Technische Universität Braunschweig

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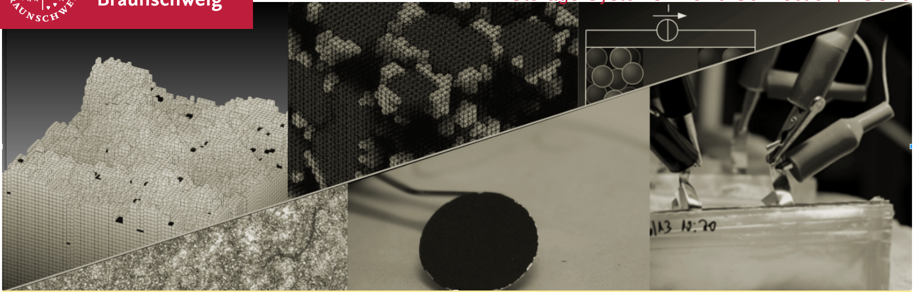
Workshop on Modeling, Control and Operation of Advanced Energy Storage Systems in Grid Connection, ECC19



Dynamic Modeling and State Analysis of Li Ion Batteries

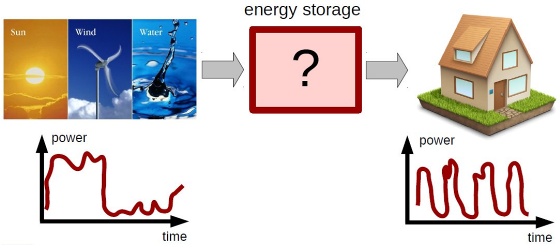
Prof. Dr.-Ing. Ulrike Krewer and co-workers[1], [2], ECC19, Naples, June 25 2019

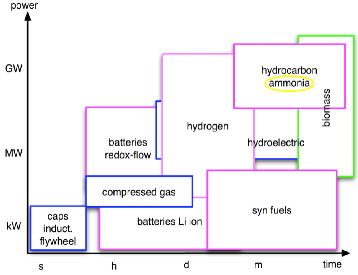
[1] Institute of Energy and Process Systems Engineering, TU Braunschweig, Germany

[2] Battery LabFactory Braunschweig, TU Braunschweig

Content

Electrochemical Systems for Renewable Energy Storage



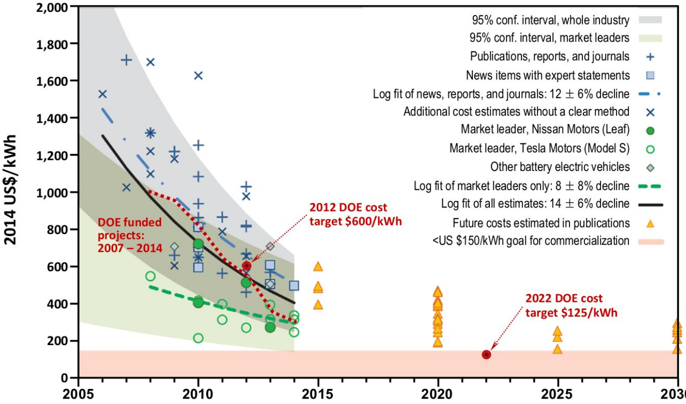


[Behrens, Schlögl]

Li Ion Batteries - Where Are We?

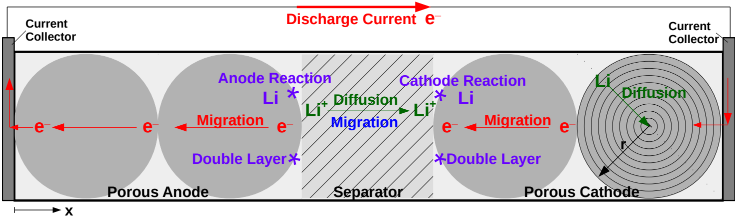
- Widely used for portable, mobile and increasingly stationary power supply
- Challenges remaining: cost, energy density, safety

