Rechargeable Batteries for Electrochemical Energy Storage: From Battery Research to Application

Workshop: Batteries – Fuelling the Alliance with the Future

Santiago de Compostela, Nov. 6th, 2018

Dr. Tobias Placke, Prof. Dr. Martin Winter

MEET Battery Research Center, University of Münster, Münster, Germany

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Münster Electrochemical Energy Technology

Official Launch
in 2009 – Entry into MEET-Arcades in 2011

Central Scientific Institution
of University of Münster since 2013

Diversity and Internationality
About 140 staff members from more than 12 nations, 30% female

Worldwide Visibility
with numerous scientific publications, conference contributions, patents, awards, *etc*.

Bridge
from Science to Industry

The Battery Value Chain

Materials

Components

Cells

Batteries

Application

2^{nd} Life

Recycling

Electrochemistry
& process development

Focus of MEET

Management system
& System integration

Technical Universities

Electrochemistry
& process development

Focus of MEET

MEET Battery Research Center: Division „Materials“

BOARD OF DIRECTORS
Scientific Leadership: Prof. Dr. Martin Winter // Management: Dr. Falko Schappacher

Project Management and MEET Administration:

Dr. Adrienne Hammerschmidt

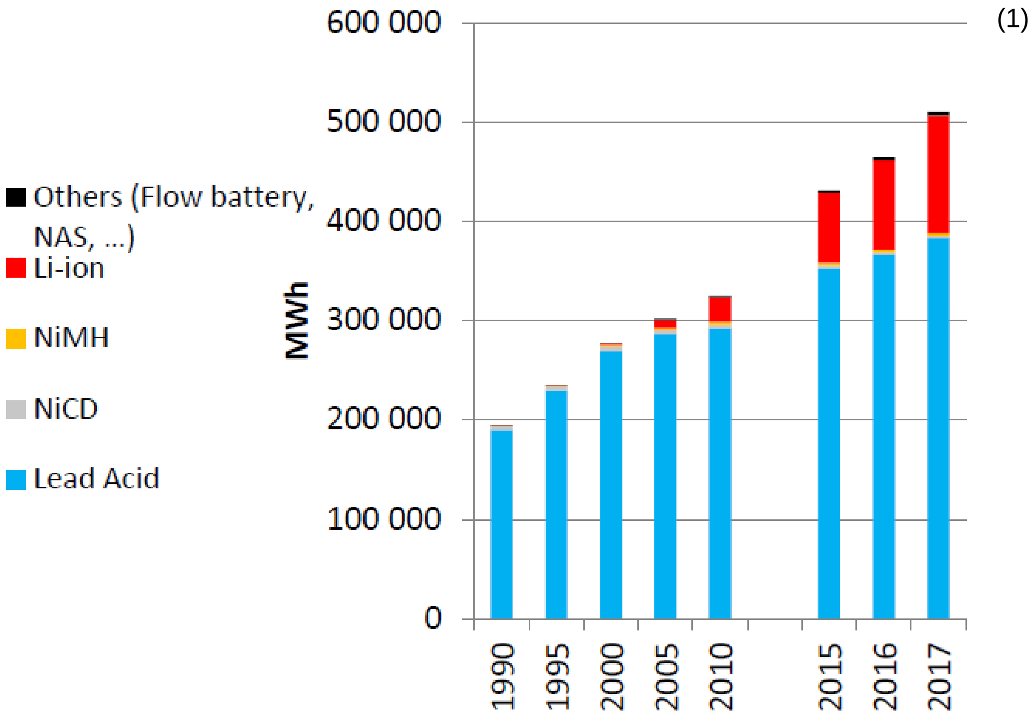
Division Cell System	Cell & Cell Design	Aging	Safety
Division Analytics & Environment	Electrolyte Aging	Recycling & Second Life	Toxicity Investigations
Division Materials	Anode Materials	Cathode Materials	Inactive Materials
Joint Groups	Next Generation	Electrolyte	

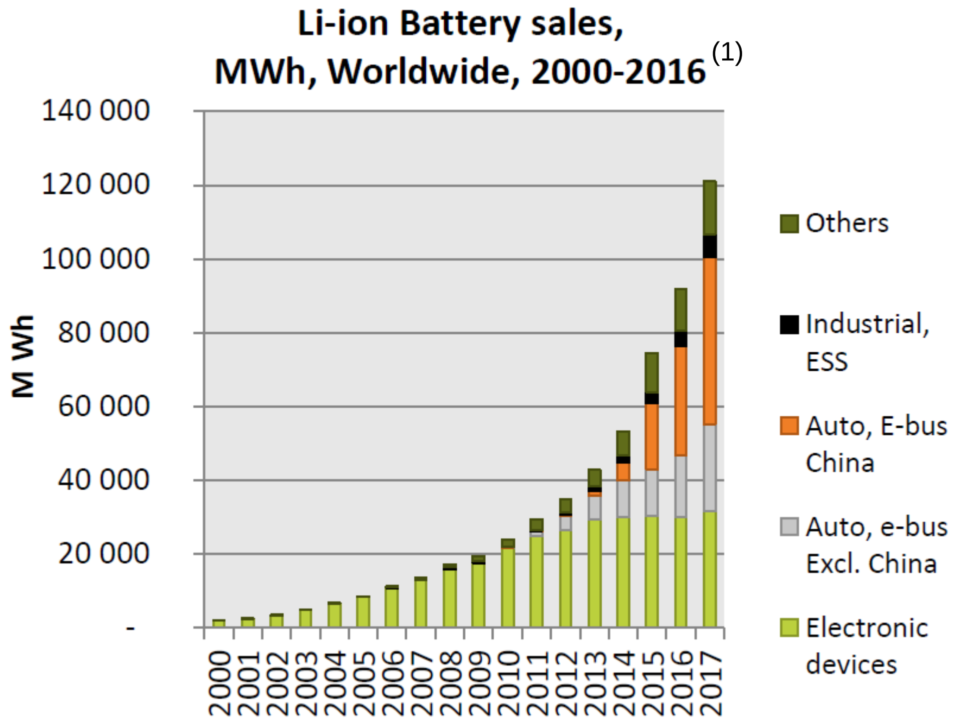
Head of Division “Materials”:
Dr. Tobias Placke

Deputy Head:
Dr. Richard Schmuch

Group size (2018):
- *5 Post Docs*
- *15 PhD students*
- *> 15 Undergraduate Students (Master, Bachelor or internship students)*

Excellent Times for Electrochemical Energy Storage (= Batteries and More)





others: power tools, gardening tools, e-bikes, medical devices, *etc*.

- Global market for lithium ion batteries (LIBs) in xEVs (HEVs, PHEVs, BEVs, etc.) and energy storage applications is huge.
- xEV market based on LIB technology has recently become the largest.

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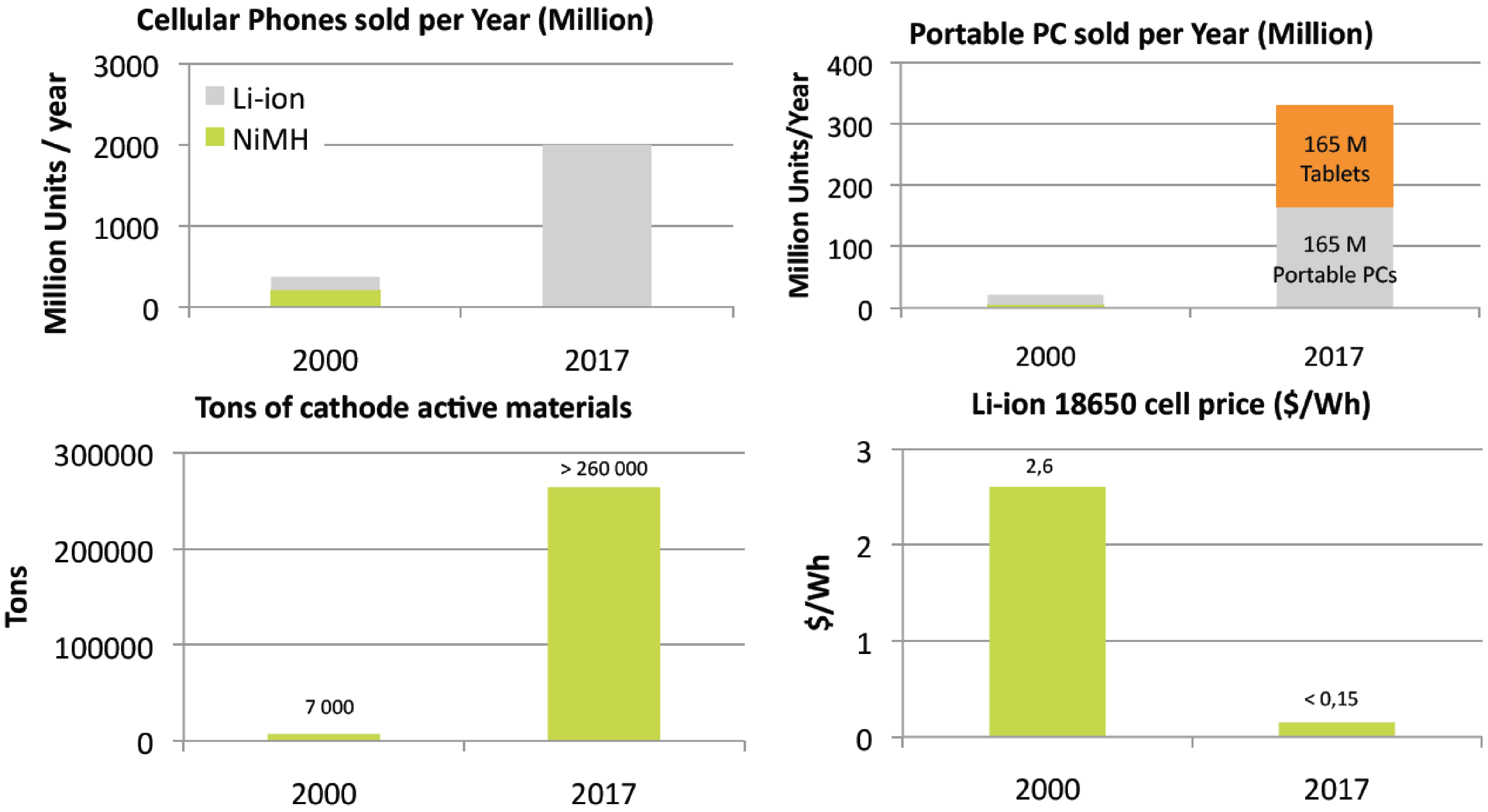
(1) Pillot, C. *Talk at Advanced Automotive Battery Conference (AABC) Europe, Mainz* **2017**.

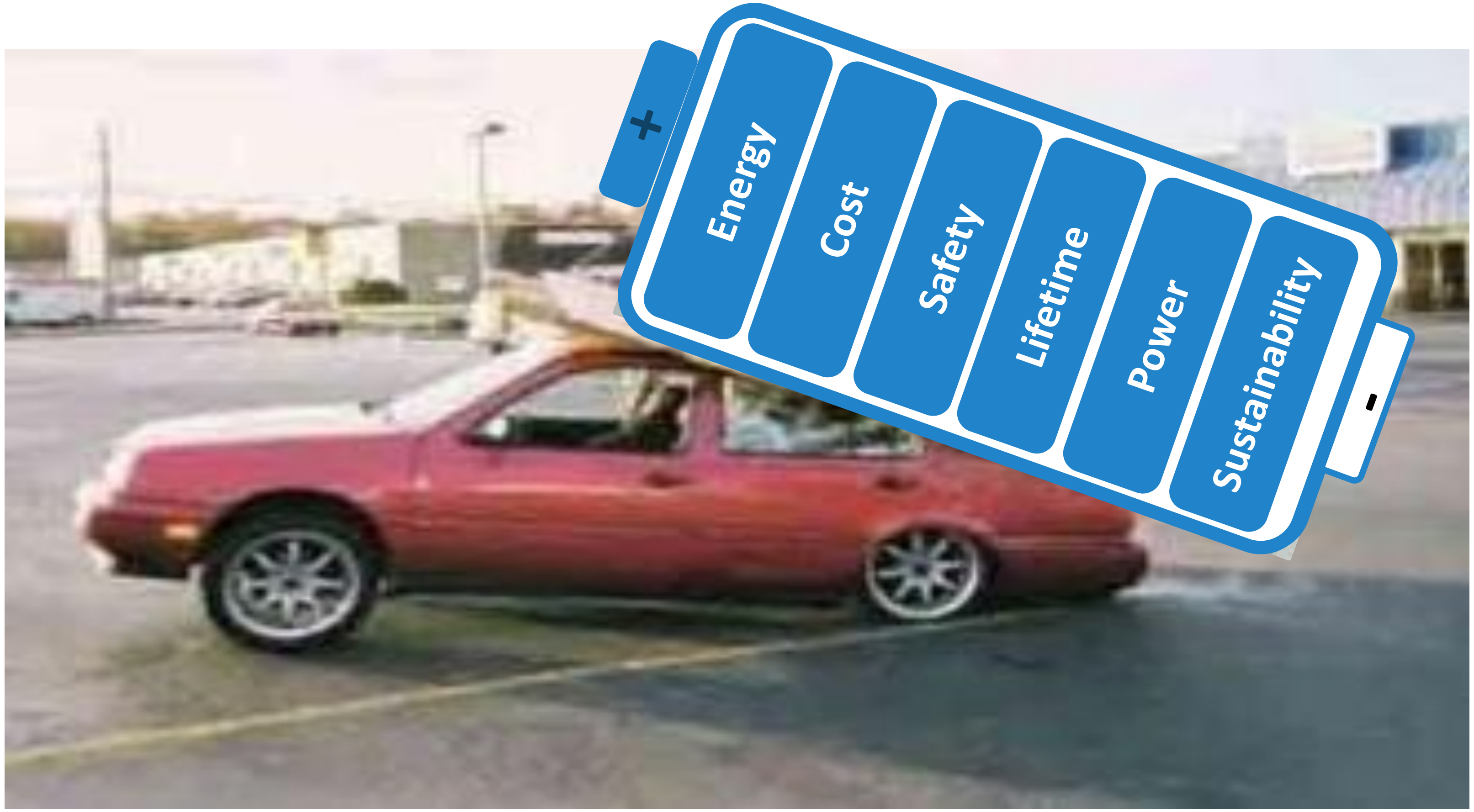
The Lithium Ion Battery (LIB): A Success Story



(1) Pillot, C. *Talk at Advanced Battery Power, Münster* **2018**.

From Today's View: Is it possible to develop a "1000 km battery"?

