Simulation elektrochemisch-thermisch-mechanischer Vorgänge in Lithium-Ionen-Batterien

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Gekürzte Version

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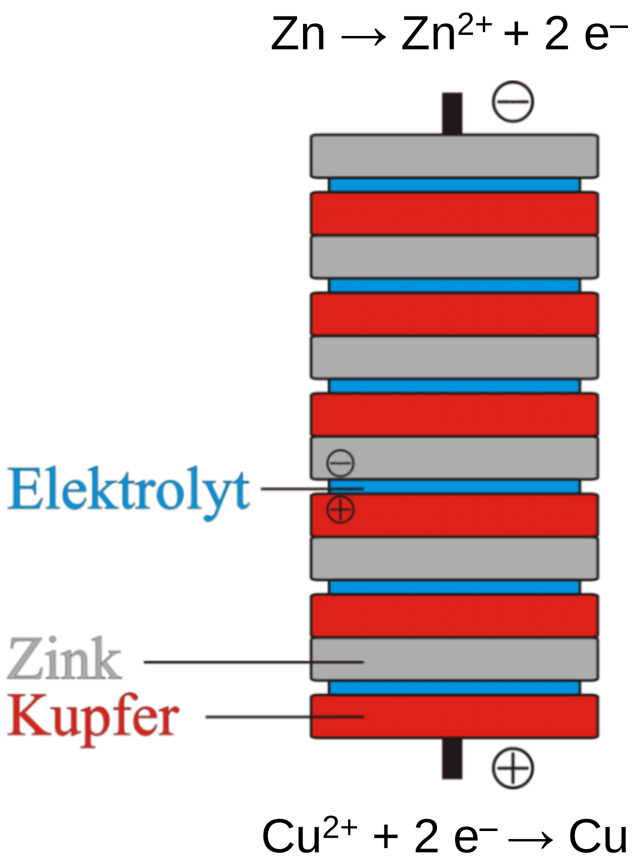
offenburg.university

1. **Einleitung**
2. Lebensdauervorhersage von Lithium-Ionen-Zellen


19.04.2018
Foto: W. Bessler

Foto: W. Bessler

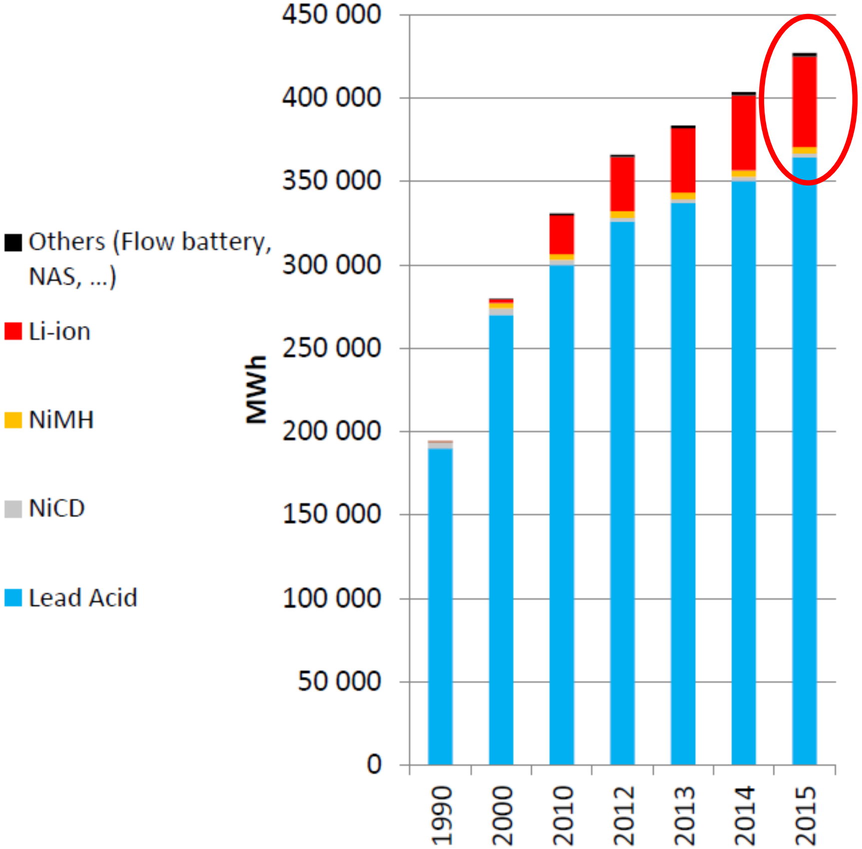
Voltasche Säule 1799



https://de.wikipedia.org/wiki/Voltasche_Säule, downloaded 07.10.2015. Fotos: W. Bessler