→ Operate at upper performance limits → optimal cell diagnosis/operation



[Nykvist, Nilsson, Nature Climate Change, 2015]

Processes and Performance Variables of Li Ion Batteries



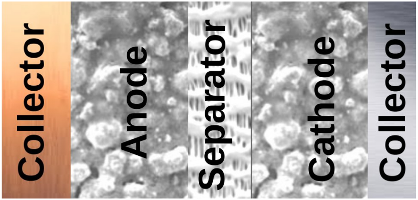
Main processes in battery

- Electrochemical reactions, e.g. $Li_xC_6 \longleftrightarrow C_6 + xLi^+ + xe^-$
- Migration, diffusion
- Double layer (dis)charging, heat transport/generation
- Degradation processes

Essential performance variables for diagnosis/operation/control

- State of charge: percentage of available capacity at time t, $(C_{max} - C(t))/C_{max}$
- State of health: percentage of remaining max. capacity, $C_{max}/C_{max,t=0}$

General Challenge for Electrochemical Technologies

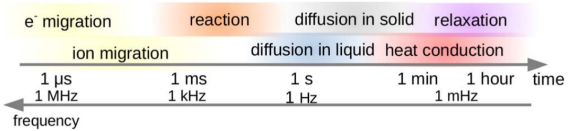


- Electrochemical cells consist of thin, sensitive layers.
- In each layer are strongly different and interacting processes.
- Only three variables easily measurable: current, voltage, (temperature).
- These conditions make it difficult to understand processes in and state of cells!
- Optimal diagnosis and operation (performance, safety, lifetime) thus challenging

Dynamic Methods for Better Diagnosis and Operation

[Krewer et al., J. Electrochem. Soc. 2018]

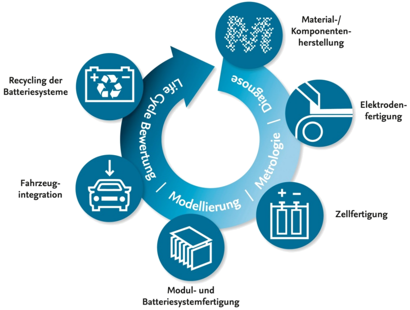
- Electrochemical cells contain processes on different time scales: slow transport processes, fast electron transport, slow and fast reactions



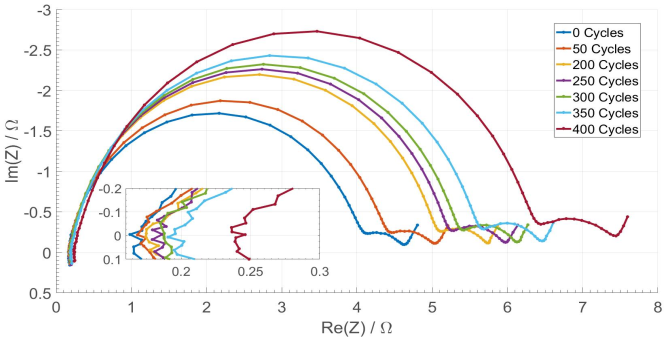
- Dynamic methods allow to separately analyse slow and fast processes
- Established dynamic techniques in electrochemistry: impedance spectroscopy (sinus), chronoamperometry (step), cyclovoltammetry (ramp)

Well Characterised LIB at Battery LabFactory Braunschweig

- Interdisciplinary R&D platform for the development, production, diagnosis and simulation of (Li ion) batteries,
- offers an engineering based infrastructure for the tailored production and analysis of electrodes, cells and systems.
- Facts: 13 Professors and PTB; $>$ 70 researchers; 900 m^2 pilot plant



Typical Impedance Spectrum of LIB



Spectrum of cell manufactured at Battery LabFactory clearly shows

- aging process of LIB
- similar features as in literature

Open Question

How to extract information from spectrum?