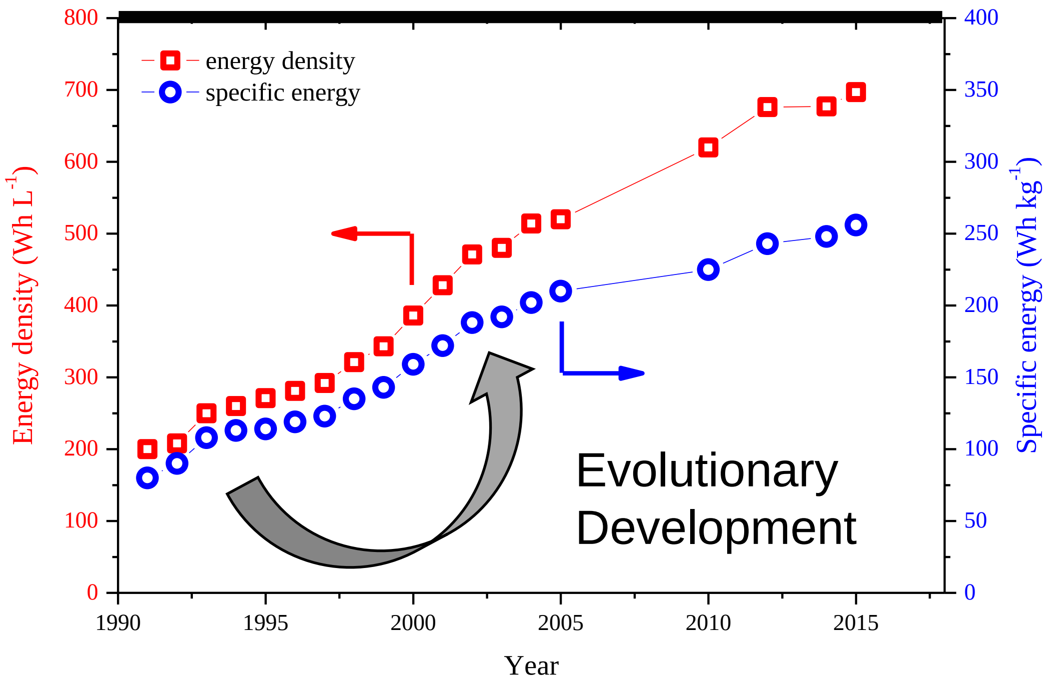
Yes, but…



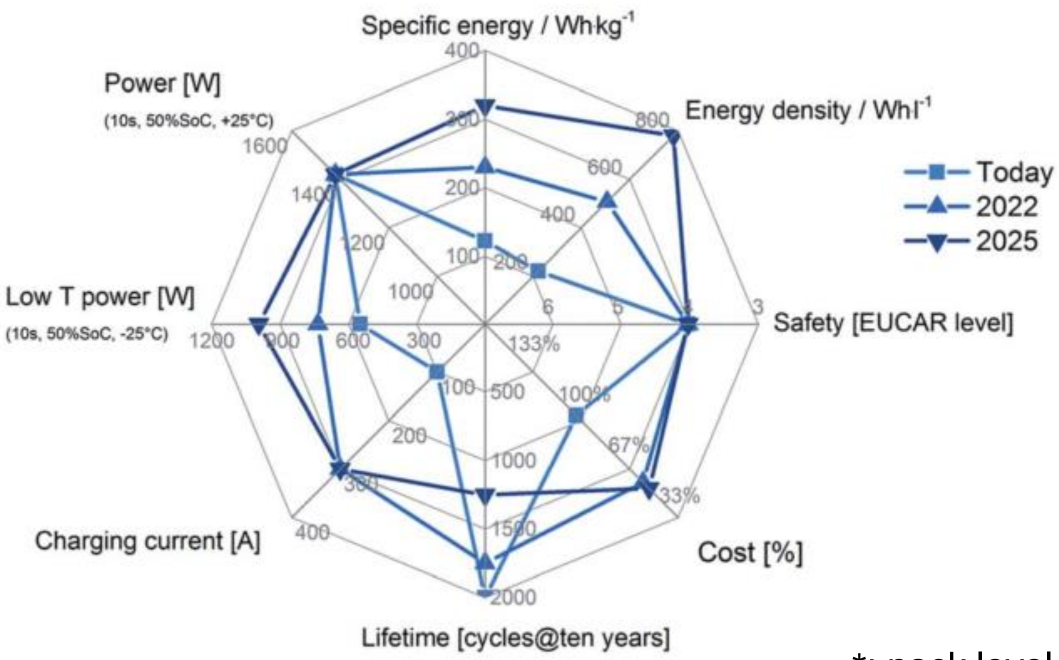
Battery Performance Targets: Energy Density and more

(1, 2)

Physicochemical limit: ≈400 Wh/kg, ≈800 Wh/L



Roadmap of key performance parameters for automotive application (from OEM perspective)[3]



*: pack level

- LIBs (intercalation/insertion) approach physicochemical limit:
  - Current energy density: ≈260 Wh/kg & ≈700 Wh/L in cylindrical 18650-type cells
  - Further energy-optimization becomes increasingly difficult

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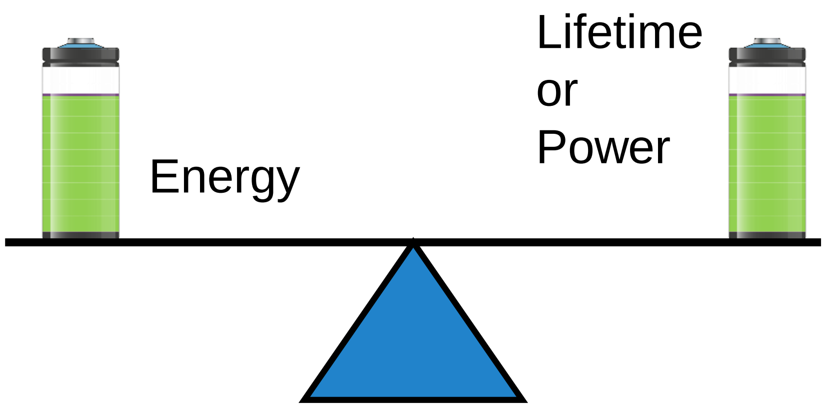
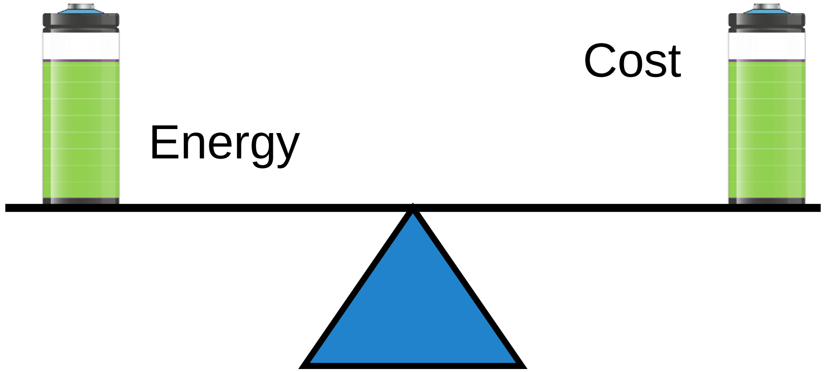
(1) Placke, T.; Kloepsch, R.; Dühnen, S.; Winter, M. *Journal of Solid State Electrochemistry* **2017**, *21*, 1939.
(2) Janek, J.; Zeier, W. G. *Nature Energy* **2016**, *1*, 16141.
(3) Andre, D.; Kim, S.-J.; Lamp, P.; Lux, S. F.; Maglia, F.; Paschos, O.; Stiaszny, B. *J. Mater. Chem. A* **2015**, *3*, 6709.

Battery Performance Targets: Energy Density and more



Performance parameters are affecting each other and need to be well balanced!



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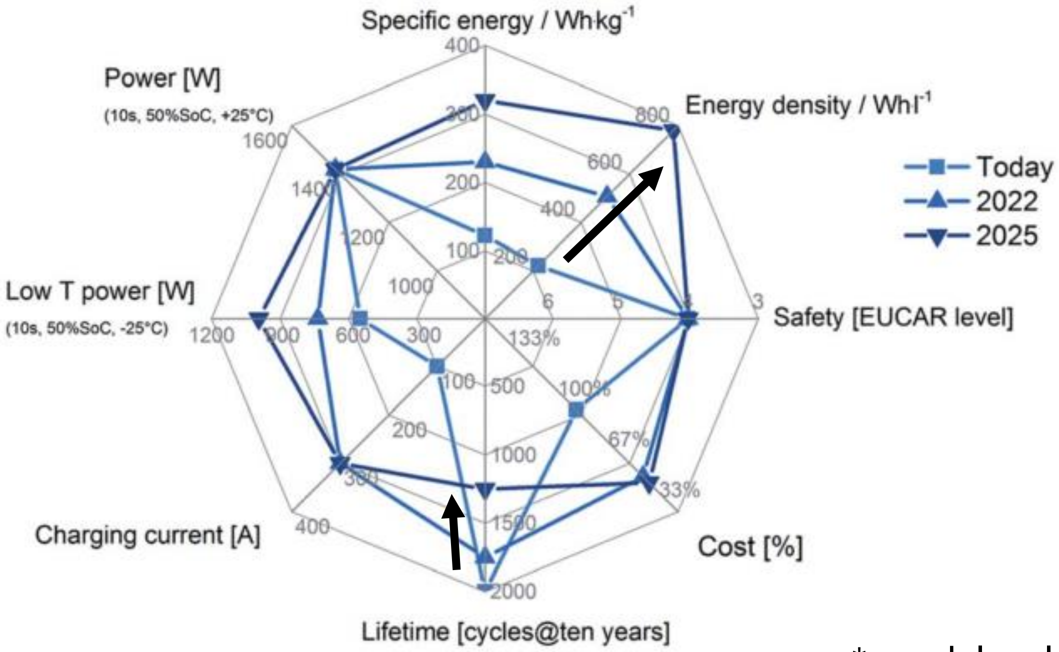

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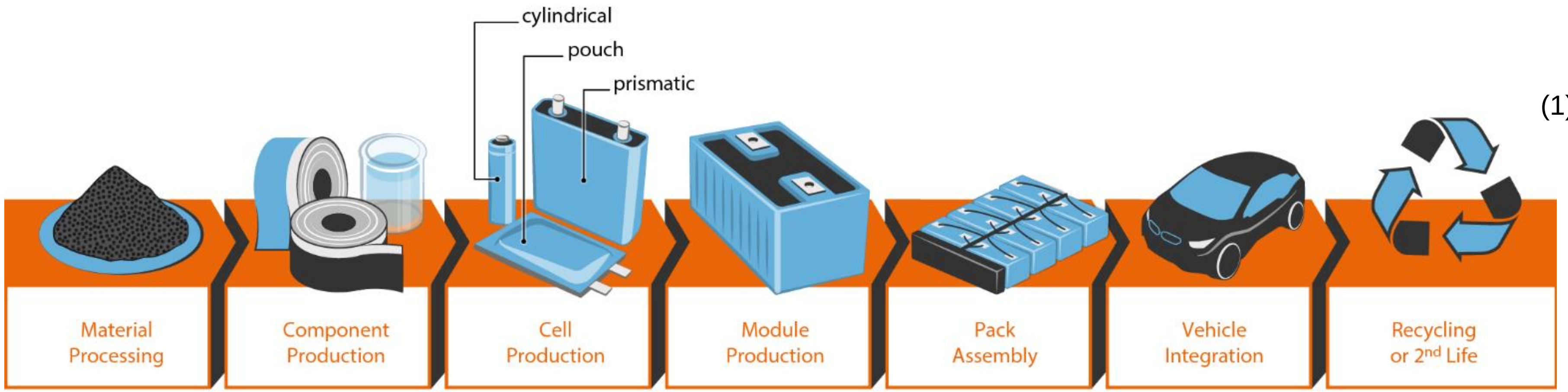
The Battery Value Chain:
From Material Level to Pack Level

(1)



Material level *(active materials)*

Electrode level *(binder, conductive additive, current collectors)*

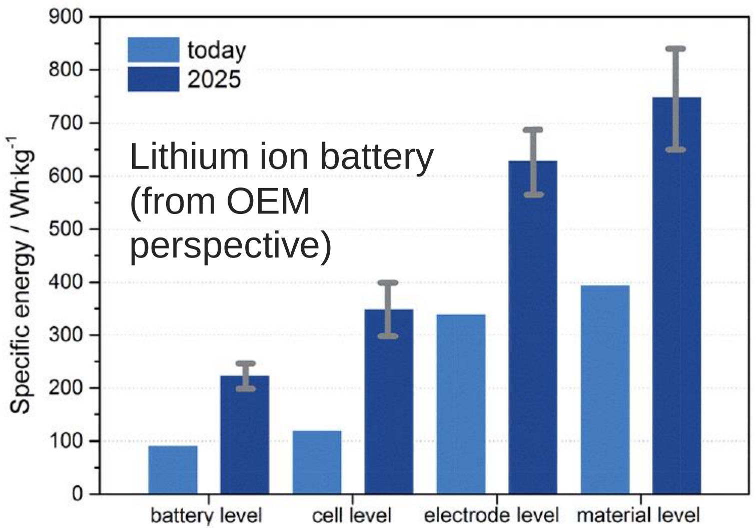
Cell level *(separator, cell housing, etc.)*

Module level *(module container, control units, sensors, etc.)*

System or Pack level *(battery management system, cooling, etc.)*

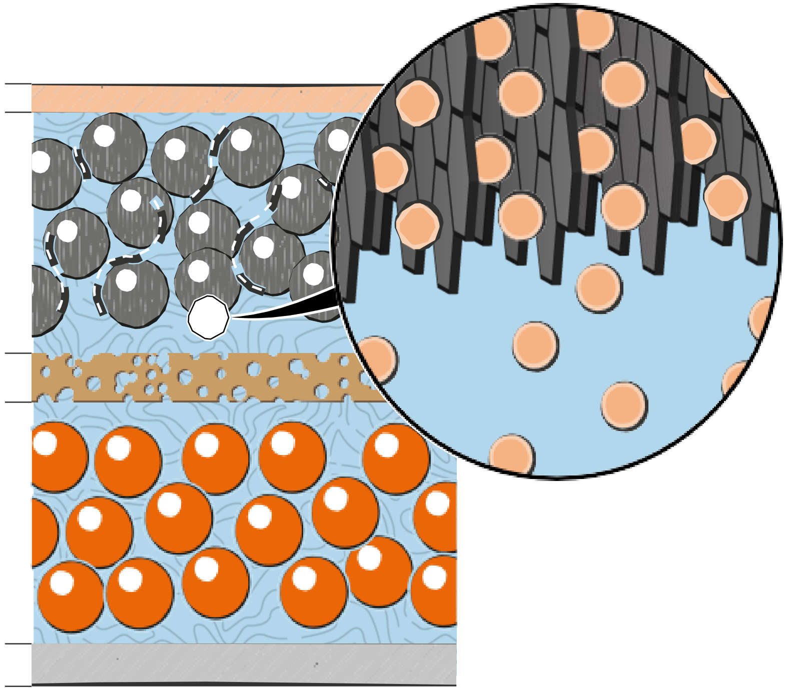
Addition of inactive materials: Decrease of energy content