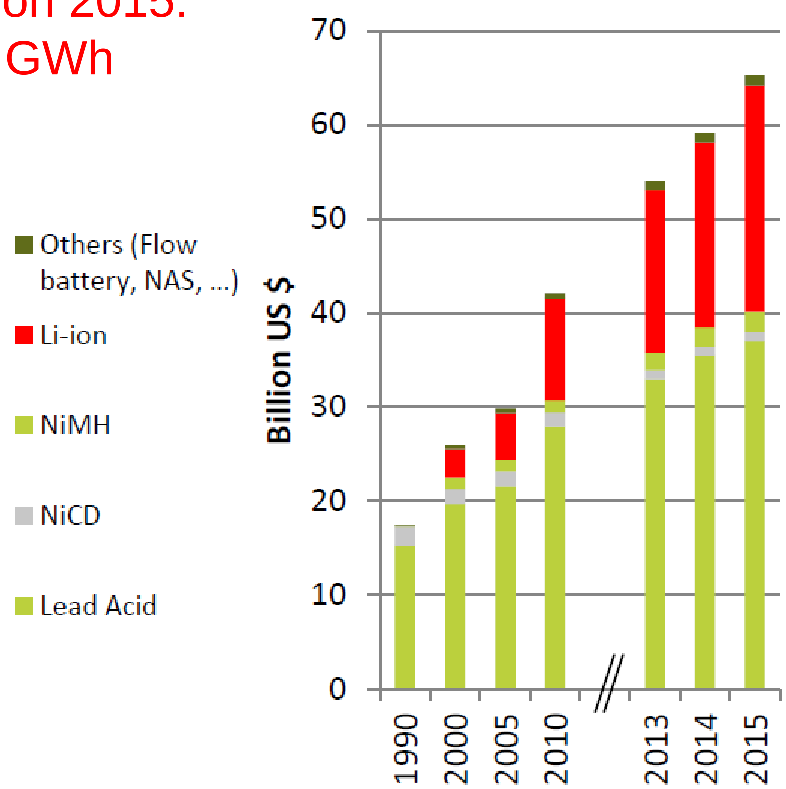
Globaler Batteriemarkt

Produzierte Speicherkapazität



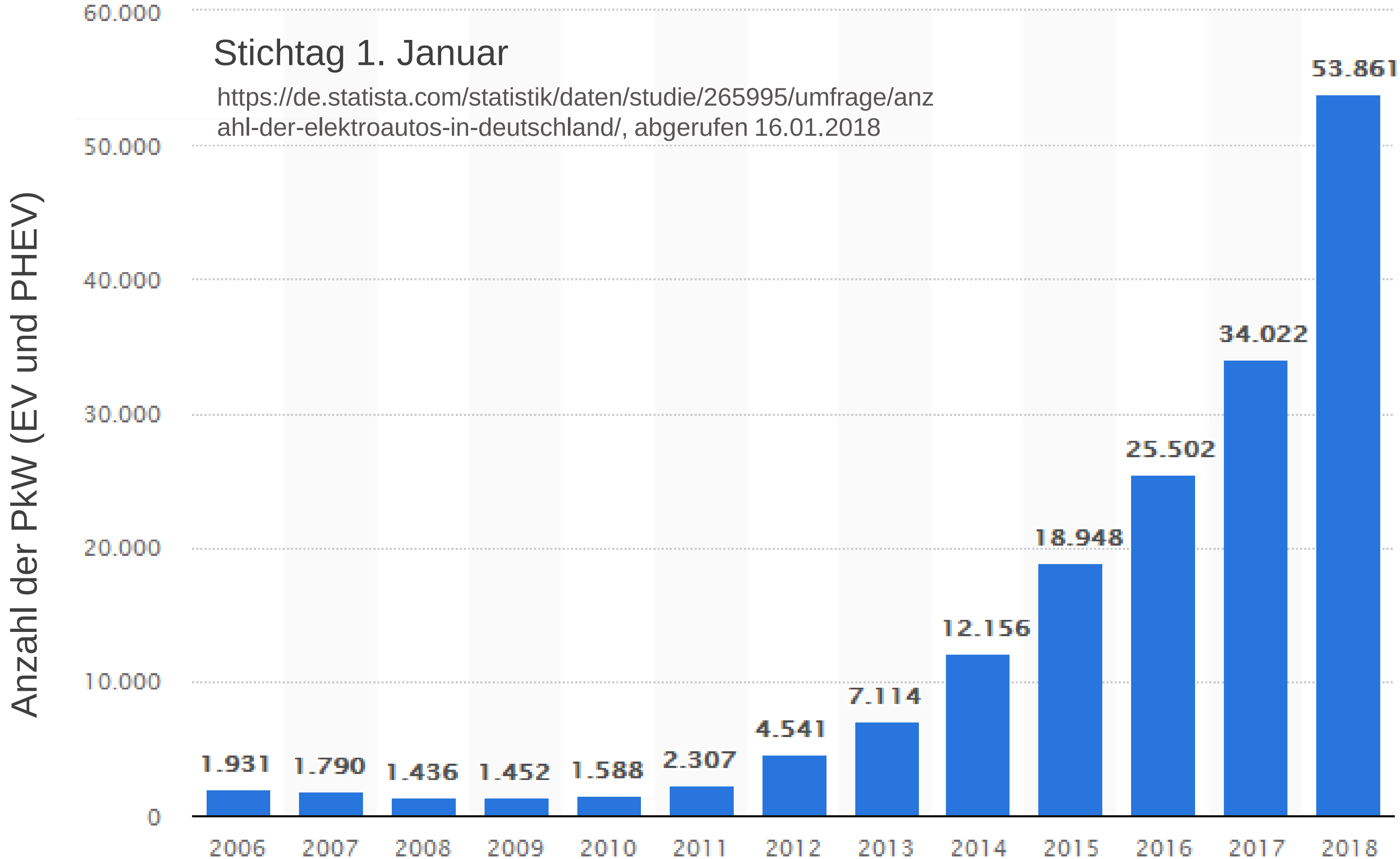
Li-ion 2015:
56 GWh

Umsatz



C. Pillot, Avicenne Energy, Future trends in the rechargeable battery market, ICBR 2015.

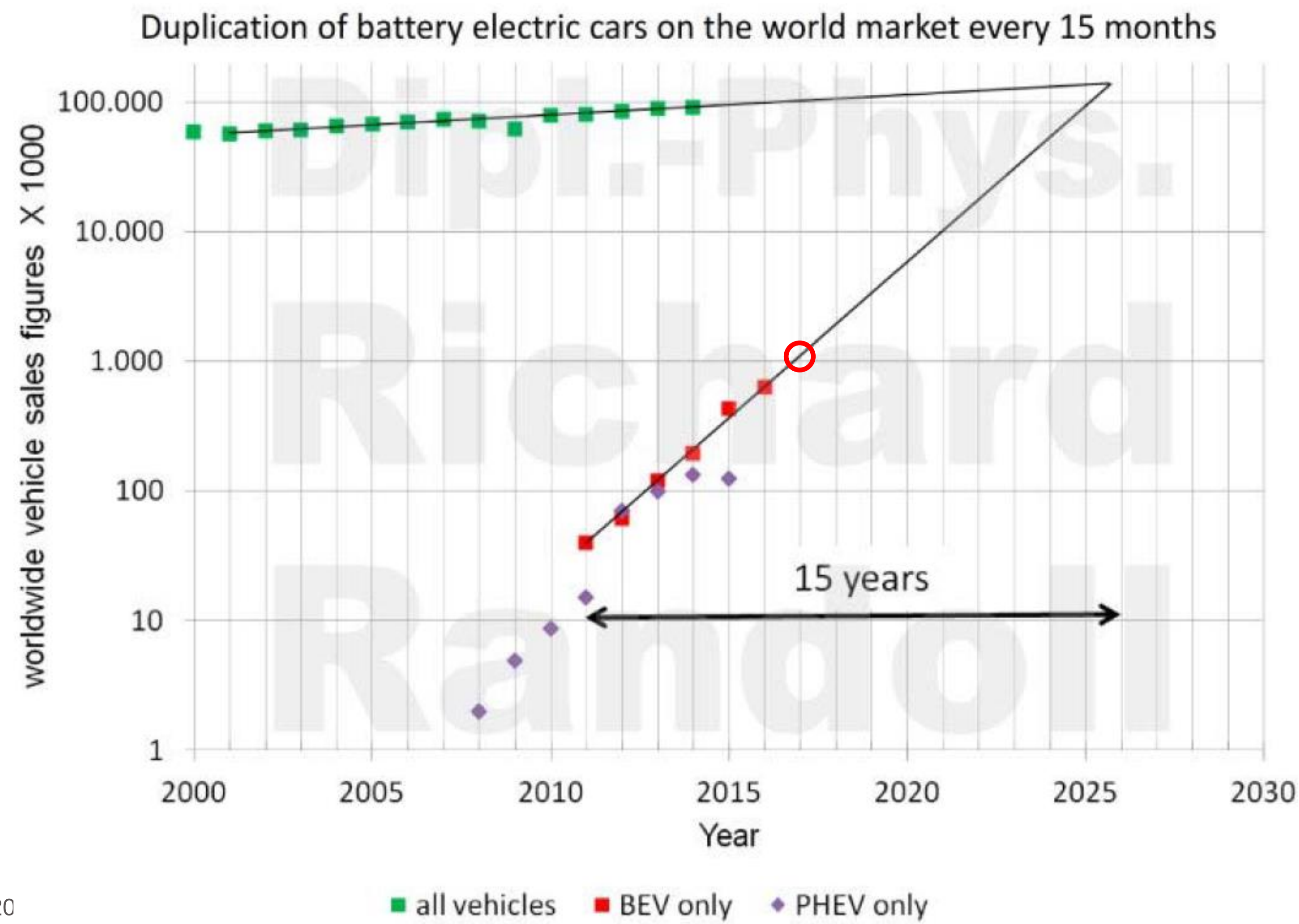
Elektrofahrzeuge in Deutschland



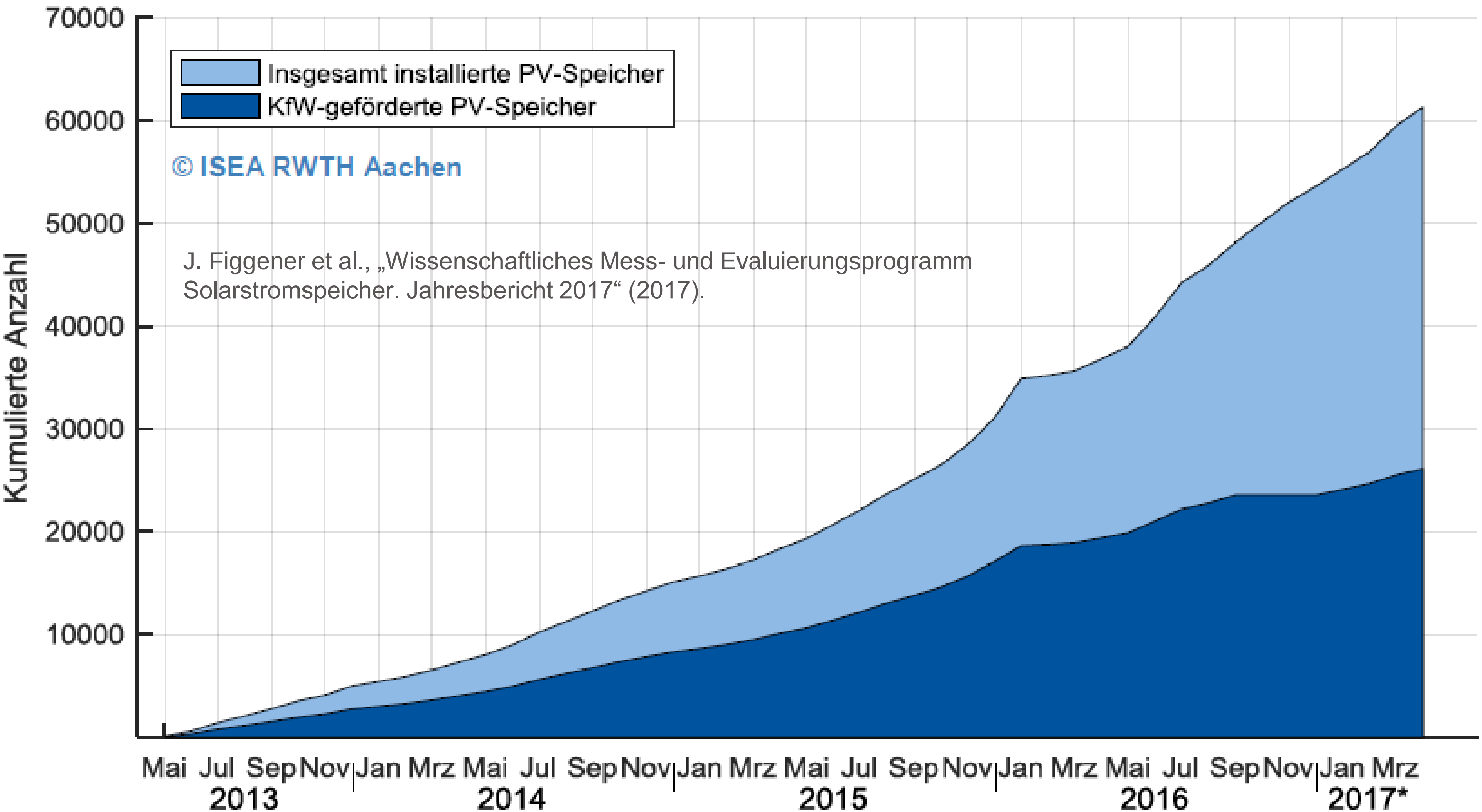
Zukunft des Autos

"2026 kommt das Aus für den Verbrennungsmotor"

Das E-Auto wird sich durchsetzen - davon sind fast alle in Politik und Wirtschaft überzeugt. Nur wann? Ein deutscher Physiker hat berechnet, wann die letzten Benziner und Diesel verschwinden.

