Performance analysis of Lithium-ion-batteries: status and prospects

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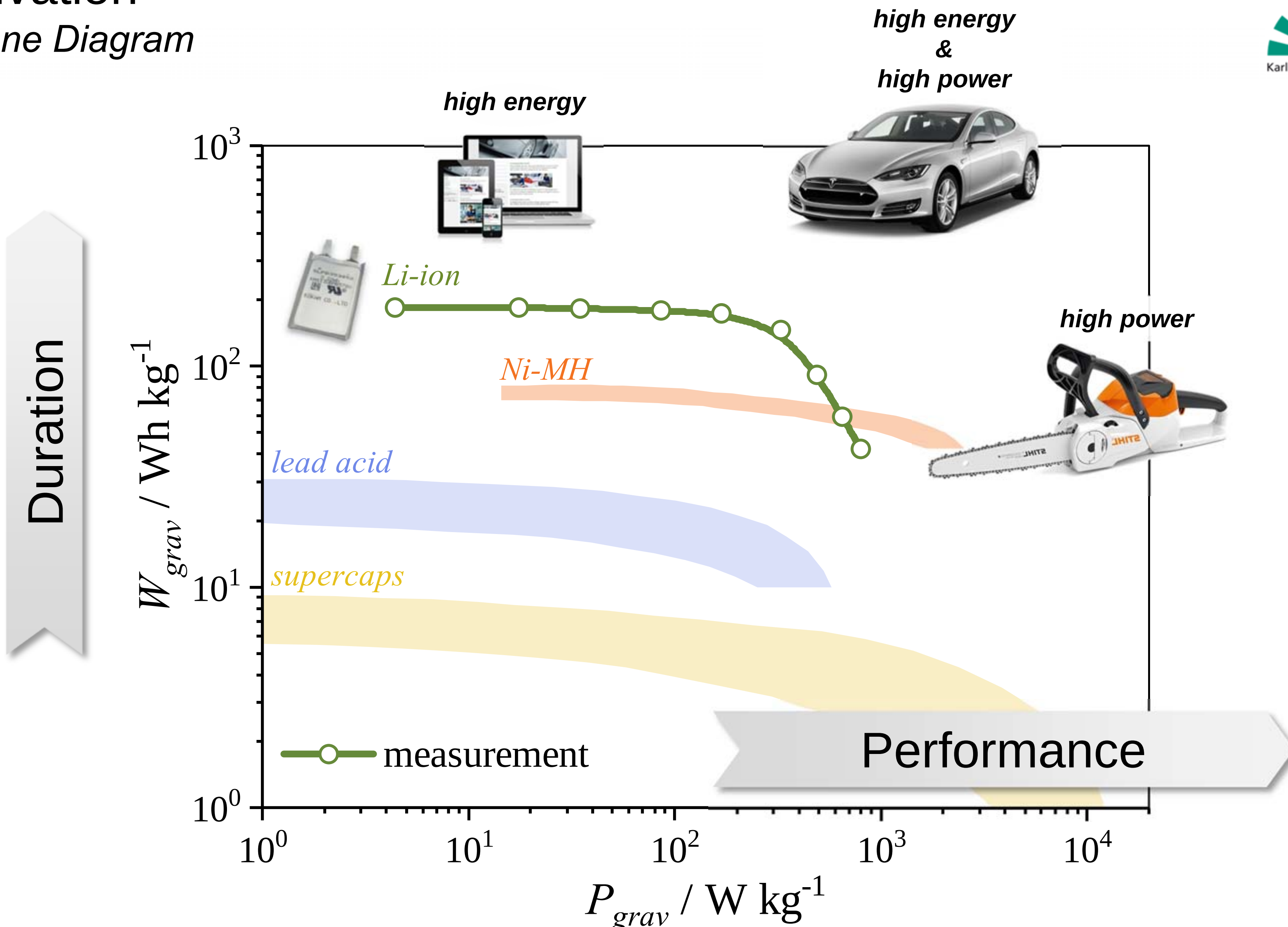
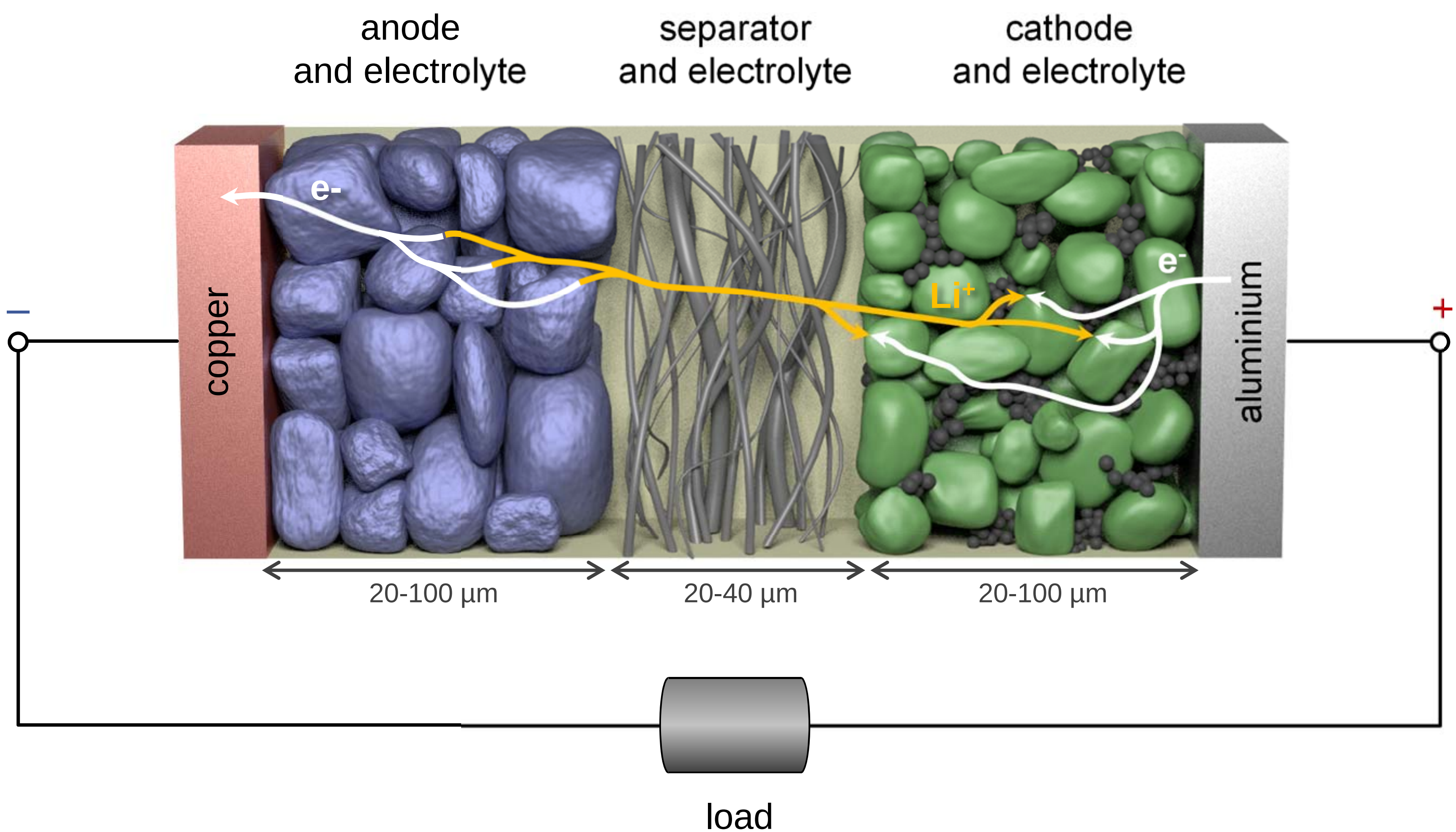
Motivation
Ragone Diagram