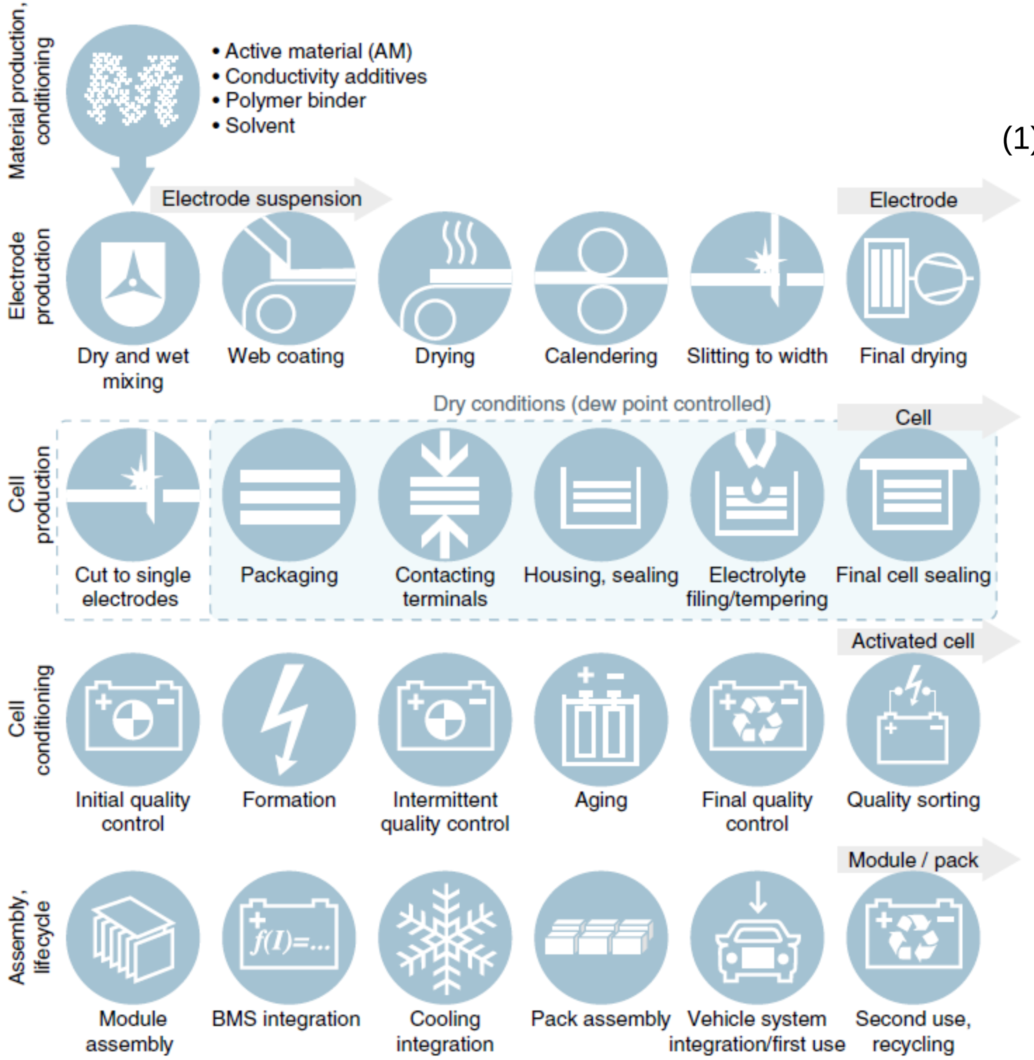
(2)



(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M. *Nature Energy* **2018**, *3,* 267.
(2) Andre, D.; Kim, S.-J.; Lamp, P.; Lux, S. F.; Maglia, F.; Paschos, O.; Stiaszny, B. *J. Mater. Chem. A* **2015**, *3*, 6709.

Battery Process Chain

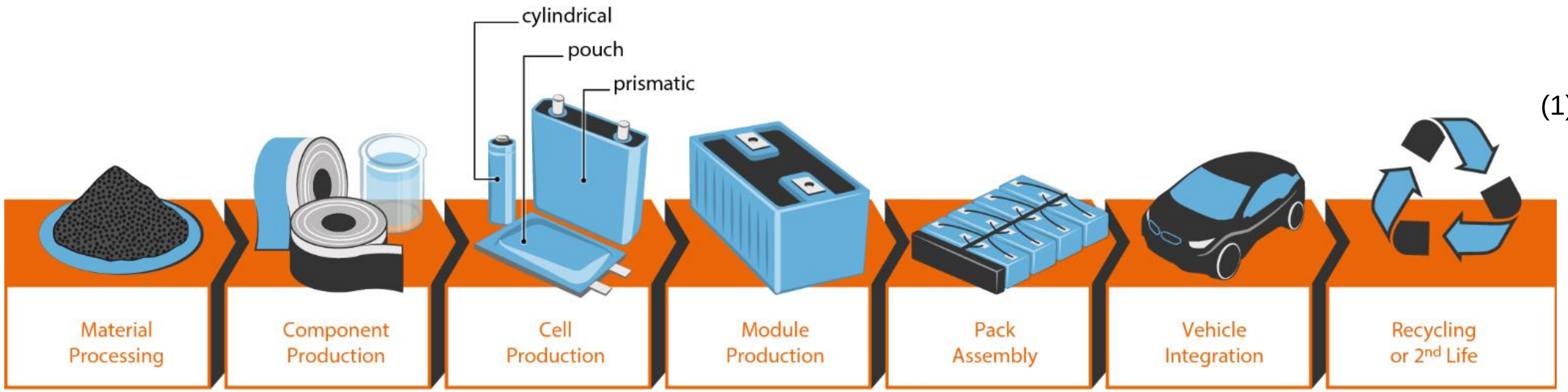




(1)

(1) Kwade, A.; Haselrieder, W.; Leithoff, R.; Modlinger, A.; Dietrich, F.; Droeder, K., *Nature Energy* **2018,** 3, (4), 290-300.

The Battery Value Chain: From Material Level to Pack Level



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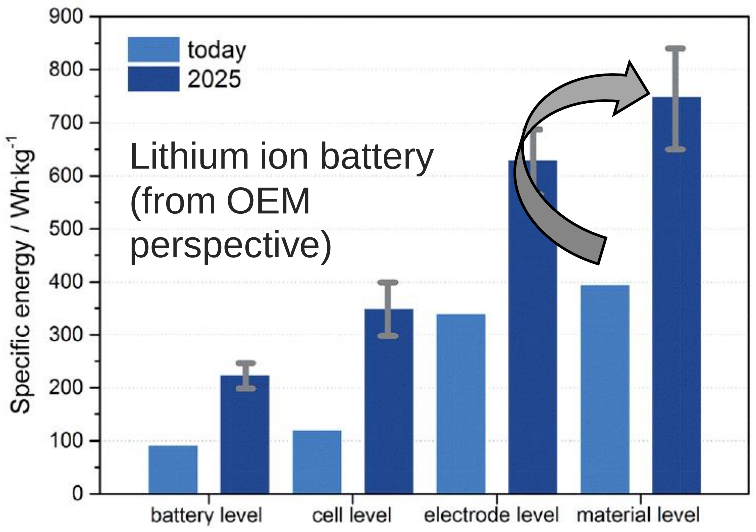
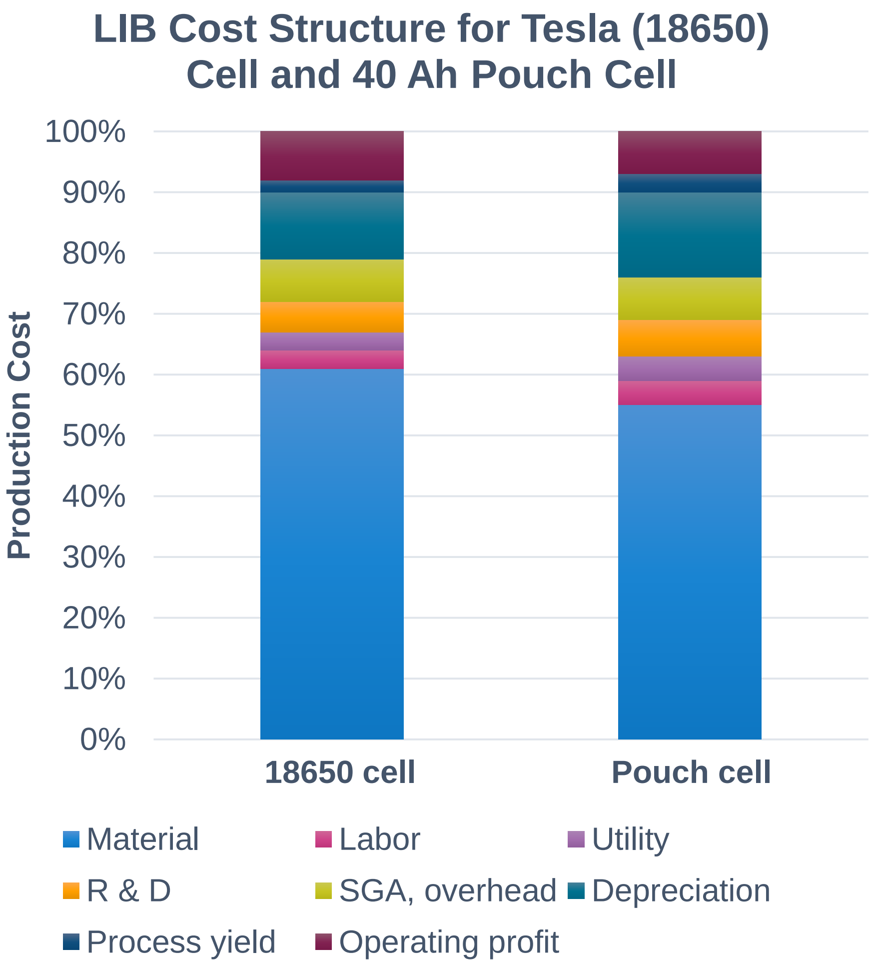
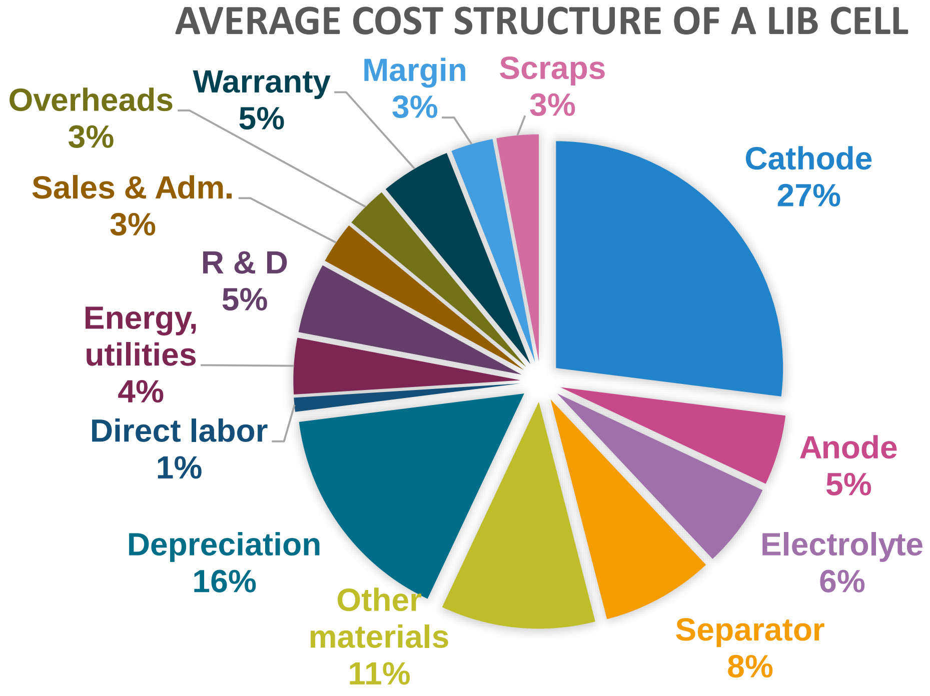


(2)

(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M. *Nature Energy* **2018**, *3,* 267.
(2) Andre, D.; Kim, S.-J.; Lamp, P.; Lux, S. F.; Maglia, F.; Paschos, O.; Stiaszny, B. *J. Mater. Chem. A* **2015**, *3*, 6709.