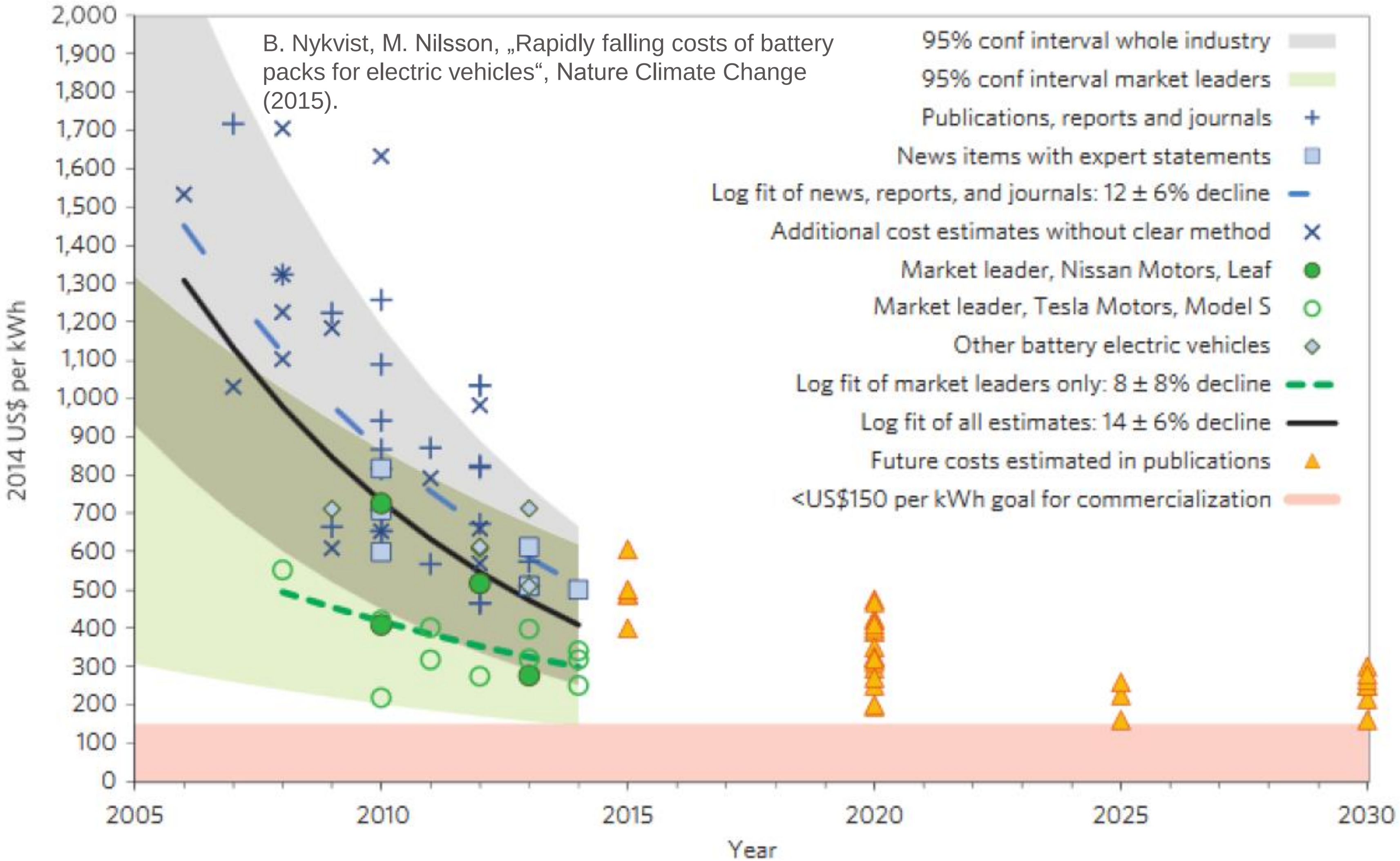


Photovoltaik-Heimspeicher in Deutschland



J. Figgener et al., „Wissenschaftliches Mess- und Evaluierungsprogramm Solarstromspeicher. Jahresbericht 2017“ (2017).

Costs of battery packs for electric vehicles



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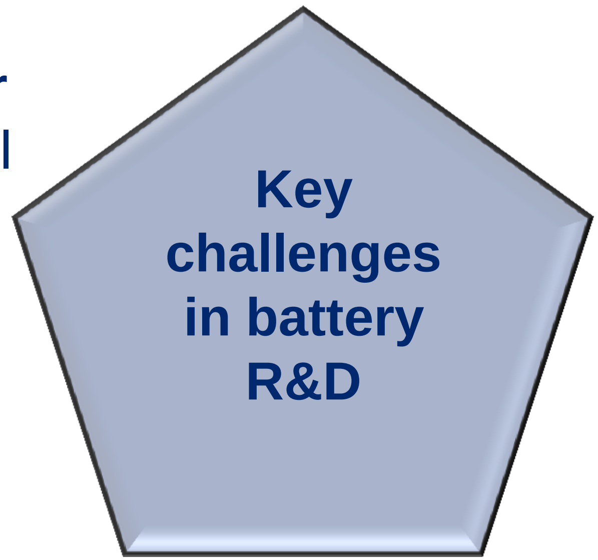
Lithium-ion batteries: Current topics

Lifetime
in years or cycles

Specific power
in kW/kg or kW/l

Safety



Specific energy
in Wh/kg or Wh/l

Cost
in €/kWh

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A battery is a multi-scale system

