Commercial Sodium-Ion Cells
Characterization & Modeling

SIMBA Final event

07.06.2024

Gereon Stahl, Moritz Schütte, Hendrik Laufen, Dirk Uwe Sauer

Center for Ageing, Reliability and Lifetime Prediction of Electrochemical and Power Electronic Systems (CARL)

CARL Center for Ageing, Reliability and Lifetime Prediction of Electrochemical and Power Electronic Systems

RWTH AACHEN UNIVERSITY

Center for Ageing, Reliability and Lifetime Prediction for Electrochemical and Electronics systems – Supporting battery applications and battery production

- State government and Federal government invest about 110 Million Euros for building this center in Aachen
- 5000 m^2 of net area for laboratories and offices

- Interdisciplinary team from chemistry, physics, mathematics, material science, electrical and mechanical engineering

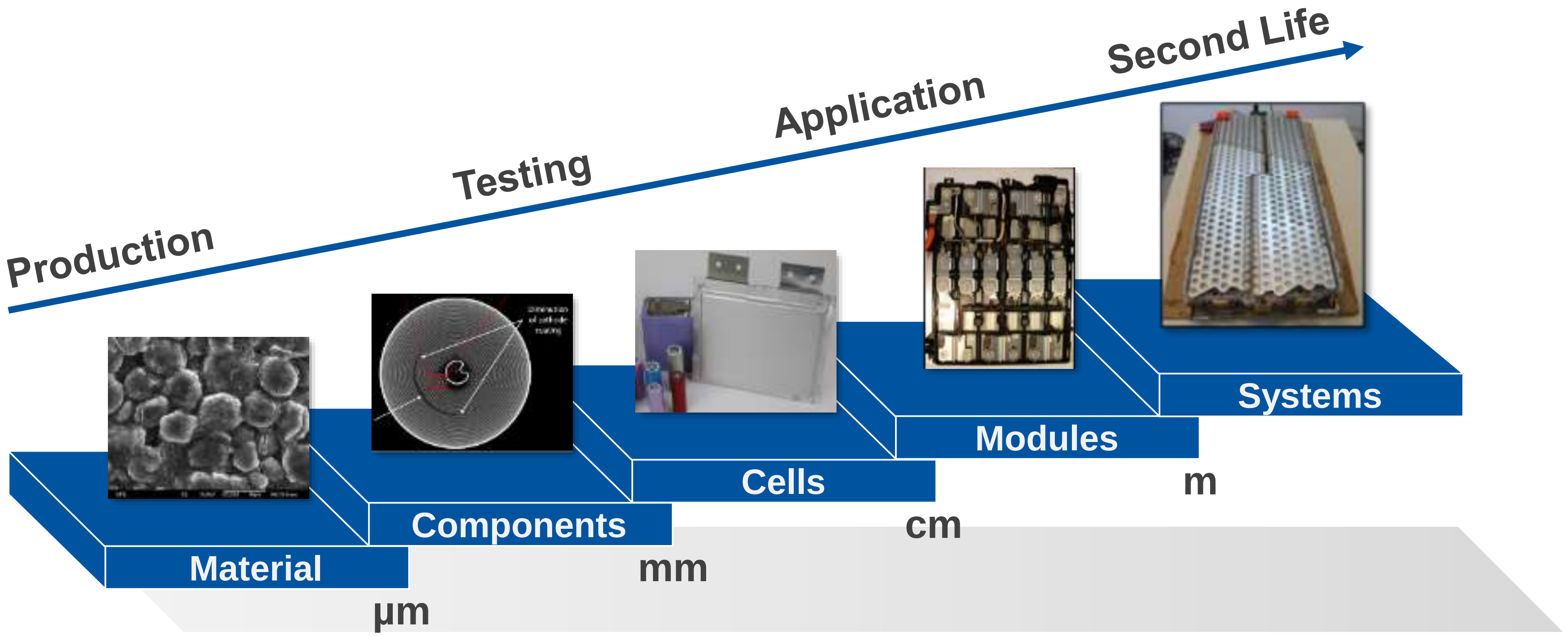
Institute for Power Electronics and Electrical Drives

- Univ.-Prof. Dr. ir. Dr. h. c. Rik De Doncker
  - Chair for Power Electronics and Electrical Drives

- Univ.-Prof. Dr. rer. nat. Dirk Uwe Sauer
  - Chair for Electrochemical Energy Conversion and Storage Systems

- Univ.-Prof. Dr. rer. nat. Egbert Figgemeier
  - Chair for Ageing and Lifetime Prediction of Batteries

Our Vision at CARL



Enabling improvements at every scale for different industries

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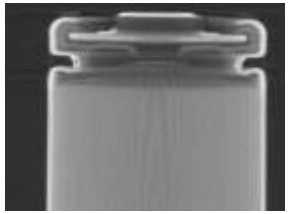
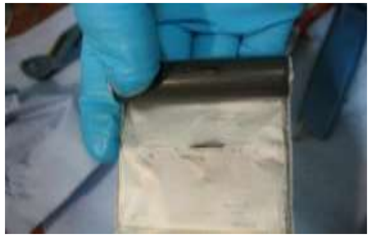
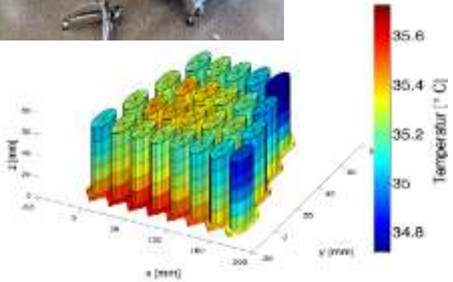
From Cell to System
Overview of the Storage Competences of ESS

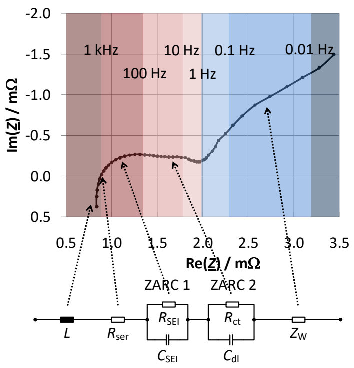




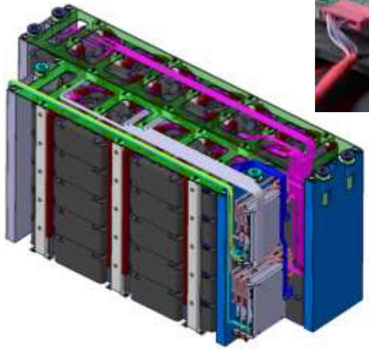


Battery-Testing → Analysis-laboratory → Modelling & Prediction of Aging → System-integration → Monitoring & Management







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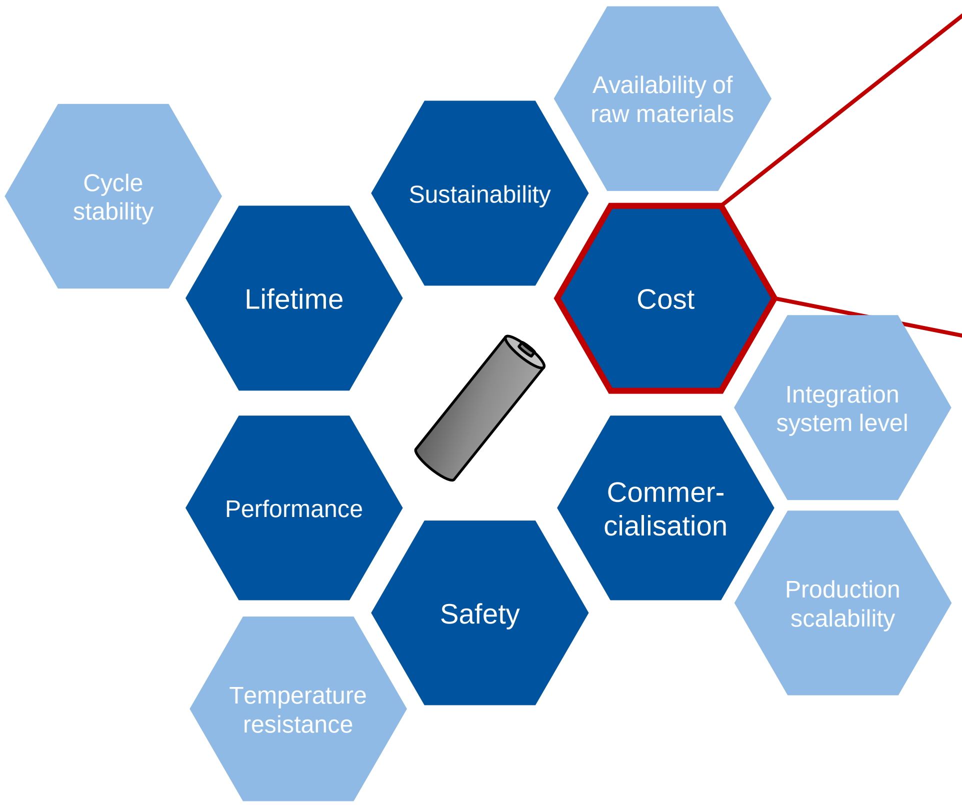
Agenda

Sodium-Ion cell	• Overview of commercial cells
Electrochemical characterization	• Cell specification • Material analysis
Performance tests	• Electrochemical impedance spectroscopy • Cycling test & fast charging • Self discharge & calendaric tests
Physio-chemical modeling	• Parametrization • Modeling • Validation

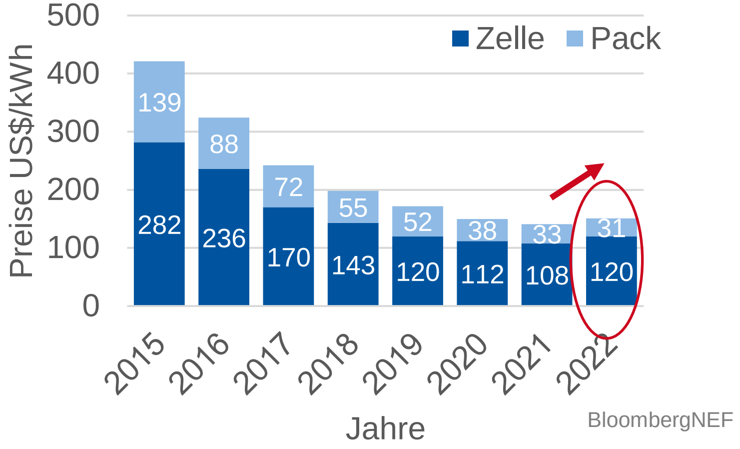
Motivation
Sodium-ion cells as an alternative battery technology

Requirements for modern battery systems



Can sodium-ion cells potentially fulfil these requirements better than lithium-ion cells?

Prices per kWh for lithium-ion batteries rose for the first time in 2022, due in particular to the increase in raw material prices.



Growing interest from research and industry in sodium-ion battery systems

https://batteriesnews.com/byd-plans-mass-produce-sodium-ion-batteries-q2-2023-report-says/

Materials for Sodium-Ion cells

Anode

- Hard carbon
- Prussian blue analogues
- Alloys as next-gen
  - Silicon
  - Zinn

Cathode

- Polyanionic materials (z.B. NVPF)
- Prussian blue analogues
- Layered oxides

Electrolyte

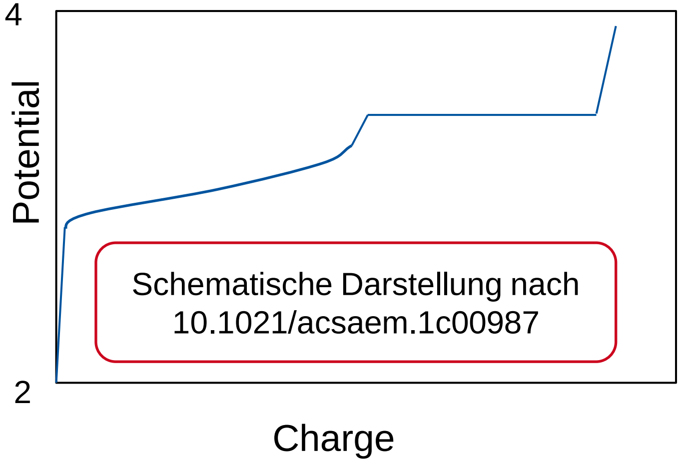
- linear + cyclic carbonates with $NaPF_6$
  - Lower solvation energy and utilisation of propylene carbonate improves low-temperature performance
- Utilisation of aqueous electrolyte solutions in theory possible

Current collector

- Aluminium or copper for anodes
  ➔ Aluminium = reduced costs, copper = reduced impedance, high energy density
- Aluminium for cathodes

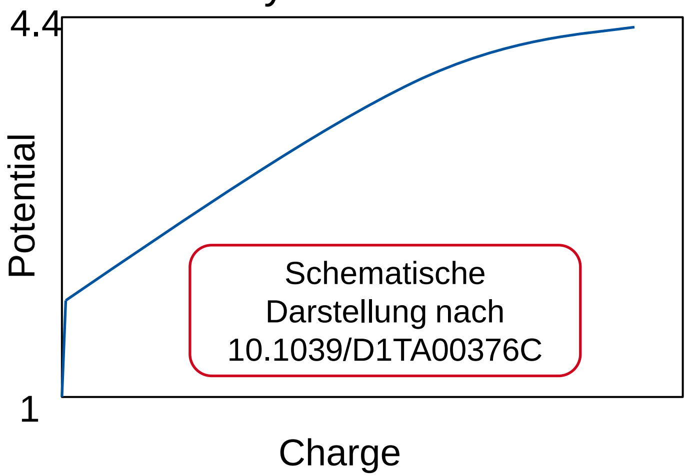
Cathode materials for different properties

Prussian blue analogues



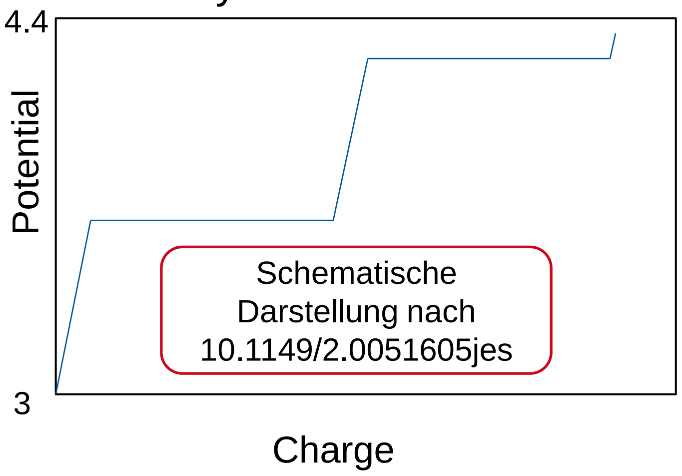
- Aqueous electrolyte possible
- Low energy density
- Commercialisation through Natron Energy
- Elements influence voltage
  - Fe, Mn, …

Layered oxides



- Similar to NMC
- Comparatively high energy density
- Commercialised by Faradion & HiNa
- Materials:
  - Cu, Fe, Mn, Ni, Ti, …

Polyanionic materials



- High performance
- Short lifetime
- NVPF in commercialisation by Tiamat (10.1016/j.jpowsour.2023.233741)

Safety

	Flammability	Temperature resistance	Risk of overcharging

Sodium-Ion

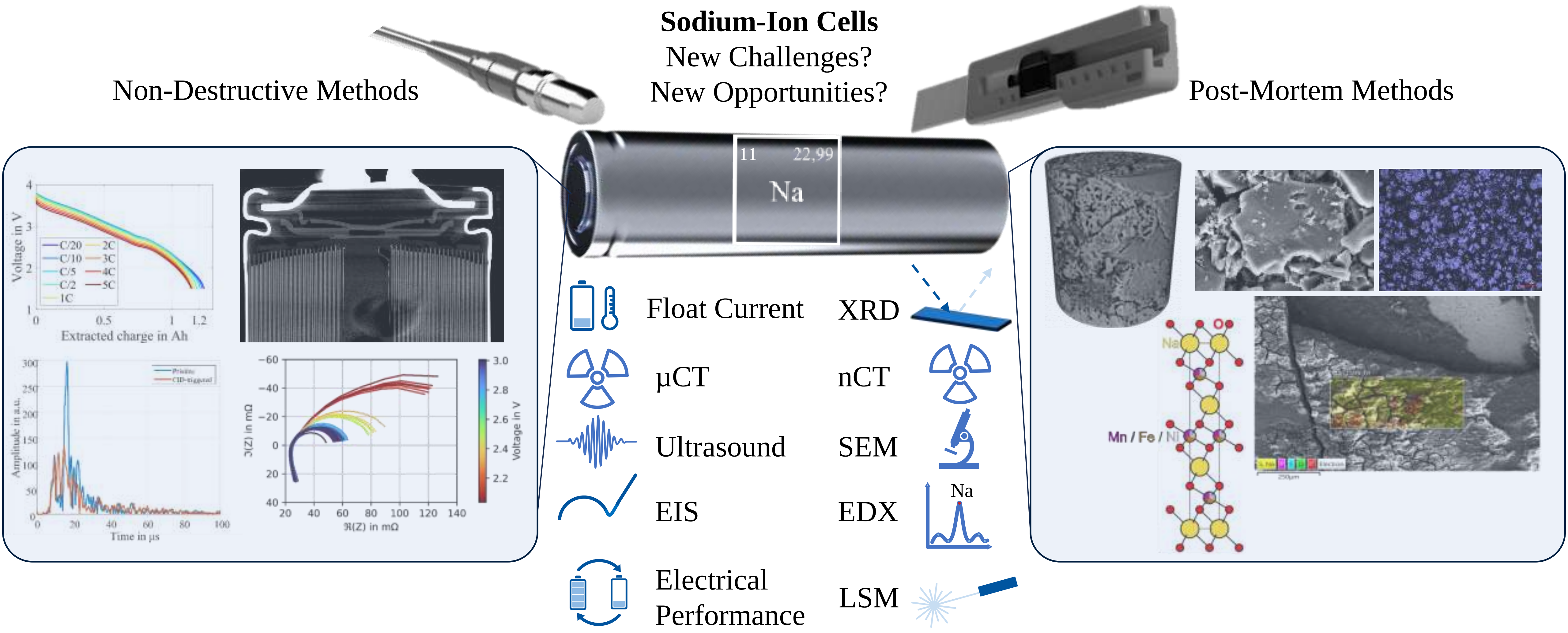
Organic electrolyte

Aqueous electrolyte — **Low energy density**

Lithium-Ion

Method overview

1.2 Ah 18650 cell made by Shenzhen Mushang Electronics



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Cell specification
1.2 Ah 18650 cell made by Shenzhen Mushang Electronics