Cost Structure of Lithium Ion Batteries: Raw Material Impact

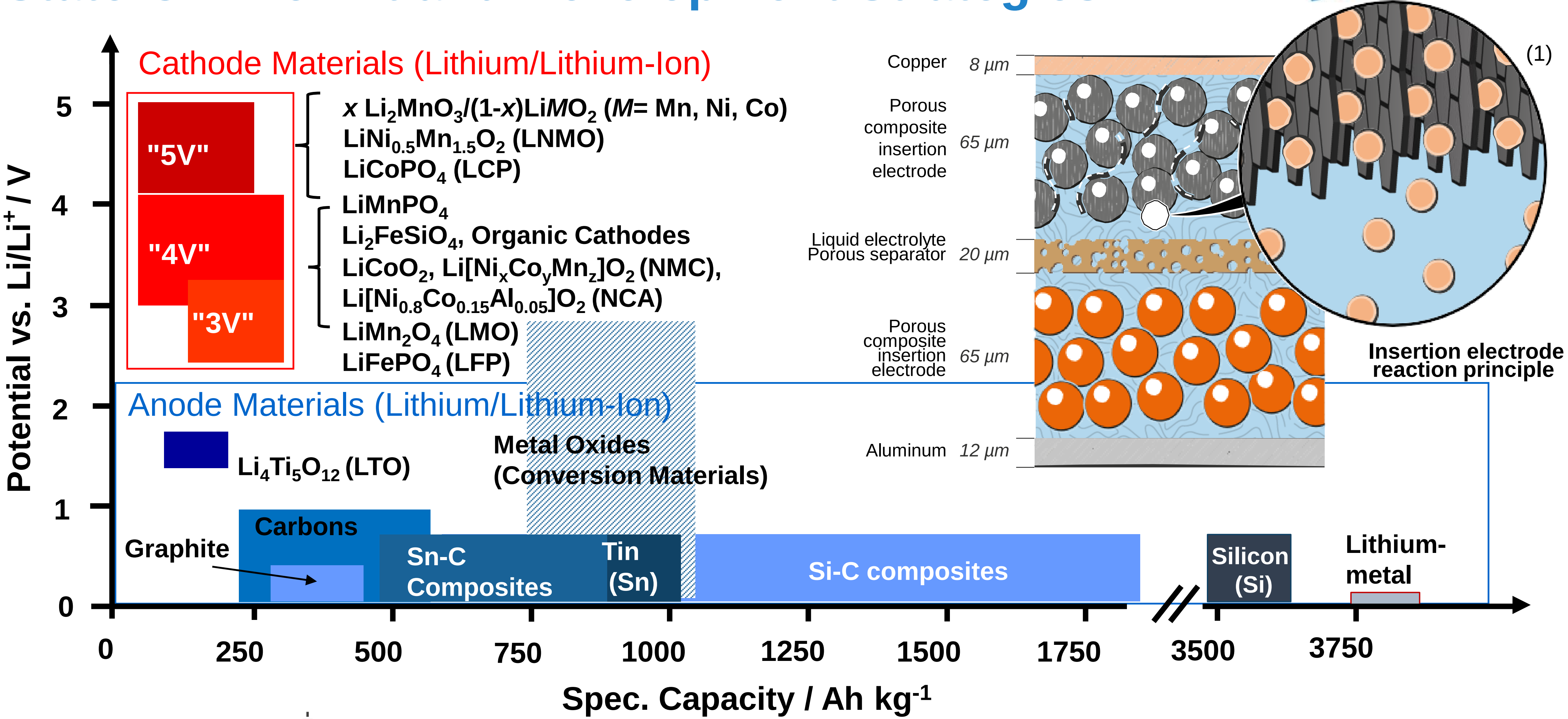




- Raw material cost account for ≈50-70 % of LIB cells
- Cathode materials are the most substantial contributor to material cost

(1) Data from: Pillot, C., Avicenne Energy, *Talk at Advanced Battery Power, Münster* **2018.**

Materials for Lithium Ion Batteries: State-Of-The-Art and Development Strategies



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(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M. *Nature Energy* **2018**, *3*, 267.

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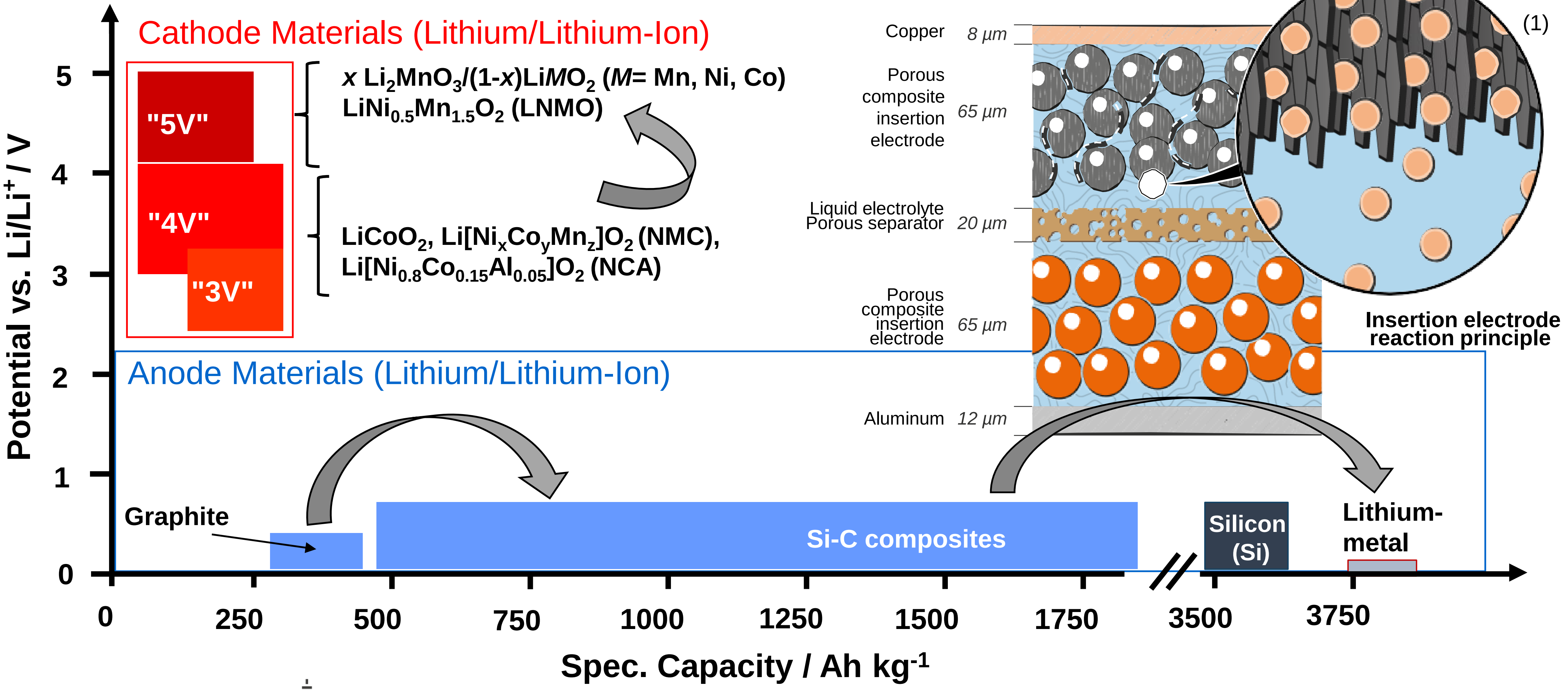
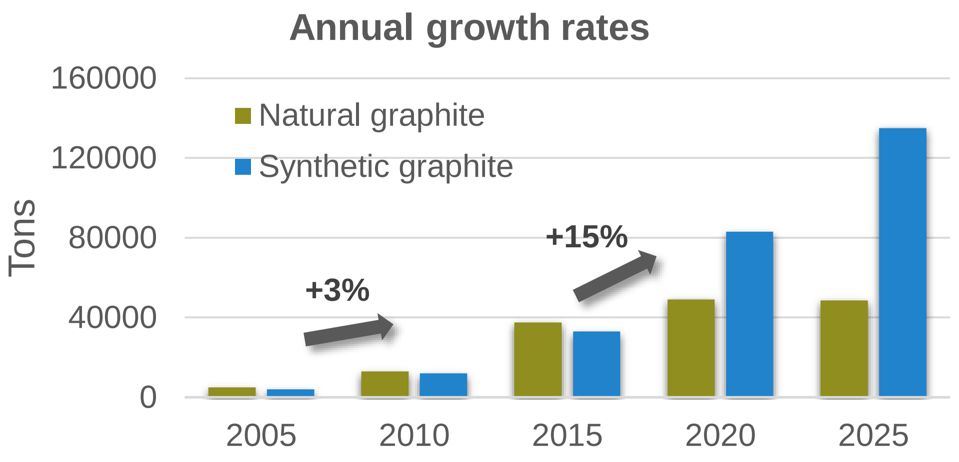
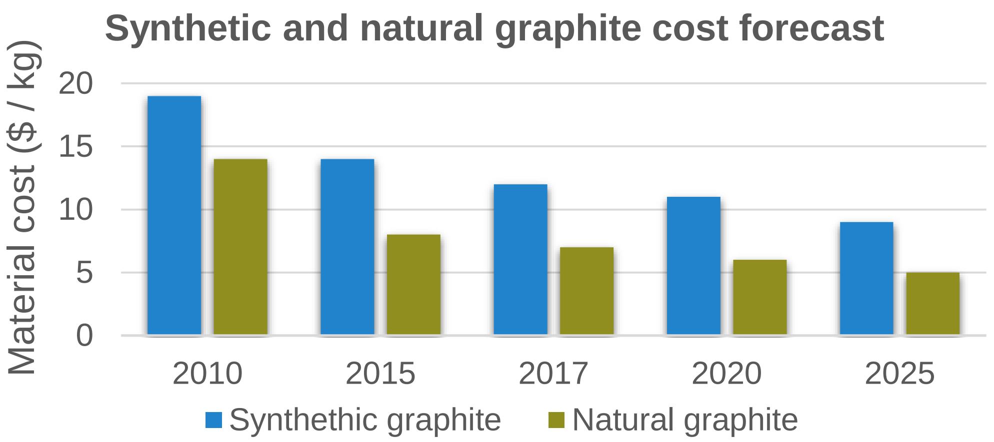


(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M. *Nature Energy* **2018**, *3,* 267.

State-of-the-Art LIB Anode Materials: Graphitic Carbons





- Carbonaceous materials: Synthetic graphite (SG; share of 54%) and natural graphite (NG; share of 39%) as well as amorphous carbons (share of 2%)(1)
- Often, mixtures of amorphous and graphitic carbons are used to optimize the P/E-ratio
- Demand for graphite increases fast, especially for synthetic graphite due to EV market
- SG shows outstandingly high levels of purity and less fluctuating quality compared to NG → SG meets EV lifetime requirements
- Cost: ≈7 $/kg for NG and ≈13 $/kg for SG (2017)
- Currently, only some commercial cells (*e.g.* Panasonic) use silicon (SiO_x) in small amounts (few wt.%)

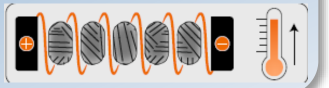
(1) Data from: Pillot, C. *Talk at Advanced Automotive Battery Conference (AABC) Europe, Mainz* **2018**.

Industrial Production of Carbons: Synthetic Graphite *vs.* Natural Graphite

Petroleum coke, coal tar pitch

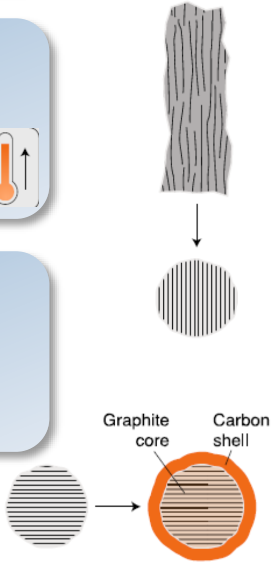
1) Pre-treatment
- Calcination: „Soft Carbon“
- Crushing, grinding
- Classifying

2) Graphitization
- T ≥ 2800 °C



3) Particle Refinement
- Conditioning, grinding
- Classifying, carbon coating

Synthetic graphite



Graphite ore

1) Mining and Flotation
- Mining from graphite ore
- Mechanical separation
- Flotation, drying, screening

2) Material processing
- Micronisation
- Spheroidization
- Purification (chem./therm.)

3) Particle Refinement
- Conditioning, grinding
- Classifying, carbon coating

Natural graphite

Major Challenges:

- High energy consumption and high cost, i.e. >25% of total production cost (*synthetic graphite*)
- *Natural graphite* is classified as „critical“ material (largest deposits: China)
- Purification of *natural graphite* is often done by acid treatment (HF) → water pollution
- China: insufficient monitoring and measures: high levels of environmental and air pollution [2]

(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M., *Nature Energy* **2018,** 3, (4), 267.
(2) The Washington Post: In your phone, in their air. [https://www.washingtonpost.com]

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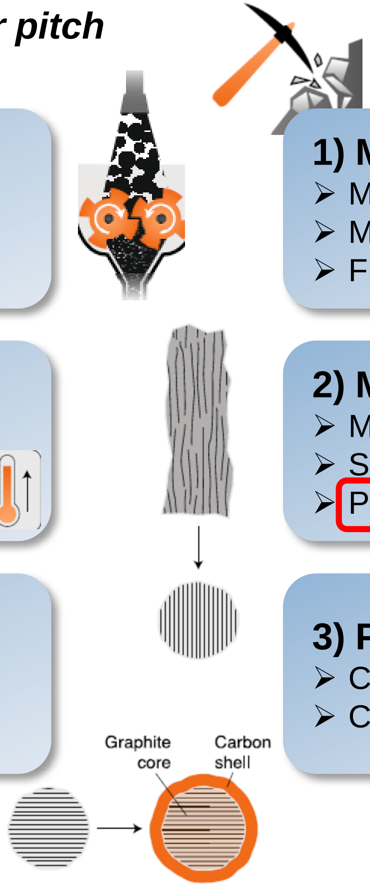

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3) Particle Refinement
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- Classifying, carbon coating

Natural graphite

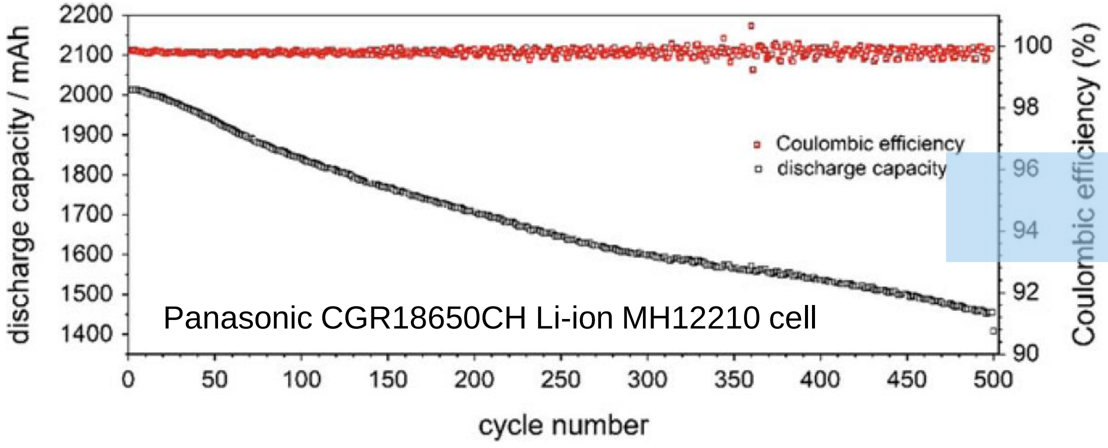
Strategies:

- Decrease of processing cost by decrease of energy consumption during graphitization: Catalytic graphitization
- Search for alternative, abundant precursor materials for synthetic graphite production (e.g. from biomass or waste products)
- Search for environmentally friendly (or friendlier) processes for natural graphite purification
- Recycling of graphite anode materials from spent lithium ion cells

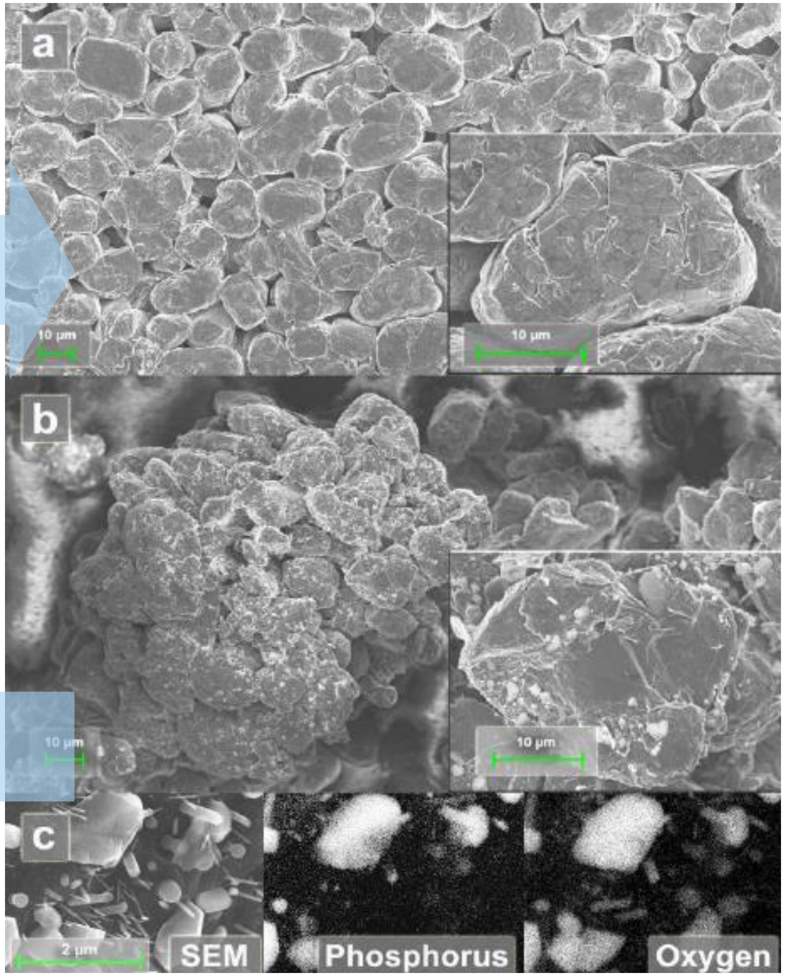
(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M., *Nature Energy* **2018,** 3, (4), 267.