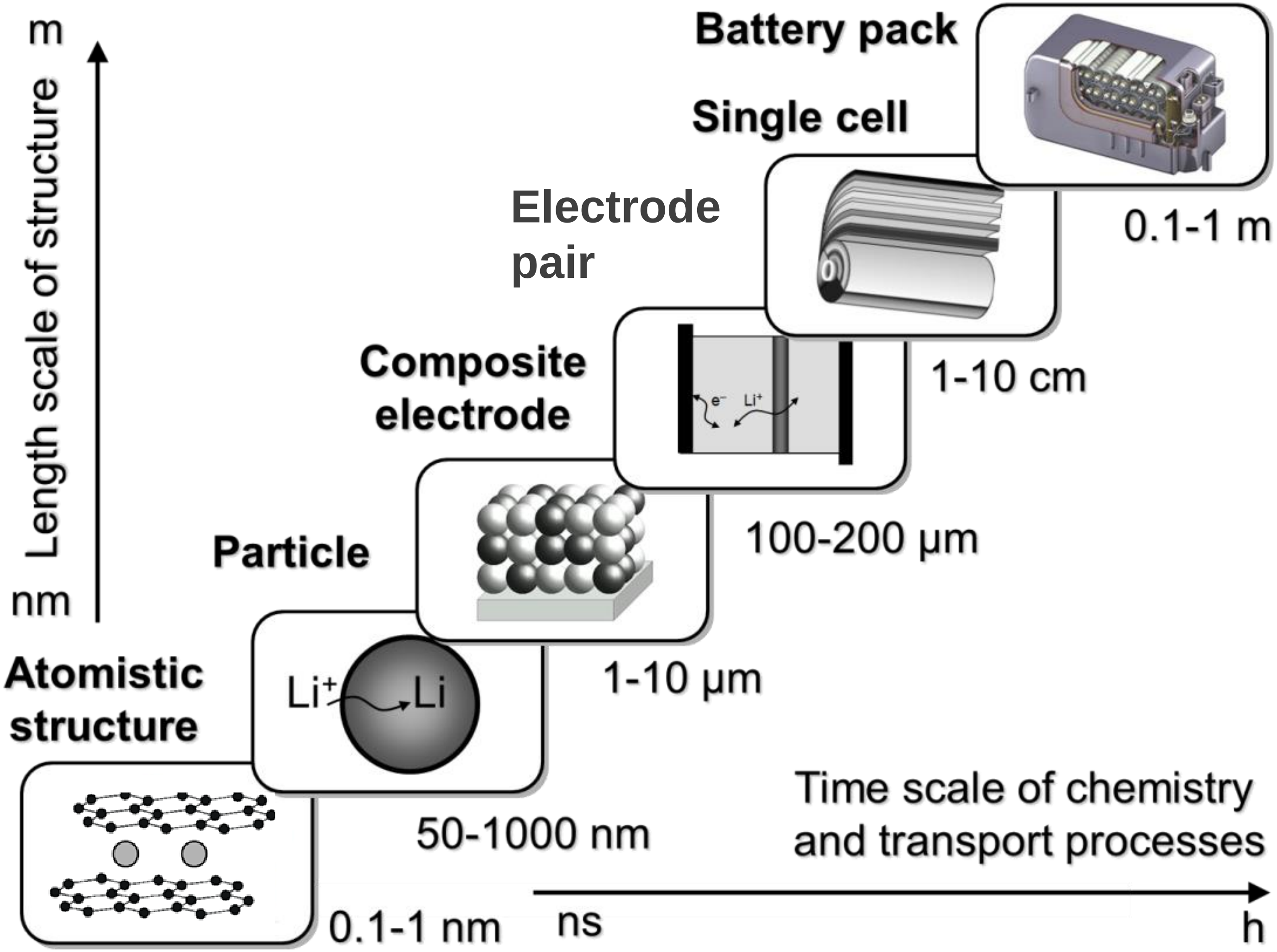
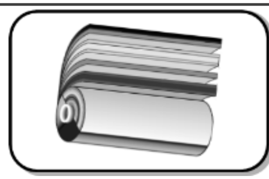
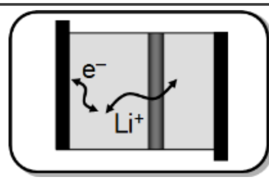
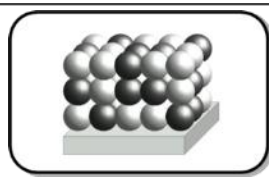
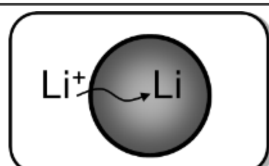
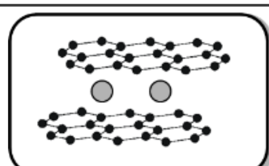


Bild rechts oben: Daimler S400, ATZ 07-08/2009

Modeling opportunities on all scales

Battery pack 0.1-1 m		Thermal & safety management SOC&SOH diagnostics Battery management	CFD modeling Equivalent circuits Control theory
Single cell 1-10 cm		Thermal & safety management SOC&SOH diagnostics Cell design	CFD modeling Equivalent circuits Control theory
Electrode pair 100-200 µm		Repeat unit design Mass and charge transport	Multiphysics modeling
Composite electrode 1-10 µm		Electrode design Mass and charge transport	Multiphysics modeling Stochastic methods
Particle 50-1000 nm		Particle design Mechanical stability Mass transport	Phase-field modeling Mechanical modeling
Atomistic structure 0.1-1 nm		Materials design Interfacial properties	Density-functional theory Molecular dynamics

Forschungsgruppe Elektrische Energiespeicherung

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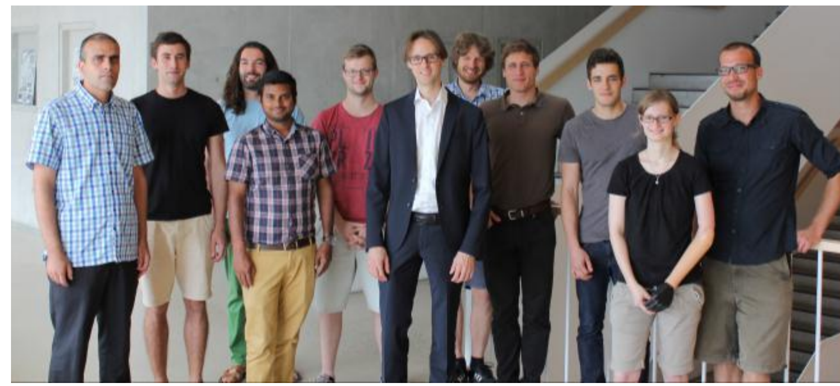
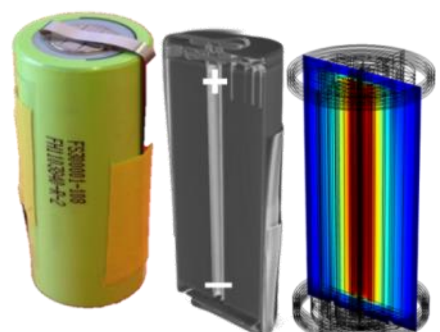
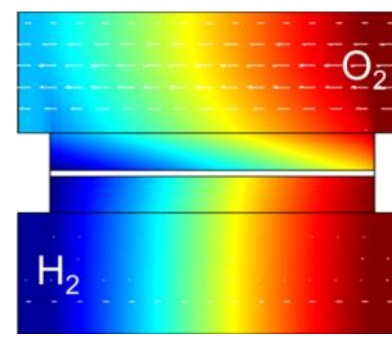
- **Leitung:** Prof. Dr. W. G. Bessler
- **Forschungsschwerpunkte**
  - Computergestützte Batterie- und Brennstoffzellentechnik
  - Lithium-Ionen-Batterien, Metall-Luft-Batterien, Batteriesysteme für Elektromobilität und PV-Speicher
- **Methoden und Kompetenzen**
  - Skalenübergreifende und multiphysikalische Modellierung
  - Experimentelle Zellcharakteri-sierung (*U*, *I*, *T*, EIS)
- **Internet:** www.ees.hs-offenburg.de







Bessler group: Computational methodology

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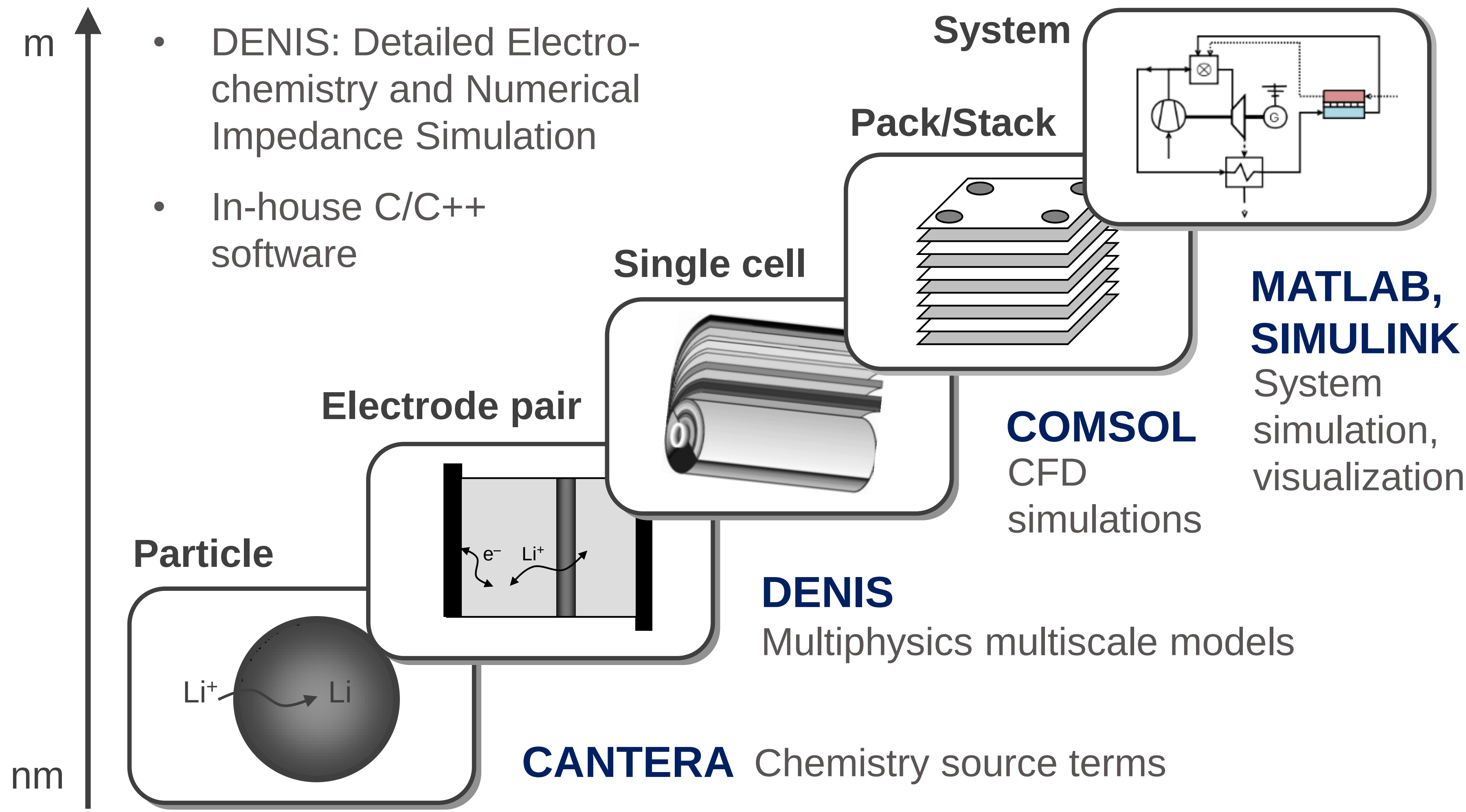
- DENIS: Detailed Electro-chemistry and Numerical Impedance Simulation
- In-house C/C++ software