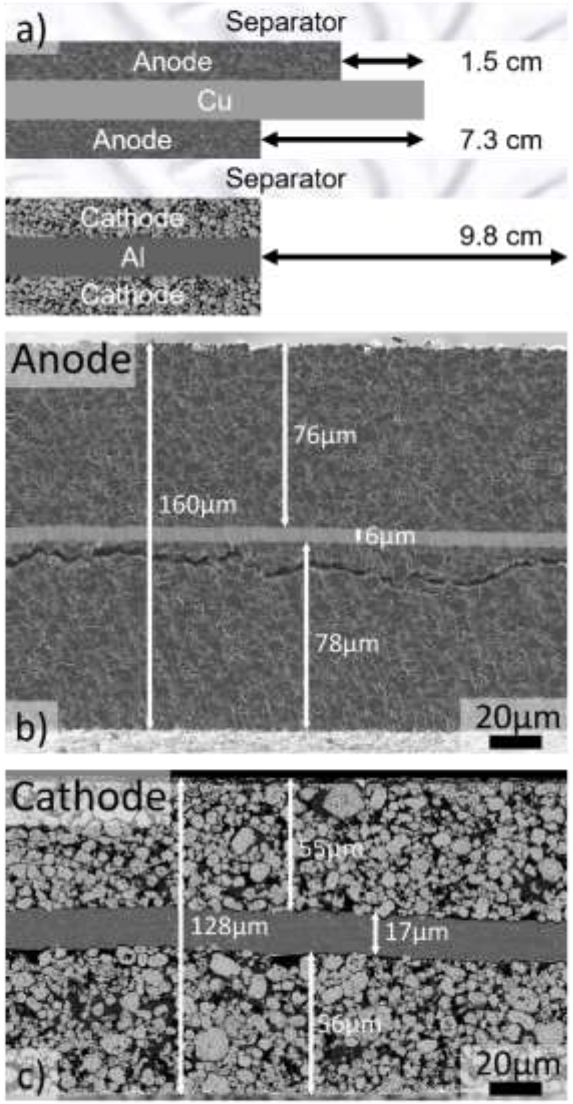
Cell specification	
Nominal capacity	1.2 Ah
Nominal voltage	3.0 V
Voltage limits	1.5–3.8 V
Continuous current limits	charge 0.6 A (0.5C) at 0°C–10°C charge 1.2 A (1C) at 10°C–20°C charge 3.6 A (3C) at 15°C–25°C charge 6.0 A (5C) at 20°C–45°C discharge 9.6 A (8C) at 10°C–50°C
Weight	37 g ≅ 97.30 Wh/kg
Internal resistance	≤ 25 mΩ (1 kHz at 50% SoC)
Power density	810 W/kg

Active material

1.2 Ah 18650 cell made by Shenzhen Mushang Electronics

Postive electrode	
Layered oxide	$Na_{0.96}Ca_{0.02}[Mn_{1/3}Fe_{1/3}Ni_{1/3}]O_2$
Thickness	55 - 56 µm
Porosity	29.9%
Current collector	17 µm aluminum

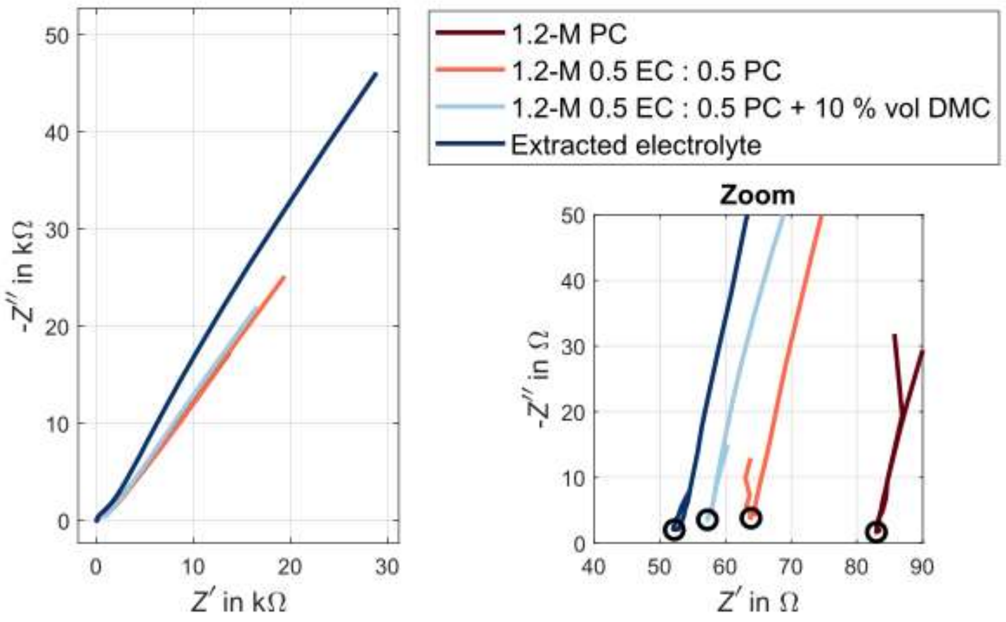
Negative electrode	
Hard carbon	
Thickness	76 µm
Porosity	31.4%
Current collector	6 µm copper



Electrolyte
Parameterization

- Centrifuge extraction of electrolyte
- ICP-OES: average measured concentration
  - Sodium: 1.42 mol/l
  - Phosphorus: 1.83 mol/l
  - $NaPF_6$ as conducting salt
- Ionic conductivity
  - 9.8 mS/cm

- GC-MS:
  - Dimethyl carbonate (DMC)
  - Ethyl-methyl carbonate (EMC)
  - Ethyl propionate (EP)
  - Ethylene carbonate (EC)
  - Propylene carbonate (PC)



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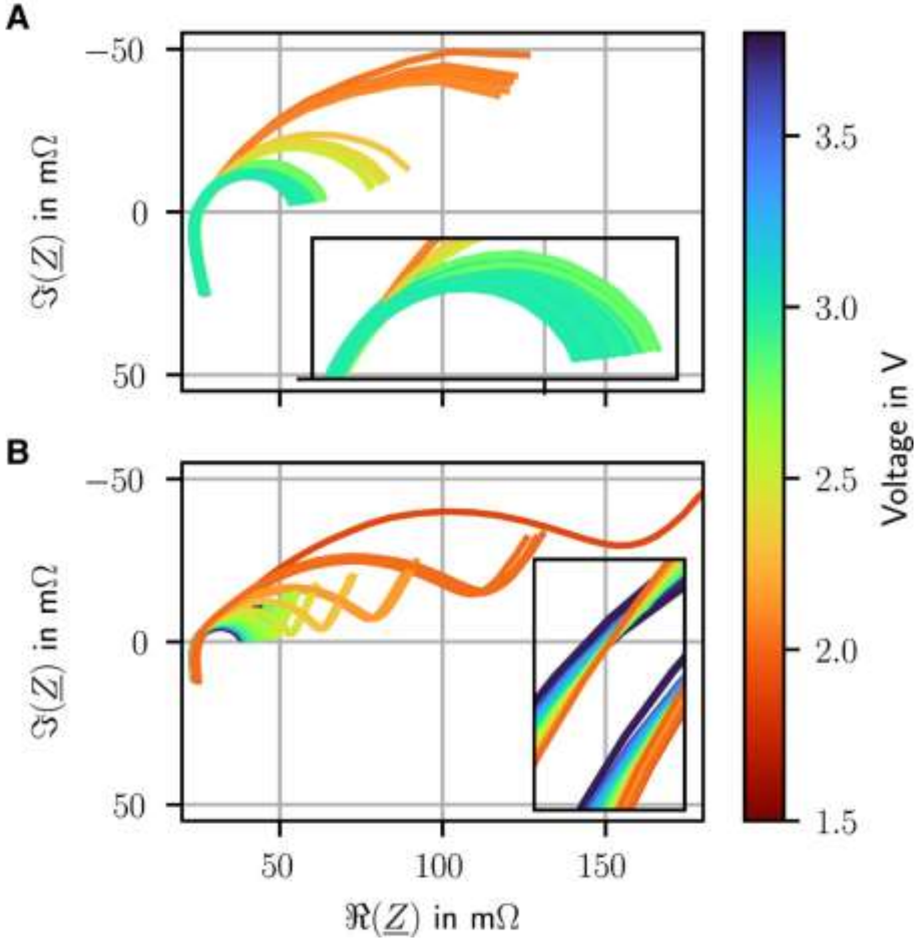
Cell performance - Electrochemical impedance spectroscopy

- Cell quality inhomogeneous
  1. Voltage at 3.0 V at delivery
  2. Self discharge: < 2.5 V
  3. Strong self discharge: < 2.0 V

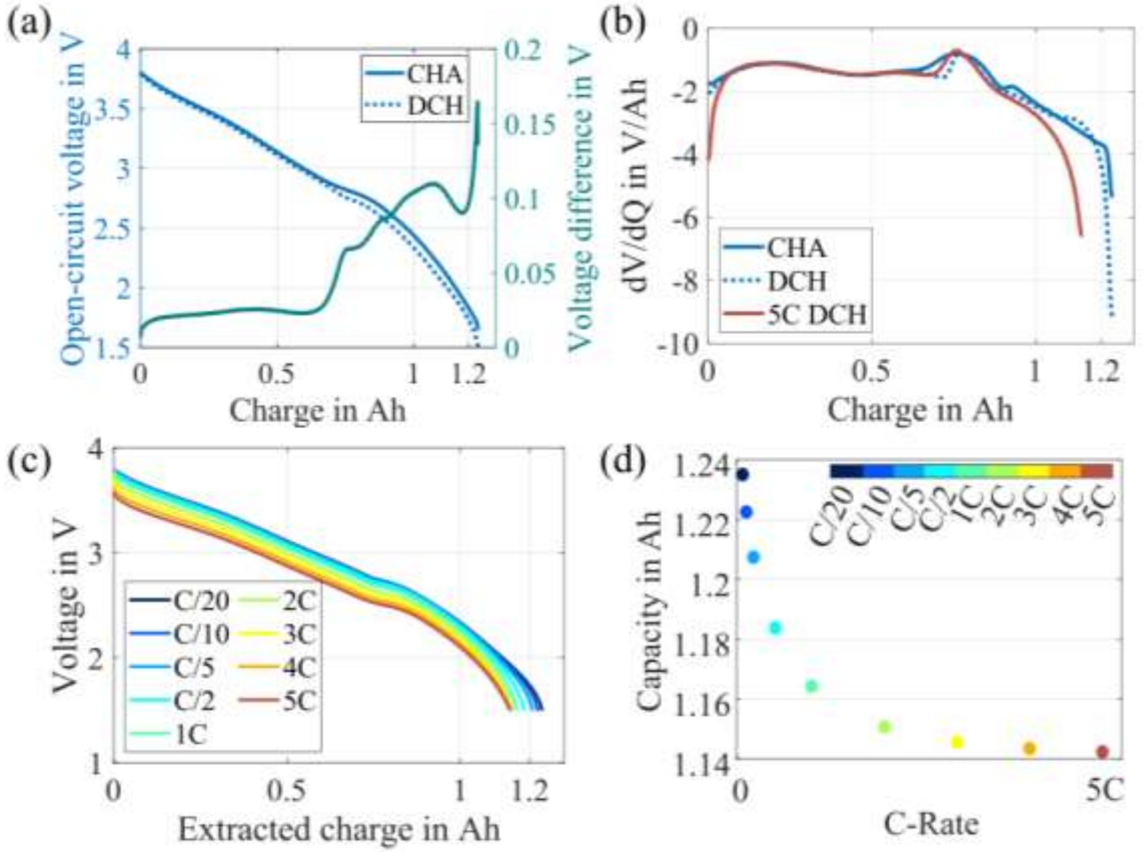
- Strong SOC-dependency on impedance
  - High impedance at low SOC

- Similar to all layered oxide cells
  - Topband, HiNA, Hakadi



Cell performance

- High hysterises in low voltage range
  - Hard carbon anode
- High capacity at high current rates
  - 98.12% at 5C compared to 1C
- Differential voltage analysis at 5C possible
- High power cell



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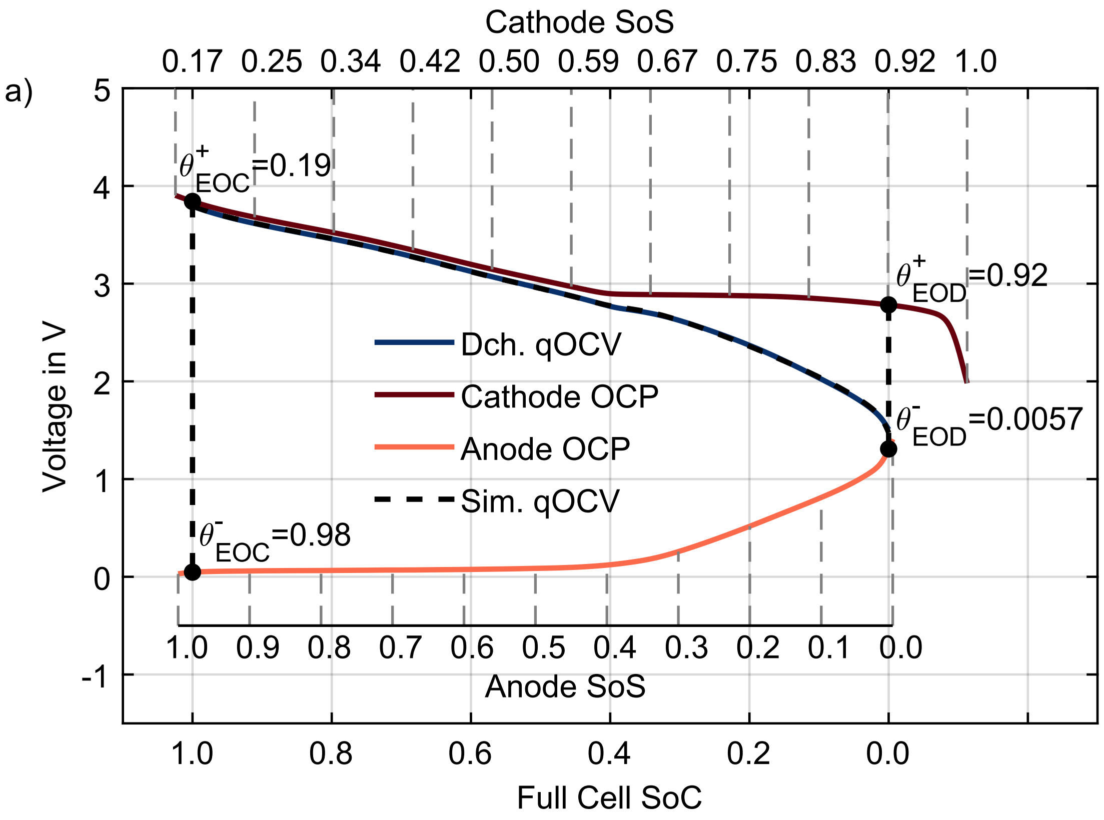
Cell performance - Balancing

- Anode and cathode half cells
  - Both materials show only one significant voltage change
  - Fitting strongly influenced by overvoltage due to sodium metal

- Initial capacity loss of cathode

- Anode determines the lower voltage



RMSE → 5.4 mV

Ageing tests

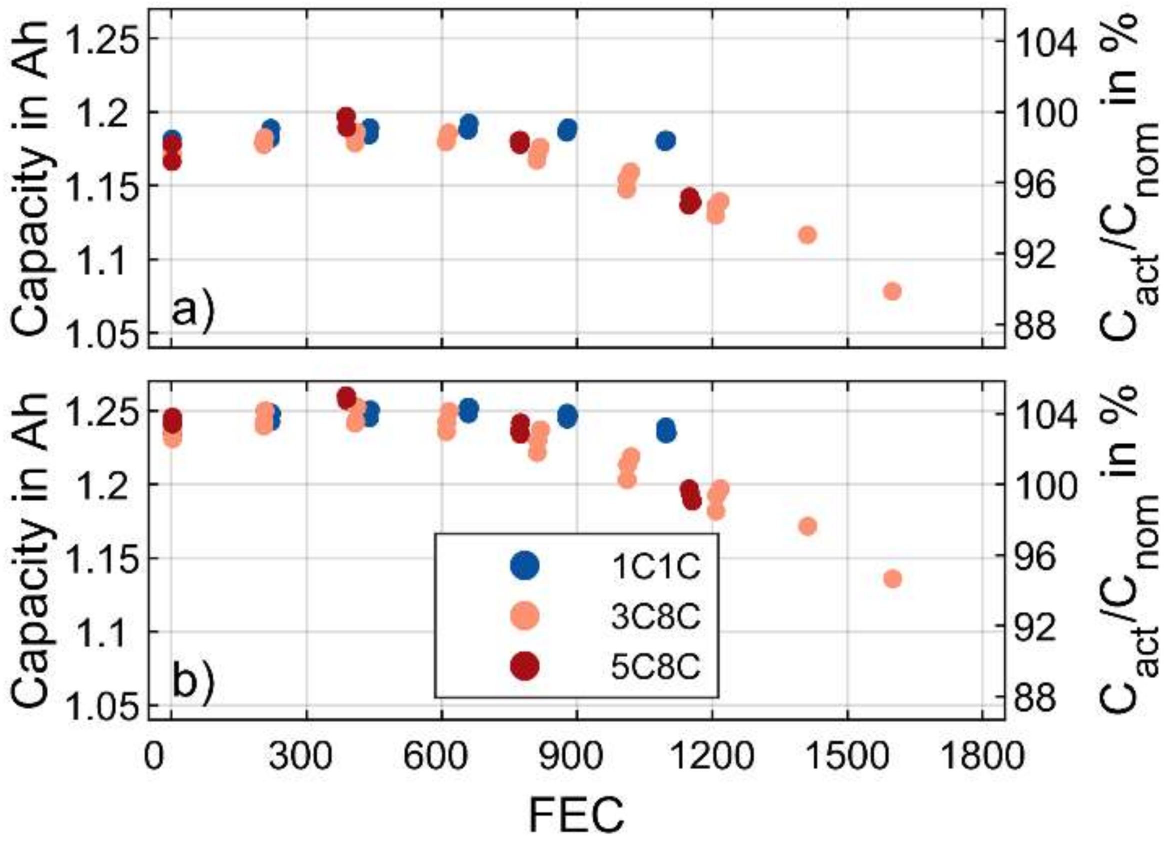
Influence of fast charging on lifetime

Limited fast-charging capability of Lithium-Ion cells

High-performance Li-ion cells expensive

Cell aging – Cell cycling

- Testprotocolls
  - 3C8C:
    - Charging: 3C
    - Discharging: 8C
- High capacity rentention
  - a) C/2 discharge capacity
  - b) C/20 discharge capacity
- Still 100% capacity compared to nominal capacity for C20
- Cell temperature
  - 47°C – 52°C (3C8C)
  - 55°C – 60°C (5C8C) → all cells failed