Modeling Approaches for Diagnosis and Operation

[Krewer et al., J. Electrochem. Soc. 2018]

Modeling

allows to predict performance, estimate (critical) state from complex measurements (e.g. EIS), optimise performance

Mechanistic Modeling

- First principles modeling
- Considers physical, electrical and chemical phenomena

+ Provides deep insight into processes and battery state

- Challenging to parameterise, computationally demanding

Equivalent Circuit (EC) Modeling

- Map ionic/electric processes to network of electric circuit componends

+ Easily adustable to reproduce measured behavior

- Often non-unique EC & effect attribution; limited in-sight

Data-driven Modeling

- Trained black box models correlate measured features to performance

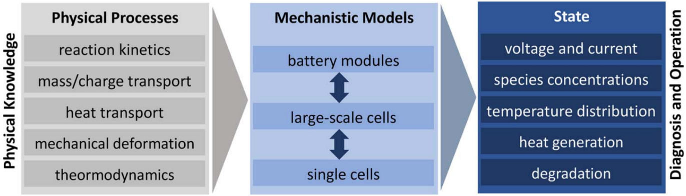
+ Allows modeling of complex, not well understood behavior

- Training/analysis time-consuming and expensive; no in-sight

Content

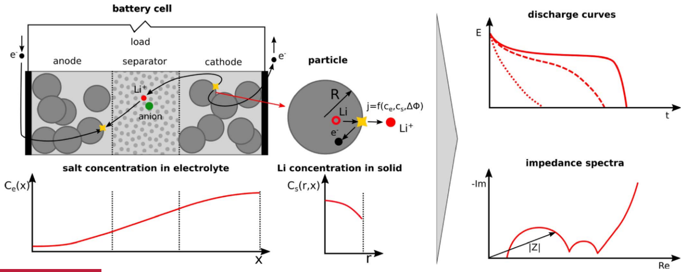
Mechanistic Modeling: Purpose and Principle

[Krewer et al., J. Electrochem. Soc. 2018]



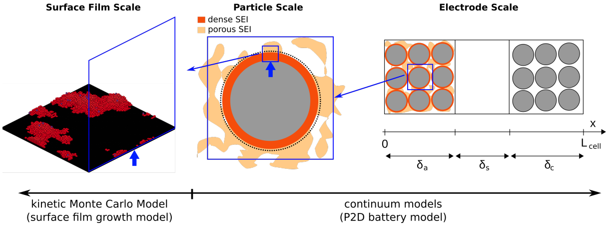
Scope

Understanding, prediction, reproduction and control of states and behavior of LiB

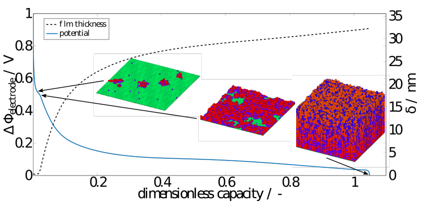


Example 1: Understanding Film Formation

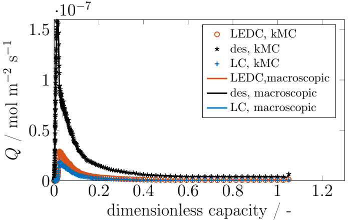
[Roeder, Braatz, Krewer, J. Electrochem. Soc. 2017]



Potential, film thickness and film structure



Reaction rates

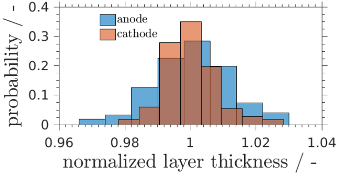


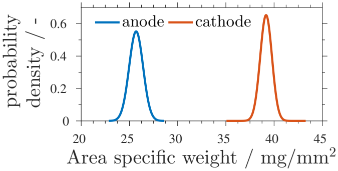
Model-based in-sight into Li loss during first cycle allows to optimise this procedure

Example 2: Assessing Uncertainty in Production

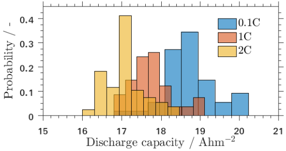
[Laue, Schmidt, Dreger, Xie, Röder, Schenkendorf, Kwade, Krewer, Energy Technol. 2019]