Bessler group: Running projects

Research topics

- Lithium-ion batteries
  - Ageing mechanisms
  - Safety and thermal runaway
- Fuel cells and metal/air cells
  - Lithium/oxygen cell
  - PEM fuel cell
- System integration
  - Stationary energy storage
  - Electric mobility
- Diagnostics: EIS, EPIS, ETIS

Running projects

- SiMET (DFG GRK 2218, 04/2017-10/2021)
- STABIL (BMBF, 01/2016-12/2018)
- LiBaLu (BMBF, 01/2016-12/2018)
- DENE (Land Baden-Württemberg, 11/2014-10/2017)
- EPISTEL (DFG, 03/2018-02/2021)
- Master and bachelor projects

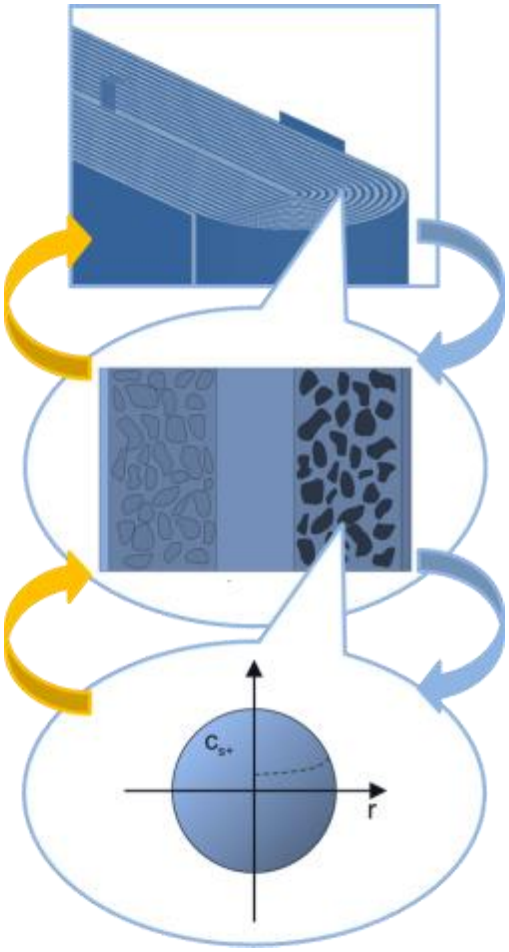
DFG-Graduiertenkolleg

SiMET

Simulation mechanisch-elektrisch-thermischer Vorgänge in Lithium-Ionen-Batterien

01.04.2017-30.09.2021

www.simet.kit.edu



„We use *quantitative* models in order to make *qualitative* predictions“

David G. Goodwin (1957-2012), California Institute of Technology

1. Einleitung
2. **Lebensdauervorhersage von Lithium-Ionen-Zellen**

Strong nonlinearity of cell ageing

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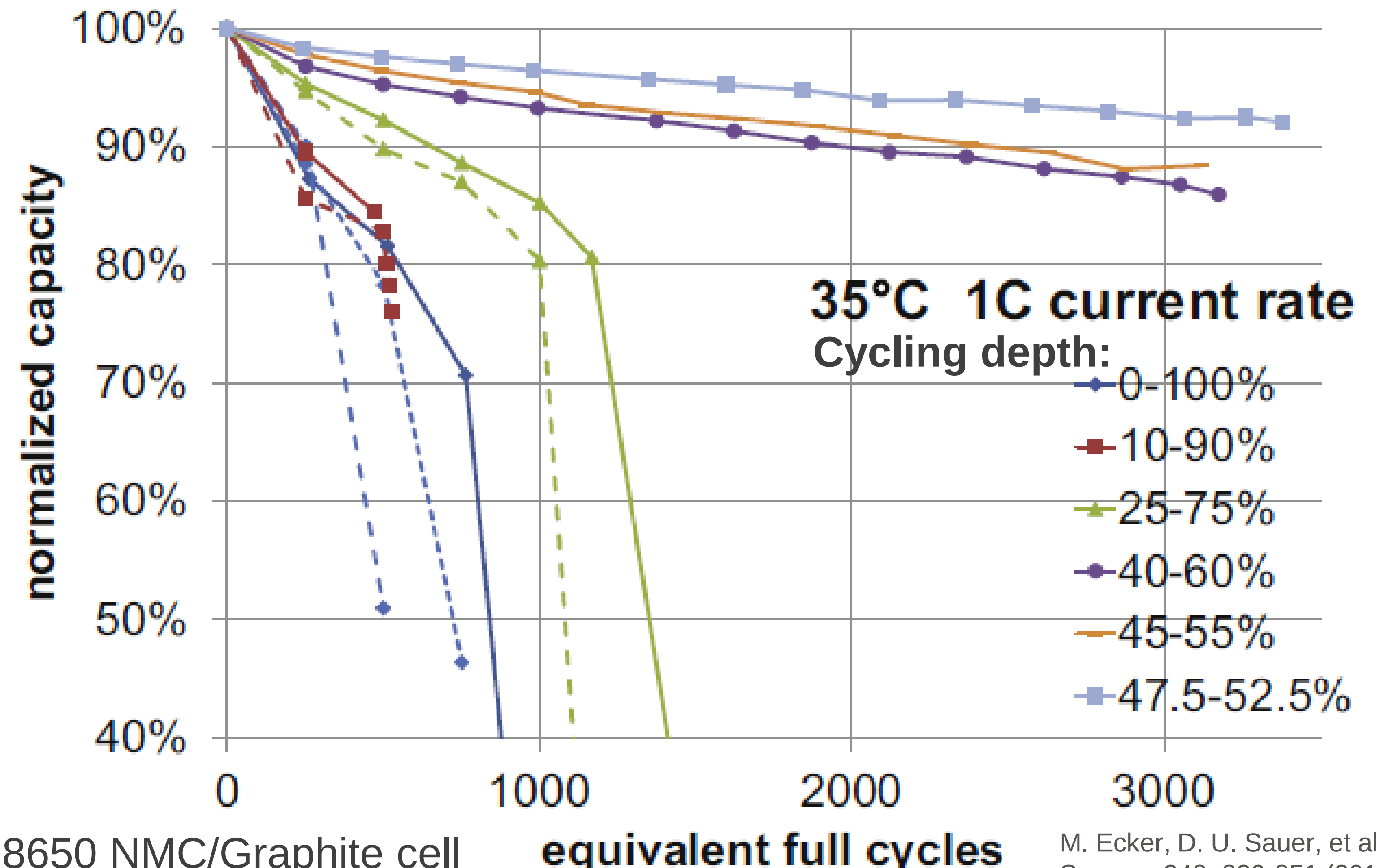