Graphite Recycling from Spent Lithium Ion Cells

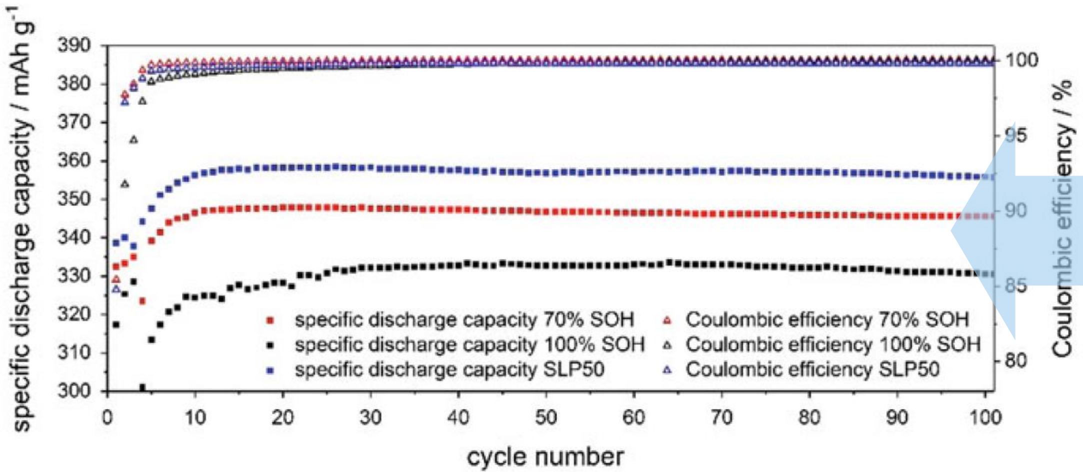
Charge/discharge cycling until 70% SOH



thermal purification



Reuse as graphite anode



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(1) Rothermel, S.; Evertz, M.; Kasnascheetw, J.; Qi, X.; Grützke, M.; Winter, M.; Nowak, S., *ChemSusChem* **2016,** 9, (24), 3473.
(2) Kwade A, Diekmann J. *Recycling of Lithium-Ion Batteries - The LithoRec Way*. *Springer International Publishing AG*, **2018**.

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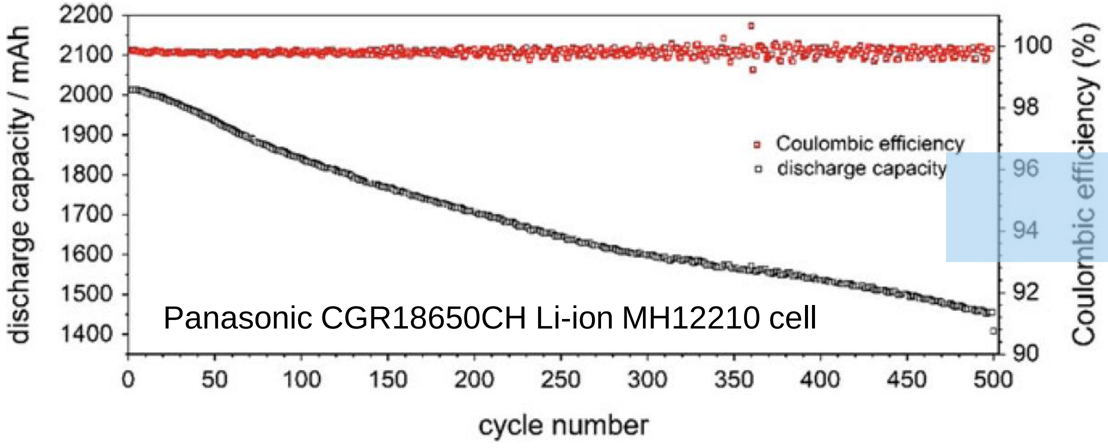

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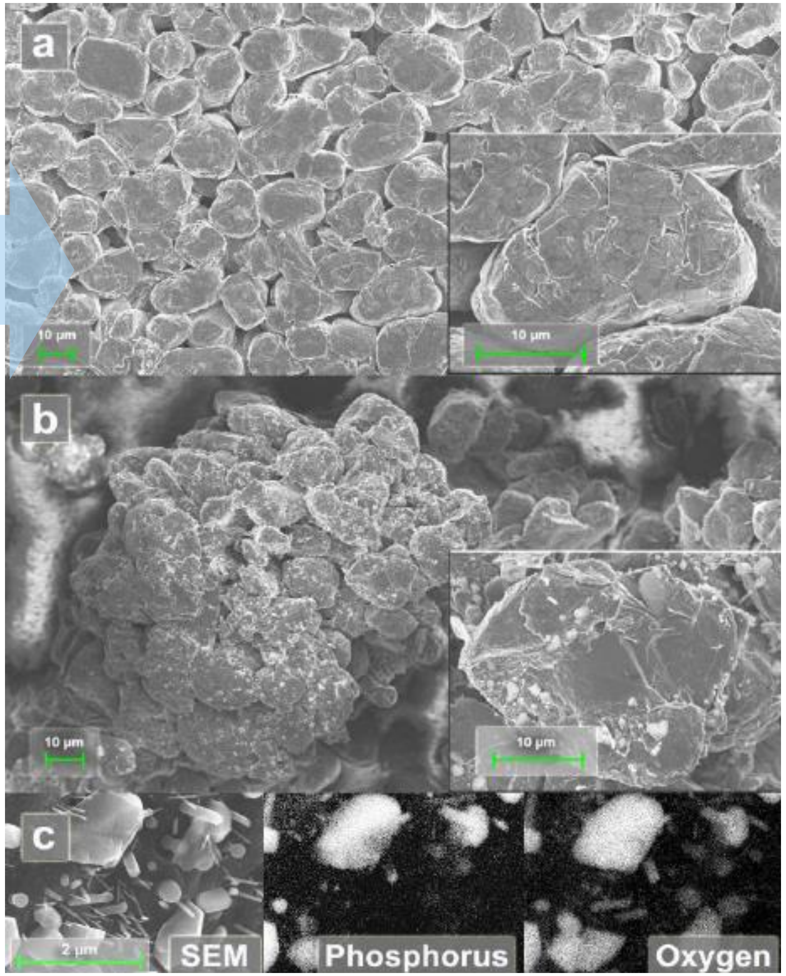


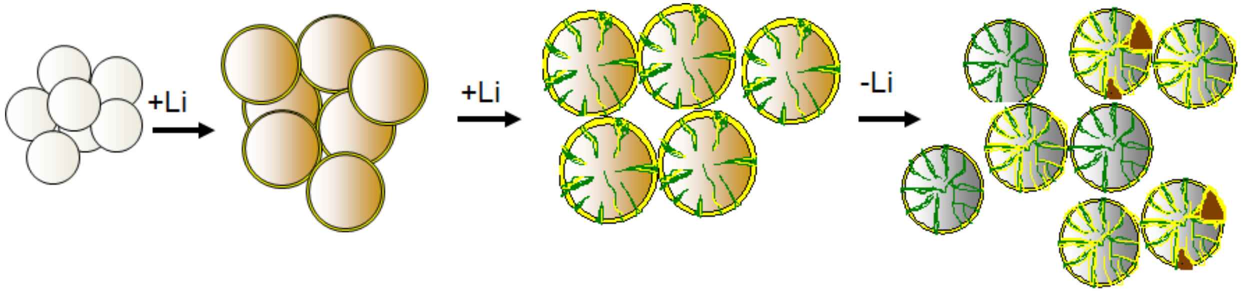
Open questions / challenges:

- Impact of electrolyte/salt residues on long-term performance (stability and rate)?
- Impact on solid electrolyte interphase (SEI) formation and stability?
- Multiple recycling of graphite possible? Degradation effects?

(1) Rothermel, S.; Evertz, M.; Kasnascheetw, J.; Qi, X.; Grützke, M.; Winter, M.; Nowak, S., *ChemSusChem* **2016,** 9, (24), 3473.
(2) Kwade A, Diekmann J. *Recycling of Lithium-Ion Batteries - The LithoRec Way*. *Springer International Publishing AG*, **2018**.

Challenges and Strategies for Si-Based Anodes

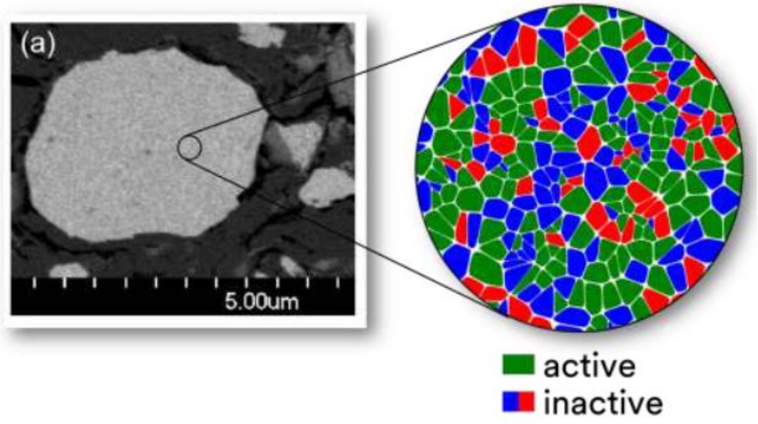
- High volume changes during lithiation/de-lithiation
- Pulverization/"cracking" of Si particles
- Contact loss of particles from electronically conductive network or current collector
- Instability of solid electrolyte interphase (SEI): Breakage and re-formation
- High active lithium losses by continuous electrolyte decomposition (low Coulombic efficiency)



Strategies

- Active/inactive matrix concept (nano-Si in inactive matrix)
  - Si/Carbon composite materials
  - Si/intermetallics/carbon composite materials

3M approach: [1]



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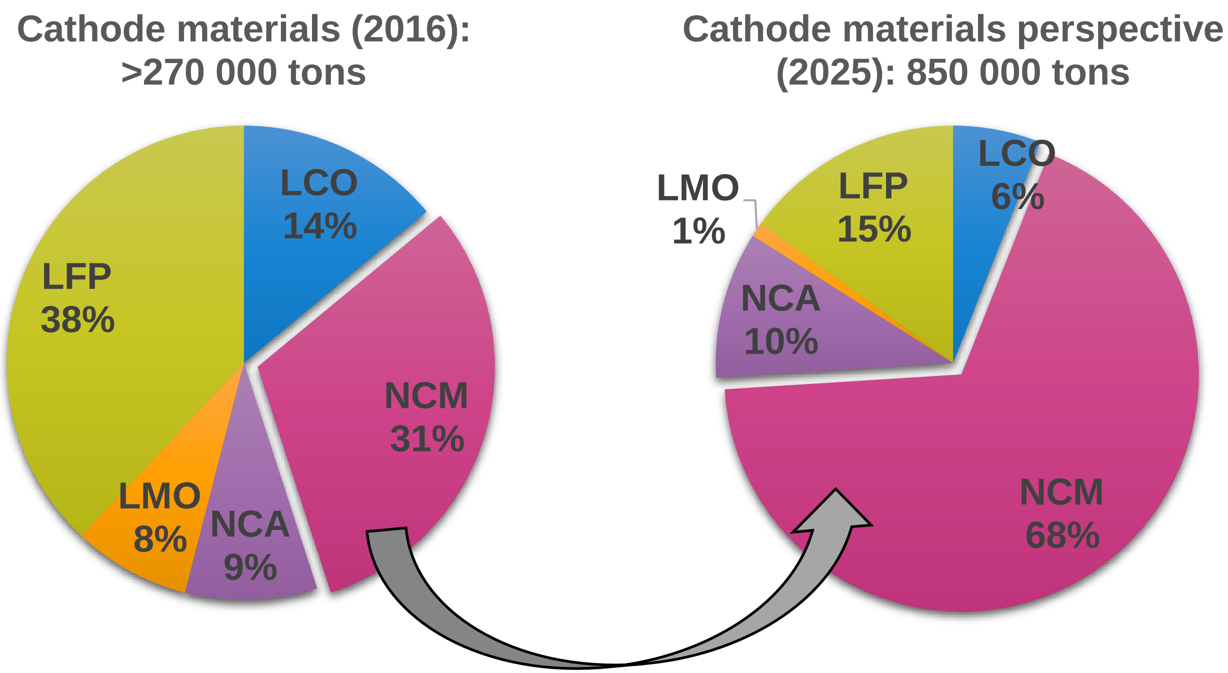
(1) Kaiser J., 3M, *Talk at the Batterieforum Deutschland*, Berlin, **2017**.