Ragone diagram on cell level

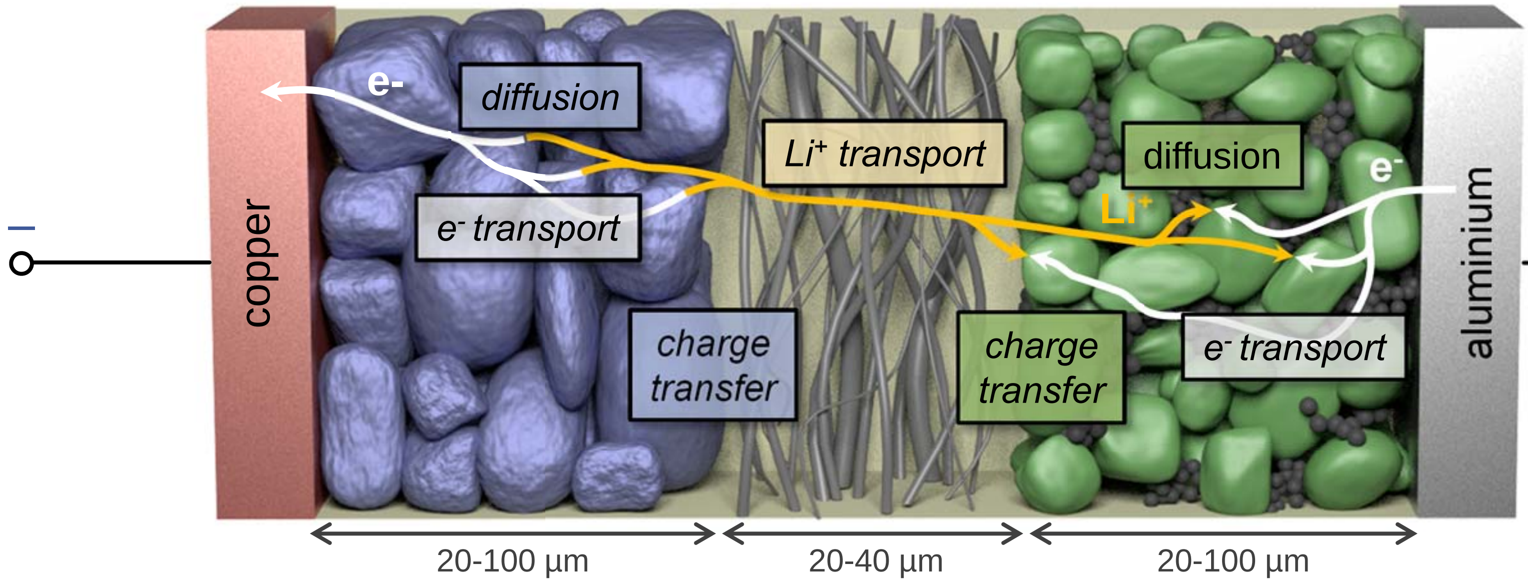
The Lithium-Ion Cell

Resistance Contributions



The Lithium-Ion Cell

overpotential

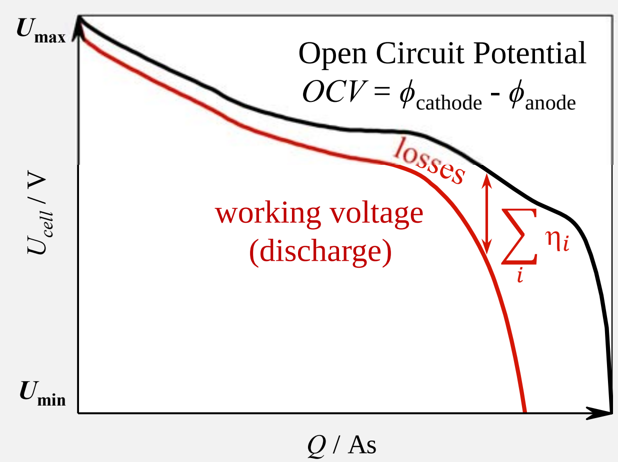


Loss processes

- Transport (Li^+, e^-)
- Charge transfer (Li^+)
- Diffusion (Li^0)

overpotential

$$\eta = I_{discharge} \cdot \sum_i R_i$$



The Lithium-Ion Cell

energy- and power density

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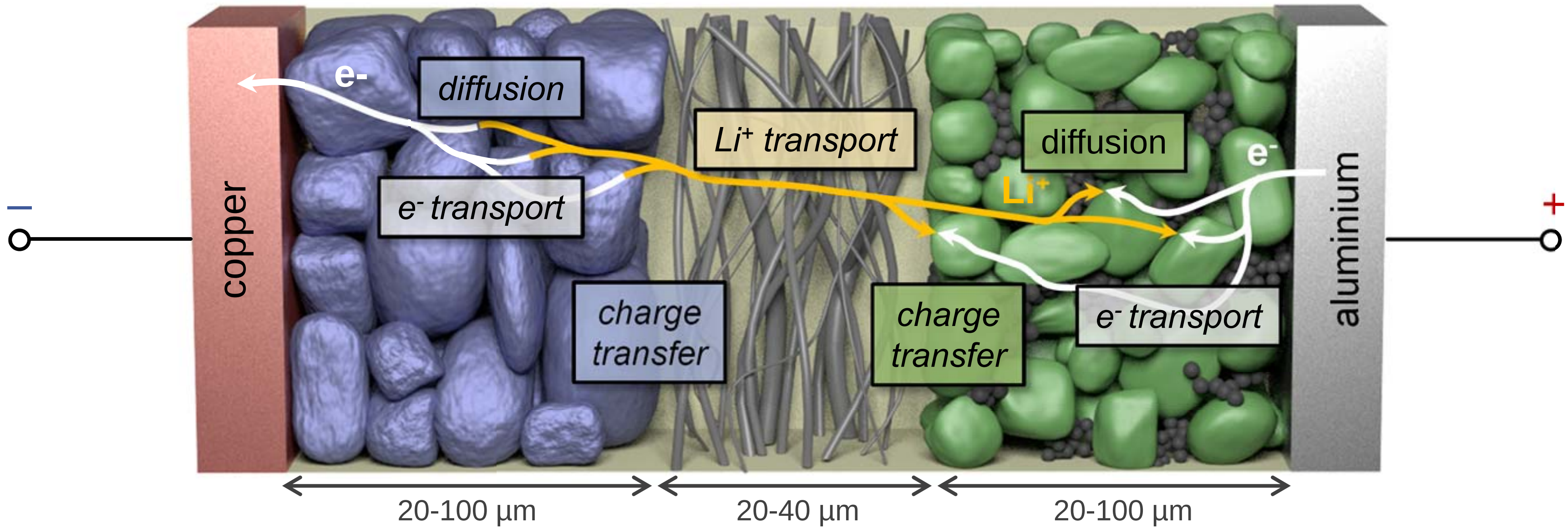
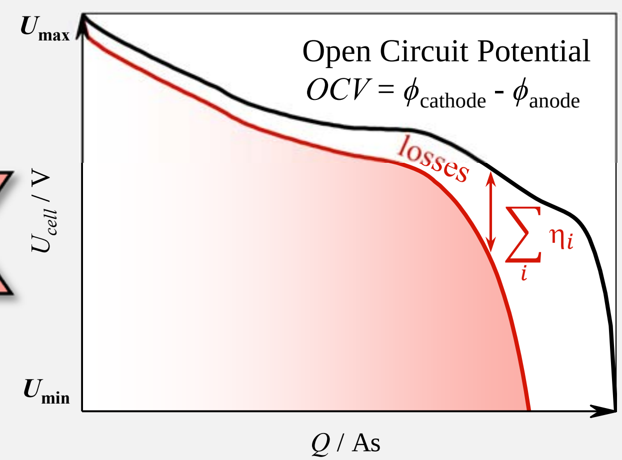


Energy- and Power-density

$$W_{grav} = \frac{energy}{m_{cell}} = \frac{\int OCV - \sum_i R_i \cdot I_{discharge} dQ}{m_{cell}}$$

$$P_{grav} = \frac{energy}{t_{discharge} \cdot m_{cell}} = \frac{\int OCV - \sum_i R_i \cdot I_{discharge} dQ}{t_{discharge} \cdot m_{cell}}$$