18650 NMC/Graphite cell

M. Ecker, D. U. Sauer, et al., J. Power Sources 248, 839-851 (2014).

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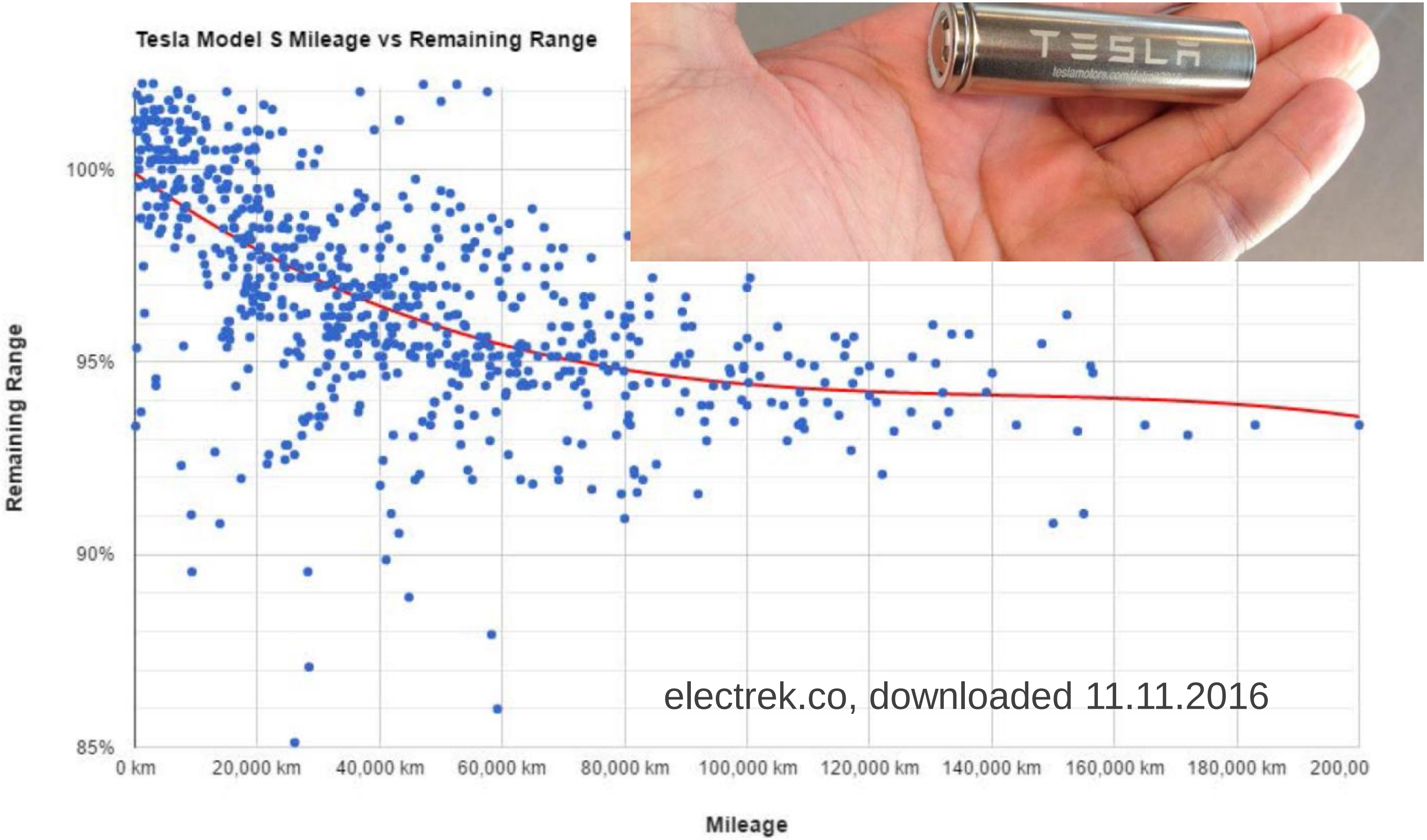
Strong nonlinearity of cell ageing



electrek.co, downloaded 11.11.2016

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Investigated graphite/LFP cylindrical cell

- 26650 type cylindrical cell (A123)
  - 2.6 cm Ø, 6.5 cm height
- 3.3 V, 2.3 Ah, 108 Wh/kg
  30 C discharge capability
- Anode: Graphite, LiC_6
- Cathode: Lithium iron phosphate, $LiFePO_4$ (LFP)

Computer tomography by D. Kohler, HS Offenburg

1D+1D+1D = Pseudo 3D (P3D) tansport model

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- Cylindrical or pouch cells
- 1 cm scale: Heat transport

$$\rho c_\mathrm{p} \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) + \dot{q}^\mathrm{V}$$

- 100 µm scale: Mass and charge transport in electrolyte

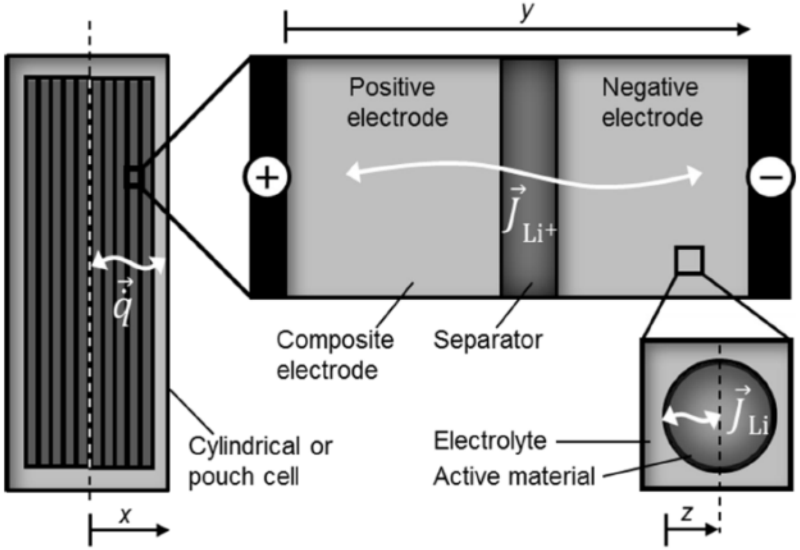
$$\frac{\partial(\varepsilon c_\mathrm{i})}{\partial t} = \frac{\partial}{\partial y}\left(D_i \frac{\partial c_\mathrm{i}}{\partial y}\right) + \frac{z_i F}{RT}\frac{\partial}{\partial y}\left(D_i c_i \frac{\partial \phi}{\partial y}\right) + \dot{s}_i^{\,V}$$

$$C_\mathrm{DL}^\mathrm{V} \frac{\partial(\Delta\phi)}{\partial t} = \sum_i z_i F \frac{\partial J_i}{\partial y} - i_F^\mathrm{V}$$

- 1 µm scale: Solid-state Li diffusion in active materials

$$\frac{\partial \rho_\mathrm{Li}}{\partial t} = \frac{1}{z^2}\frac{\partial}{\partial r}\left(z^2 D(c_\mathrm{Li}) \frac{\partial \rho_\mathrm{Li}}{\partial z}\right)$$

- In-house code DENIS



C. Kupper and W. G. Bessler, “Multi-Scale Thermo-Electrochemical Modeling of Performance and Aging of a $LiFePO_4$/Graphite Lithium-Ion Cell,” Journal of the Electrochemical Society 164, A304-A320 (2017)

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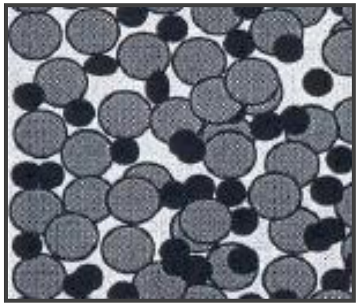
Generalized phase management

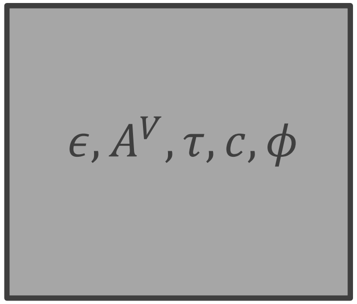
- Multi-phase modeling
  - Solid, liquid and/or gaseous **bulk phases** j
  - **Interfaces** k
- Homogenization
  - Volume fractions ϵ_j, interfacial areas A_k^V
- Continuity for each phase

$$\frac{\partial(\epsilon_j \rho_j)}{\partial t} = \sum_{i,k} A_{ki}^V \dot{s}_i M_i$$

- Volume fractions sum up to one, gas phase is compressible

$$\sum \epsilon_j = 1 \qquad p_{\text{gas}} = \rho_{\text{gas}} RT/\bar{M}_{\text{gas}}$$





J. P. Neidhardt, D. N. Fronczek, T. Jahnke, T. Danner, B. Horstmann, W. G. Bessler, J. Electrochem. Soc. 159, A1528 (2012).