Uncertainties in production

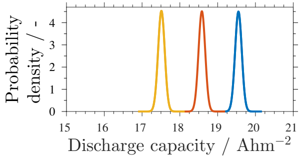




Experimental Performance



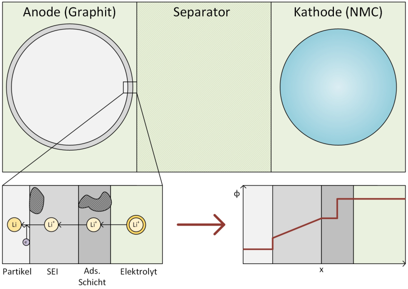
Predicted performance



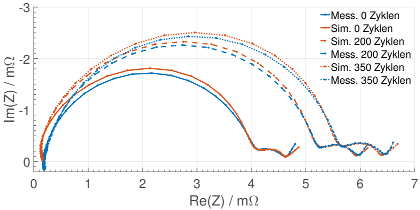
- Uncertain product parameters lead to uncertain performance
- Product deviation detrimental for balancing cells, i.e. performance/life-time loss
- Knowledge uf production uncertainty impact important for battery system

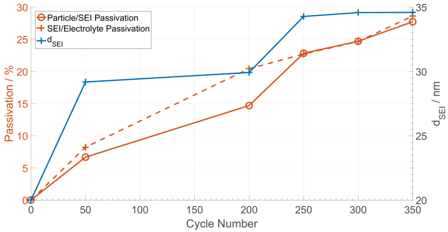
Example 3: Estimating Degradation Parameter

[Heinrich, Wolff, Roeder, Seitz, Krewer, Batteries and Supercaps, 2019]



- Mechanistic model for identification of degradation causes and progress
- Here: film thickness and surface passivation



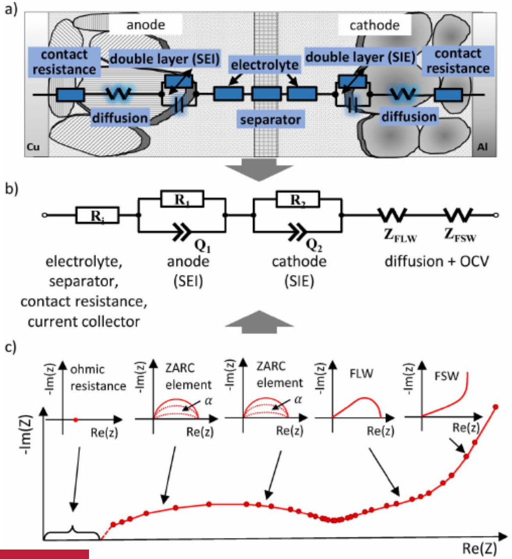


- Model able to reproduce spectra during aging
- Degradation cause/progress located

Content

Equivalent Circuit Modeling: Purpose and Principle

[Krewer et al., J. Electrochem. Soc. 2018]



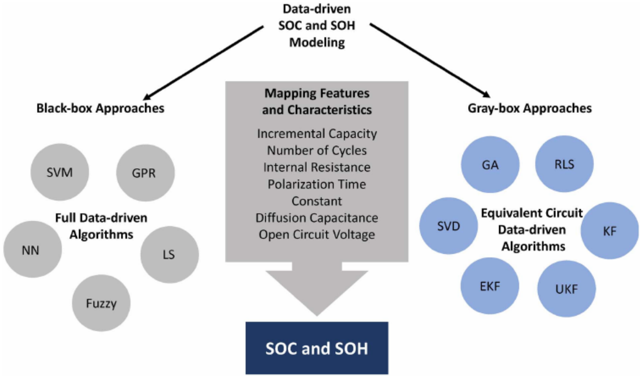
Scope

Reproduce and estimate state of health/charge of LiB with electric circuit elements

Besides classical electric circuit elements, introduction of new (nonlinear) elements, which emulate reaction and diffusion process behavior