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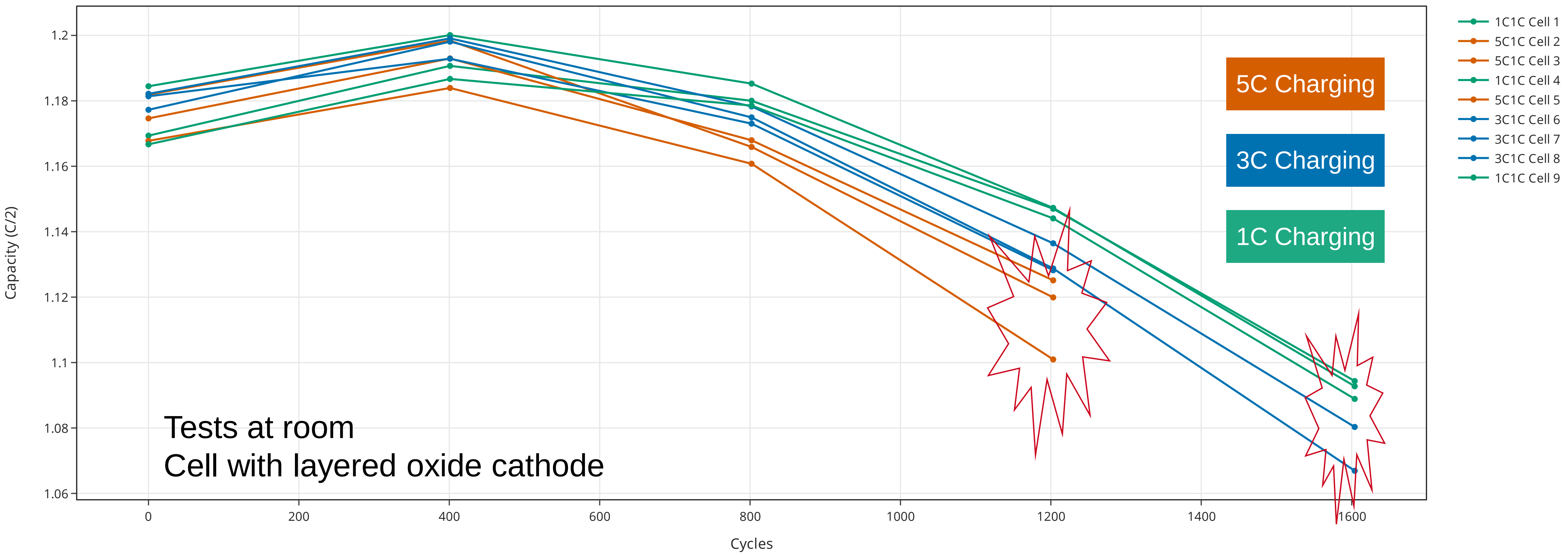
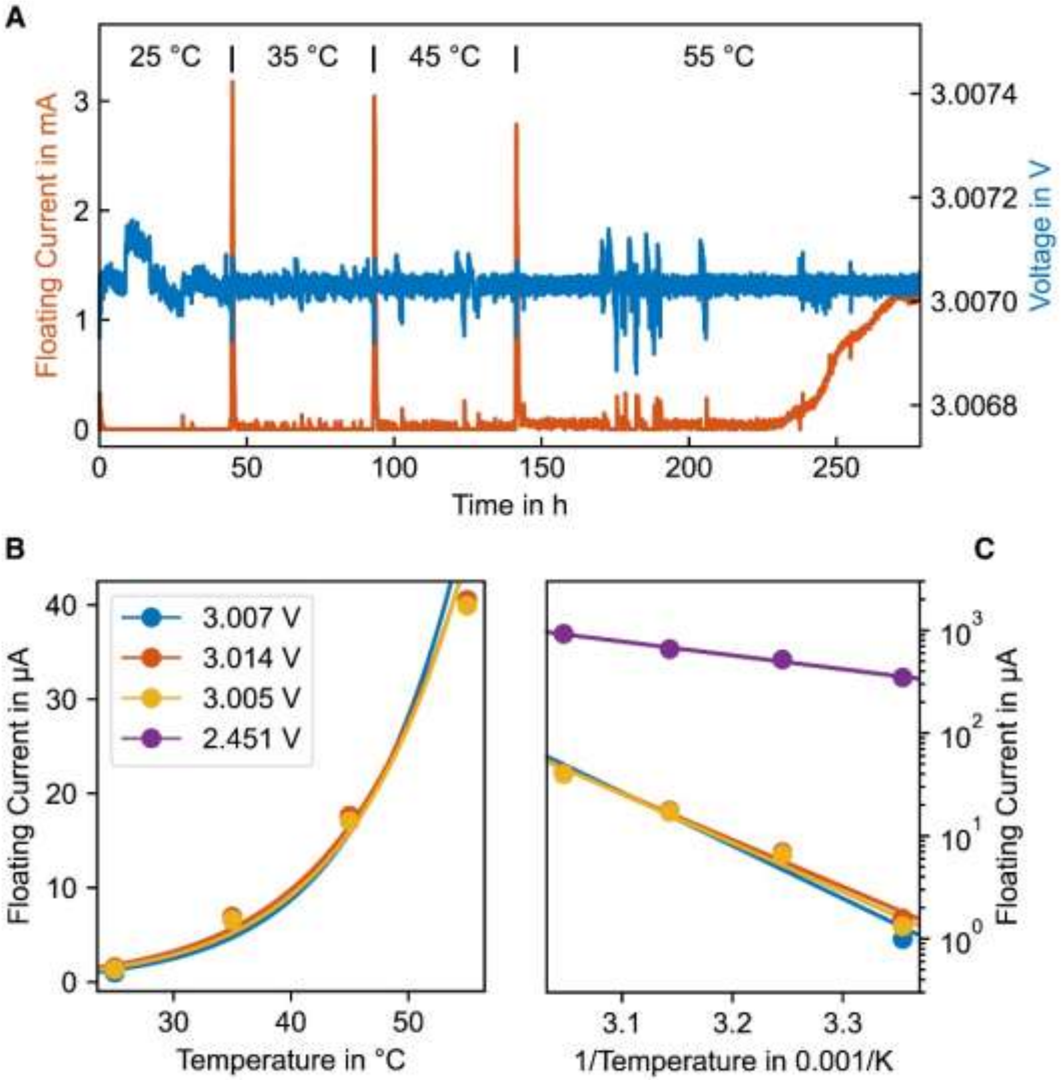
Cell aging - Fast charging



No strong influence of charge rate on capacity loss

Cell aging - Self discharge

- Voltage hold at cell voltage
  - Self discharge
- Activation energy:
  - 92 ± 5 kJ/mol
- Strong increase at 55 °C
  - → Instability



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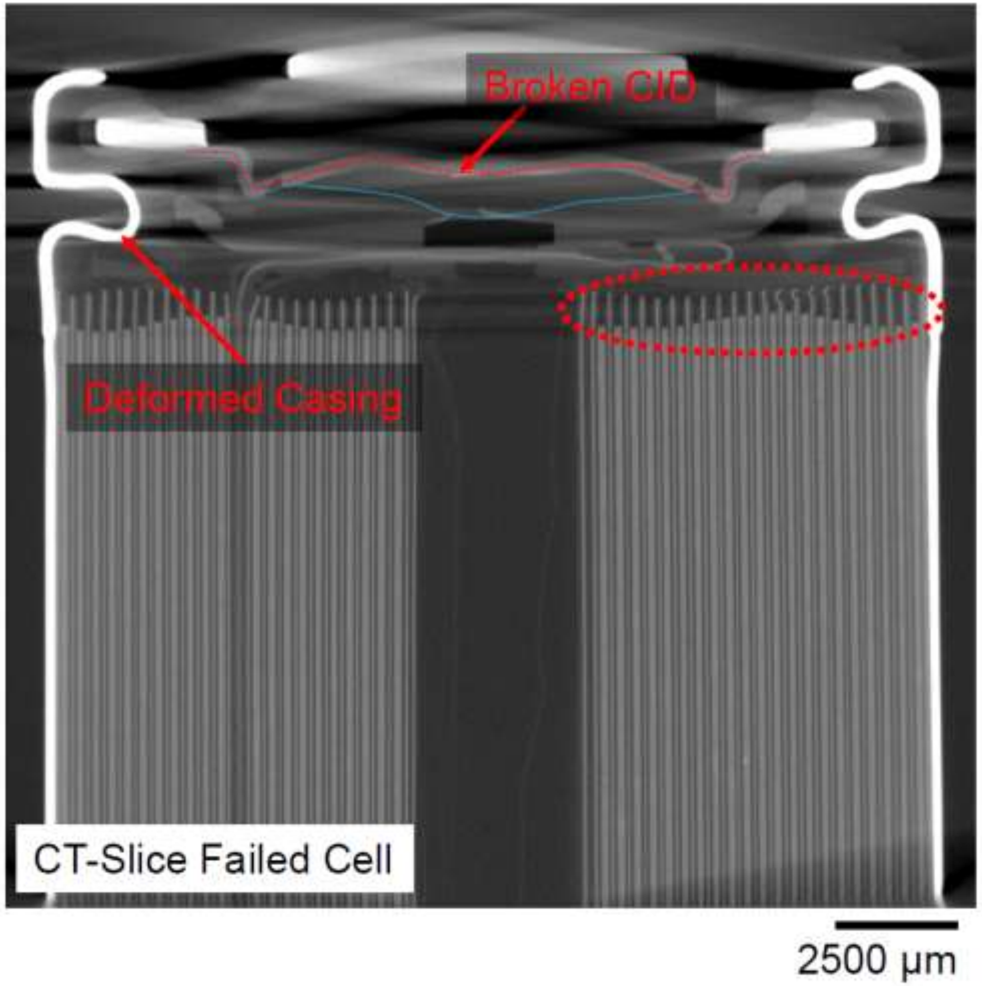
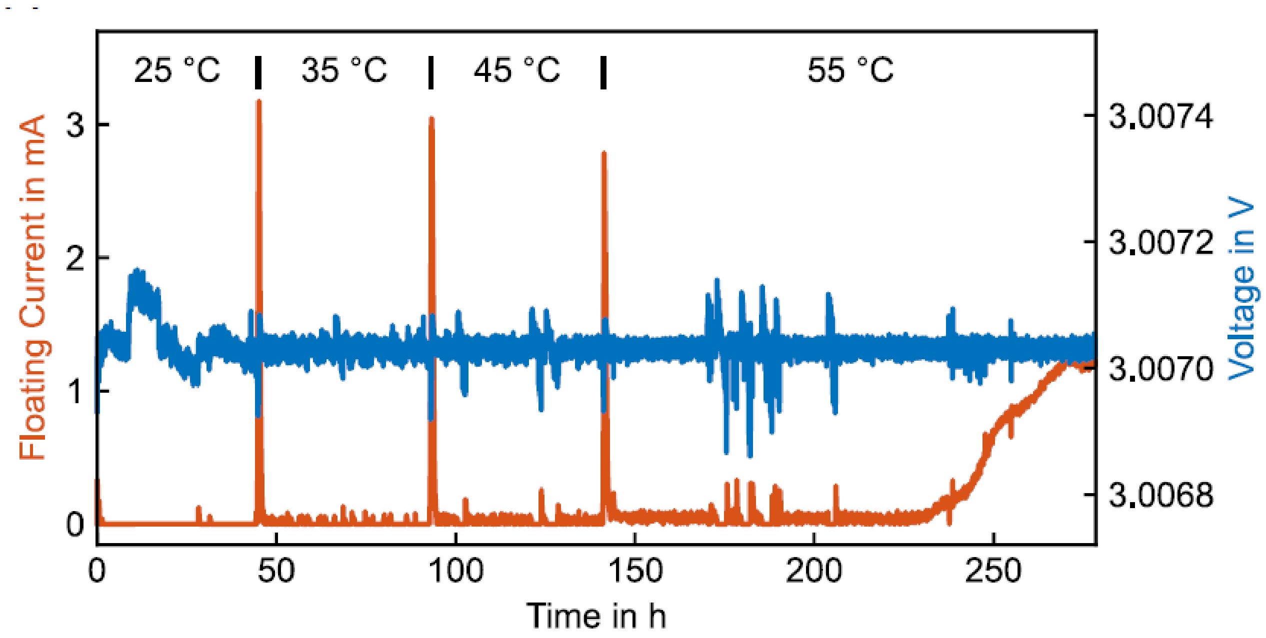
Self discharge - high temperatures



- Increased temperature accelerates side reactions
  - Gas formation leads to increasing pressure
  - CID triggering leads to cell failure



From Laufen et al. *Multi-method Characterization of a Commercial 1.2 Ah Sodium-Ion Battery Cell Indicates Drop-in Potential.* Accepted Paper. Cell Reports Physical Science 2024.

Conclusion
1.2 Ah 18650 cell made by Shenzhen Mushang Electronics

- High power cell
  - Stable capacity retention

- Instability at high temperature
  - Na-Plating
  - Cathode instability
  - Gassing → cell failure
  - Temperature sensitive cell

- How can we better understand the battery behaviour?
  - Physio-chemical modeling

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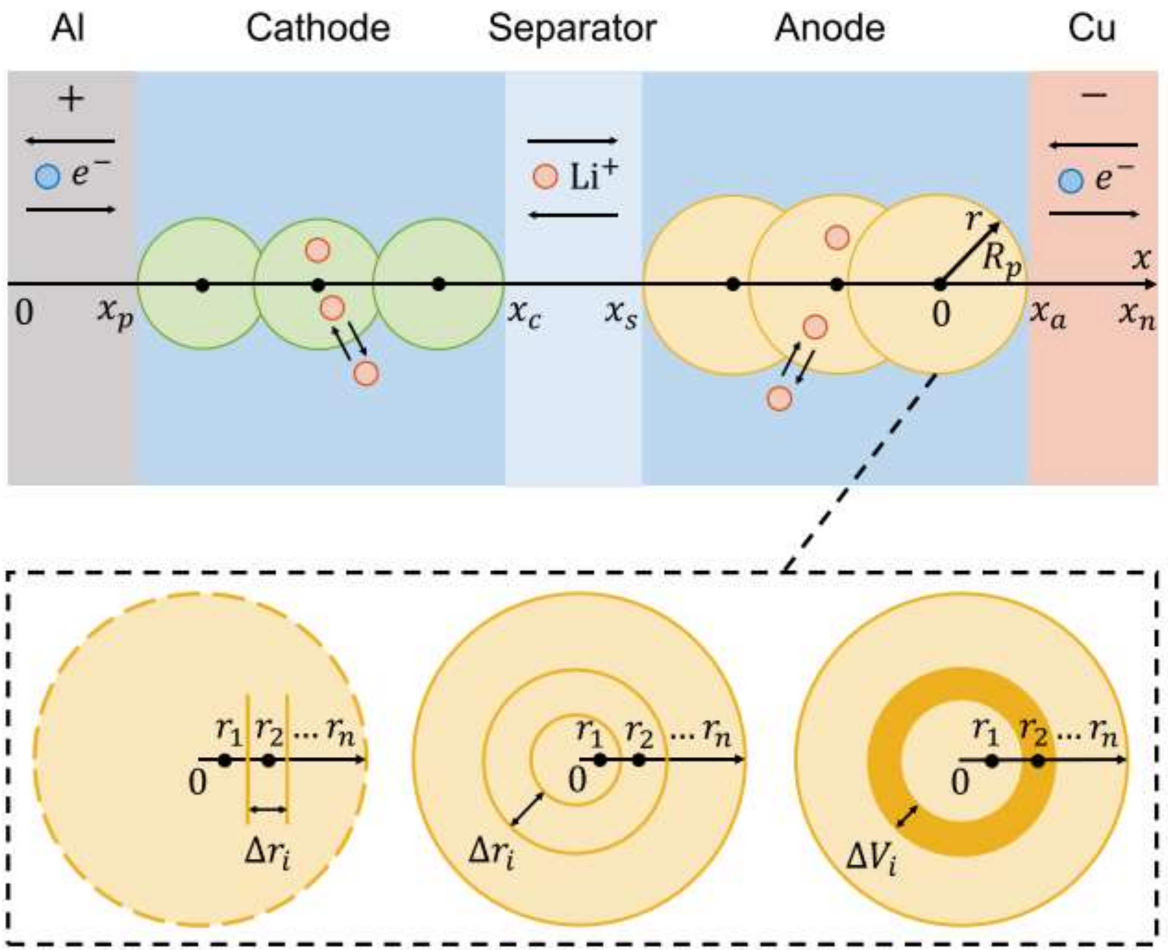
Physio-chemical model

Features of the PCM

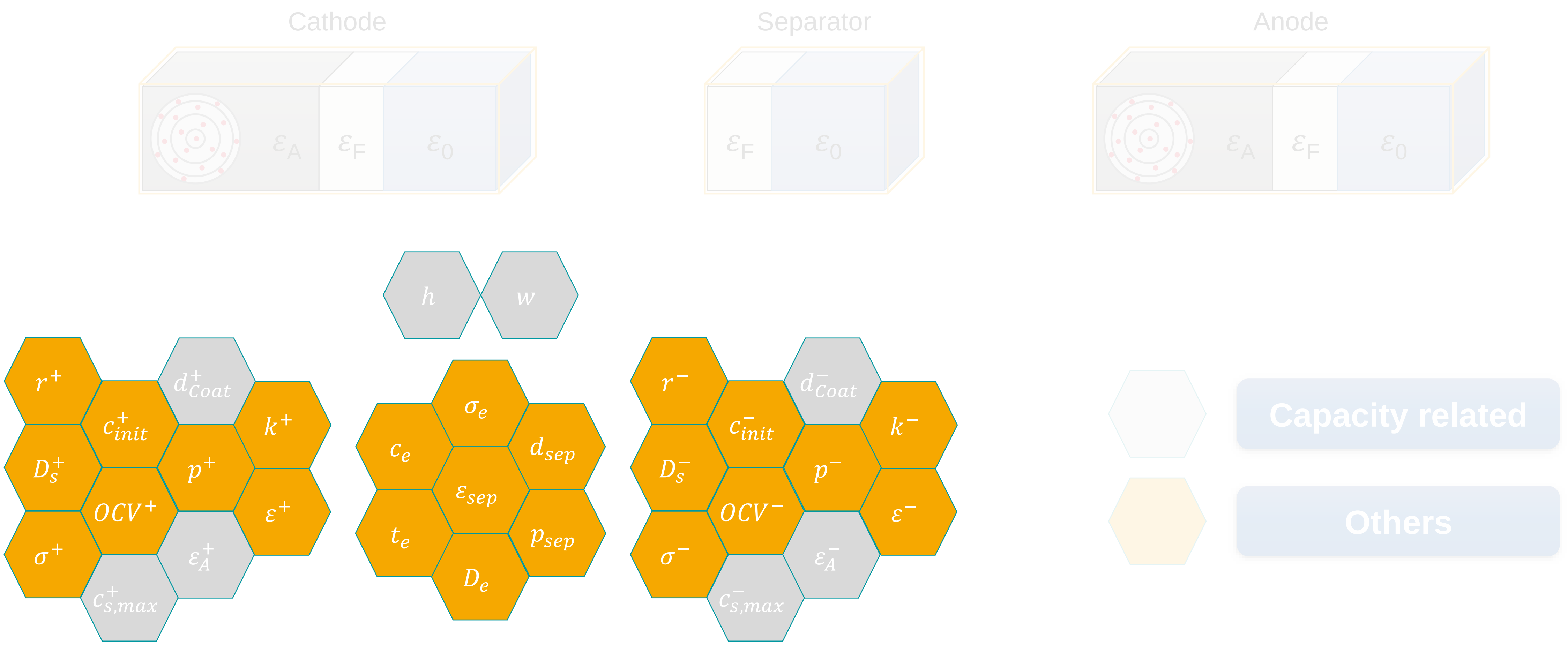
- **3D-capable DFN P2D type physico-chemical battery model (PCM)**
- **Coded in C++, realtime-capable and can be built to .exe for deployment**
- **All inputs presented in .yml files or via CLI, outputs generated for Matlab and as .csv**
- **Covers double-layer effects and capable of EIS simulation with internal profiles**



