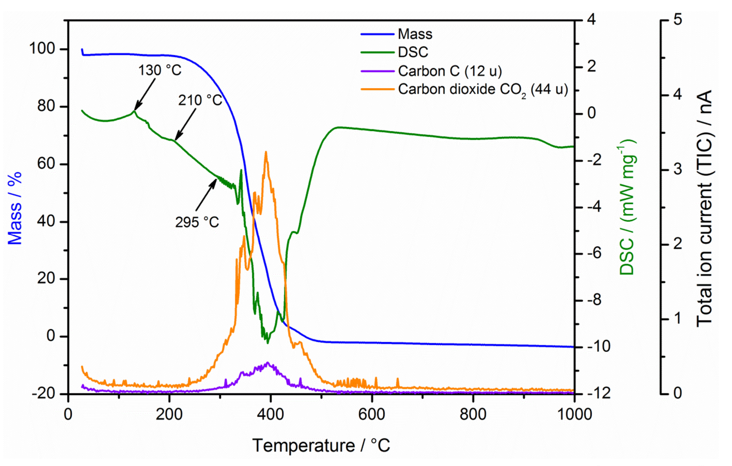
Accelerating rate calorimetry (ARC): thermal stability tests

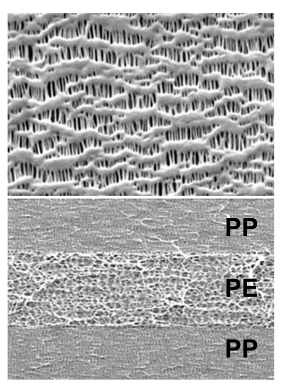


Commercial battery: Energizer 2032 (Li/MnO_2)

- Heat-Wait-Search → two characteristic temperatures: 148 °C and 185 °C
- Lower temperature: separator begins to melt
- Higher temperature: separator begins to decompose; melting of lithium metal electrode
- Energizer 2032: separator is unknown

Thermogravimetric analysis (TGA) of separator material

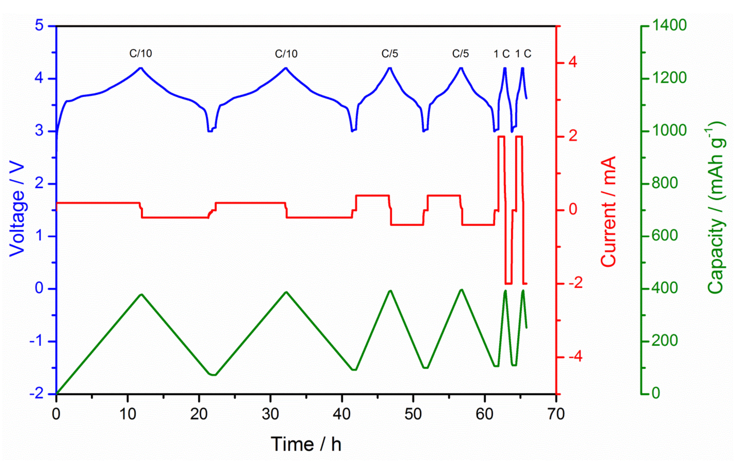




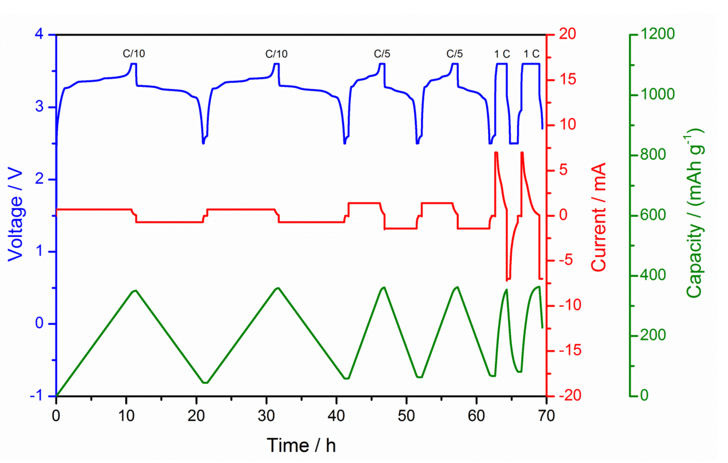
> 130 °C: beginning of melting process
> 210 °C: melting process and combustion → formation of carbon and carbon dioxide
> 295 °C: only combustion (C and CO_2)