Data-driven Modeling: Purpose and Principle

[Krewer et al., J. Electrochem. Soc. 2018]



support vector machine (SVM), Gaussian process regression (GPR), least squares (LS), neural network (NN), genetic algorithm (GA), recursive least square (RLS), unscented/extended Kalman filter (KF/UKF/EKF), and singular value decomposition (SVD)

Principle

Correlate features with state of health/charge using trained black-box algorithms

Hybrid Modeling: Data-Driven and EC/Mechanistic Modeling

[Krewer et al., J. Electrochem. Soc. 2018]

Lumped First-principles Modeling

Equivalent Circuit (EC) Modeling

$$\dot{x} = f(x, I, p);$$

x – states of battery model
x_{OCV} – Open circuit voltage (one of states in x)
I – Current
p – EC parameters, e.g., { Internal resistance; Polarization resistance and Capacitance; Diffusion resistance and Capacitance }

+

Data-driven Modeling

OCV-SOC Modeling

e.g., Lookup table
Analytical expression:
$x_{OCV} = g(SOC)$

EC parameter – SOH Modeling

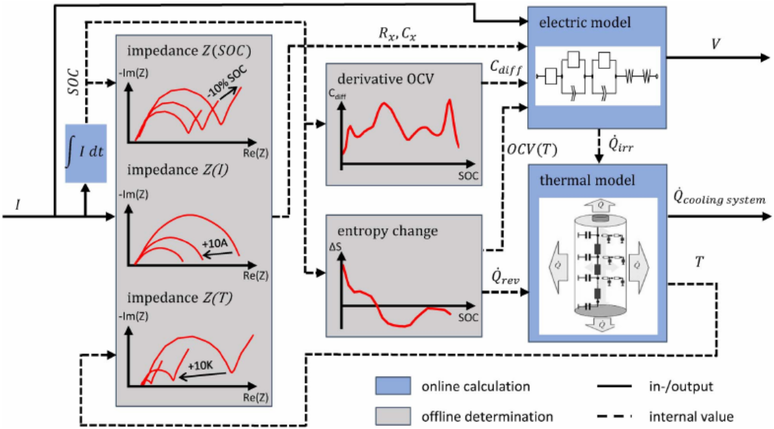
e.g., Analytical expression:
$C_{diff} = h(SOH, T)$, C_{diff} – diffusion capacitance
$R_{int} = l(SOH, T)$, R_{int} – internal resistance
T – temperature

Hybrid Modeling

Hybrid modeling as promising way to include physical effects and rapid estimation with limited data

Hybrid Model for Performance Estimation

[Krewer et al., J. Electrochem. Soc. 2018]



Combination of EC, mechanistic model with data correlation allows rapid estimation for better operation.

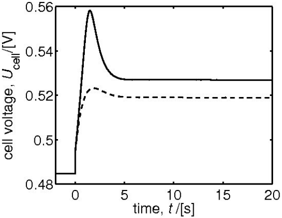
Content

- Challenging Li-Ion Battery
- Mechanistic Modeling
- Equivalent Circuit, Data Driven and Hybrid Modeling
- **Advanced Dynamic Analysis using Nonlinearities**

Why Nonlinear Methods?

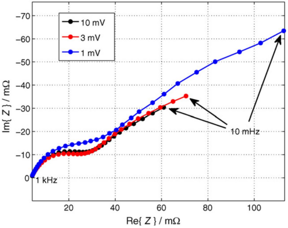
- EIS is a linear system analysis tool
- I.e. nonlinear systems deflected only so much that linear response obtained
- Advantage: Signal independent; extensive theory on linear systems analysis available
- Yet: loss of nonlinear information
- Dependence of I on E highly nonlinear (Butler-Volmer)
- Nonlinear system analysis as complementary method

- Nonlinear vs. linearised model: response of fuel cell voltage to current step



[Krewer]