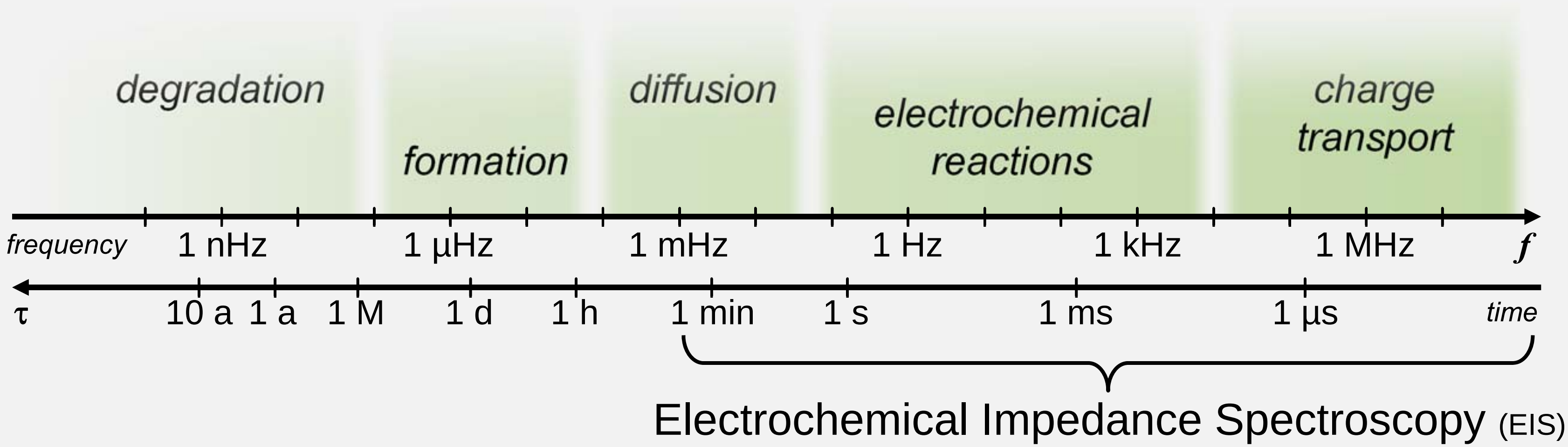
$$energy = \int U \, dQ$$



Characterization of Lithium-Ion Cells

Electrochemical Impedance Spectroscopy (EIS)

Characteristic time constants of different loss mechanisms in Lithium-ion cells:



Characterization of Lithium-Ion Cells

Electrochemical Impedance Spectroscopy (EIS)

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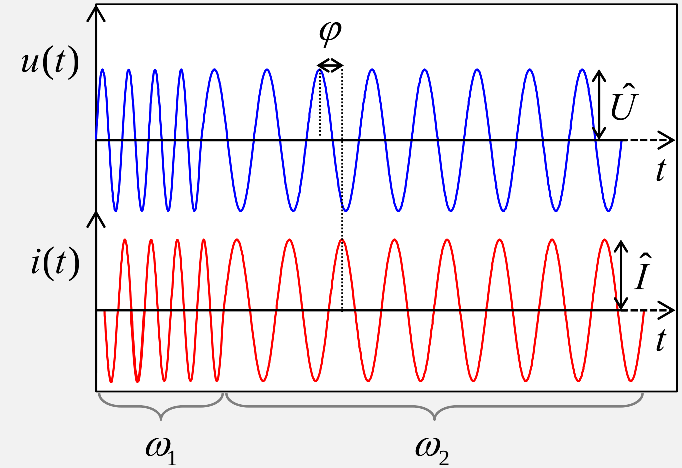
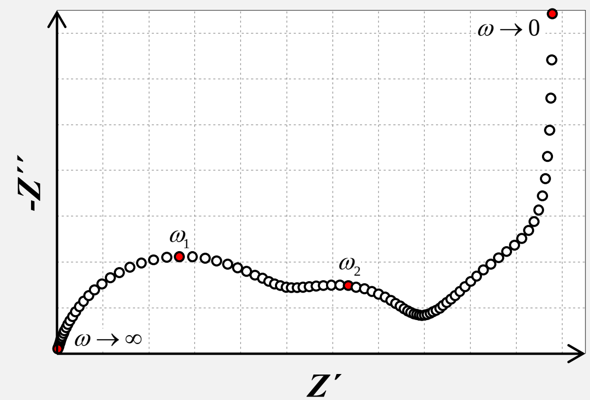
AC Small Signal Perturbation:



Frequency Response Analyzer:

$$Z(\omega) = \frac{\hat{U}(\omega)}{\hat{I}(\omega)} \cdot e^{j\varphi(\omega)} = Z'(\omega) + jZ''(\omega)$$

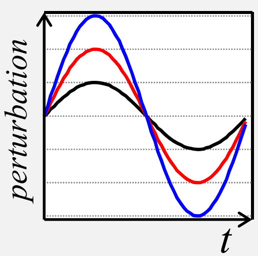
Nyquist Plot:



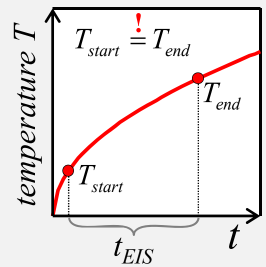
synthetic battery-like spectrum

System Requirements:

causality



linearity



time invariance

Kramers-Kronig Validity Test:

$$Z_{\mathrm{Re}}(\omega) = \frac{2}{\pi} \cdot \int_0^\infty \frac{\omega' \cdot Z_{\mathrm{Im}}(\omega')}{\omega^2 - \omega'^2}\, d\omega'$$

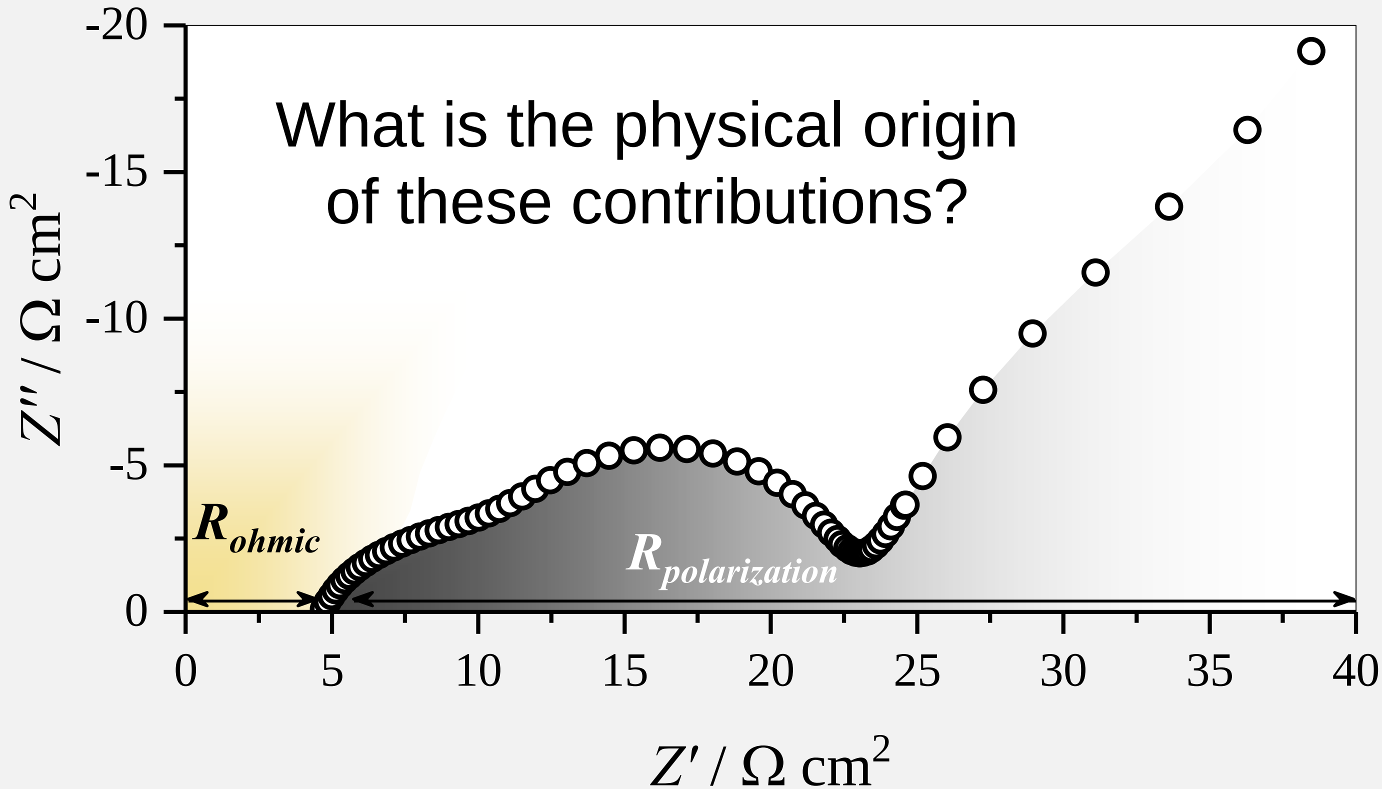
$$Z_{\mathrm{Im}}(\omega) = -\frac{2}{\pi} \cdot \int_0^\infty \frac{\omega \cdot Z_{\mathrm{Im}}(\omega')}{\omega^2 - \omega'^2}\, d\omega'$$

M. Schönleber, D. Klotz, and E. Ivers-Tiffée, “A Method for Improving the Robustness of linear Kramers-Kronig Validity Tests,” Electrochim. Acta, vol. 131, pp. 20–27, 2014.