Celgard® 2320 (20 µm thickness; 39 % porosity): Trilayer PP/PE/PP (polypropylene/polyethylene/polypropylene) separator

Coin cell formation procedure after assembling



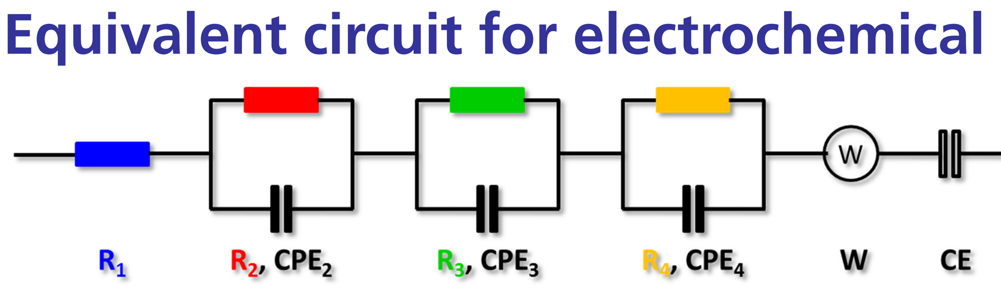
NCM-111 vs. C (high energy electrode)



LFP vs. C (high energy electrode)

Cell formation procedure: charge: CC+CV (up to 1/10 of C-rate current), discharge: CC+CV (up to 1/10 C-rate current), 30 min resting phase; 2 x C/10, 2 x C/5, 1 x 1C

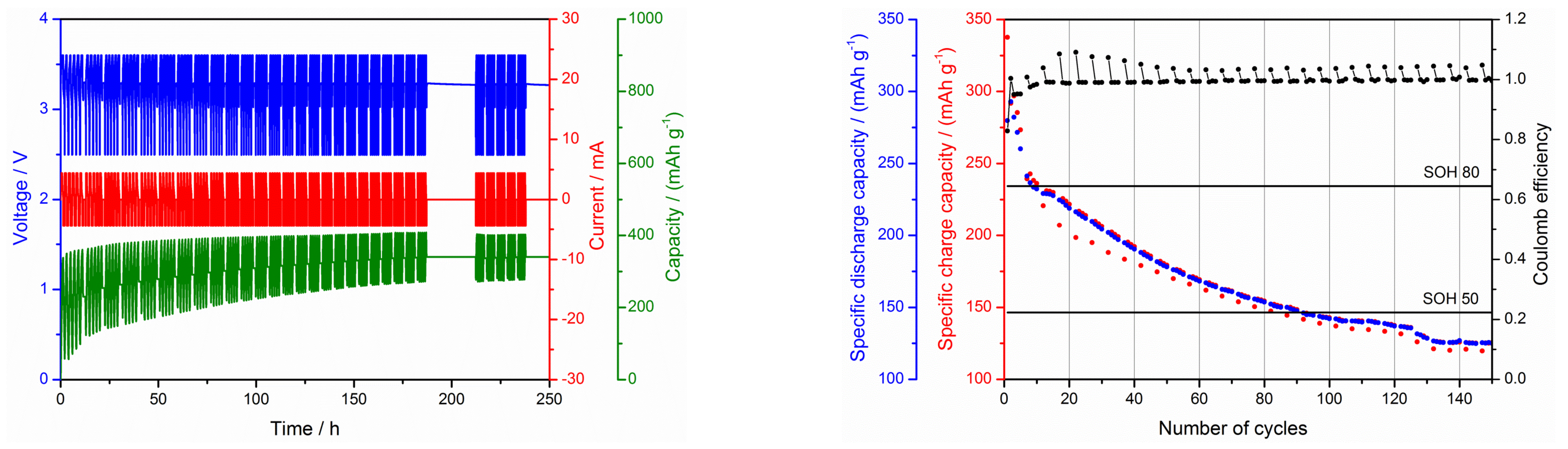
Equivalent circuit for electrochemical impedance spectroscopy