- Experiment: EIS of Pb acid battery

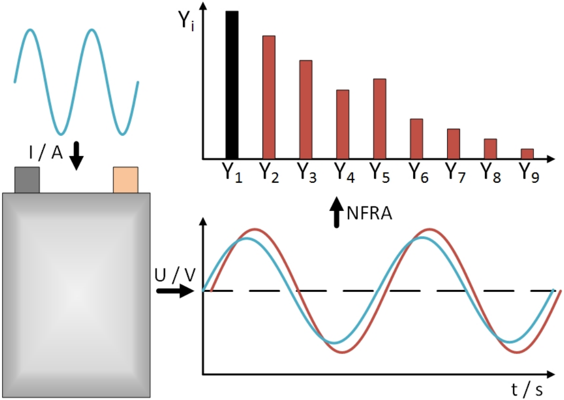


[Sauer]

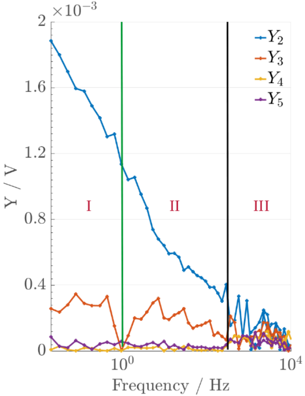
Nonlinear Frequency Response

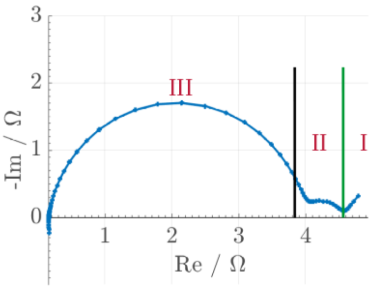
Nonlinear frequency response analysis (NFRA)

- analyses the higher harmonic responses (e.g. due to reactions)
- to a sinusoidal input signal of large amplitude
- Compare: Impedance analyses only linear part, i.e. less information



NFRA on Lithium-Ion-Batteries: NFRA vs. EIS





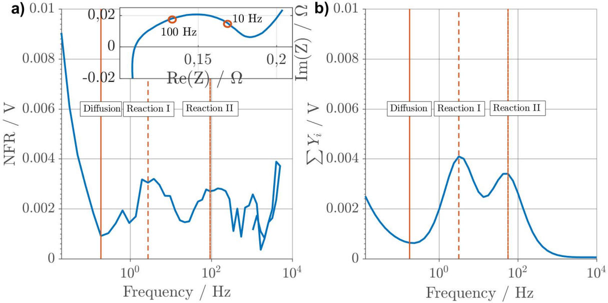
Range	Frequency	Typ. processes
I	0 to ∼ 1 Hz	Diffusion
II	1 to ∼ 300 Hz	Electrode Reactions
III	300 to ∼ 1 kHz	Transport in SEI

- Characteristic features of NFRA and EIS at same frequencies
- Area III may be correlated to the typically linear transport in SEI

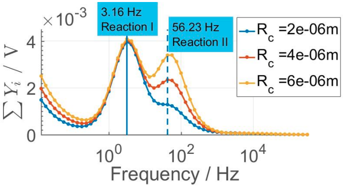
Understanding NFRA via Mechanistic Model

[Wolff, Harting, Krewer, El. Acta 18]

Exp. commercial 18650 cell vs. P2D model simulation (lit. parameters)



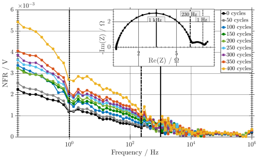
Impact of cathode particle radius



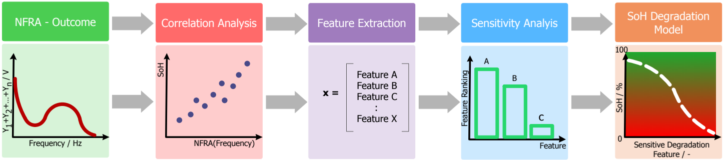
- Successful correlation of model to experiment for commercial cells
- Simulation aids in interpretation of NFR spectra