Required parameters
Physical-chemical model

Doyle-Fuller-Newman Model

$\varepsilon_A + \varepsilon_F = \varepsilon_S$



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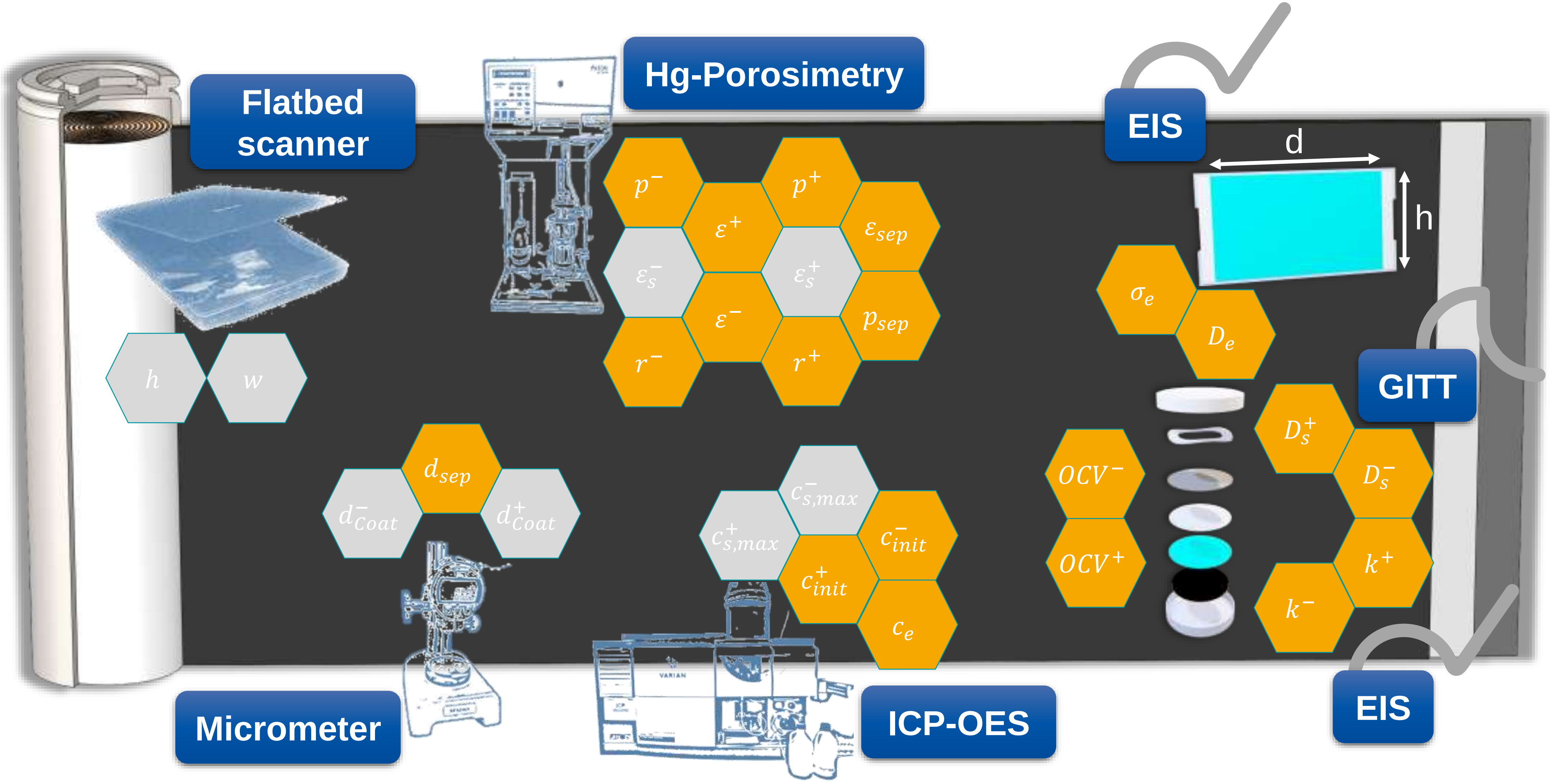


Flatbed scanner
h
w
Hg-Porosimetry
p^-
p^+
ε^+
ε_{sep}
ε_s^-
ε_s^+
ε^-
p_{sep}
r^-
r^+
EIS
d
h
σ_e
D_e
GITT
D_s^+
D_s^-
OCV^-
OCV^+
k^+
k^-
EIS
d_{sep}
d_{Coat}^-
d_{Coat}^+
Micrometer
$c_{s,max}^-$
$c_{s,max}^+$
c_{init}^-
c_{init}^+
c_e
ICP-OES

Cell and Geometry
Parameterization

Cell Specs	
Capacity	1.2 Ah @0.5C & 25 °C
Voltage limits	1.5 V to 3.8 V
Nominal voltage	3.0 V
Grav. Energy density	97 Wh/kg
Max. charge current	6 A (5C) @20 – 45 °C
Max. discharge current	9.6 A (8C) @10 – 50 °C

Flatbed scanner

h | h^+ | **57.5 mm**

h^- | **59 mm**

w | w^+ | **1.388 m**

w^- | **1.454 m**

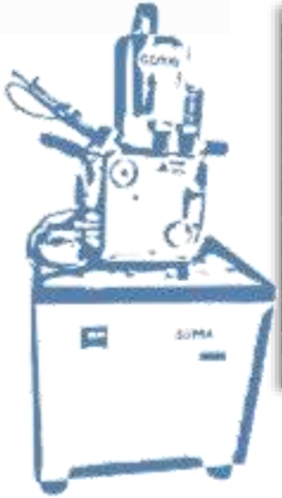
Micrometer

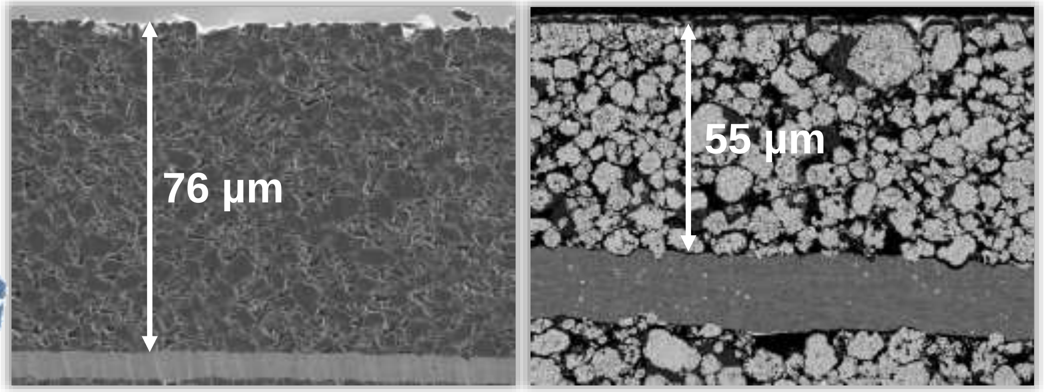
d_{Coat}^- | **76 – 78 µm**

d_{Coat}^+ | **55 – 56 µm**

d_{sep} | **15 µm**

SEM





Laufen et al. https://dx.doi.org/10.2139/ssrn.4542213
Poster P2-074 Schütte et al.

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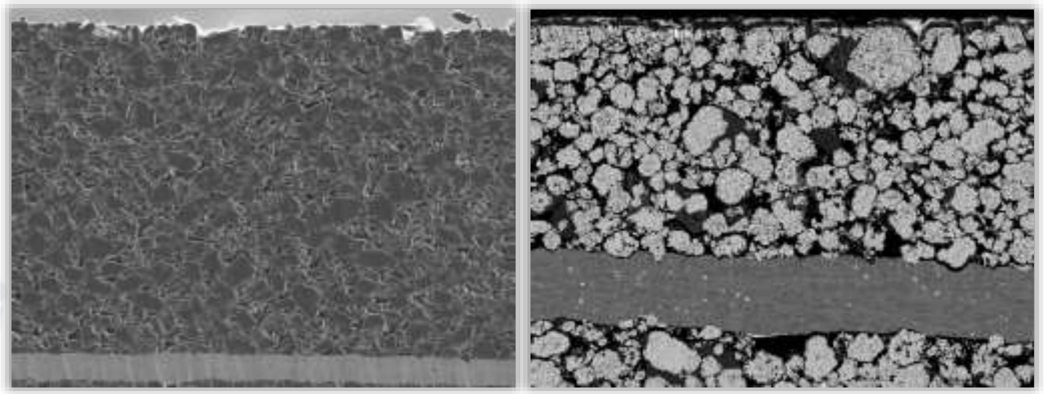

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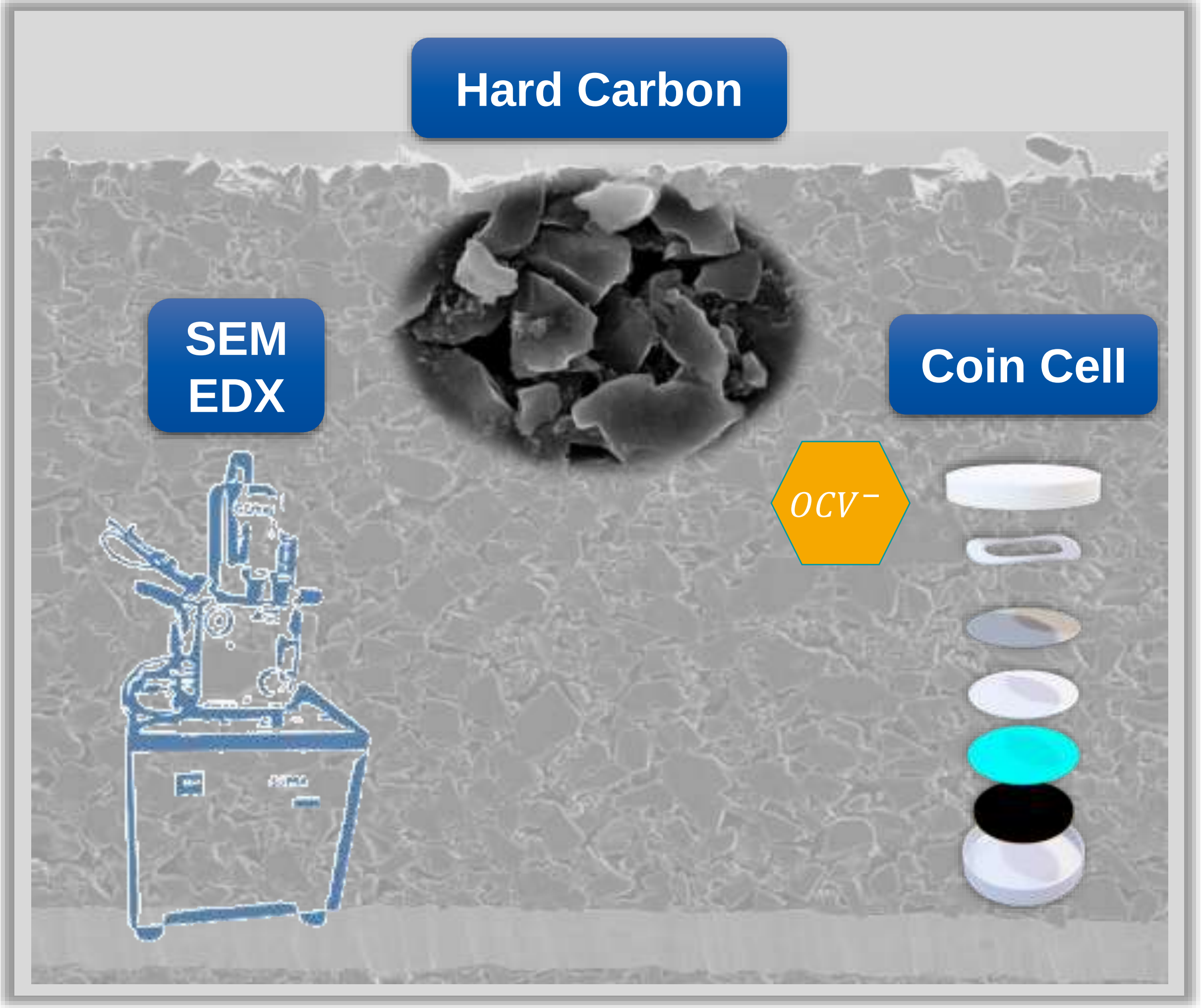
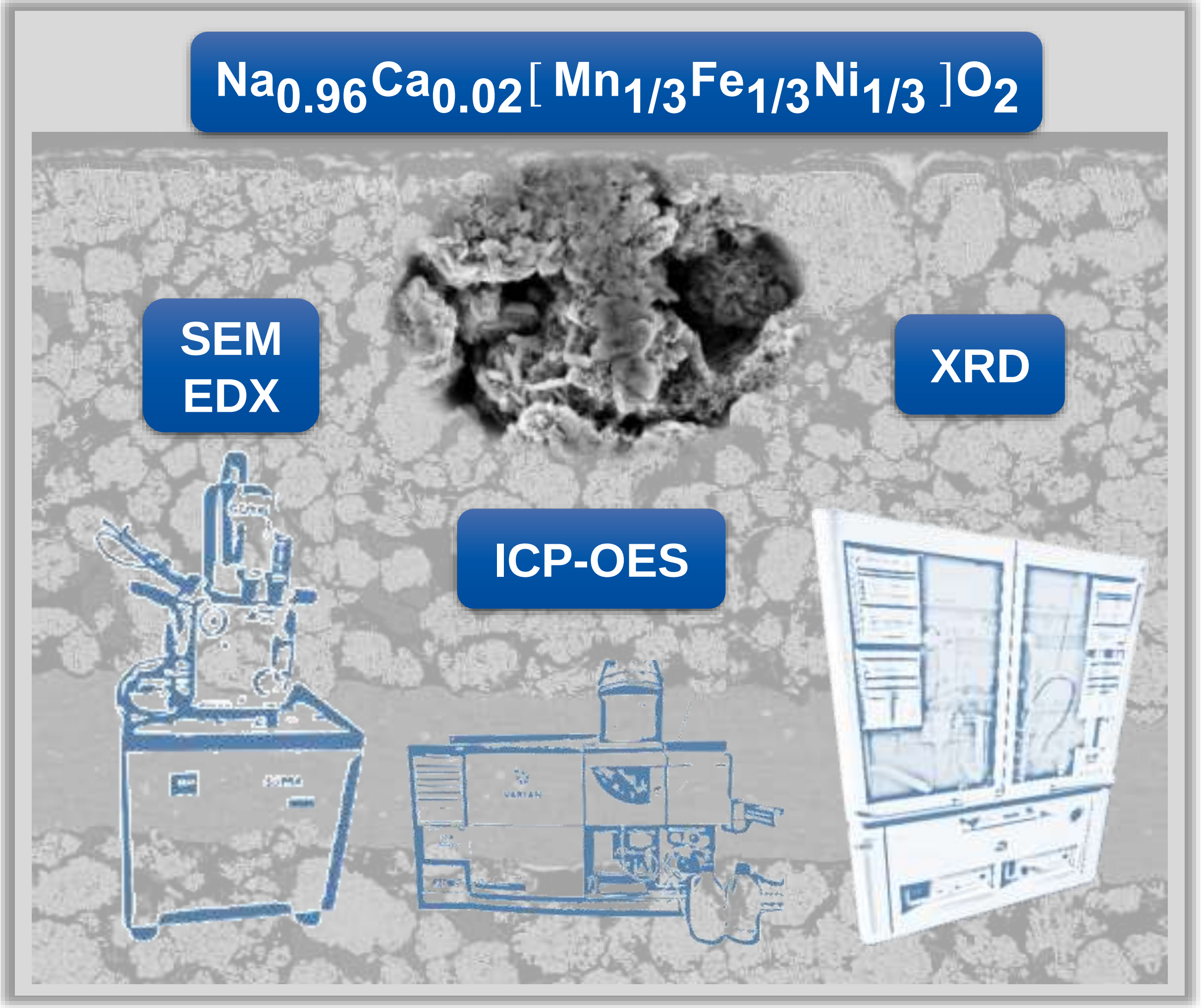
Poster P2-074 Schütte et al.