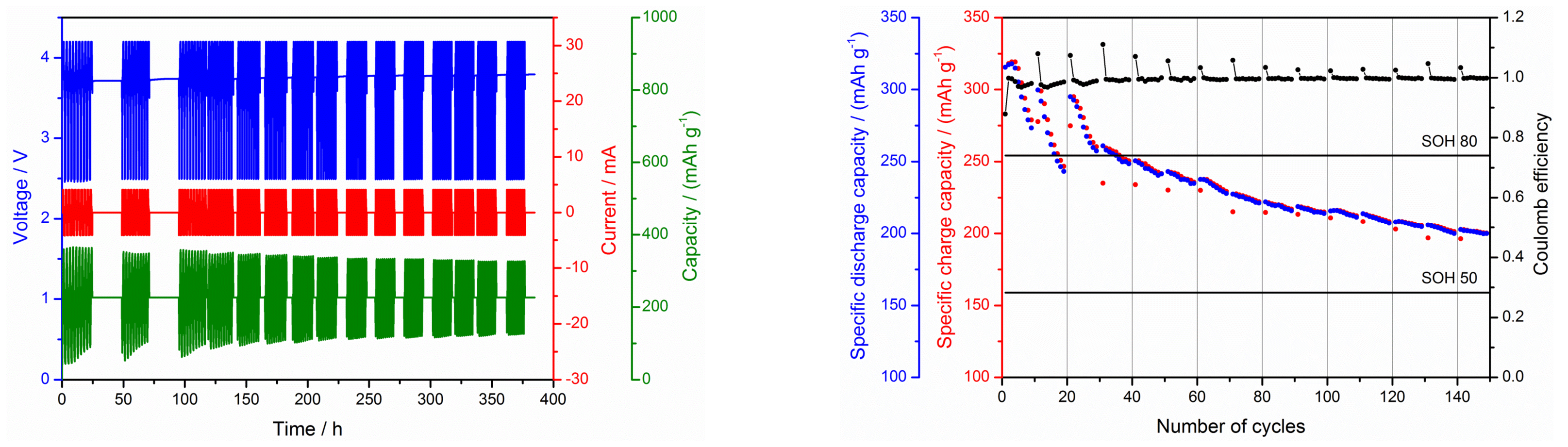
R_x: ohmic resistance
CPE_x: constant phase element
W: Warburg element
CE: capacitance element

Long-term test: load cycling aging behavior

LFP vs. C, 3.7–2.5 V, 1 C, 1 M $LiPF_6$, EC/DEC 3:7, charging/discharging: CC+CV



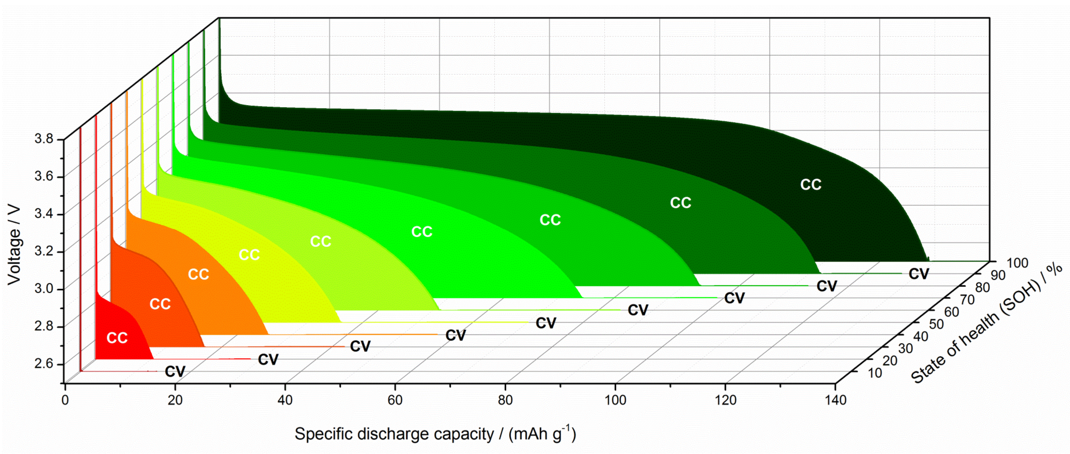
NCM-111 vs. C, 4.2–2.5 V, 1C, 1 M $LiPF_6$, EC/DEC 3:7, charging/discharging: CC+CV