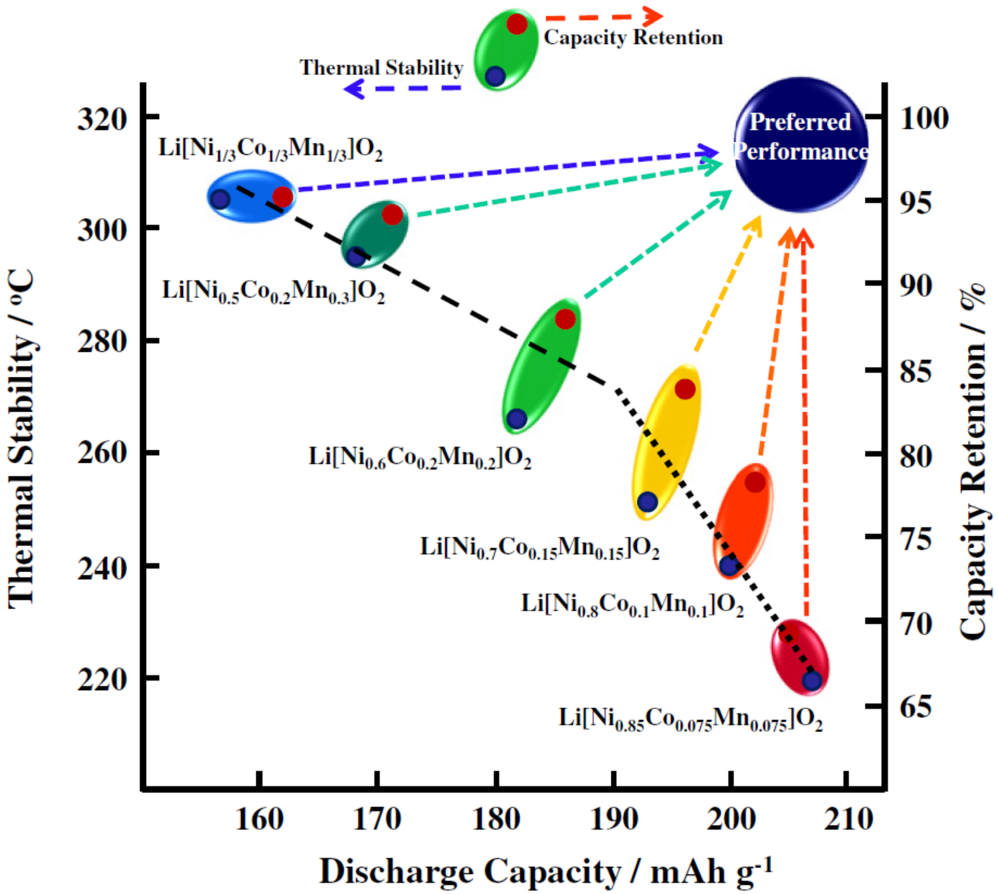
State-of-the-Art LIB Cathode Materials



- LCO is mostly used for handheld consumer electronics (pouch cell lithium ion cells for mobile phones, tablets, *etc*.)
- NCM is used in other electronic devices and in large cells (EV applications)
- NCA is primarily used in 18650 cells (Panasonic, Tesla) and as blend with LMO for EV cells
- LMO is typically blended with NCM for EVs to adjust the P/E ratio:
  Trend: LMO/NCM 75:25 → LMO/NCM 25:75
- LFP is primarily used for EVs and electric buses in China, as well as for industrial or stationary applications

(1) Data from: Pillot, C., Avicenne Energy, *Talk at Advanced Battery Power, Münster* **2018.**

State-of-the-Art LIB Cathode Materials: NCM-based Layered Oxides



NCM111 (Gen2a)	NCM523 (Gen2b)	NCM622 (Gen2b-3a)	NCM811 (Gen3a)	NCM910 (Gen3a/b)
Ni: 33%	Ni: 50%	Ni: 60%	Ni: 80%	Ni: 90%
Co: 33%	Co: 20%	Co: 20%	Co: 10%	Co: 10%
Mn: 33%	Mn: 30%	Mn: 20%	Mn: 10%	Mn: 0%

Increasing nickel content →

Increasing capacity →

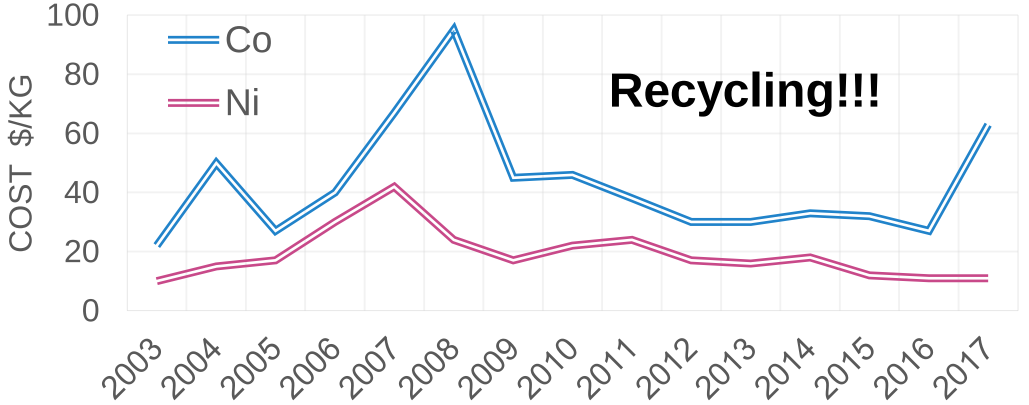
- NCM523 and NCM622 (and NCA) can be considered as state-of-the-art materials for xEV applications
- NCM811: short-term goal for EV applications
- Higher Ni-content
  - Lower cost of raw materials
  - Challenges: Safety, lifetime and manufacturing

(1) Noh, H.-J.; Youn, S.; Yoon, C. S.; Sun, Y.-K. *Journal of Power Sources* **2013**, *233*, 121.

State-of-the-Art LIB Cathode Materials: NCM-based Layered Oxides

- **Cost drivers:**
  - Lithium is not considered as potential cost driver[2]
  - Cost increase risk: especially Cobalt and Nickel pricing

NICKEL AND COBALT COST FROM 2003-2017 [3]



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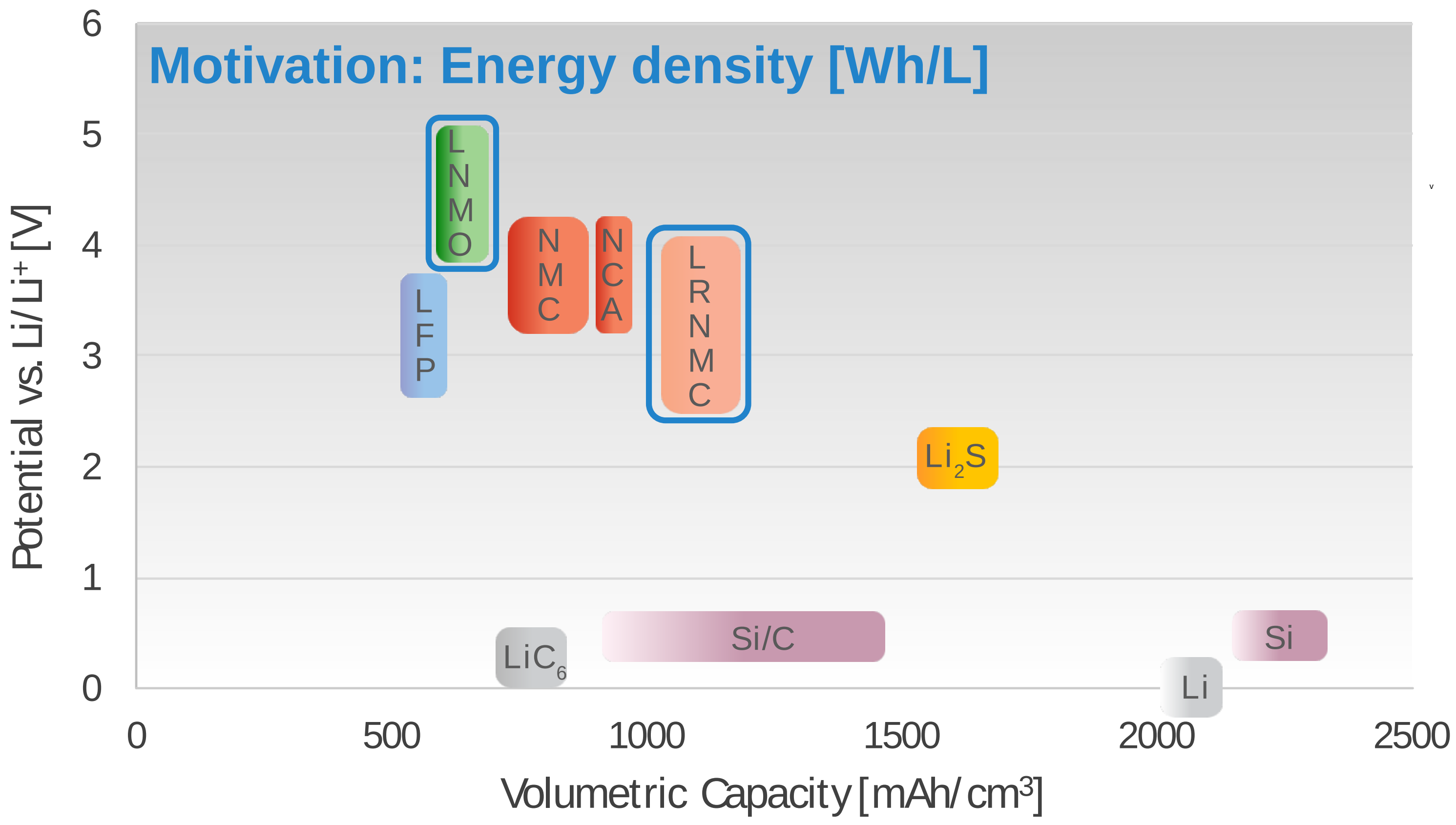
(1) Noh, H.-J.; Youn, S.; Yoon, C. S.; Sun, Y.-K. *Journal of Power Sources* **2013**, *233*, 121.
(2) Ciez RE, Whitacre JF. *Journal of Power Sources* 2016, **320:** 310-313.
(3) Data from: Pillot, C., Avicenne Energy, *Talk at Advanced Battery Power, Münster* **2018**.

Promises of High-Capacity/High-Voltage Cathode Materials



- Volumetric energy density [Wh/L] is of higher importance for mobile applications than specific energy [Wh/kg]
- With respect to cathodes:
  - High capacity
  - High redox potential
  - High material density

LNMO: **High-voltage spinel (HVS; $LiNi_{0.5}Mn_{1.5}O_4$)**

LRNMC: **Li-rich NMC (HE-NMC; x LiMO_2 · 1-x Li_2MnO_3)**

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(1) Placke, T.; Kloepsch, R.; Dühnen, S.; Winter, M. *Journal of Solid State Electrochemistry* **2017**, *21*, 1939.

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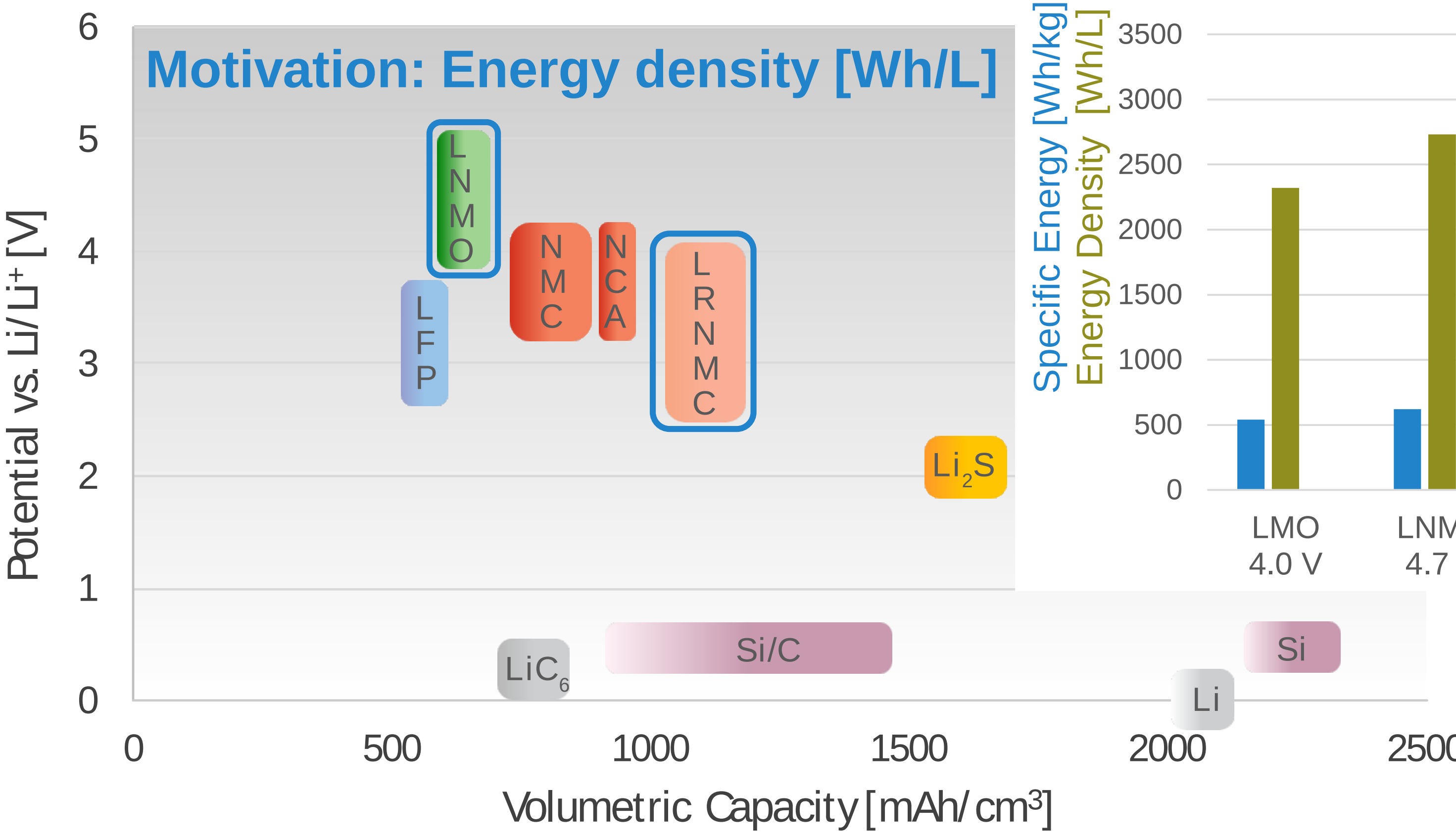