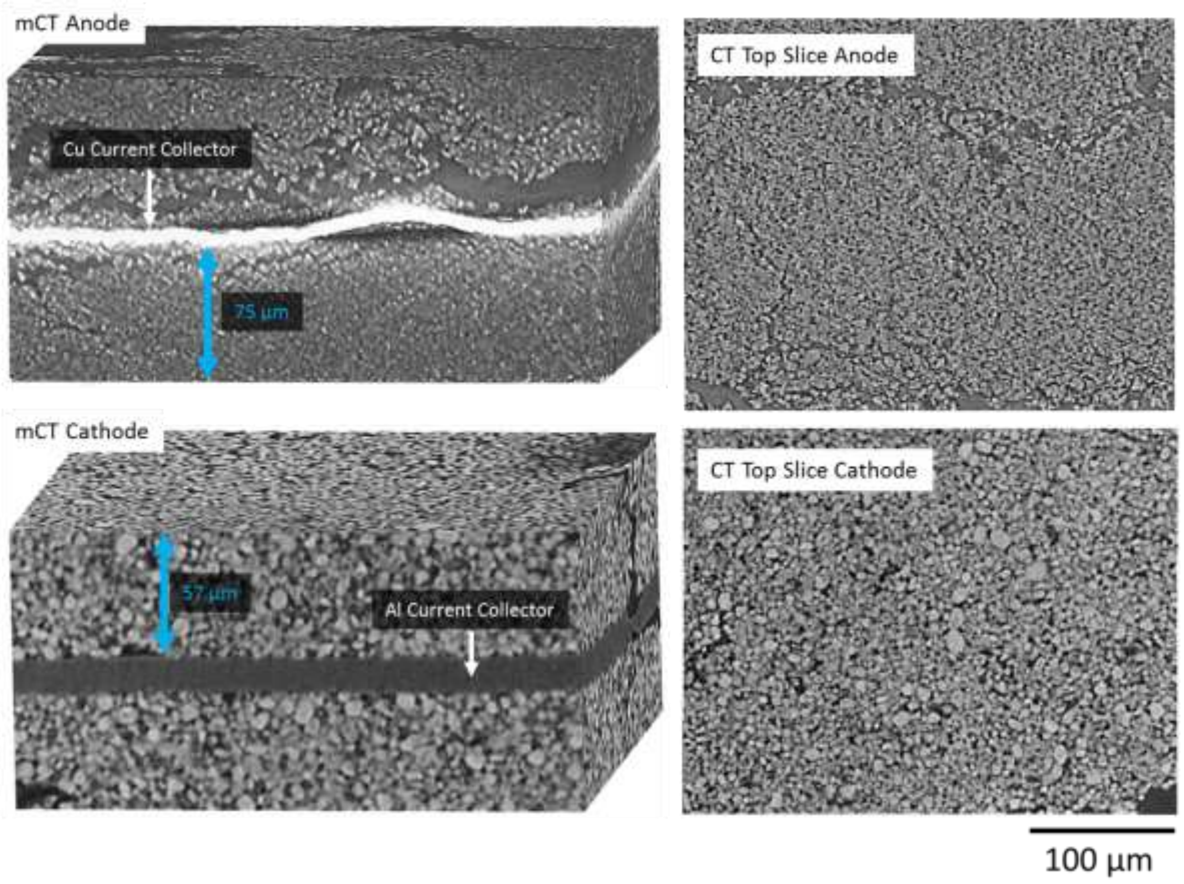
Active Materials
Parameterization

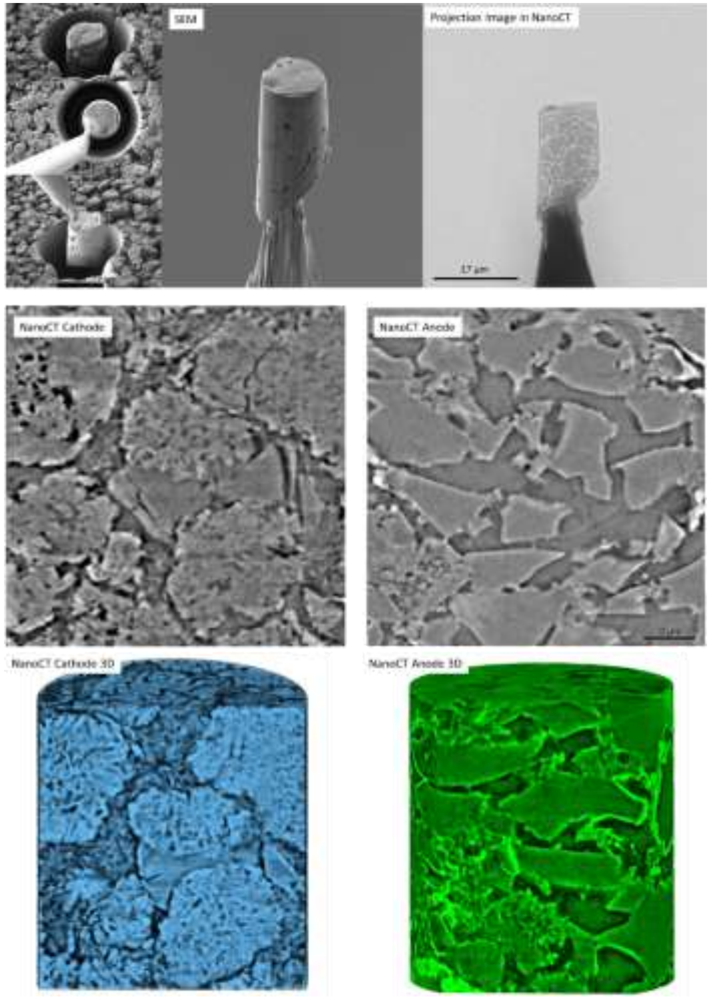




Laufen et al. https://dx.doi.org/10.2139/ssrn.4542213 | Poster P2-074 Schütte et al.

Active Materials
Parameterization – Micro- and Nano-CT





Electrolyte Analysis
Parameterization

Conducting salt

$NaPF_6$

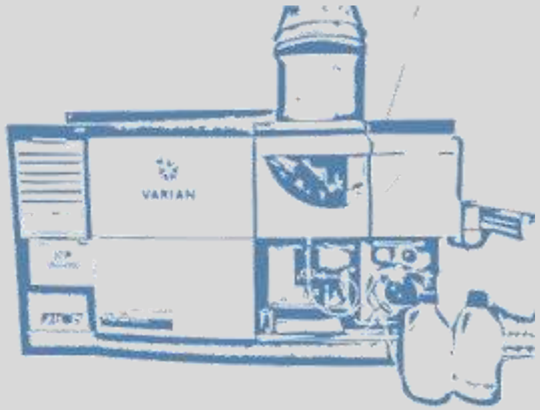
SEM EDX

c_e

Conducting salt concentration

$1.42\ mol\ L^{-1}$

ICP-OES

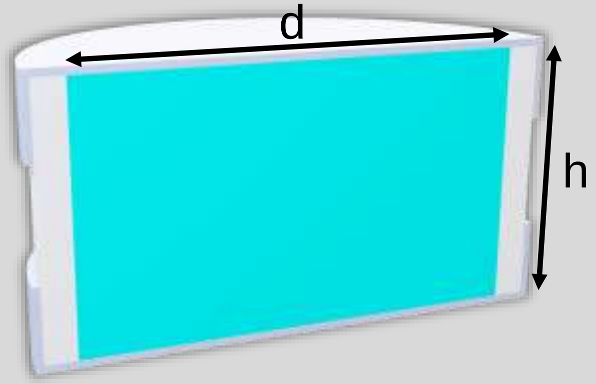


σ_e

Conductivity

$0.98\ S\ m^{-1}$

EIS

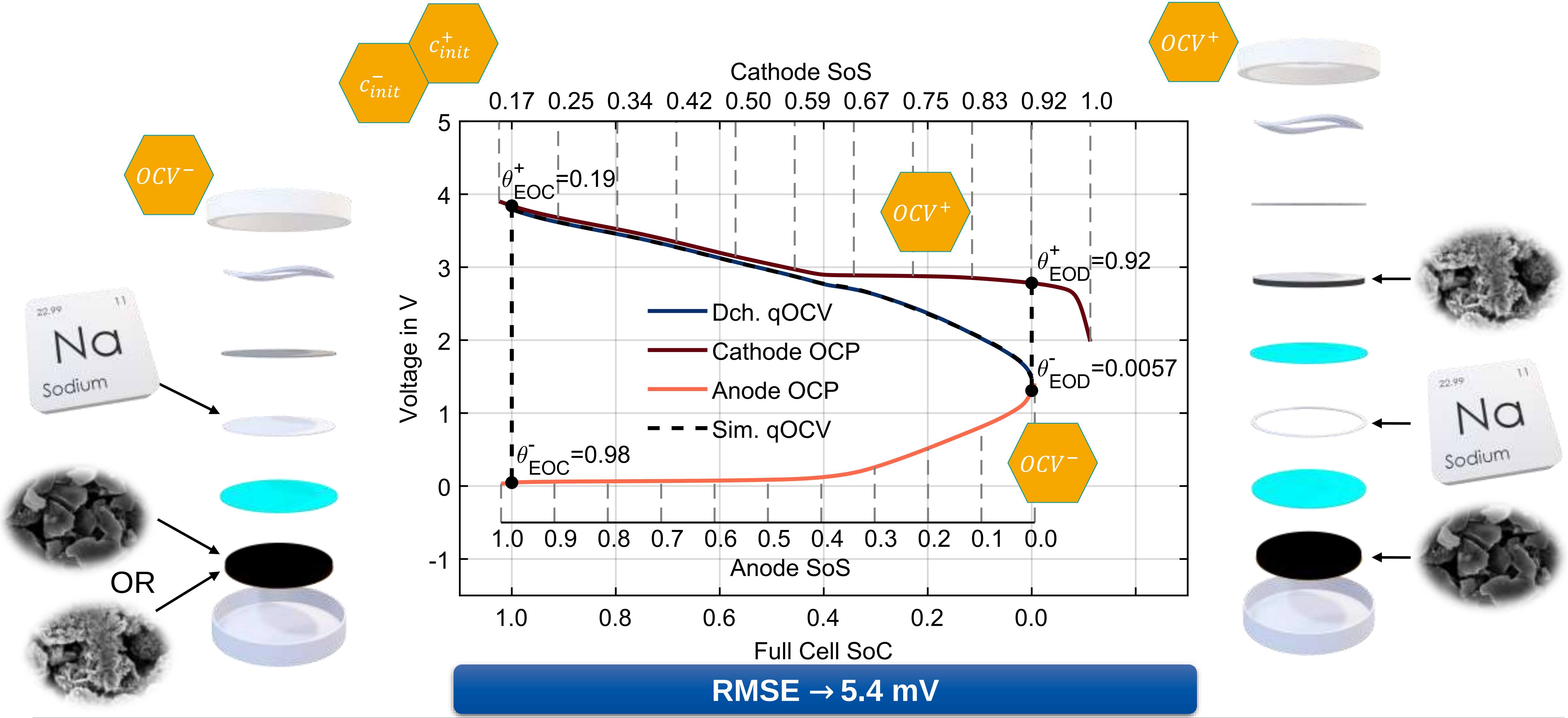


D_e

Diffusion Coefficient

$1.8 \cdot 10^{-10}\ m^2 s^{-1}$

qOCV Fitting
Parameterization



RMSE → 5.4 mV

Overview Parameter
Parameterization

h	$57.5\ mm$	c_e	$1.42\ mol\ L^{-1}$	ε_A^+	0.3712	ε_A^-	0.5609
w	$1.388\ m$			ε^+	0.299	ε^-	0.314
d_{Coat}^-	$76 - 78\ \mu m$			p^+	1.53	p^-	1.54
d_{Coat}^+	$55 - 56\ \mu m$			r^+		r^-	
d_{sep}	$15\ \mu m$	OCV^+		k^+	$2 \cdot 10^{-11}\ m^{2.5} s^{-1} mol^{-0.5}$ https://doi.org/10.1149/2.0551701jes	k^-	$2 \cdot 10^{-11}\ m^{2.5} s^{-1} mol^{-0.5}$ https://doi.org/10.1149/2.0551701jes
ε_{sep}	0.406	OCV^-		$c_{s,max}^+$	$39085\ mol\ m^{-3}$	$c_{s,max}^-$	$13488\ mol\ m^{-3}$
p_{sep}	1.63	c_{init}^+	0.4811	σ^+	https://doi.org/10.18154/RWTH-2017-04693	σ^-	https://doi.org/10.1073/pnas.2111119118
		c_{init}^-	0.5903	D_s^+	$5 \cdot 10^{-15}\ m^2 s^{-1}$ doi/10.1002/aenm.201701610; 10.1149/2.0211916jes	D_s^-	$5 \cdot 10^{-15}\ m^2 s^{-1}$ https://doi.org/10.1002/batt.202000161

Width → w

Anode coating thickness → d_{Coat}^-

Cathode coating thickness → d_{Coat}^+

Cathode reactivity → k^+

Anode reactivity → k^-

Cathode particle diffusion coefficient → D_s^+

Anode particle diffusion coefficient → D_s^-

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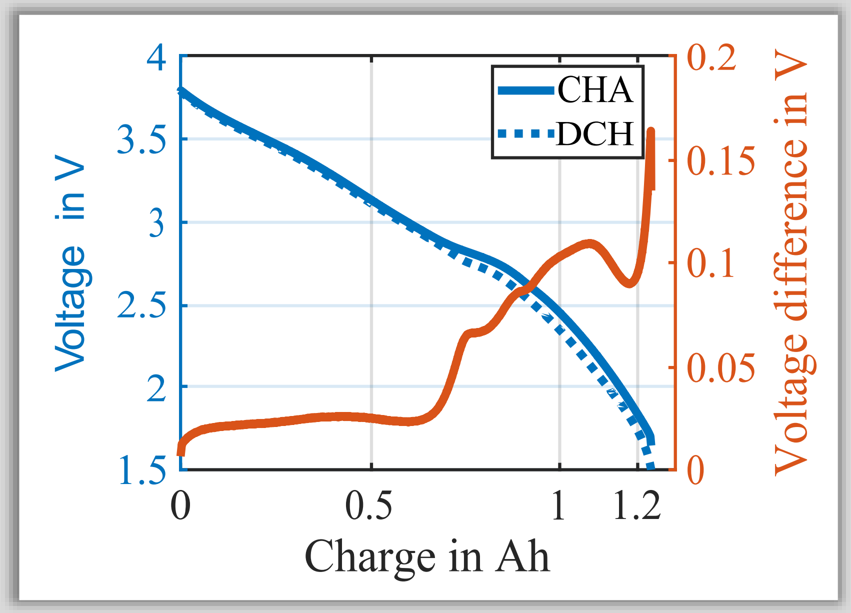
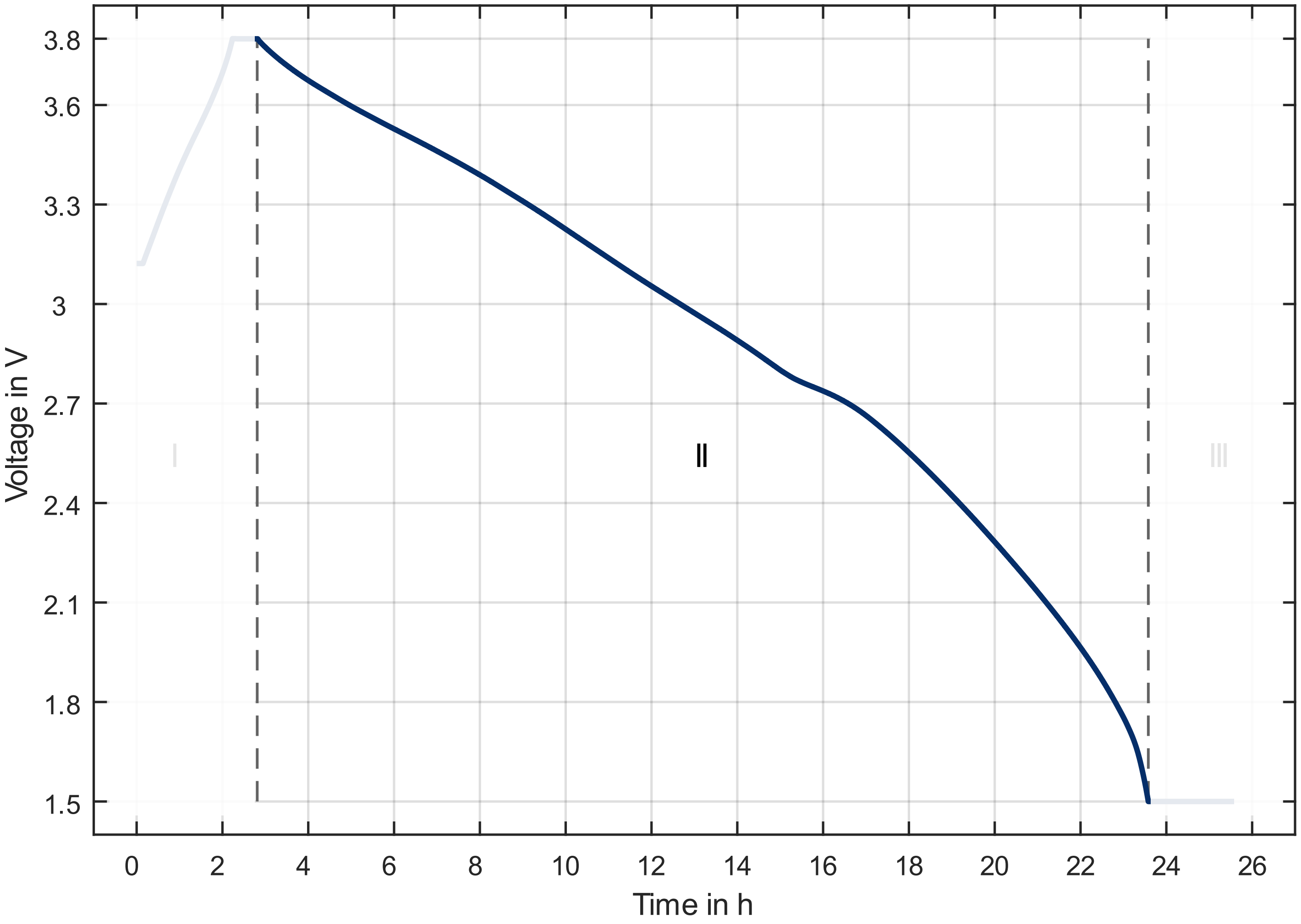
Simulation Profile
Validation

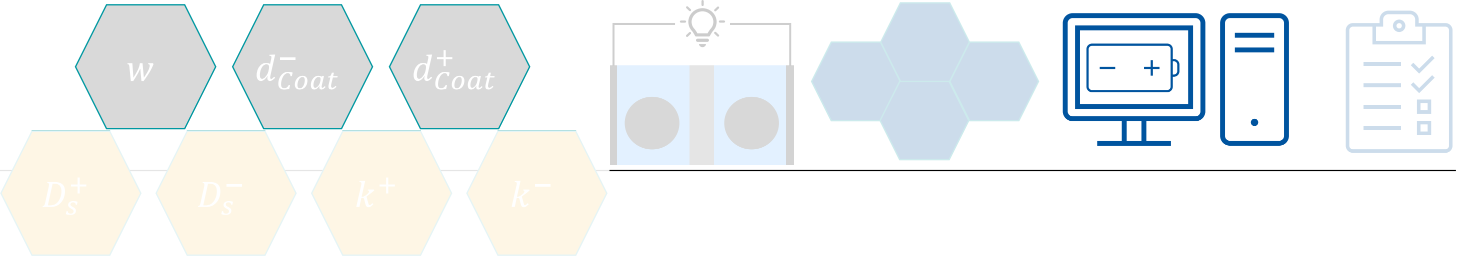


Laufen, Quade et al. https://dx.doi.org/10.2139/ssrn.4542213

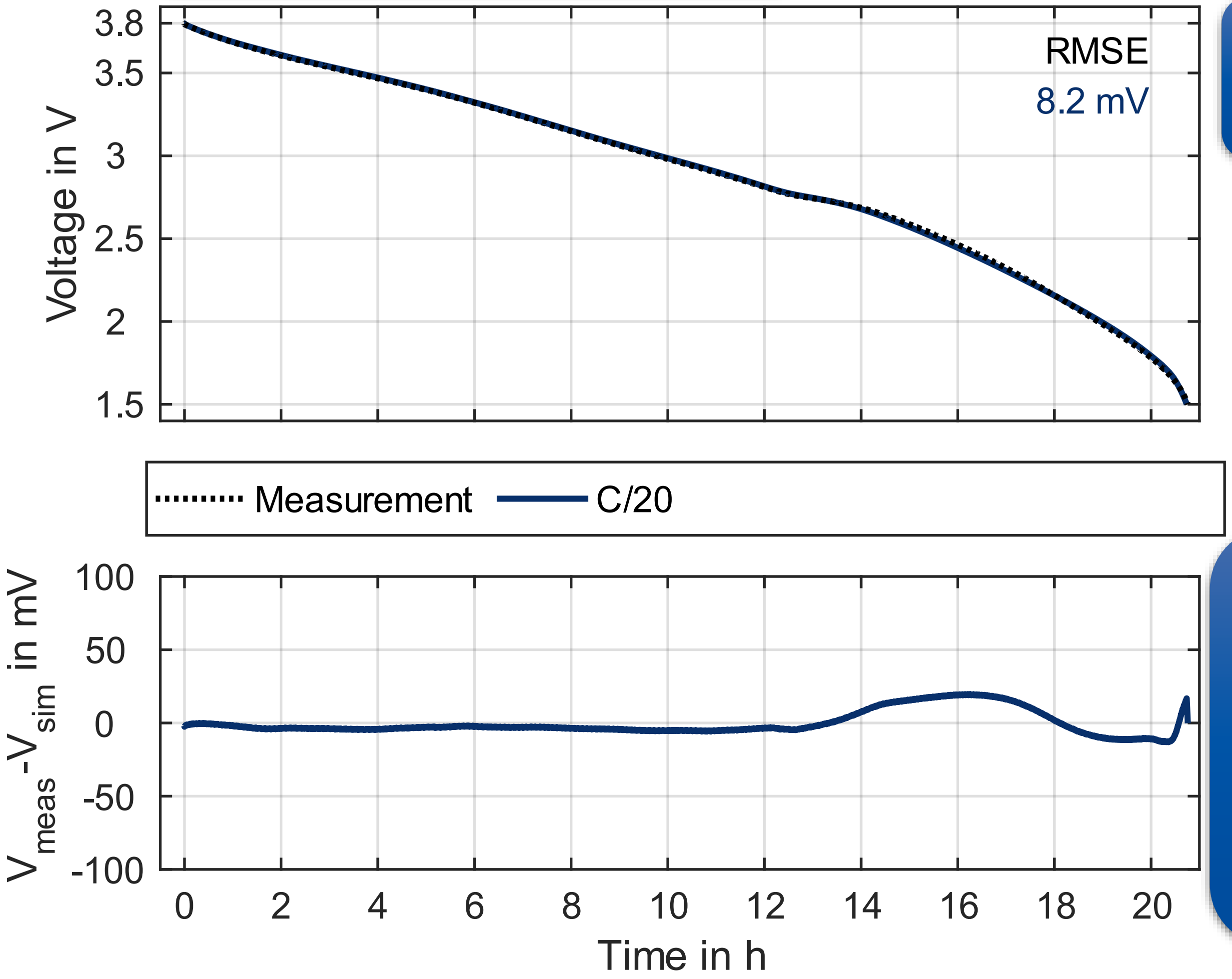
Due to hysteresis only simulation of discharge