Test sequence: 1. Cell formation, 2. EIS at SOC50, 3. 10 load cycles, 4. EIS at SOC50, …

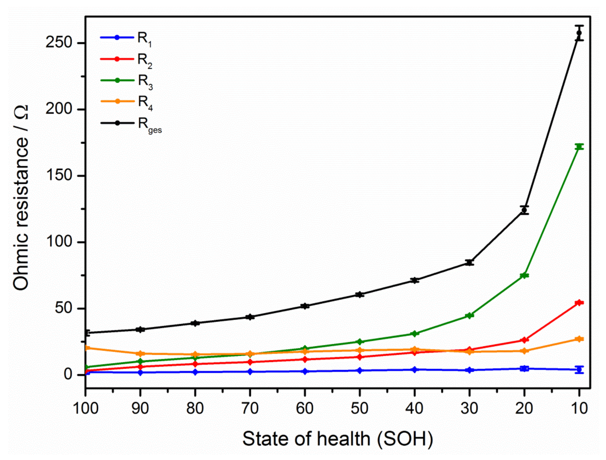
- LFP vs. C shows higher degradation rates compared to NCM-111 vs. C
- Exponential aging behavior with nearly linear degradation at end of life
- Coulomb efficiency (specific discharging capacity/specific charging capacity) close to 1
- Relaxation behavior due to EIS measurement and break → temporary efficiency above 1

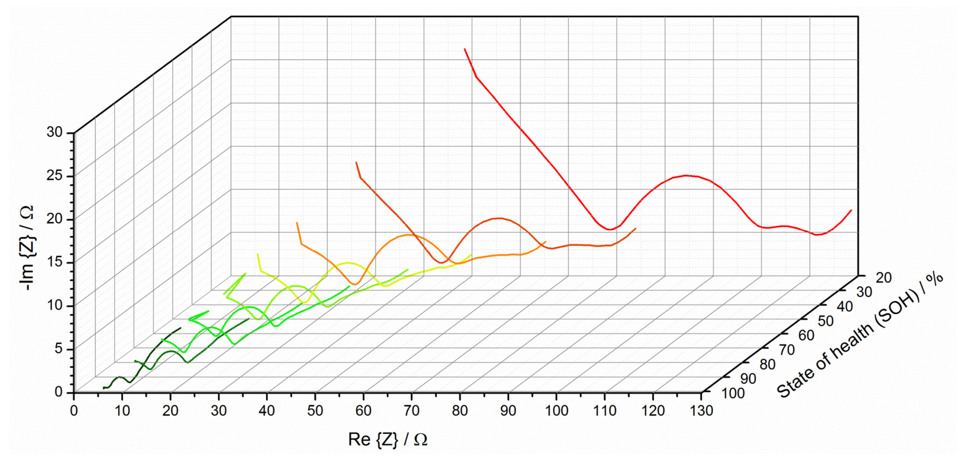
Half cell tests: e.g. lithium iron phosphate (LFP) vs. lithium (Li)



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; should be nearly constant 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 this work (FKZ: 03X4636B)

Knowledge for Tomorrow

Wissen für Morgen

DLR Deutsches Zentrum für Luft- und Raumfahrt
German Aerospace Center