Generalized electrochemistry: Transition state theory

- Electron transfer rate

  $$k_\mathrm{f} = k_\mathrm{f}^0 \cdot \exp\left(-\frac{E_\mathrm{act,f}}{RT}\right) \cdot \exp\left(-\frac{\alpha_\mathrm{f} zF}{RT}\Delta\phi\right)$$

- Reverse rate (thermodynamically consistent)

  $$k_\mathrm{r} = k_\mathrm{f}^0 \cdot \exp\left(-\frac{E_\mathrm{act,f}}{RT}\right) \cdot \exp\left(\frac{\Delta G}{RT}\right) \cdot \exp\left(\frac{(1-\alpha_\mathrm{f})zF}{RT}\Delta\phi\right)$$

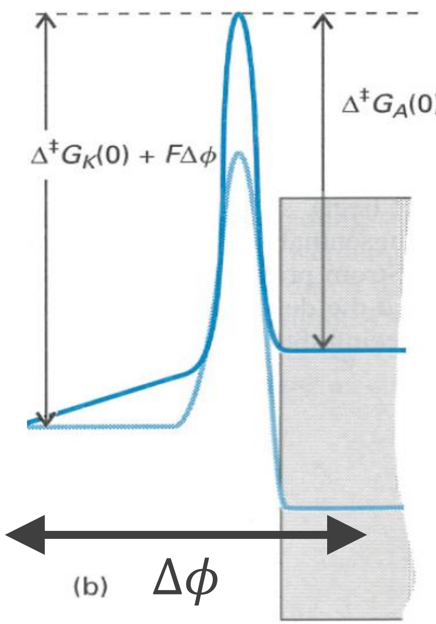
- Mass action kinetics

  $$r = k_\mathrm{f} \prod_{i=1}^{N_\mathrm{R}} c_i^{|\nu_i|} - k_\mathrm{r} \prod_{i=1}^{N_\mathrm{P}} c_i^{|\nu_i|}$$

- Heat release

  $$\dot{q}_\mathrm{heat} = r\,(-\Delta H + F\nu_\mathrm{e}\Delta\phi)$$

- Implemented in CANTERA
- Formalism valid for **electrochemical and thermochemical reactions**
- Formalism hosts both, **Butler-Volmer and Nernst equations**



P. W. Atkins, *Physical chemistry*, 6th ed (Oxford University Press, Oxford, 1998).

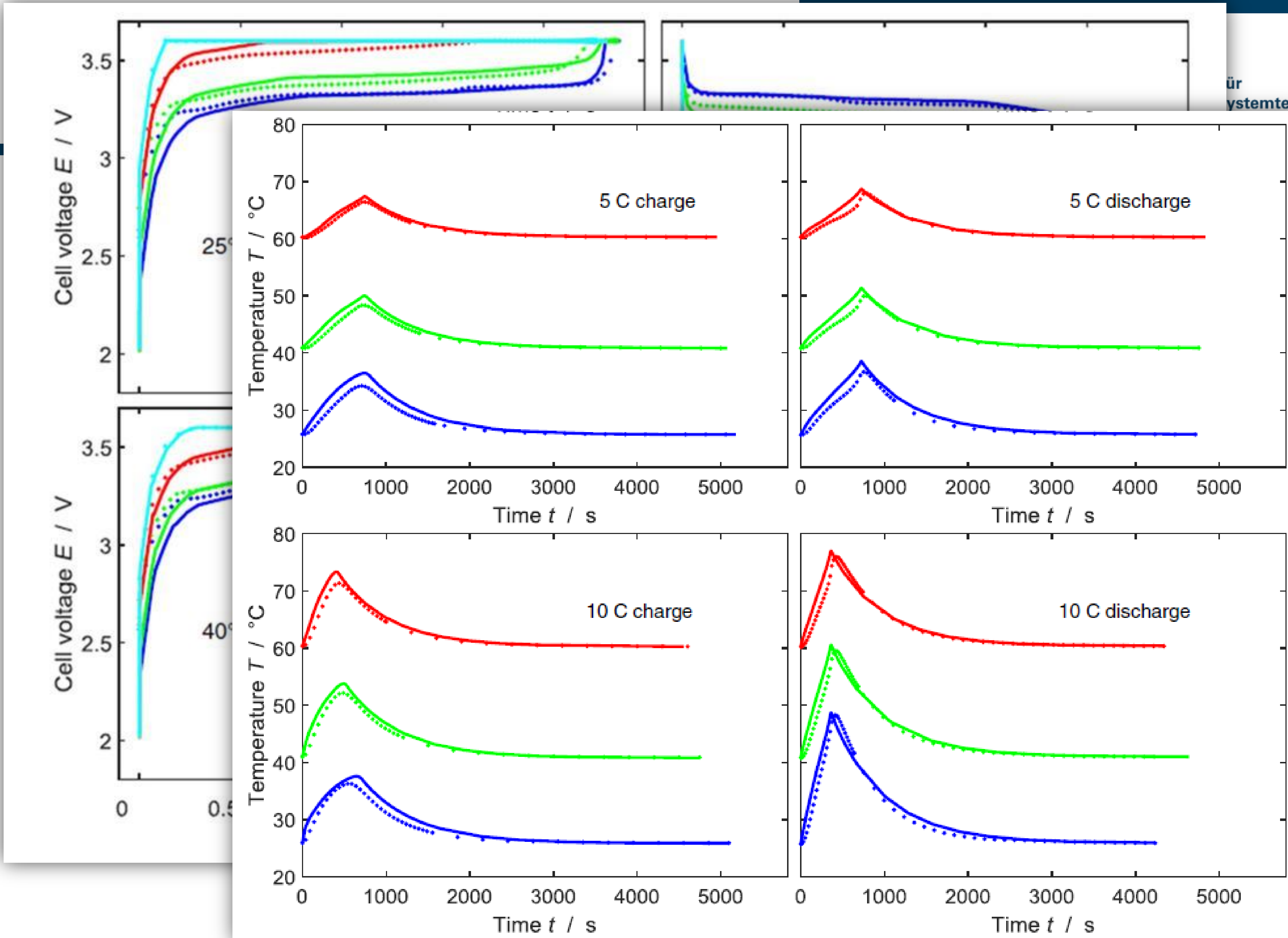
D. G. Goodwin, H. K. Moffat, and R. L. Speth, “Cantera: An Object-Oriented Software Toolkit for Chemical Kinetics, Thermodynamics, and Transport Processes, http://www.cantera.org

Investigated graphite/LFP cylindrical cell

- 26650 type cylindrical cell (A123)
  - 2.6 cm ∅, 6.5 cm height
- 3.3 V, 2.3 Ah, 108 Wh/kg
  30 C discharge capability
- Anode: Graphite, LiC_6
- Cathode: Lithium iron phosphate, $LiFePO_4$ (LFP)
- Validated electrical and thermal behavior

  C. Kupper and W. G. Bessler, "Multi-Scale Thermo-Electrochemical Modeling of Performance and Aging of a LiFePO4/Graphite Lithium-Ion Cell," Journal of the Electrochemical Society 164, A304-A320 (2017)

Computer tomography by D. Kohler, HS Offenburg


Cell voltage E / V
3.5
3
2.5
2
25°
40°
0
0.5
Temperature T / °C
80
70
60
50
40
30
20
0
1000
2000
3000
4000
5000
Time t / s
5 C charge
5 C discharge
10 C charge
10 C discharge

a) Calendaric SEI formation

b)

c)

Cell ageing due to SEI formation

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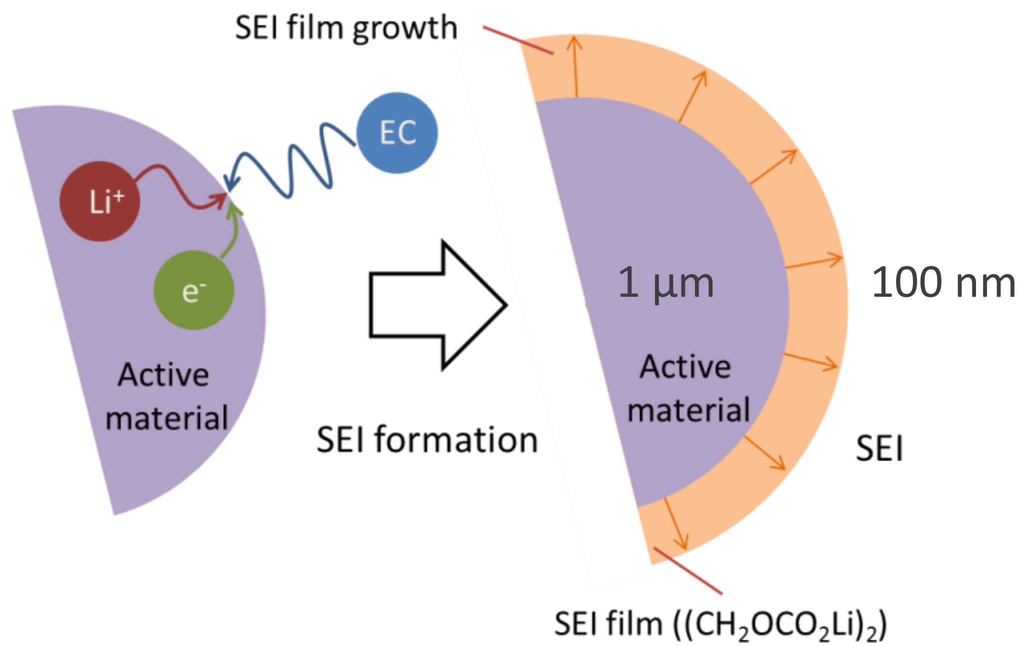
- Solid Electrolyte Interface (SEI) formation as main ageing mechanism:

$$2\ C_3H_4O_3\ (EC) + 2\ e^- + 2\ Li^+ \rightleftarrows (CH_2OCO_2Li)_2\ (SEI) + C_2H_4$$



R. Spotnitz and J. Franklin, “Abuse behavior of high-power, lithium-ion cells,” J. Power Sources 113, 81–100 (2003).
N. Tanaka and W. G. Bessler, “Numerical investigation of kinetic mechanism for runaway thermo-electrochemistry in lithium-ion cells,” Solid State Ionics 262, 70-73 (2014).