Simulation with optimized →
Validation

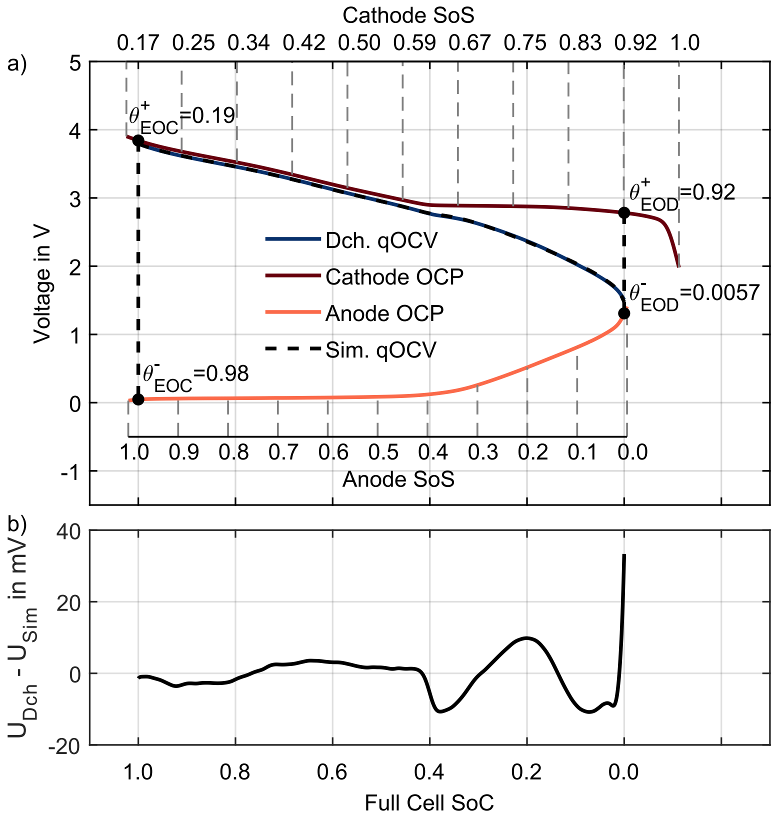


C/20



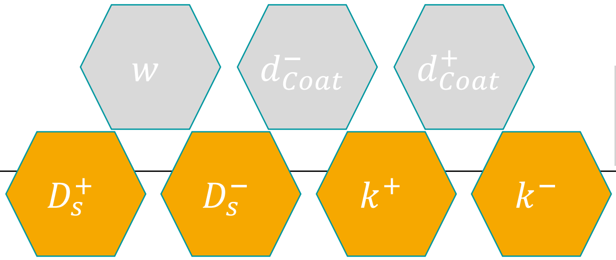
Capacity of the C/20 discharge is matched well

Error in lower SOC region partially originates from qOCV-fitting

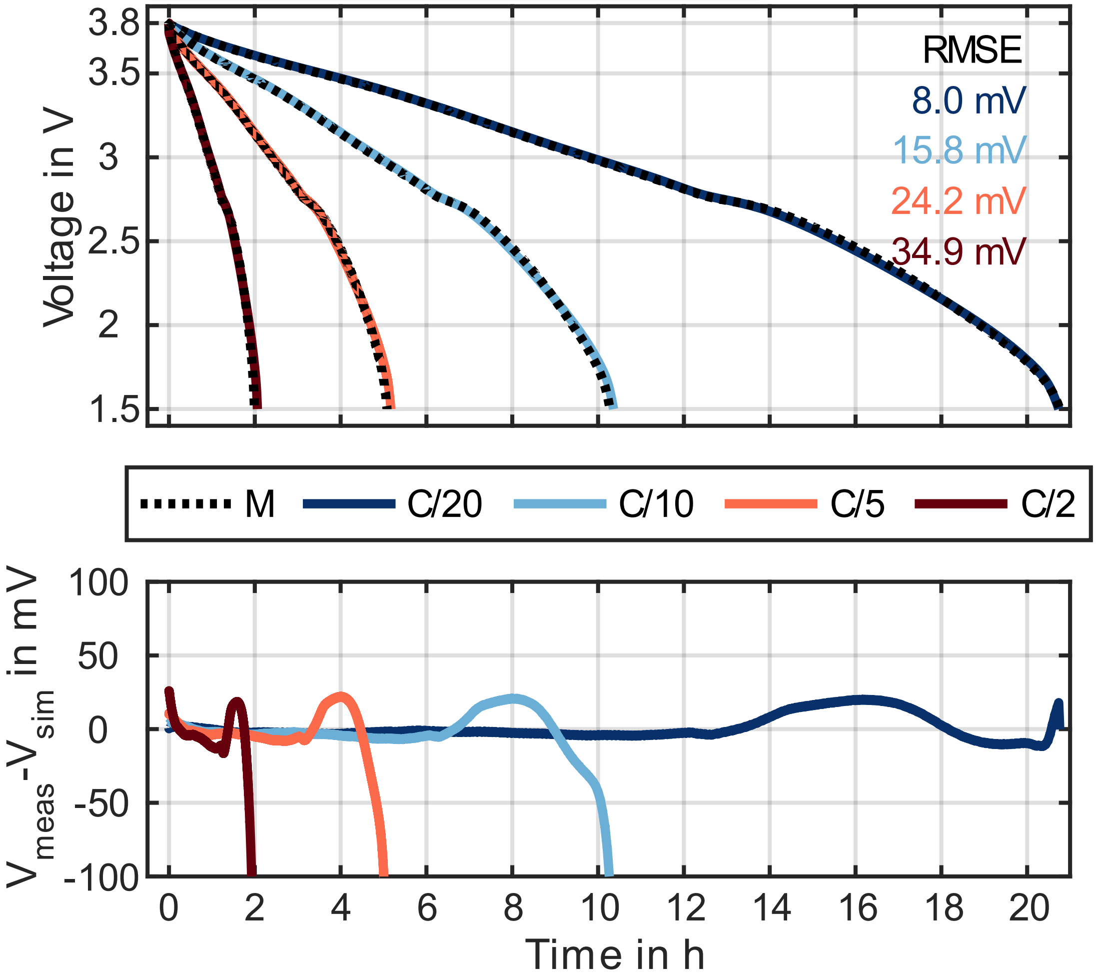


Simulation with optimized

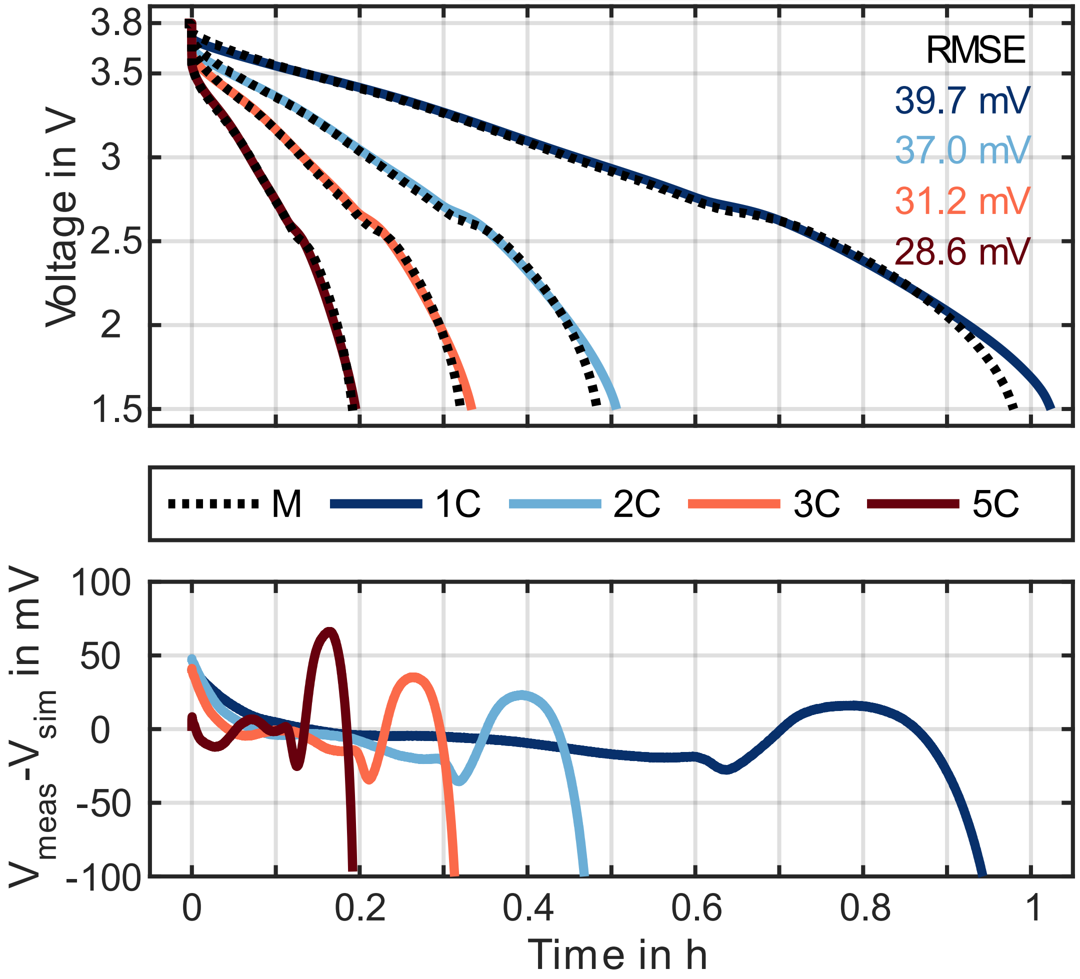
Validation



Low C-Rates

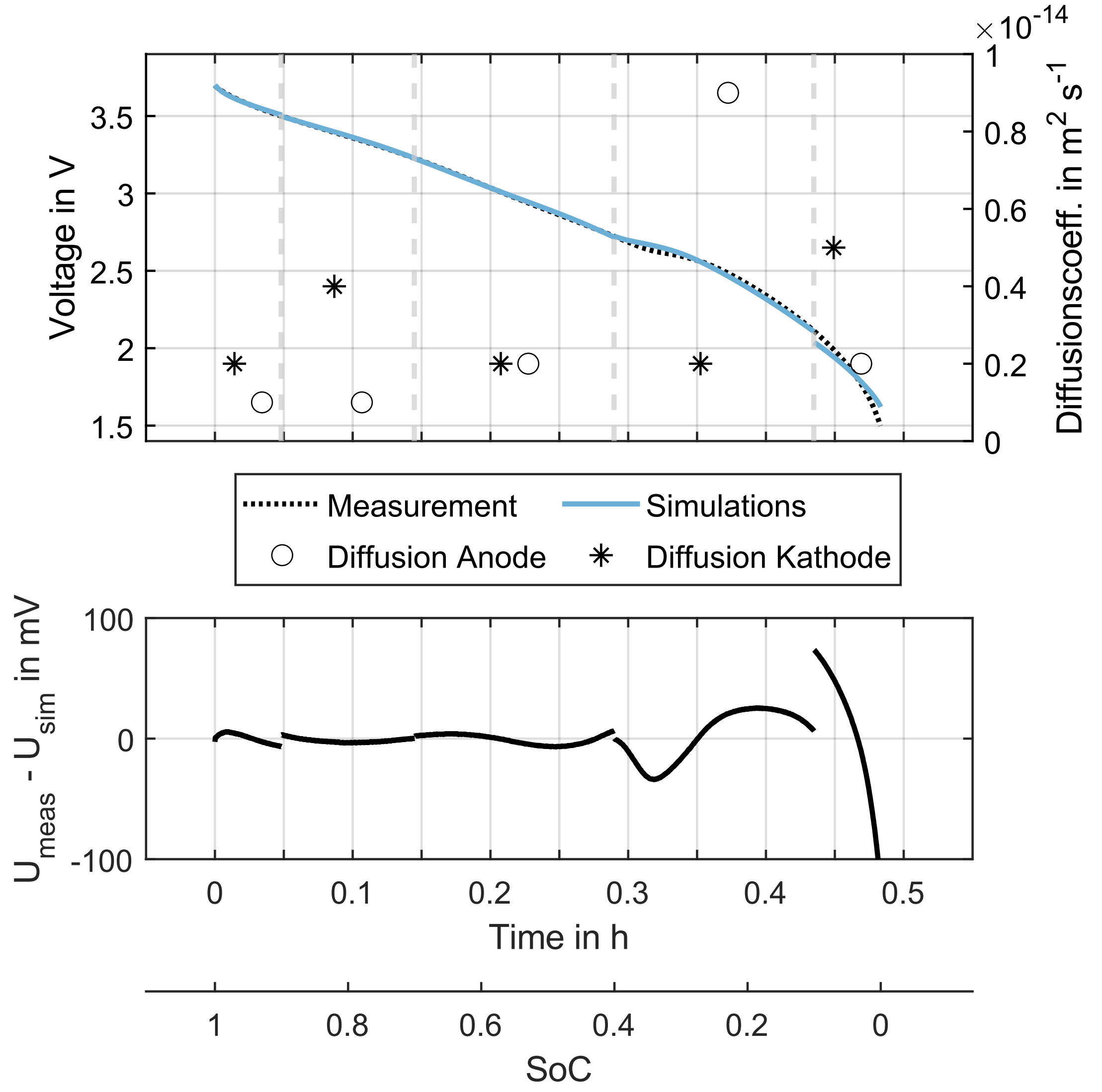


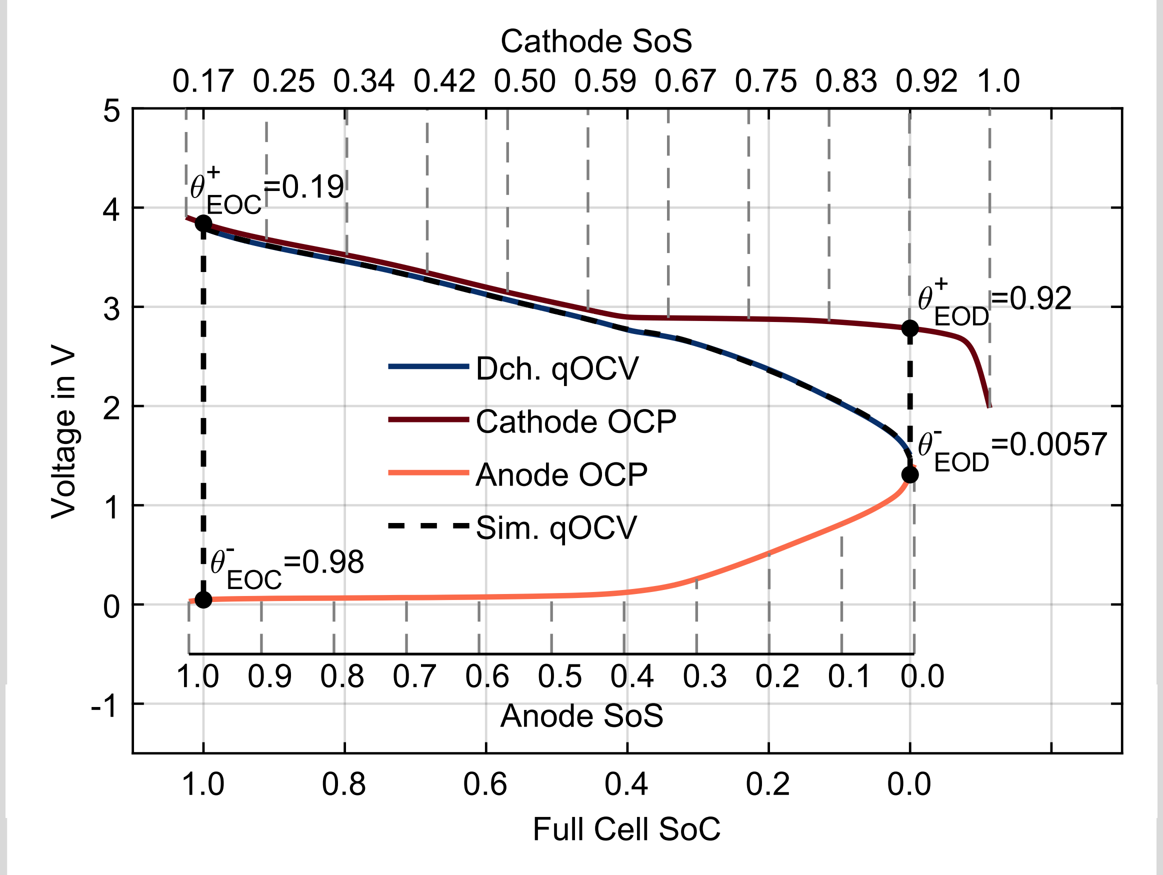
High C-Rates



Merged Interval Optimization
Validation

D_s^+ D_s^-





Does HC (anode) exhibit odification dependent diffusion coefficient?