Characterization of Lithium-Ion Cells

Electrochemical Impedance Spectroscopy (EIS)

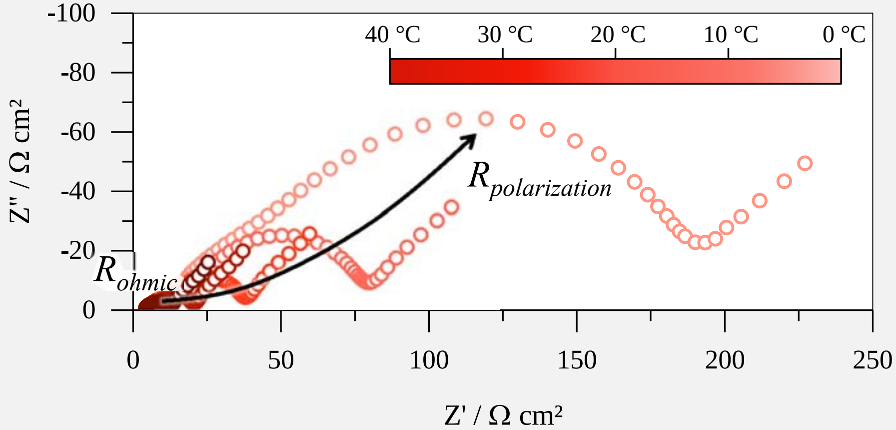
Impedance Analysis:



Characterization of Lithium-Ion Cells

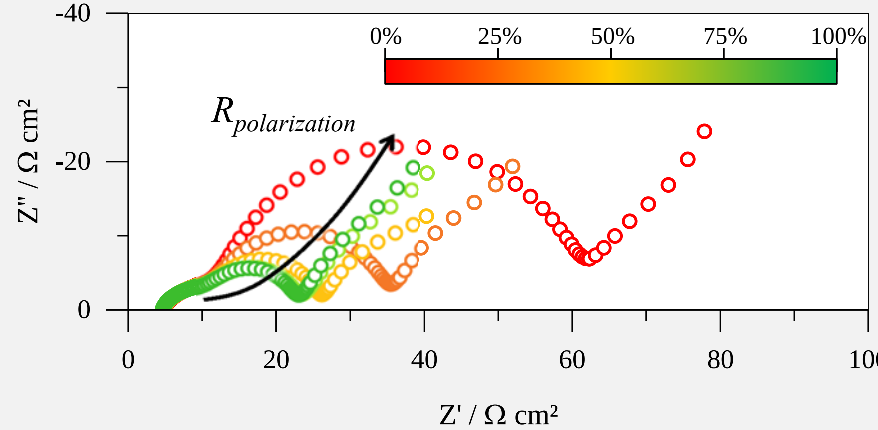
Electrochemical Impedance Spectroscopy (EIS)

Temperature variation at SoC 80 %:



→ *Strong dependency of R_{ohmic} and $R_{polarization}$ on temperature*

State-of-charge (SoC) variation at 25 °C:



→ *Strong dependency of $R_{polarization}$ on SoC*

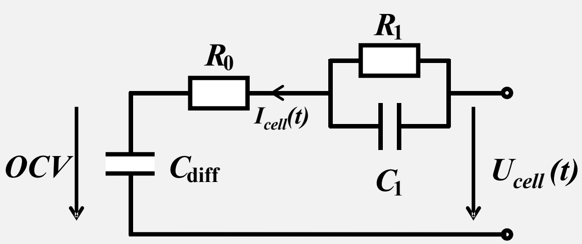
→ How to predict the performance of lithium-ion cells?

Modelling of Lithium-Ion Cells

Behavior Model

"Simple" Equivalent Circuit Model:

- *no physical meaning*
+ *simple parameterization*
+ *very short computation time*



"Advanced" Equivalent Circuit Model

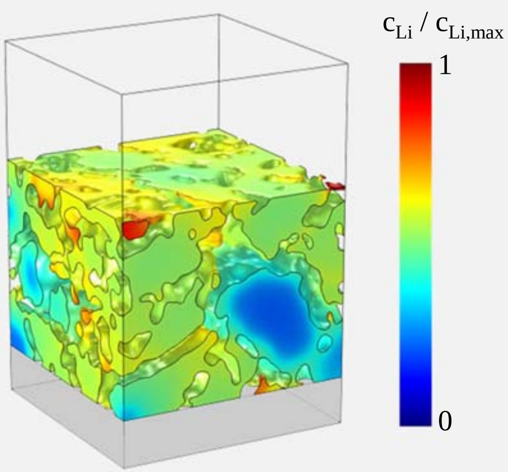
Transmission Line Models:

+ *physically motivated*
+ *feasible parameterization*
+ *short computation time*

Multiphysics Model

Finite Element Method:

+ *physically correct*
- *challenging parameterization*
- *long computation time*



Modeling of Lithium-Ion Cells

Transmission Line Model (TLM)

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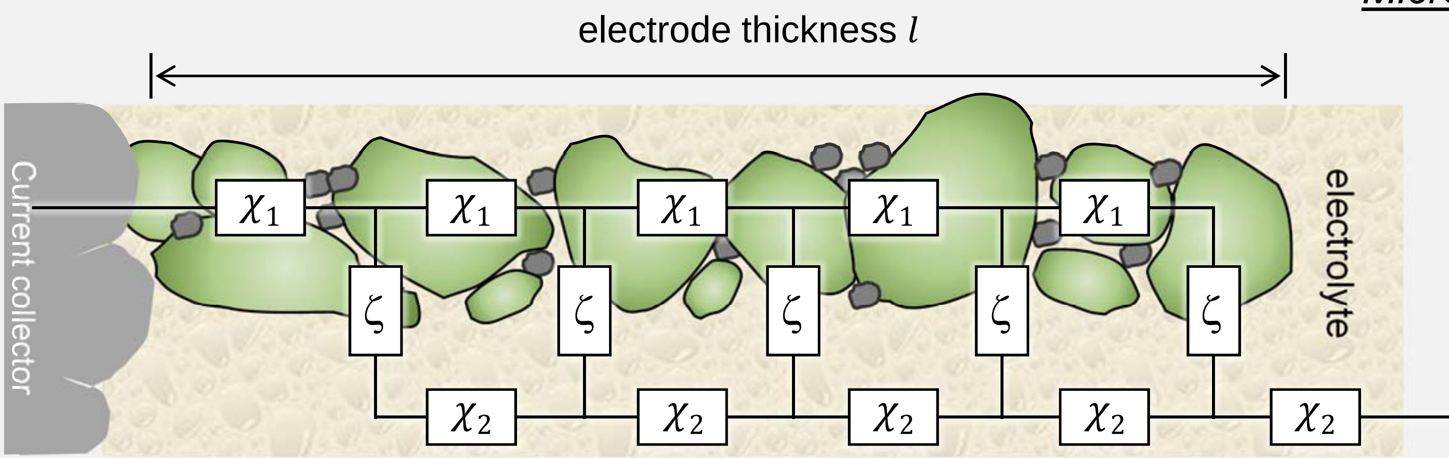


Microstructure parameters:

- *Volume fractions*
- *Tortuosity*
- *Active Surface Area*
- *Particle Size*
- *Diffusion Length*

ionic path

$$\chi_2 = \frac{1}{\sigma_{ion}} \cdot \frac{\tau}{\varepsilon} \cdot \frac{1}{A}$$

τ *tortuosity (pore)*

ε *volume fraction of pores*

A *electrode area*

charge transfer

$$Z_{CT} = \frac{\rho_{CT}}{V \cdot a_{AM}} \cdot l$$

ρ_{CT} *specific charge transfer resistance*

a_{AM} *active surface area per unit volume*

V *electrode volume*

solid-state diffusion

$$\lambda = \frac{j \cdot \omega \cdot l_{Diff}^{2}}{D_{Diff}} \qquad Z_{Diff} = \frac{1}{C_0} \cdot \frac{l_{Diff}}{D_{diff}} \cdot \frac{I_0 \cdot \sqrt{\lambda}}{\sqrt{\lambda} \cdot I_1 \cdot \sqrt{\lambda}}$$

Finite-Space Warburg Impedance

l_{Diff} *diffusion length*

D_{Diff} *diffusion coefficient*

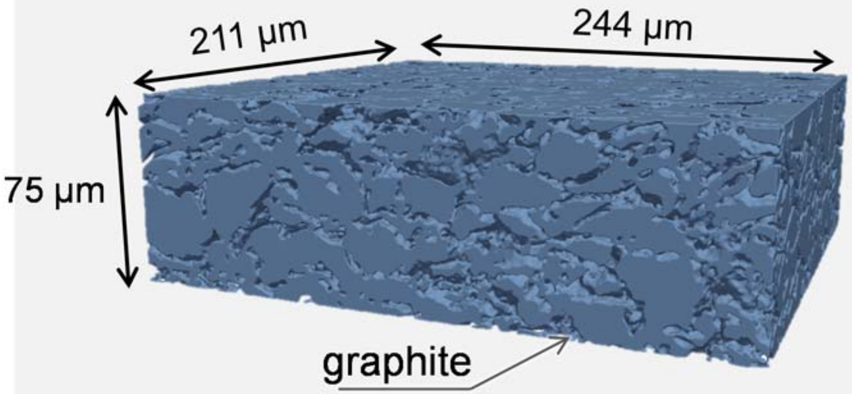
C_0 *differential capacity*

[1] J. Bisquert, G. Garcia-Belmontea, F. Fabregat-Santiagoa, and A. Compteb, “Anomalous transport effects in the impedance of porous film electrodes,” *Electrochemistry Commun.*, vol. 1, no. 9, pp. 429–435, 1999.

Characterization of Lithium-Ion Cells

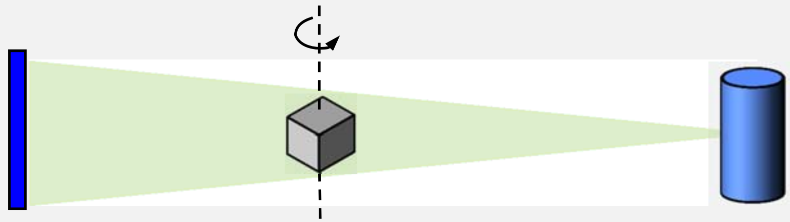
Microstructure: Anode

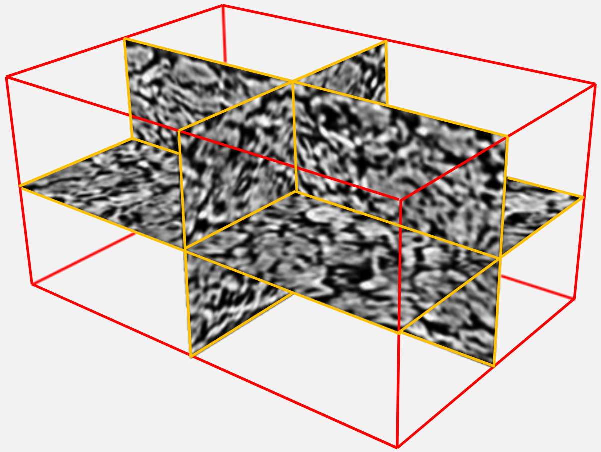
Anode: Graphite



electrode thickness	$l_{electrode}$	$= 90\ \mu m$
volume fraction	$\varepsilon_{graphite}$	$= 0.75$
	ε_{pore}	$= 0.25$
tortuosity	τ_{pore}	$= 5.12$
active surface area	$a_{graphite}$	$= 0.314\ \mu m^{-1}$
particle size	$d_{graphite,vol\text{-}av}$	$= 12.07\ \mu m$

X-ray nano-tomography:



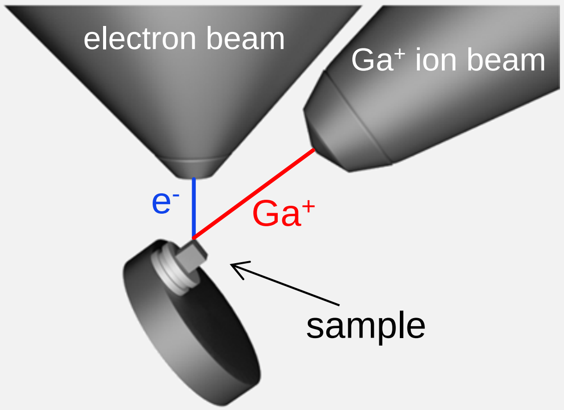


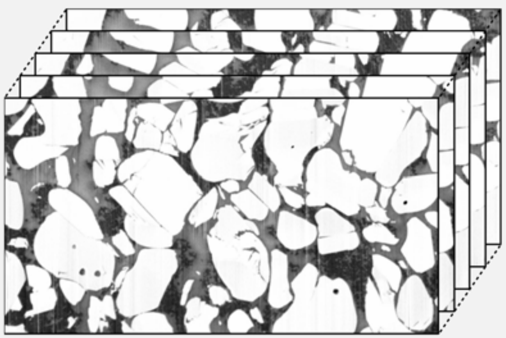
M. Ender, J. Joos, A. Weber, and E. Ivers-Tiffée, *"Anode microstructures from high-energy and high-power lithium-ion cylindrical cells obtained by X-ray nano-tomography," J. Power Sources*, vol. 269, pp. 912–919, 2014.

Characterization of Lithium-Ion Cells

Microstructure: Cathode

Focused ion beam (FIB) tomography:

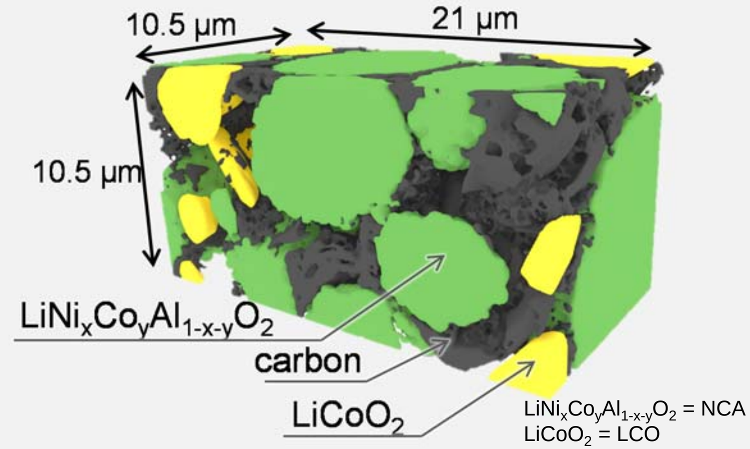




M. Ender, J. Joos, T. Carraro, and E. Ivers-Tiffée, *"Three-dimensional reconstruction of a composite cathode for lithium-ion cells," Electrochem. commun.*, vol. 13, no. 2, pp. 166–168, 2011.

M. Ender, J. Joos, T. Carraro, and E. Ivers-Tiffée, *"Quantitative Characterization of $LiFePO_4$ Cathodes Reconstructed by FIB/SEM Tomography," J. Electrochem. Soc.*, vol. 159, no. 7, pp. A972–A980, Jan. 2012.