Cell ageing due to SEI formation

- Solid Electrolyte Interface (SEI) formation as main ageing mechanism:

  $2\ C_3H_4O_3\ (EC) + 2\ e^- + 2\ Li^+ \rightleftarrows (CH_2OCO_2Li)_2\ (SEI) + C_2H_4$

- Potential-dependent and temperature-dependent formation kinetics and diffusion-limited film growth:
  - Formation rate:

    $$r_{\mathrm{SEI}} = 1/\delta_{\mathrm{SEI}} \cdot \left(k_{\mathrm{f}} \prod_{i=1}^{N_{\mathrm{R}}} c_i^{|\nu_i|} - k_{\mathrm{r}} \prod_{i=1}^{N_{\mathrm{P}}} c_i^{|\nu_i|} \right)$$

  - Forward rate constant

    $$k_{\mathrm{f}} = k_{\mathrm{f}}^0 \cdot \exp\left(-\frac{E_{\mathrm{act,f}}}{RT}\right) \cdot \exp\left(-\frac{\alpha_{\mathrm{f}} z F}{RT} \Delta\phi\right)$$

- Conservation equation for SEI volume fraction and gas phase:

$$\frac{\mathrm{d}(\rho_{\mathrm{SEI}}\epsilon_{\mathrm{SEI}})}{\mathrm{d}t} = \dot{s}_{\mathrm{SEI}} \cdot M_{\mathrm{SEI}} \qquad \frac{\mathrm{d}(\rho_{\mathrm{gas}}\epsilon_{\mathrm{gas}})}{\mathrm{d}t} = \dot{s}_{\mathrm{C_2H_4}} \cdot M_{\mathrm{C_2H_4}} \qquad p = \rho RT/\bar{M}_{\mathrm{gas}}$$

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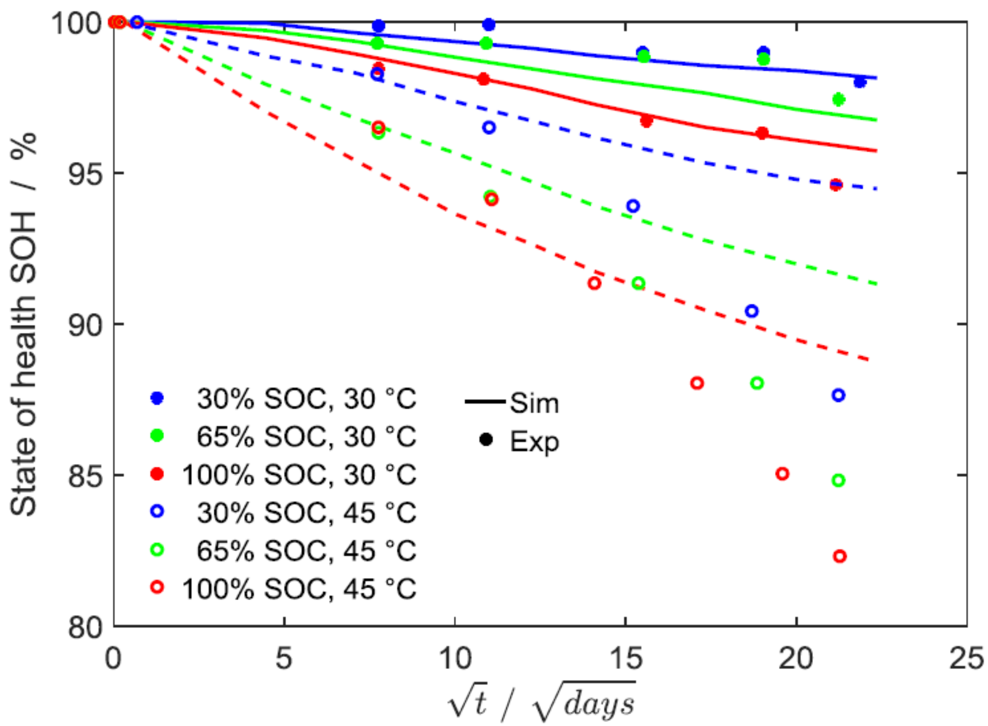
Calendaric ageing simulations

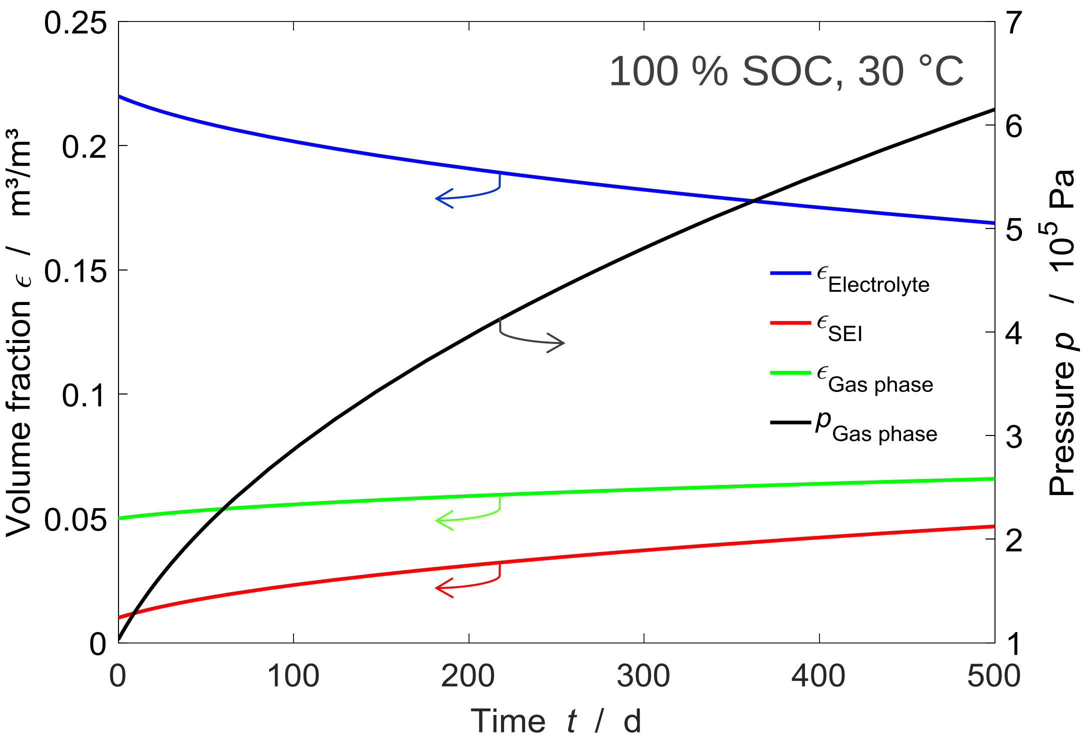
- $\mathrm{SOH} = \frac{C}{C_{\mathrm{BOL}}} \times 100\ \%$
- Experiments: LFP/Graphite cell
  S. Grolleau, A. Delaille, H. Gualous, P. Gyan, R. Revel, J. Bernard, E. Redondo-Iglesias, J. Peter, „Calendar aging of commercial graphite/$LiFePO_4$ cell predicting capacity fade under time dependent storage conditions," J. Power Sources 255, 450-458 (2014).
- Simulation wall-clock time ca. 1 min.
- **Prediction of calendaric ageing possible**



C. Kupper and W. G. Bessler, "Multi-Scale Thermo-Electrochemical Modeling of Performance and Aging of a $LiFePO_4$/Graphite Lithium-Ion Cell," J. Electrochem. Soc. 164, A304-A320 (2017).

Calendaric ageing simulations

- Electrolyte consumption and gas formation in cell
- SEI formation
- Pressure increase inside cell
- **Prediction of internal states possible**



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a) Calendaric SEI formation

b)

Mechanisms and results for cyclic ageing simulations: Publication under preparation

c)

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2. Lebensdauervorhersage von Lithium-Ionen-Zellen
3. **Zusammenfassung**

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Thank you for your attention!

Bundesministerium für Bildung und Forschung

FORSCHUNG AN FACHHOCHSCHULEN

E-Werk Mittelbaden
Daheim gut versorgt

Baden-Württemberg

DFG Deutsche Forschungsgemeinschaft