Conclusion & Outlook

First parameterization of SIB with $Na_{0.96}Ca_{0.02}Mn_{1/3}Fe_{1/3}Ni_{1/3}O_2$ and hard carbon shows promising simulation results – established PCMs can be used for sodium-ion

Established methods for cell parameterization of lithium-ion batteries can be transferred to sodium-ion cells

Merged interval optimization shows better RMSE
Should be used instead of overall RMSE

CARL Center for Ageing, Reliability and Lifetime Prediction of Electrochemical and Power Electronic Systems
RWTH AACHEN UNIVERSITY

Thank you
for your attention

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We thank

GEFÖRDERT VOM
Bundesministerium
für Bildung
und Forschung

Commercial Sodium-Ion Cells
Characterization & Modeling

SIMBA Final event

07.06.2024

Gereon Stahl, Moritz Schütte, Hendrik Laufen, Dirk Uwe Sauer

Center for Ageing, Reliability and Lifetime Prediction of Electrochemical and Power Electronic Systems (CARL)

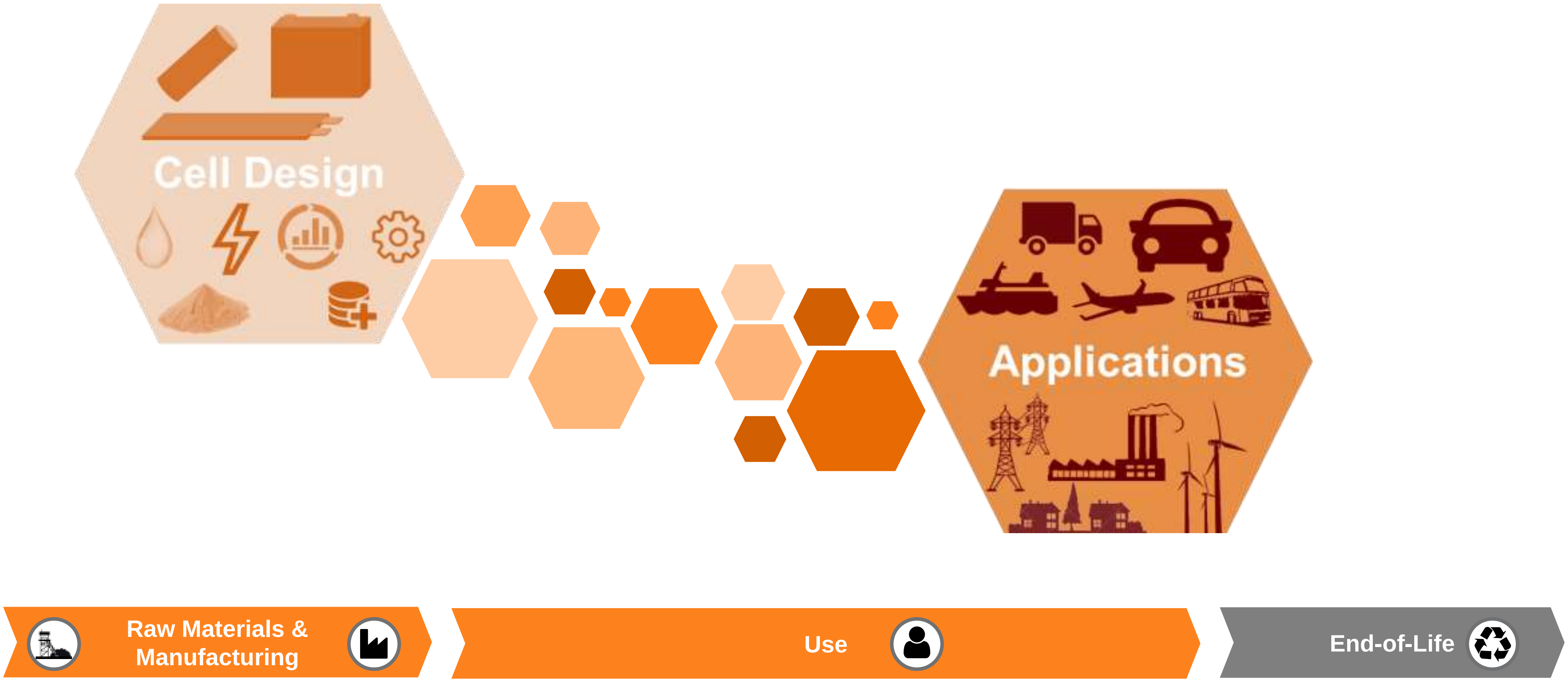
CARL Center for Ageing, Reliability and Lifetime Prediction of Electrochemical and Power Electronic Systems | RWTH AACHEN UNIVERSITY

Data sheet: commercial cells

Format	18650	26700	26700	33140	Prismatisch	18650 HP
Nominal capacity in Ah	1,5	3	3,3	10	220	1,2
Charge vo[illegible]	[illegible]	[illegible]	[illegible]	[illegible],9	3,95	3,8
Discharge voltage in V	[illegible]	1,5	1,5	1,5	1,5	1,5
Max. current (Charge/Discharge)	1C/3C	1C/3C	1C/3C	1C/3C	1C/3C	5C/8C
Energy density (grav.|vol.)	128 Wh/kg 268 Wh/l	109 Wh/kg 233 Wh/l	127 Wh/kg 271 Wh/l	110 Wh/kg 250 Wh/l	155 Wh/kg 271 Wh/l	97 Wh/kg 217 Wh/l
Price (for academia)			1,9 $		75$	1,1 $
Price/kWh			186 $/kWh		110 $/kWh	306 $/kWh
Nominal voltage	3,1 V	3,05 V	3,1 V	3	3,1 V	3 V
Resistance	<20 mΩ	<20 mΩ	<20 mΩ	<5 mΩ	<0,5 mΩ	<25 mΩ

Performance strongly temperature dependet: max. current rate only allowed at mild temperatures (10-35°C)

Motivation
Bridging the Gap between Battery Design and Application Demands



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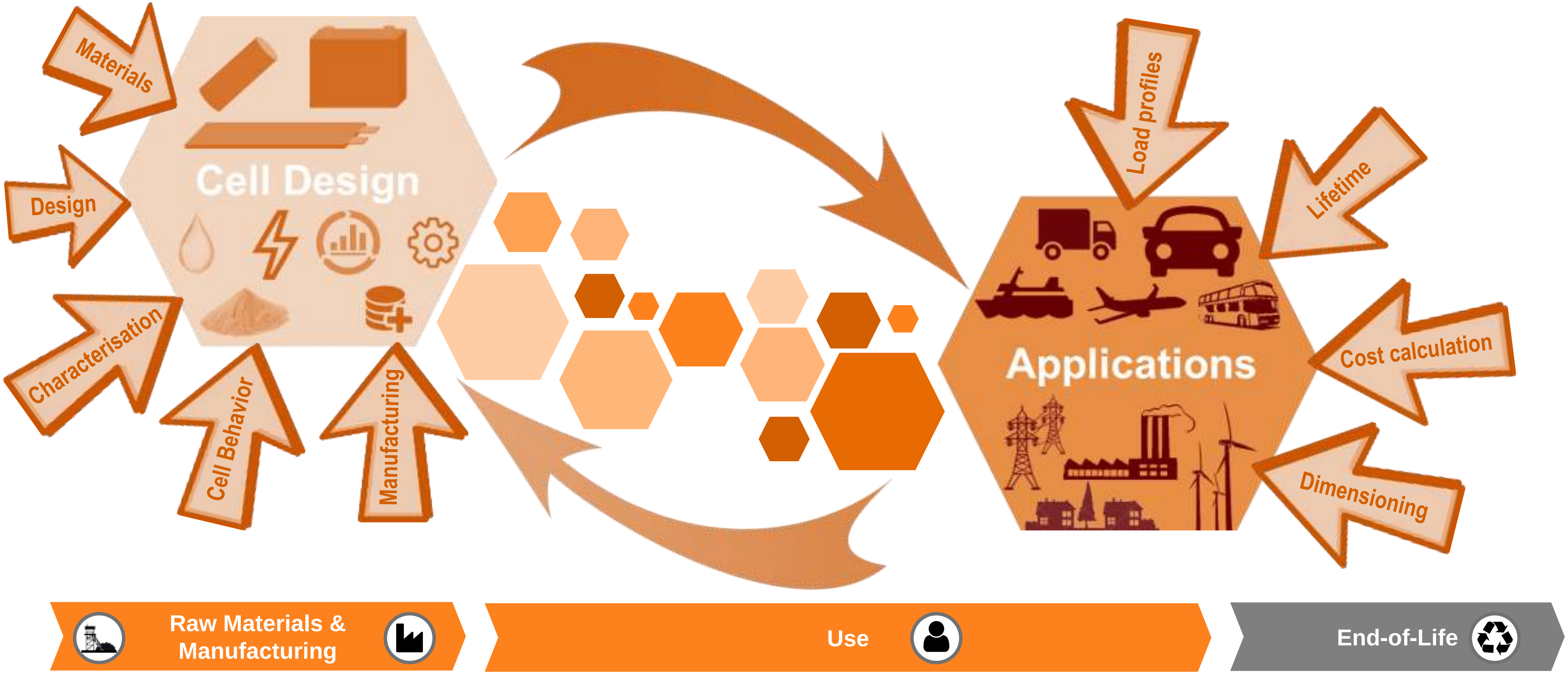
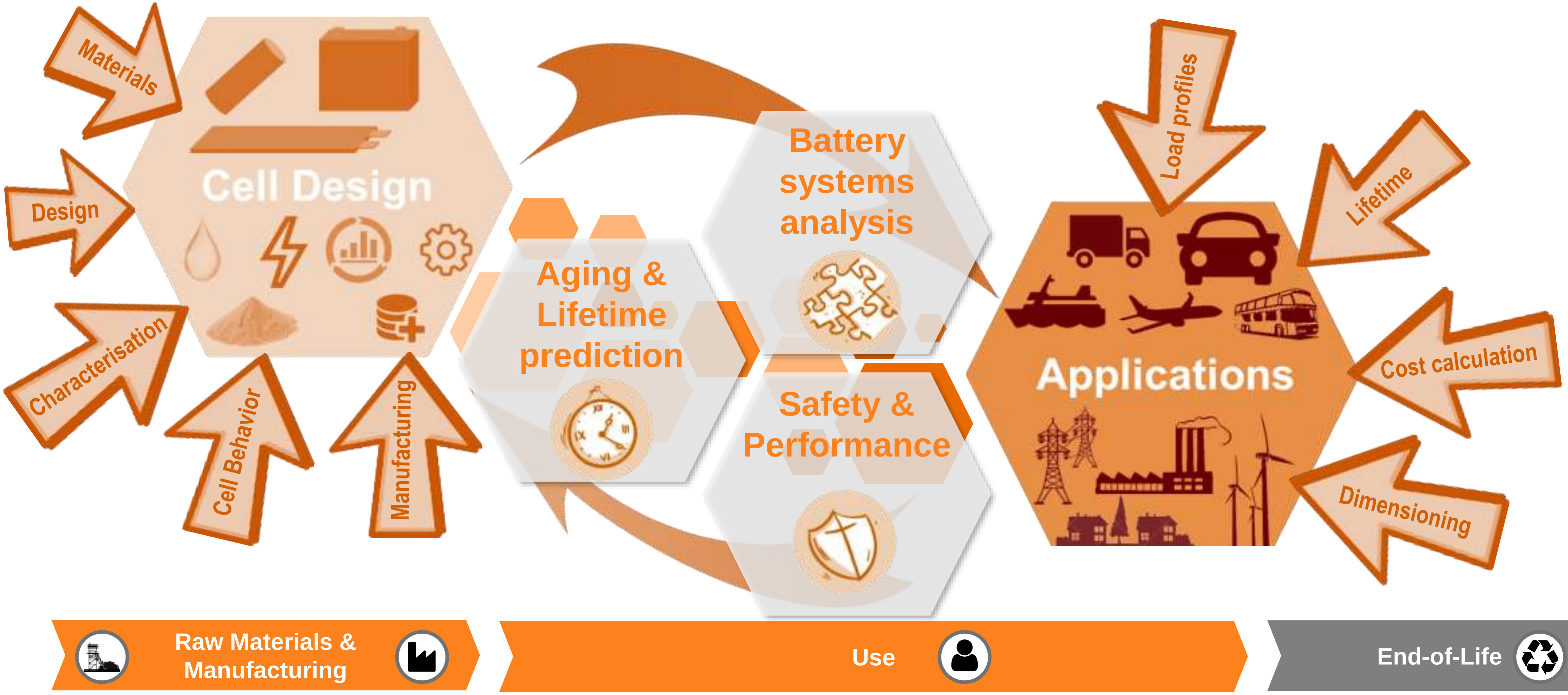
Motivation
Bridging the Gap between Battery Design and Application Demands



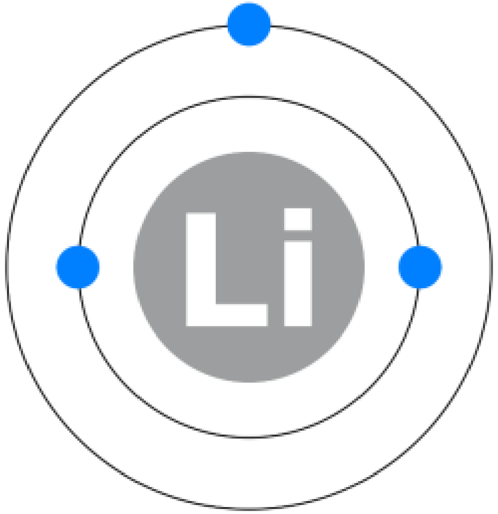
Motivation
Bridging the Gap between Battery Design and Application Demands



Models

ICPD

iSEA FRAME



Motivation of the ICPD
Overview

Extensive models and data about different battery cells, modules and packs are needed to evaluate them in the context of a wide variety of applications. The ICPD combines the approach of a data base and the linking of analysis and design of battery systems.

Material database

- All components of a battery
  - Active material
  - Conductive additive
  - ….
- Calculation of electrical, physical and chemical parameters of the materials
- Bottom-up cell, module and pack creation

Performance Analysis

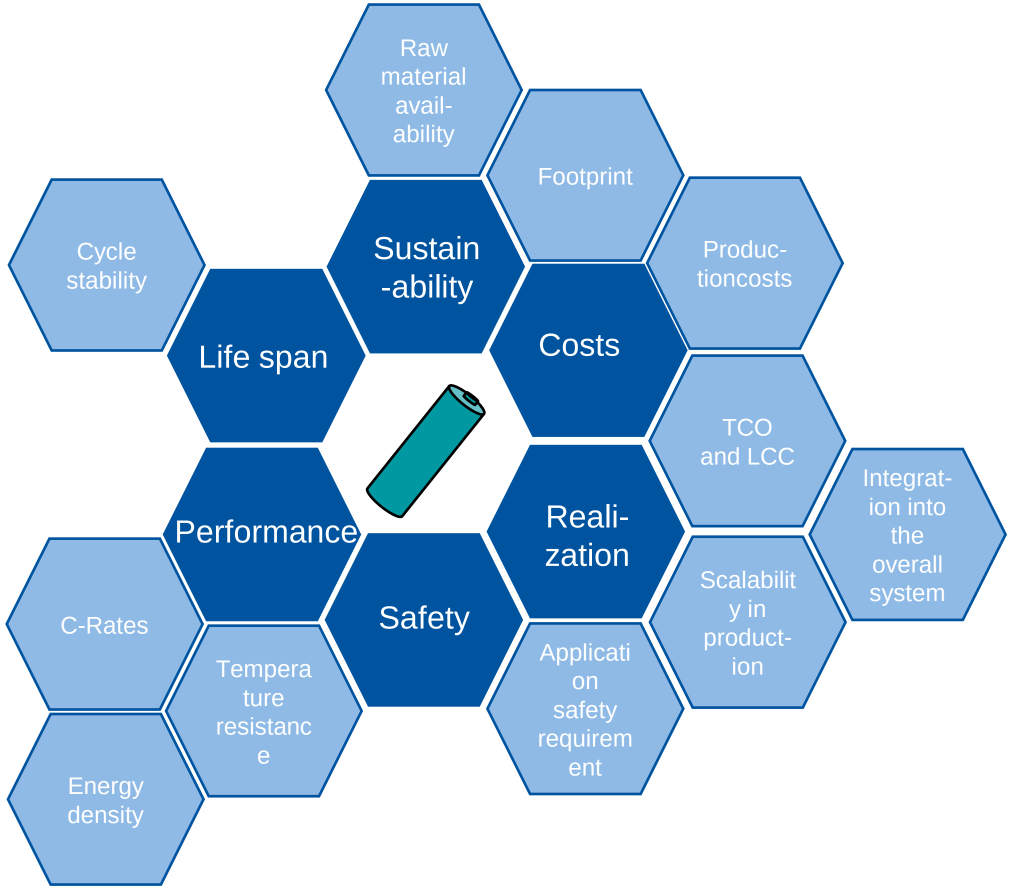
- Consideration of cell-specific properties
  - Energy, power, inner resistance
  - Gravimetric and volumetric energy and power density
- Simulation of the Cells with ECM- and physical-chemical simulations (via SBMT)
- Aging and thermal simulation based on load profiles

Cost and LCA

- Cost calculation of cells, modules and packs
- Life cycle assessment for a given field of application
- Evaluation of the battery system for given application