SOH Extraction via Support Vector Regression

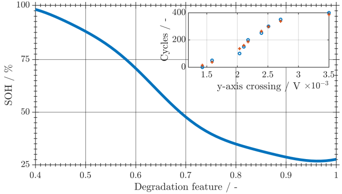
[Harting et al., Applied Sciences 18]



Data-based algorithms for estimating SOH



SOH Degradation Model

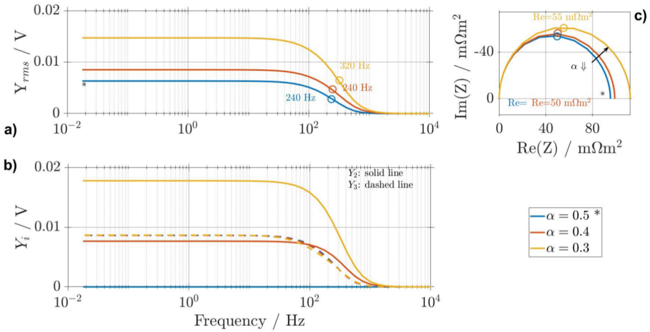


Successful validation of SOH extraction from NFR

Cell	Type	SoH_i	SoH_{SVM}	Accuracy / %
B	identical	28	29	3
C	identical	63	66	4
D	non-identical	100	96	4

Basic Butler-Volmer model for Electrochemical Reaction

[Wolff, Krewer, Europ. Phys. J. ST 2019]

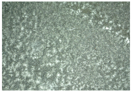


- Asymmetric electrochemical reactions ($\alpha \neq 0.5$) increase NFR and EIS
- Unique discrimination feature only in NFRA: Y_2 and Y_3 react differently to asymmetric processes

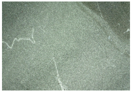
Detection of Safety-critical Li-Plating with NFRA

[Harting et al., El. Acta 2018]

- Cycling aging mechanism = f(T)
- Only low T caused Li plating (safety risk)

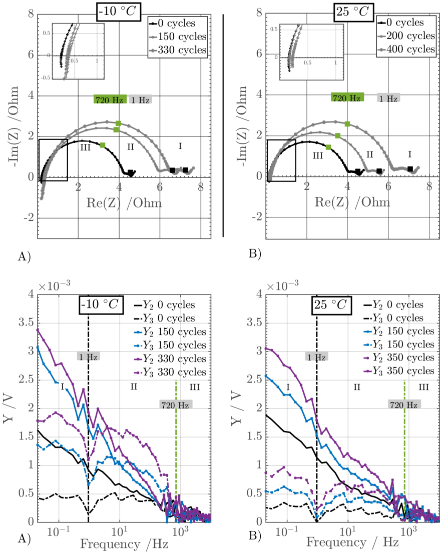


T: -10°C



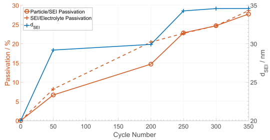
T: 25°C

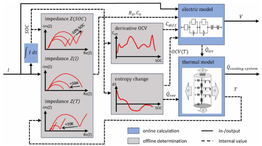
- NFRA shows unique feature for plating detection ($Y_2 > Y_3$)
- Plating changes asymmetry of reactions at anode

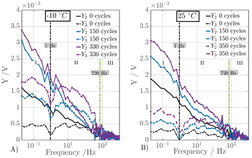


Dynamic Models for Li Ion Batteries

- Batteries operated at upper limit → Estimation of state of health/charge/safety essential
- Modeling essential for interpreting experiments, state estimation and safe operation
- Mechanistic, equivalent circuit and data-driven models usable
- Combination of modeling approaches especially practical.
- Non-linear frequency response analysis as new powerful analysis method







Institute of Energy and Process Systems Engineering

Max Planck: ‘Insight must precede application”

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EINE EINRICHTUNG DES NFF

pvz Zentrum für Pharmaverfahrenstechnik

IMPRS Magdeburg
International Max Planck Research School for Analysis, Design, and Optimization in Chemical and Biochemical Process Engineering

InES

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- and thanks you for your attention!