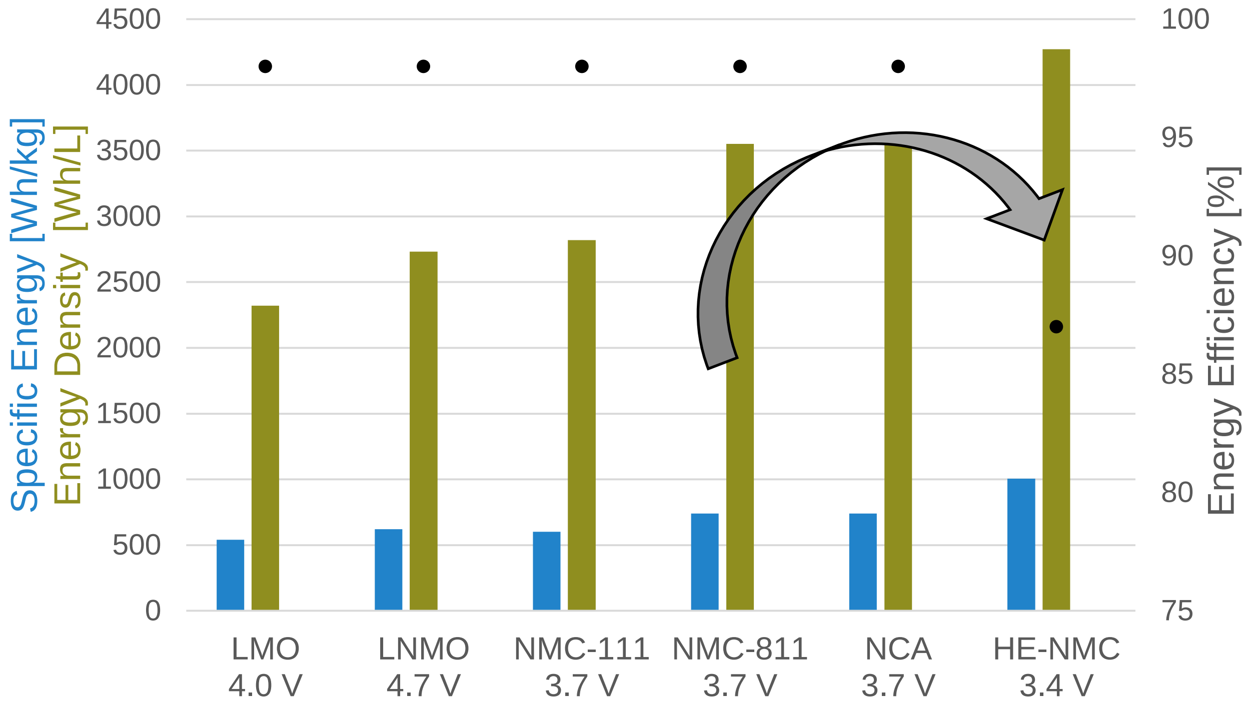

LNMO: **High-voltage spinel (HVS; $LiNi_{0.5}Mn_{1.5}O_4$)**

LRNMC: **Li-rich NMC (HE-NMC; $x\ LiMO_2 \cdot 1\text{-}x\ Li_2MnO_3$)**

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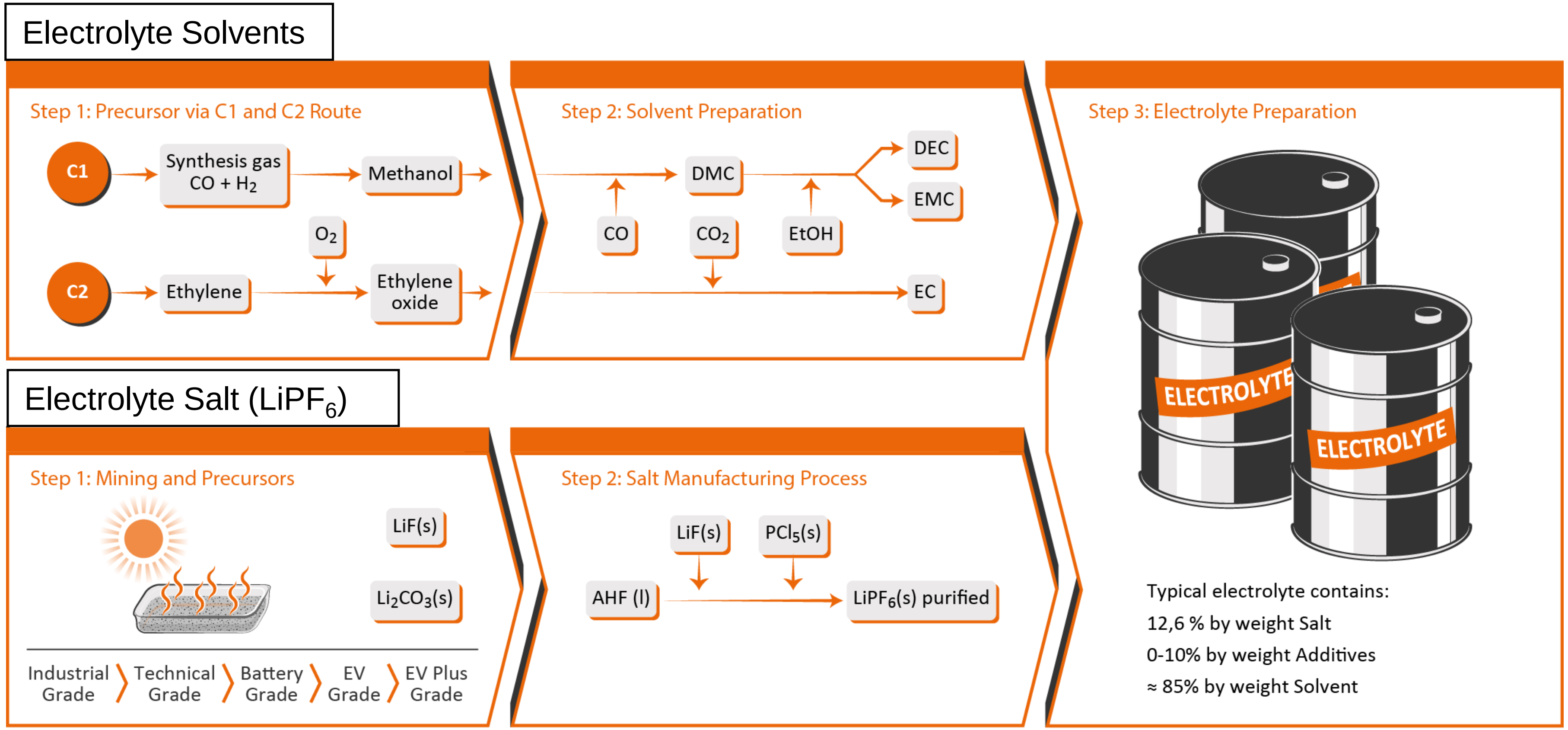
(1) Placke, T.; Kloepsch, R.; Dühnen, S.; Winter, M. *Journal of Solid State Electrochemistry* **2017**, *21*, 1939.

State-of-the-art Electrolyte: Mixtures of Carbonates and $LiPF_6$



Current research focusses on novel additives for interface stabilization:

- Anode: Solid electrolyte interphase ("SEI")
- Cathode: Cathode electrolyte interphase ("CEI")
- High voltage (>4.5 V) electrolyte additives and solvents

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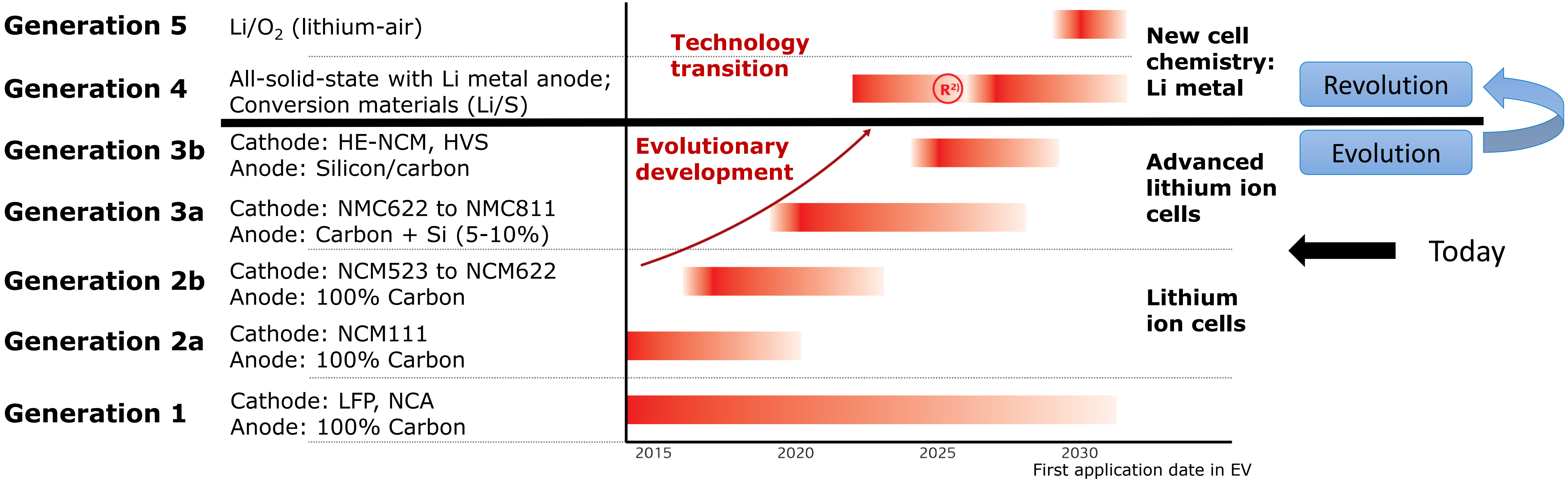
(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M. *Nature Energy* **2018**, *3*, 267.

Technological Roadmap of Battery Cell Chemistries

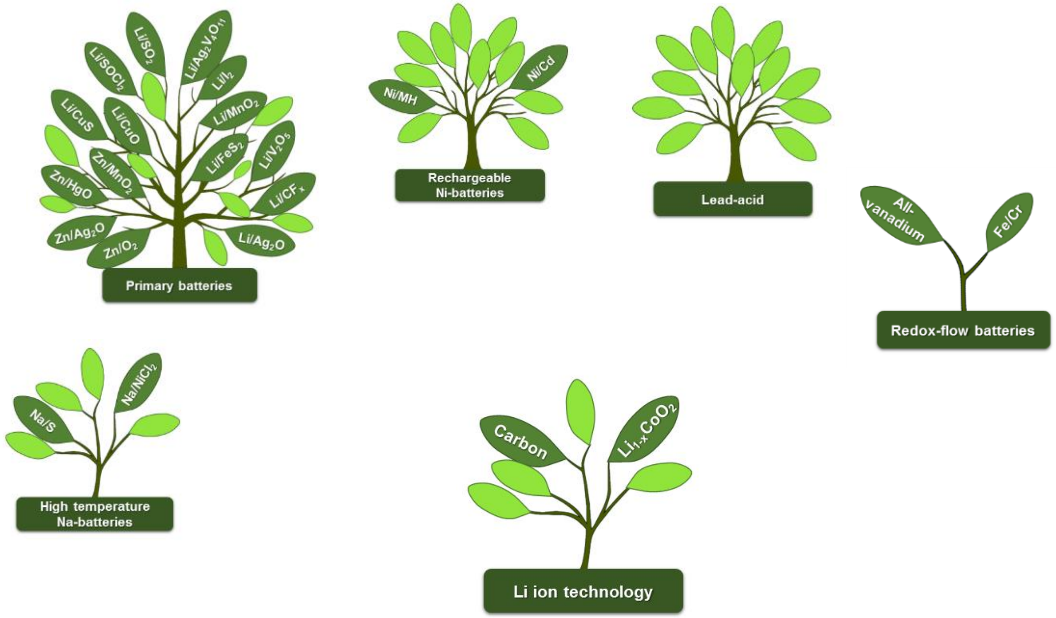


2) Risk of earlier market entrance

(1) Adapted from: Nationale Plattform Elektromobilität (NPE), *Roadmap integrierte Zell- und Batterieproduktion Deutschland*, **2016**.

Research & Development of Battery Technologies: Past, Present and Future

1991:



- The demand as well as the economic and social importance of rechargeable batteries increases rapidly (electronics, electro mobility, home storage, *etc.*)
- Versatile requirements: Significant diversification of battery technologies in the past >25 years

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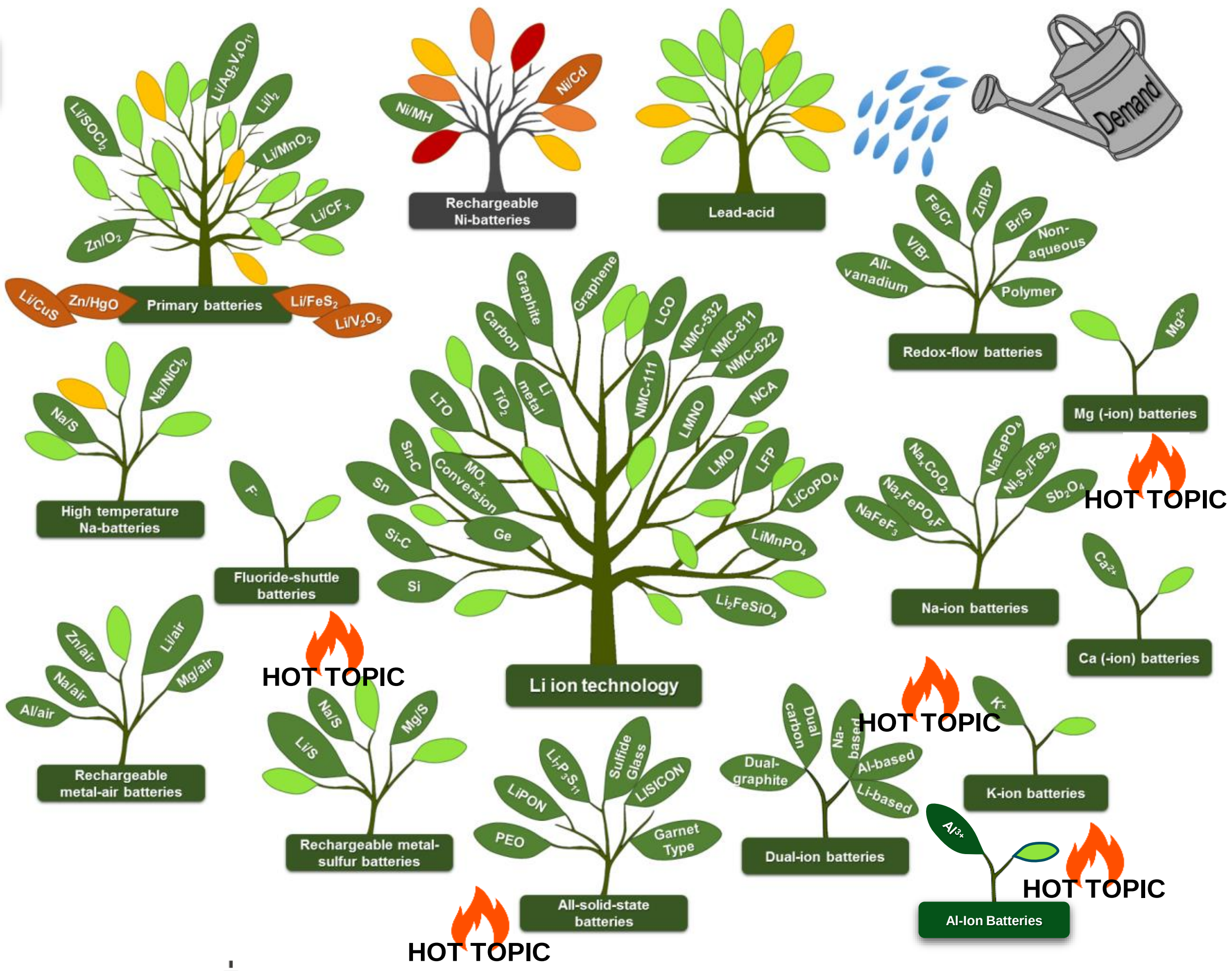
(1) Placke, T.; Kloepsch, R.; Dühnen, S.; Winter, M. *Journal of Solid State Electrochemistry* **2017**, *21*, 1939.