Motivation of the ICPD
Battery system requirements

Requirements for modern battery systems

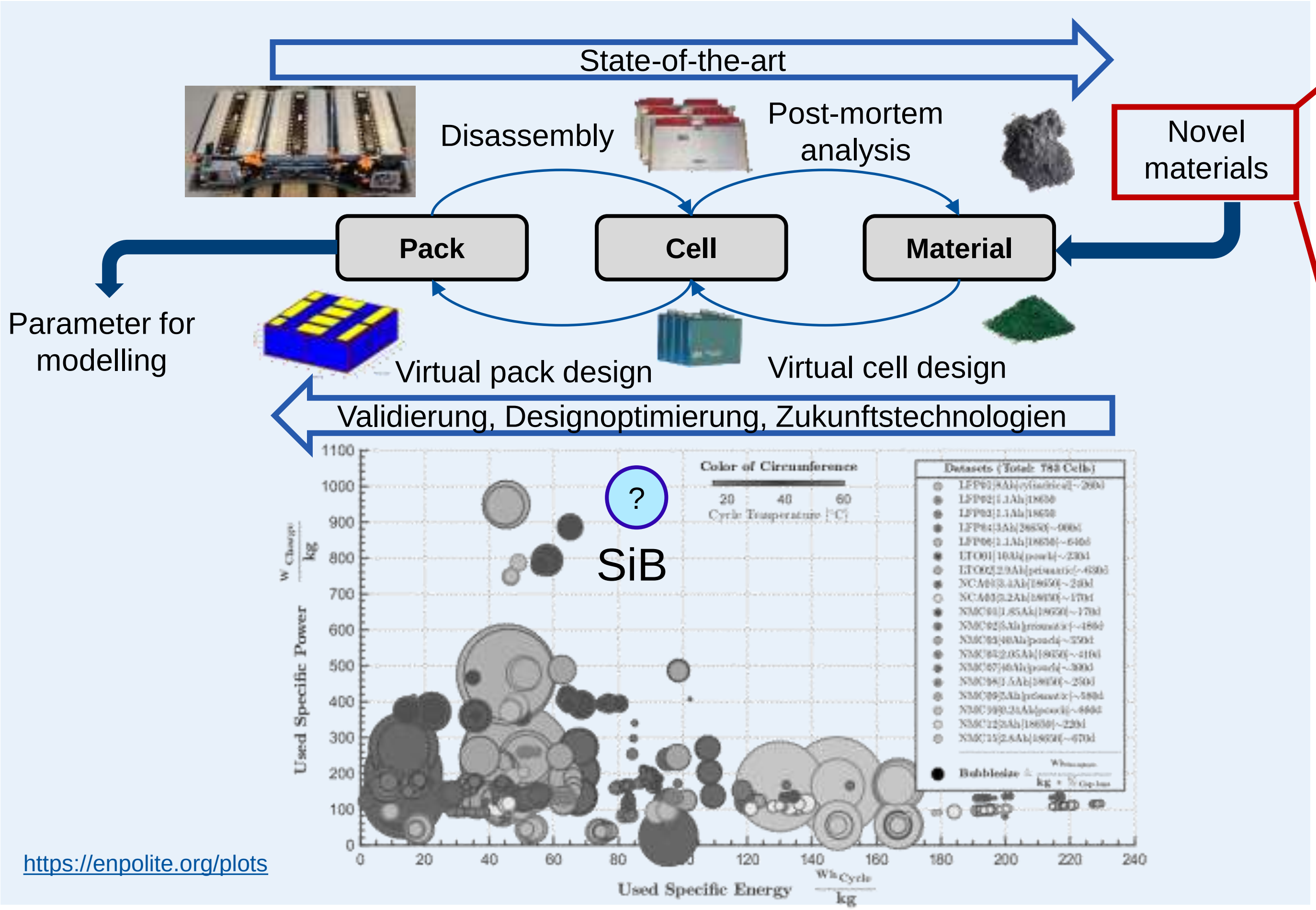


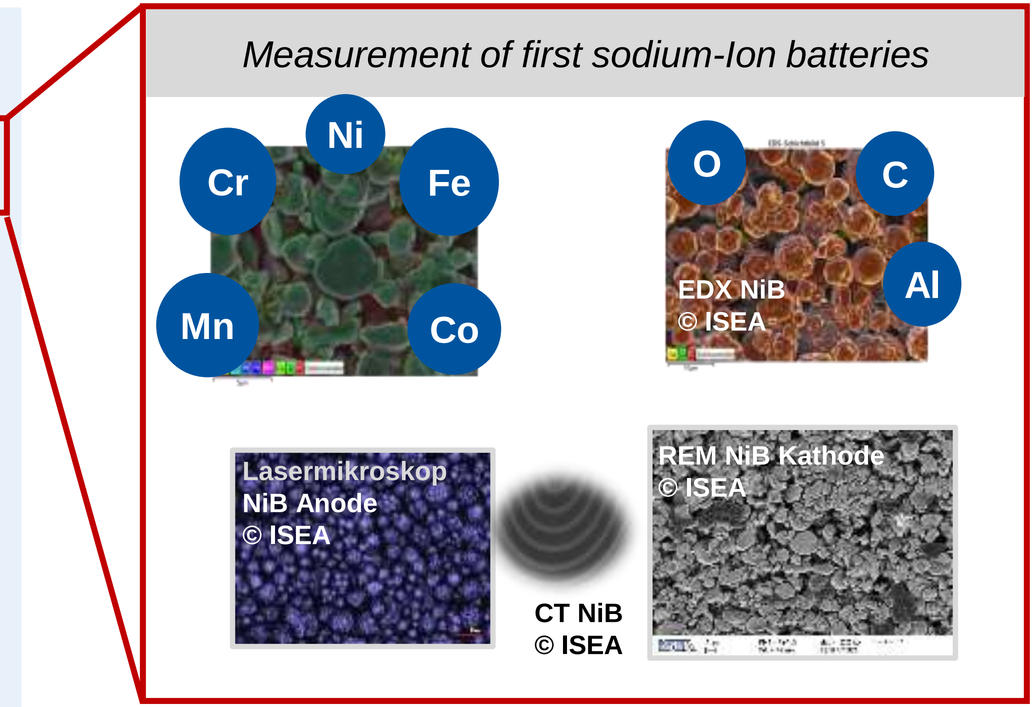
ICPD as an integral tool:

- Cost, performance, sustainability and life span analysis in one tool
- Intelligent algorithm for an optimized battery cell design
- Guided and algorithm based cell and module modelling/design
- Analysis of the battery cell, module and pack in different applications
- Application depending TCO and LCC analysis

ICPD

Investigation of State-of-the-Art and Novel Technologies





ISEA cell and pack designer

Analysis options

Simulation 3D-Lithium

- ISEA Tool of a P2D-Model
- Simulate cells with different profiles (e.g. EIS, qOCV etc.)
- With different environmental settings (e.g. Temperature)

Analysis parameter

- Halfcell simulations
- Sensitivity analysis of the P2D-parameters
- DRT Analysis of EIS

Advanced algorithm of the ICPD

Physical-chemical model of the cell

Simulation with ISEAFrame

Analysis design

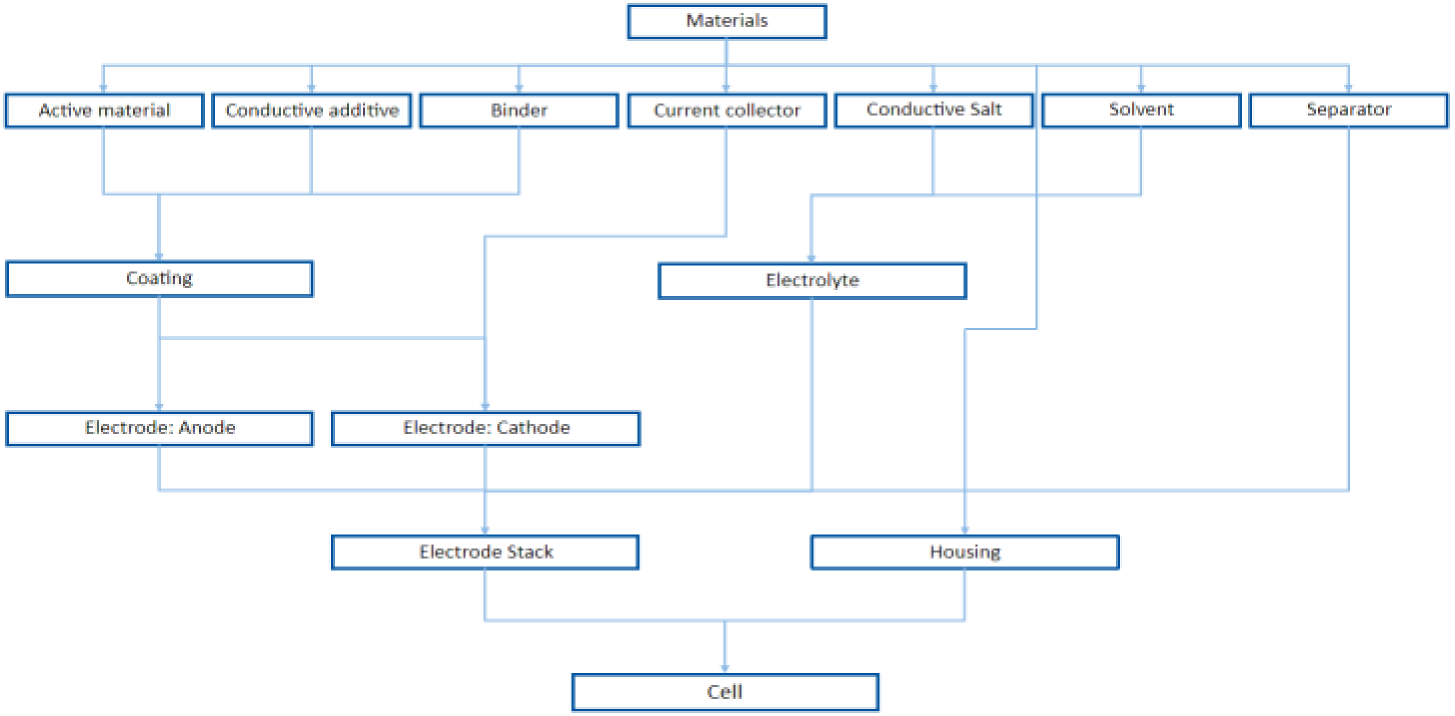
- Parameter variation of design parameter
- Identify potentials for design improvement

ISEAFrame

- Automatic export to ISEAFrame
- ECM based electrical and thermal simulation
- Ageing simulation based on empirical model

ISEA cell and pack designer

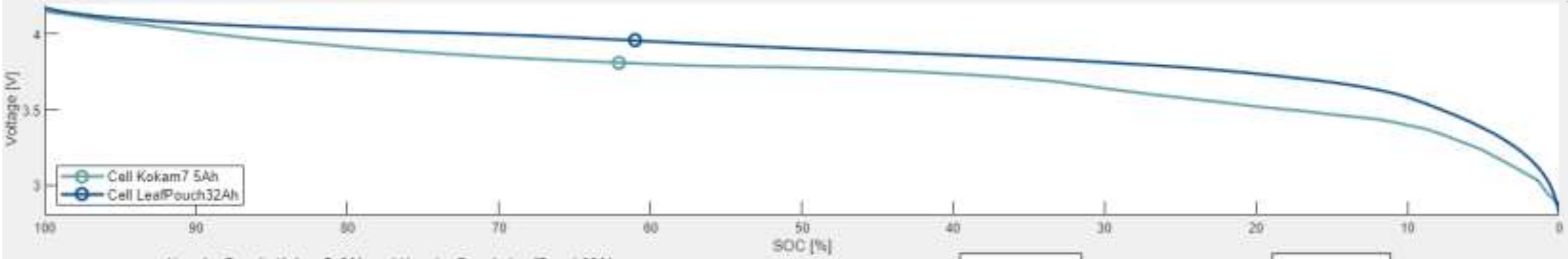
Cell creation process – Bottom-Up

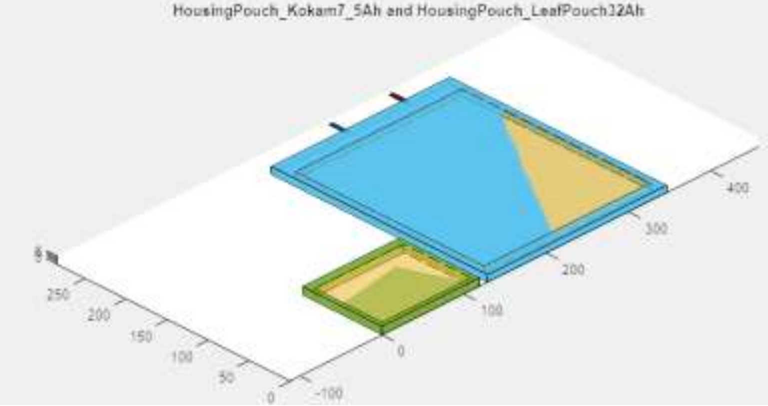


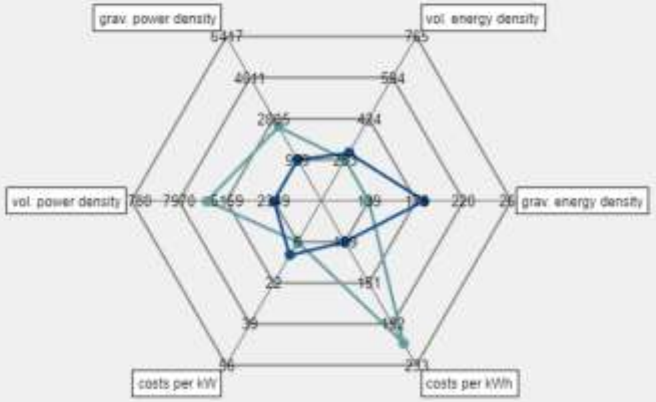
- Step-by-step cell creation
- Determination of cell and component-specific electrical, physical and geometric properties via advanced algorithms (e.g. energy, OCV)
- Different cell creation methodologies: Fit to housing, fit cell to capacity and no change of components (standard)

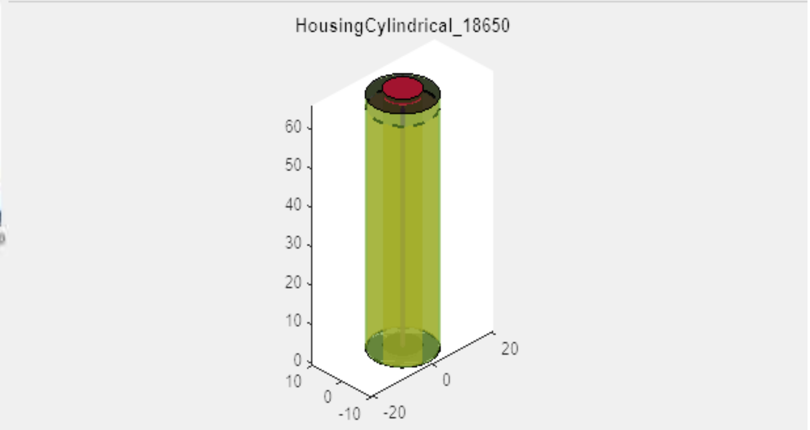
ISEA cell and pack designer

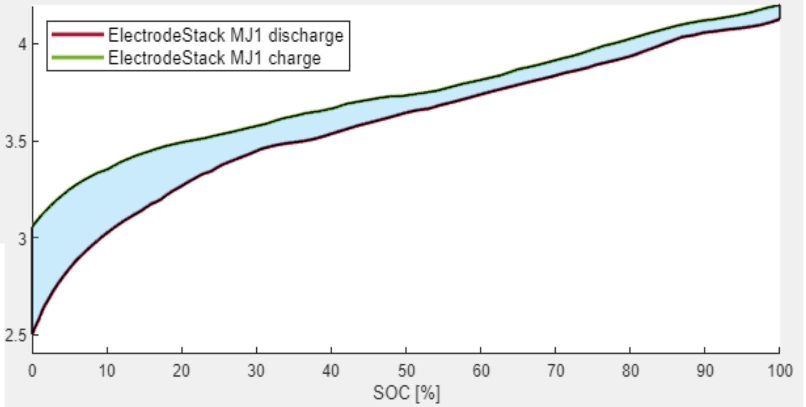
Investigation of the created cell









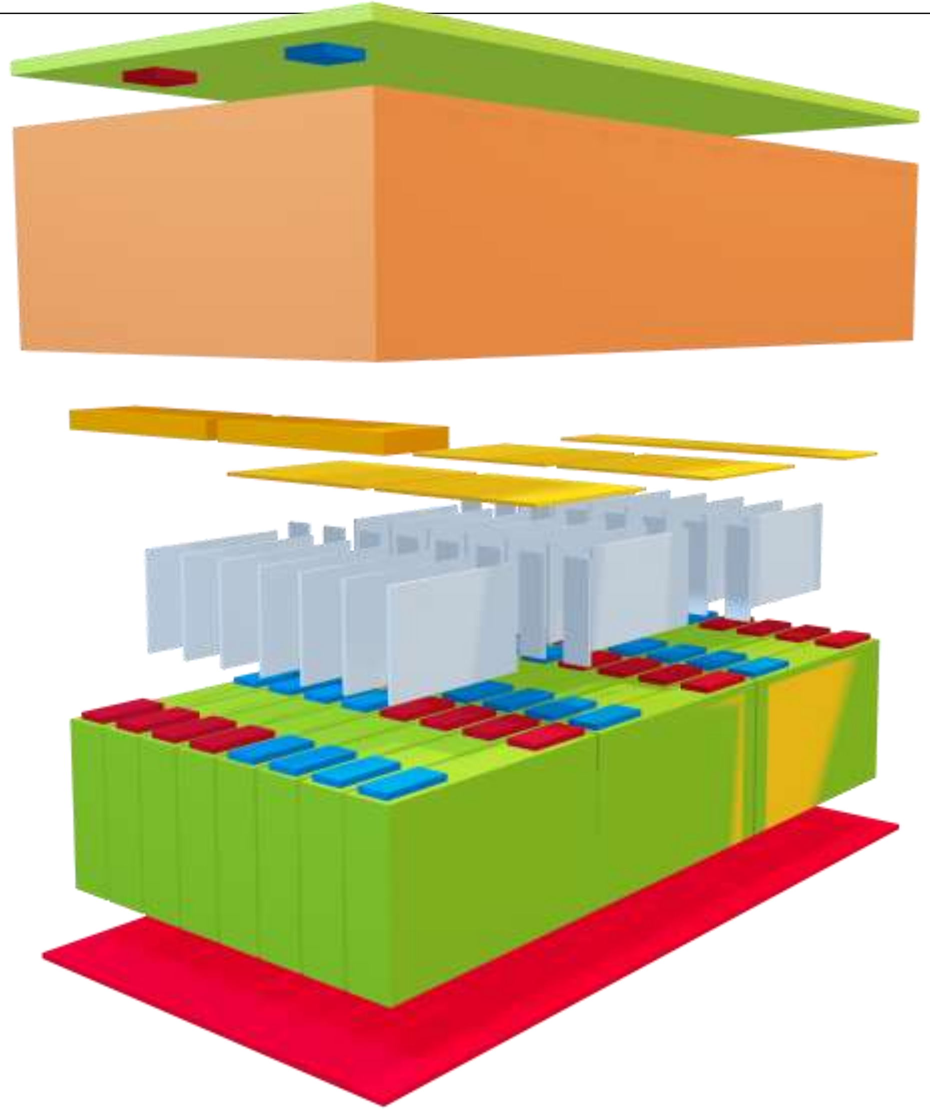


Spider diagram to compare the cells

- Compare the OCV of different cells
- Compare the geometry of the cells
- Comparison of the cell properties with spider diagram
- Show Hysteresis of specific cell

ISEA Cell & Pack designer

Module modelling



Module modelling

- Modelling of the cell connectors, busbars, compression pads, glue or cell holders and module housing
- Automatic interconnection and placing of all related objects
- Algorithm fits cell connector and busbar thickness to max. current
- Calculation of all electrical and physical properties of the module (inner resistance, densities etc.)
- Export of the module as CAD-File (.3mf) or (.stl) → Post-processing with CAD program possible
- True-to-scale size comparison between modelled modules possible
- Detailed thermal model of the module