Cathode: NCA/LCO Blend

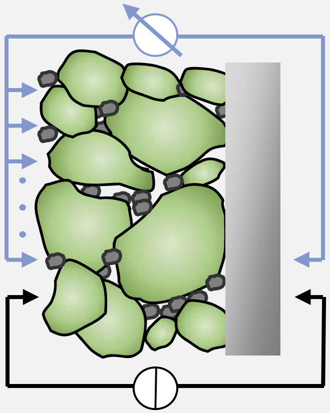


electrode thickness	$l_{electrode}$	= 75 µm
volume fraction	ε_{AM}	= 0.57
	ε_{carbon}	= 0.17
	ε_{pore}	= 0.26
tortuosity	τ_{pore}	= 4.29
active surface area	a_{AM}	= 0.73 µm^{-1}
particle size	$d_{AM,vol\text{-}av}$	= 4.06 µm

Characterization of Lithium-Ion Cells

Parametrization of transition line models

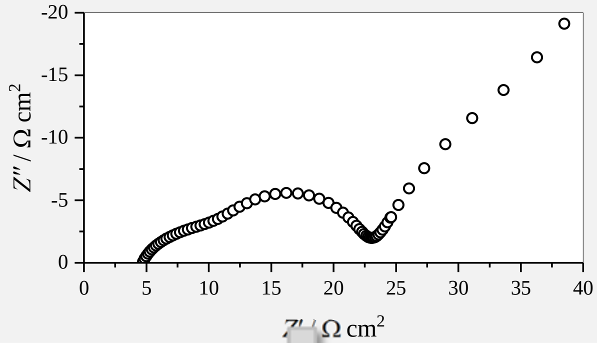
e⁻ conductivity



electronic conductivity σ_{e-}

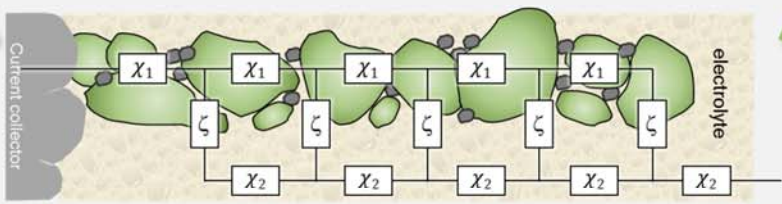
M. Ender, A. Weber, and E. Ivers-Tiffée, "A novel method for measuring the effective conductivity and the contact resistance of porous electrodes for lithium-ion batteries," *Electrochem. commun.*, vol. 34, pp. 130–133, 2013.

impedance measurement

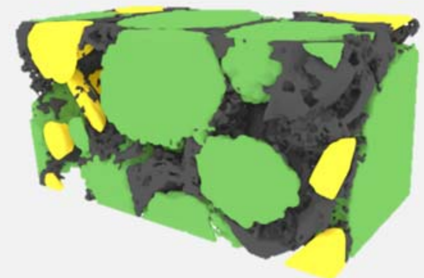


transmission line model (TLM)

σ_{ion} ✓



microstructure



ε volume fractions

τ tortuosity

l electrode thickness

a_V active surface area

ps particle size

M. Ender, J. Joos, T. Carraro, and E. Ivers-Tiffée, "Quantitative Characterization of LiFePO4 Cathodes Reconstructed by FIB/SEM Tomography," J. Electrochem. Soc., vol. 159, no. 7, pp. A972–A980, Jan. 2012.

conclusion

Electrochemical and microstructure parameters for anode and cathode are determined

Li-Ion Battery Model

Homogenized 1D Model

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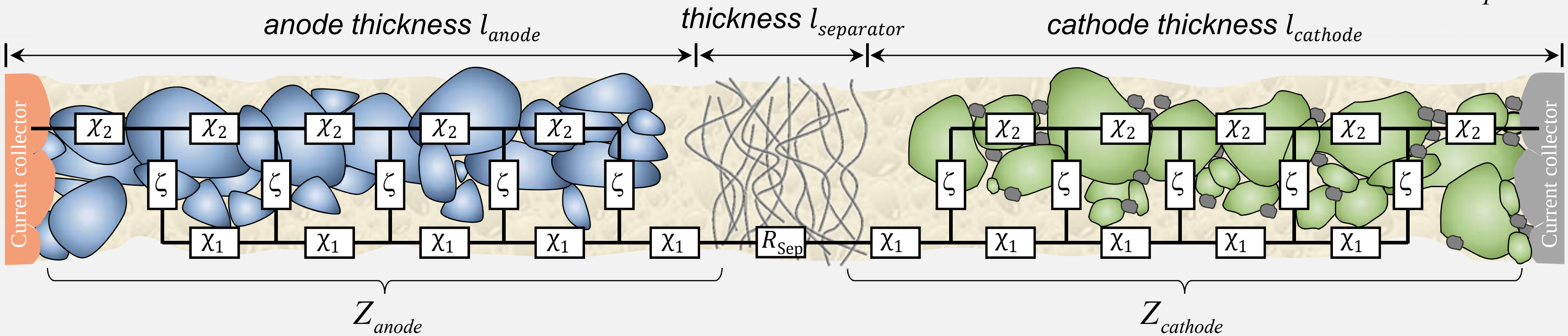
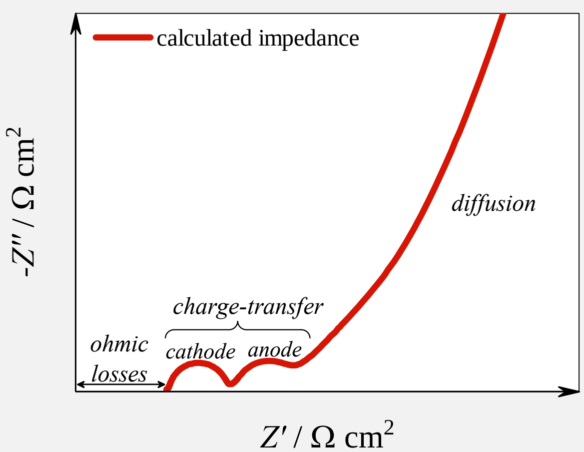
"Advanced" Equivalent Circuit Model:

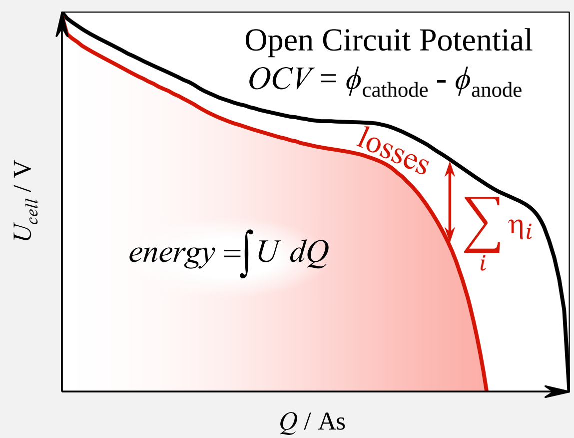
$$Z_{total} = Z_{anode} + R_{Sep} + Z_{cathode}$$



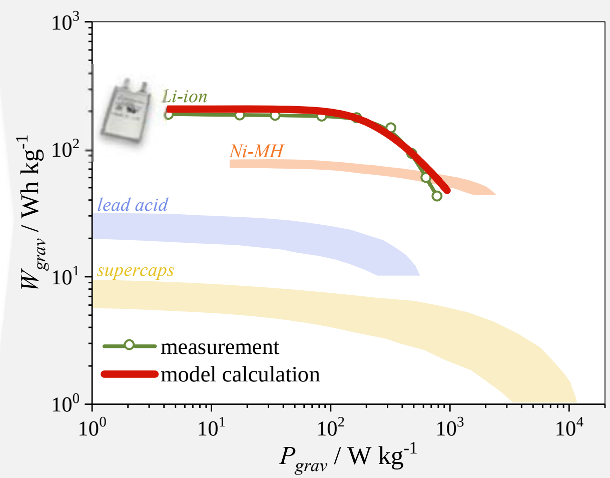
Impedance:



Discharge curve:



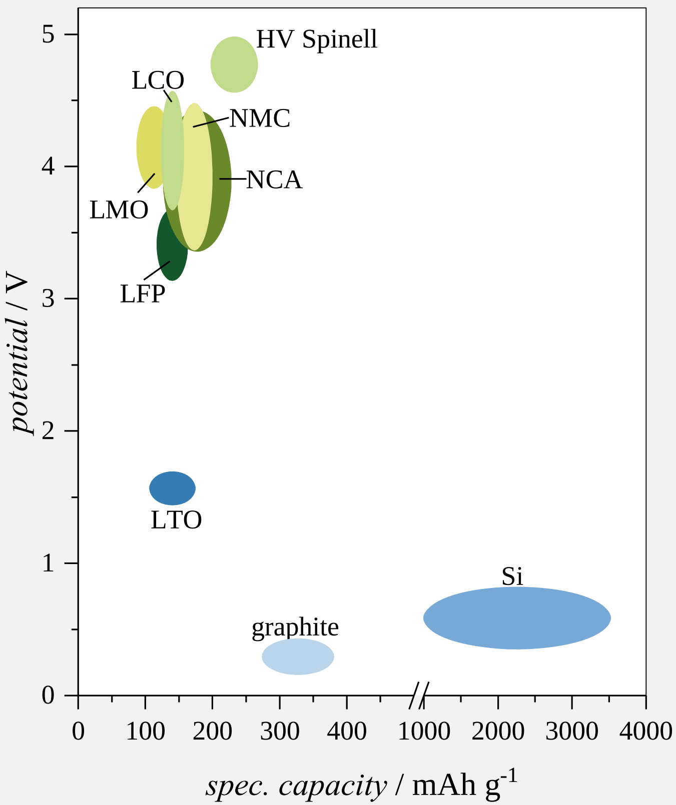
Ragone Plot:



Model-Based Optimization

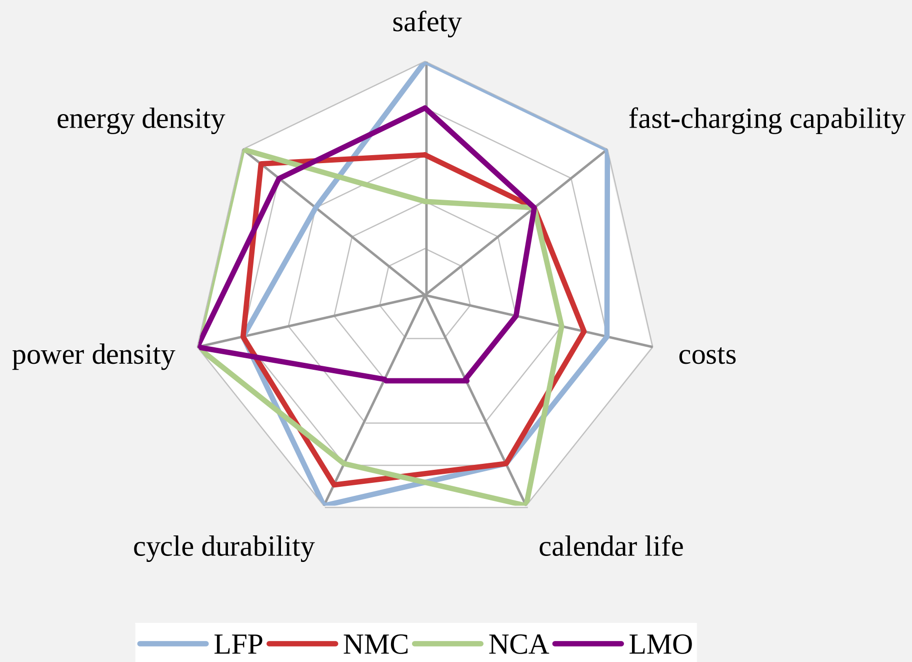
Energy Optimization

$$energy = \int \underbrace{\phi_{cathode} - \phi_{anode}}_{\text{y-axis}} \, \underbrace{dQ}_{\text{x-axis}}$$



Relevant Design Factors

Example: cathode active materials



LFP: $LiFePO_4$
NMC: $LiNi_{1-x-y}Co_xMn_yO_2$
HV Spinell: $0.3Li_2MnO_3\ 0.7LiNi_{0,5}Mn_{1,5}O_4$
NCA: $LiNi_{1-x-y}Co_xAl_yO2$
LMO: $LiMn_2O_4$

Model-Based Optimization

→ change parameters of "state-of-the-art" active materials

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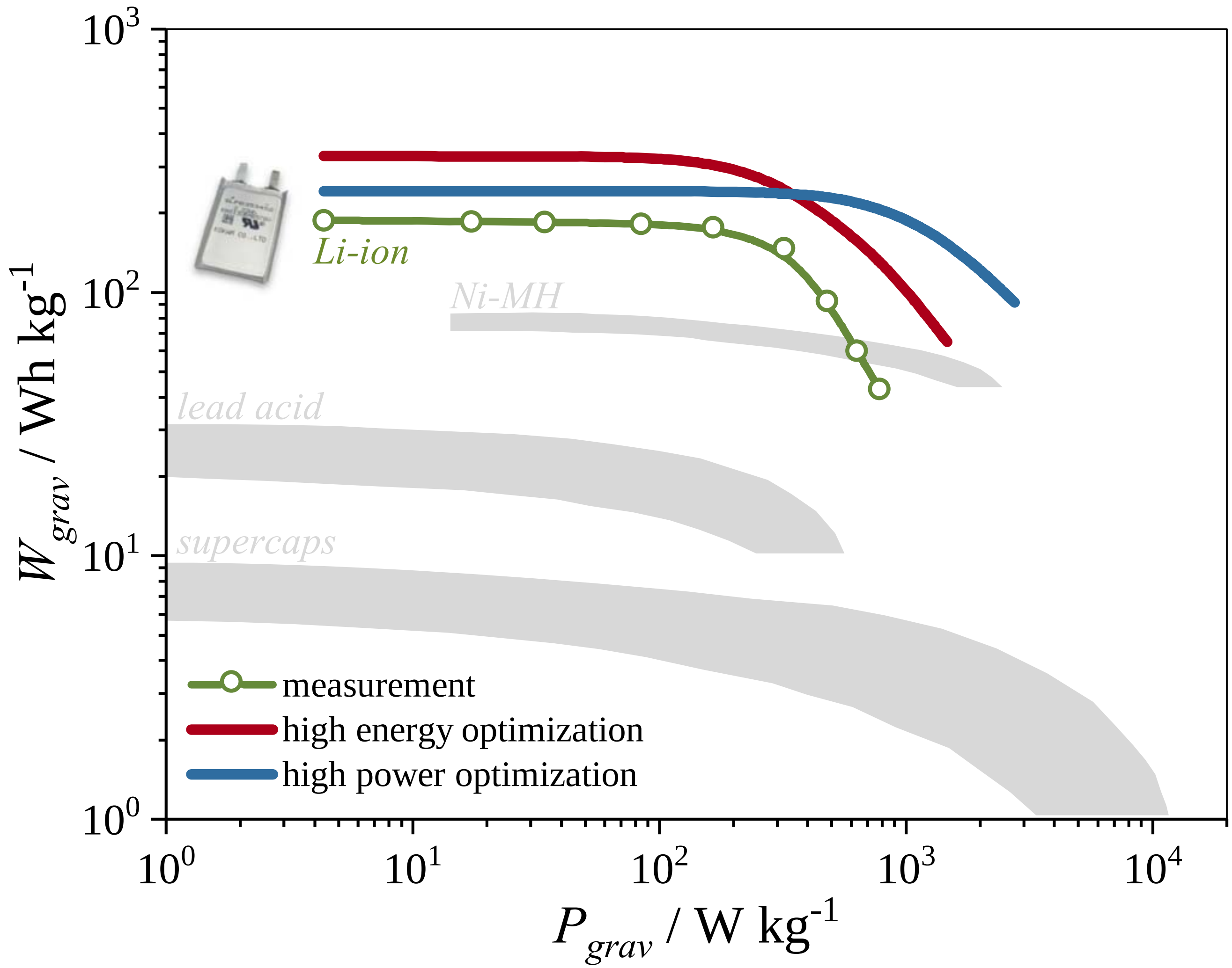
	Anode	*Cathode*	*Passive Components*
High Energy Optimization Increase capacity Reduce mass	*Specific Capacity:* graphite (350 mAh g^{-1}) + 30% graphite + 15% Si (450 mAh g^{-1})	*Specific Capacity:* LCO / NCA (145 mAh g^{-1}) + 40% NMC811 (200 mAh g^{-1}) *Volume Fractions:* *57%* NCA/LCO → *70%* NMC811 + 20%	*current collectors:* l_{cc} = 20 μm - 50% l_{cc} = 10 μm
High Power Optimization Increase surface area Reduce electrode thickness	*Particle Size:* *12.1 μm* → *0.5 μm* - 95% *Thickness:* *90 μm* → *40 μm* - 55%	*Particle Size:* *4.1 μm* → *0.5 μm* - 88% *Thickness:* *75 μm* → *30 μm* - 60%	**+** *all high energy optimization steps*

Model-Based Optimization

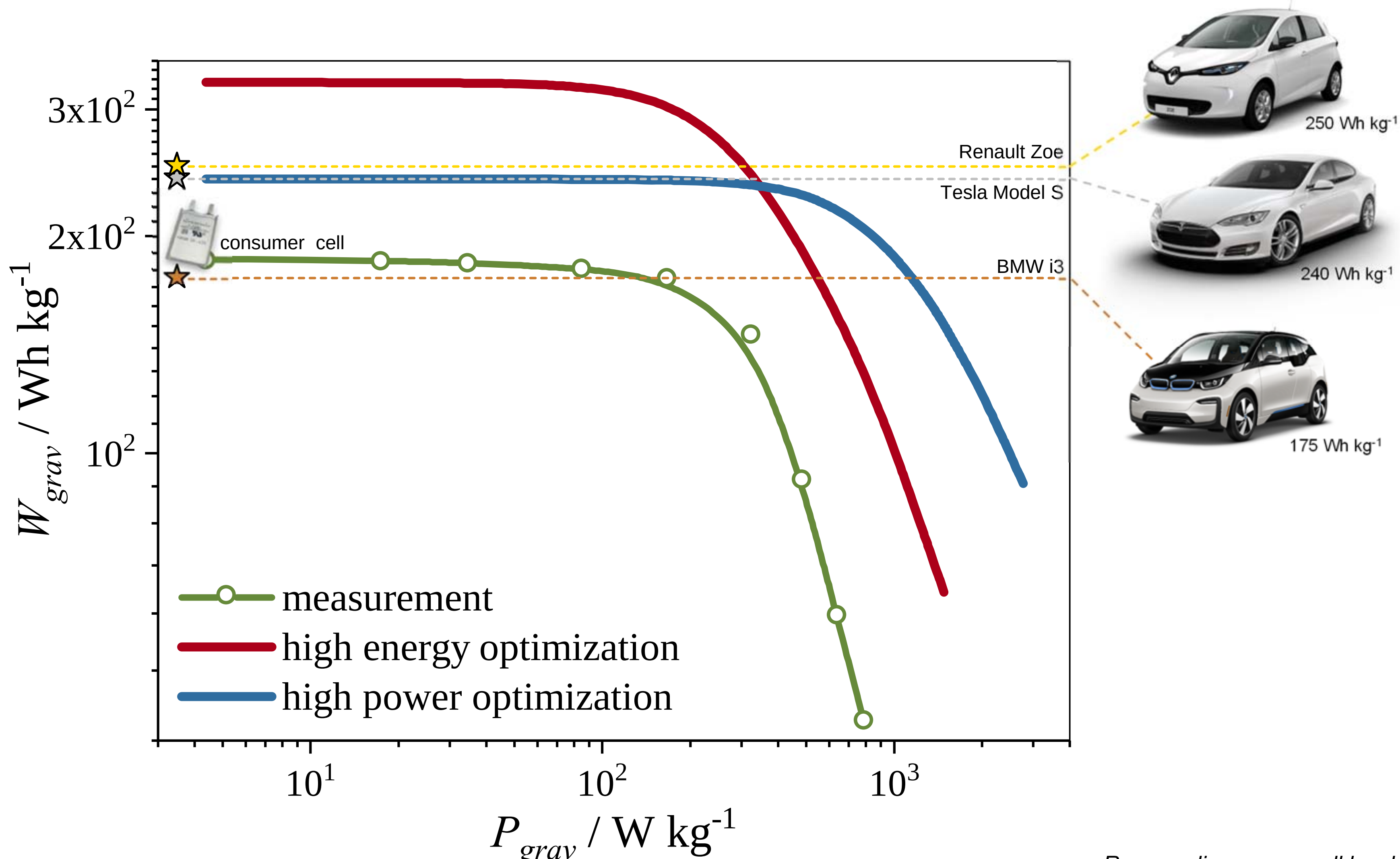
→ change parameters of "state-of-the-art" active materials



Ragone diagram on cell level

Model-Based Optimization

→ change parameters of "state-of-the-art" active materials



Ragone diagram on cell level

State-of-the-arte electric vehicles

comparison from cell to car

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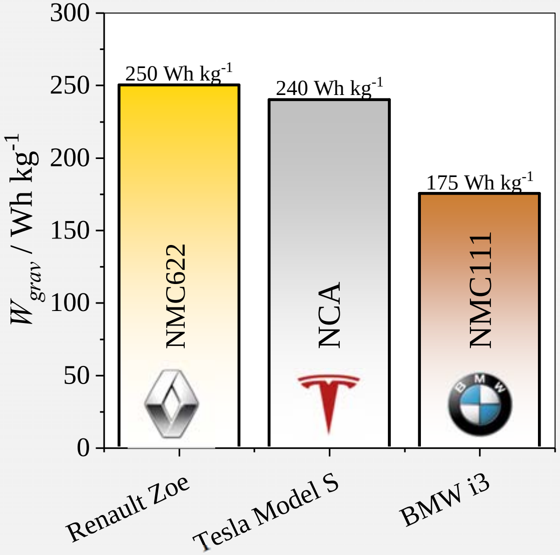
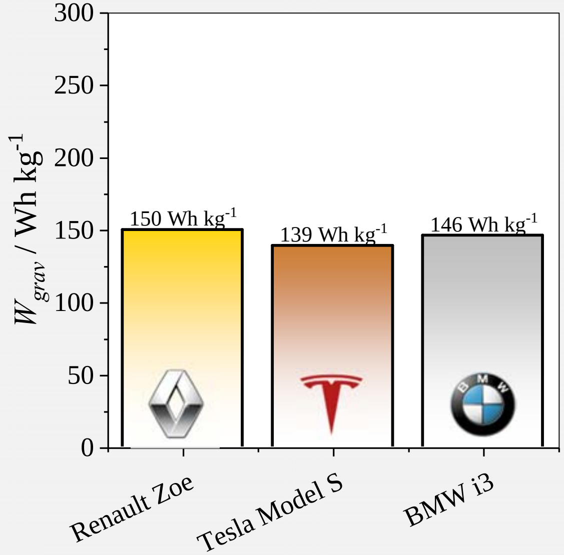
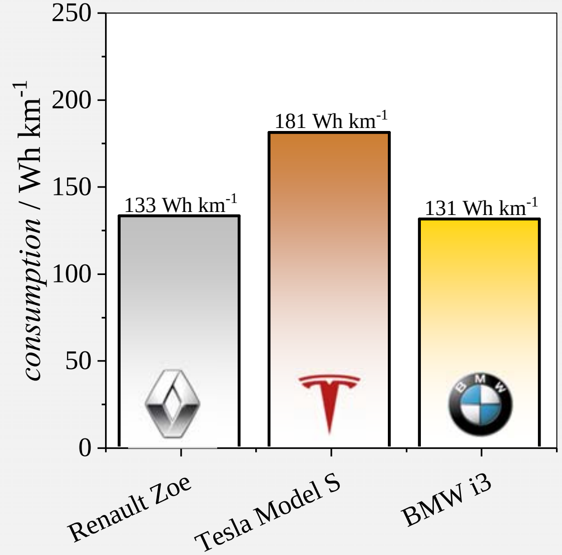
Energy-Density: Cell-Level



Energy-Density: Battery-Level



Consumption



192 pouch cells

7104 cylindrical cells

96 prismatic cells

Electric Range Prediction

Thank you very much for your kind attention!

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Bundesministerium
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BMW

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