Research & Development of Battery Technologies: Past, Present and Future

2018:



- The demand as well as the economic and social importance of rechargeable batteries increases rapidly (electronics, electro mobility, home storage, *etc.*)
- Versatile requirements: Significant diversification of battery technologies in the past >25 years
- Lithium ion batteries (LIBs): Global market in xEVs (HEVs, PHEVs, BEVs, etc.) and energy storage applications is huge and will be the largest in the near future
- LIBs approach their physicochemical limit in terms of energy: *Next generation? Alternatives? New Cell Chemistries?*

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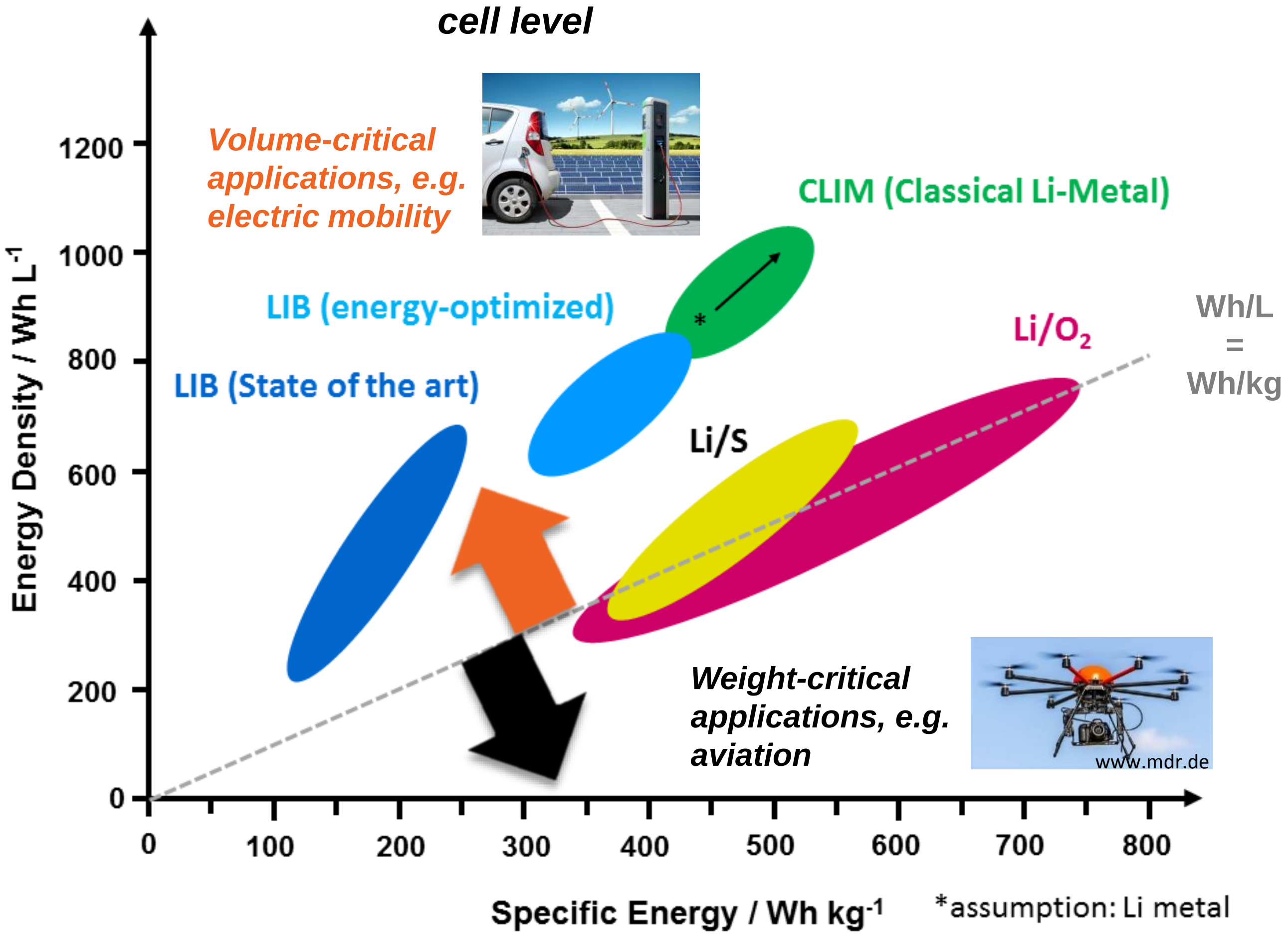
(1) Placke, T.; Kloepsch, R.; Dühnen, S.; Winter, M. *Journal of Solid State Electrochemistry* **2017**, *21*, 1939.

Performance Targets: Energy Density



- Different battery technologies will be available at the market in parallel
- Application-specific usage of different battery systems (*e.g.* high energy *vs*. high power)
- Evolutionary development of each specific battery technology
- Classification of battery technologies:
  - Lithium ion systems
  - Lithium metal systems (ASSB, Li/S, Li/O_2)
  - Other/alternative battery systems (Na, Mg, Ca, Al, Dual-ion, *etc.*)

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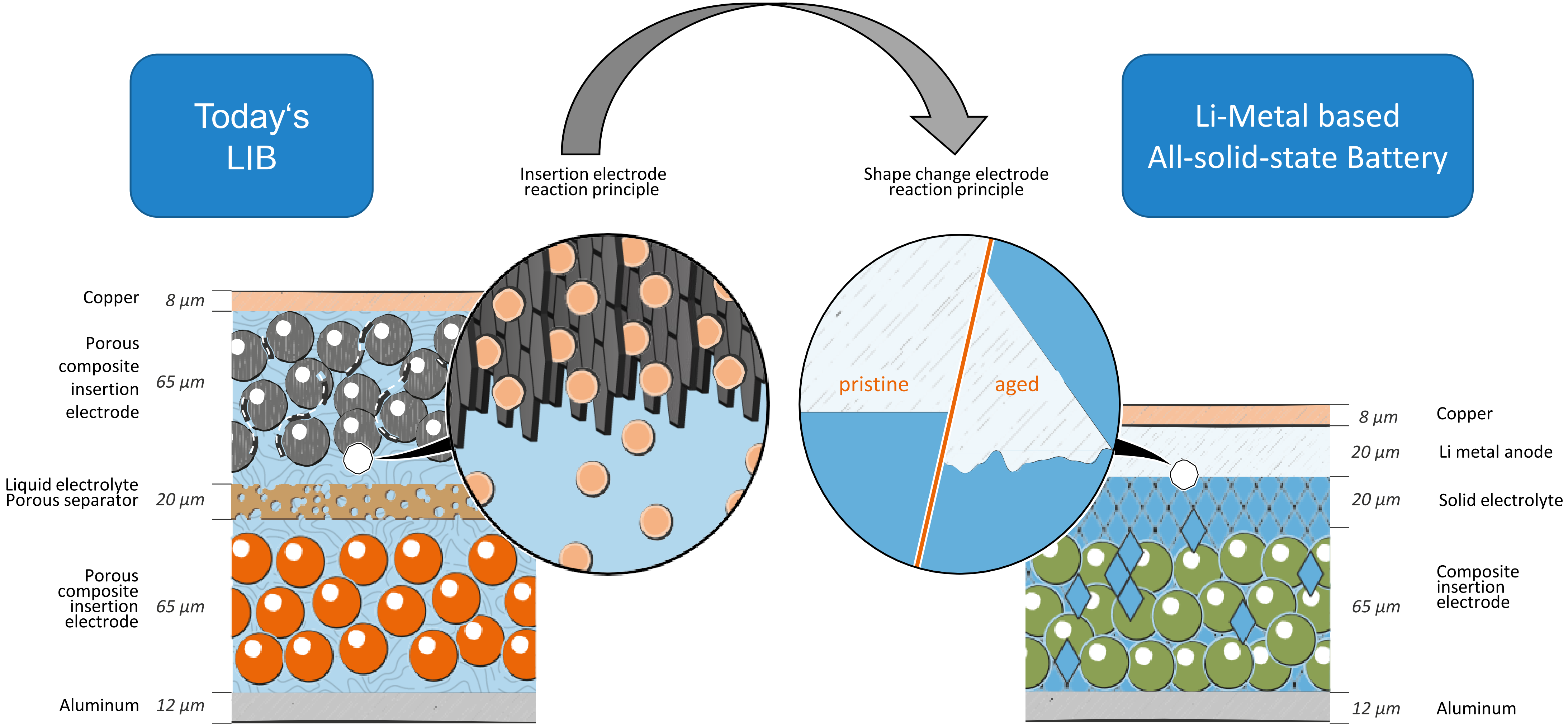
(1) Placke, T.; Kloepsch, R.; Dühnen, S.; Winter, M. *Journal of Solid State Electrochemistry* **2017**, *21*, 1939.

Lithium Metal Anodes:
Enabled by Solid Electrolytes?



(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M. *Nature Energy* **2018**, *3*, 267.

Solid Electrolytes: A Reality Check

Expectations

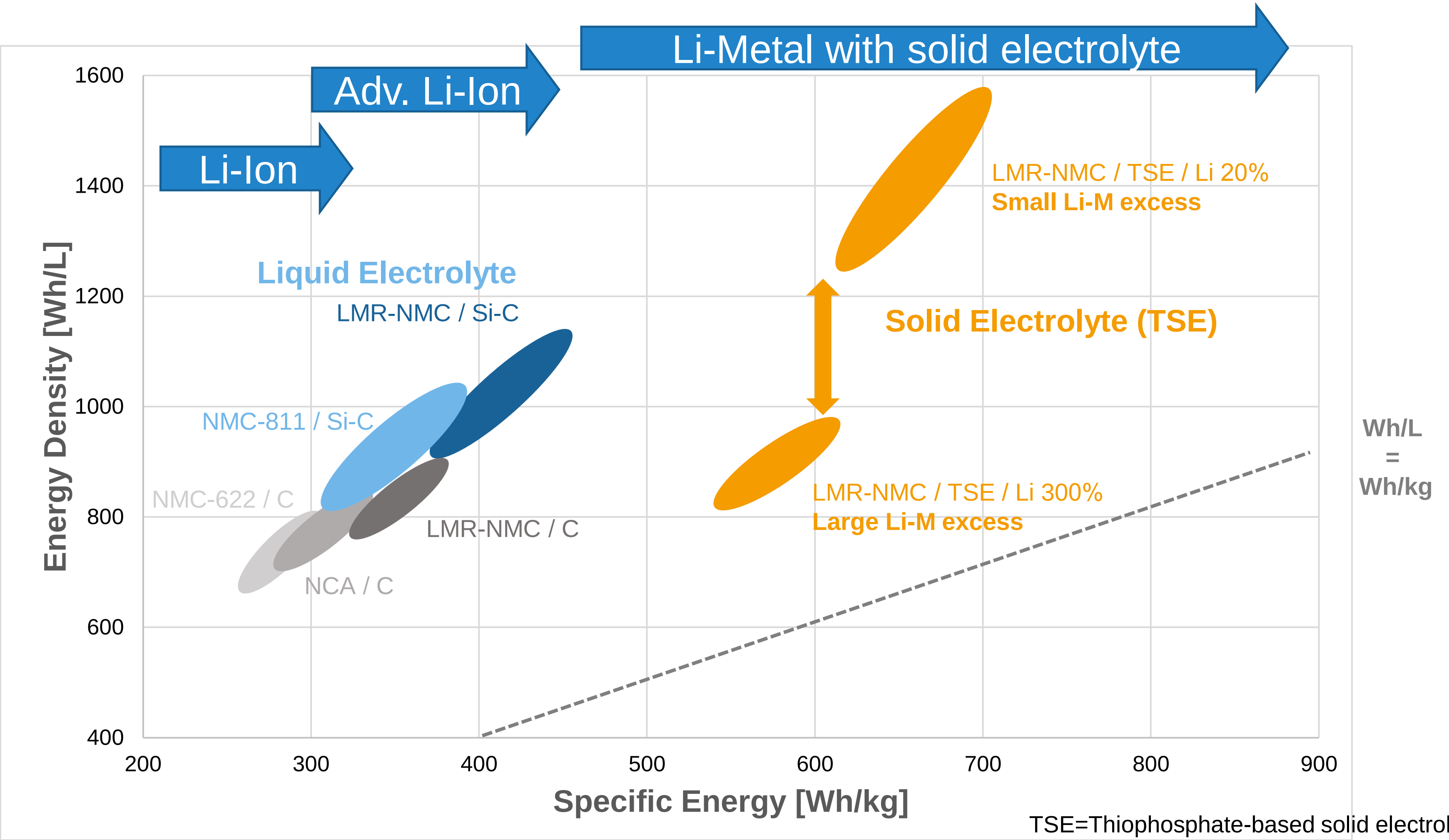
- Higher safety
- No cross-contamination of transition metals in electrode compartments (cross-talk)
- No dendrite formation, use of Li metal
- Higher voltages (higher energy density)
- Wide range of operation temperatures
- Long-term stability (cycle life, calendar life)
- Less expensive materials for inactive materials (current collection)
- Simplified thermal management

Unsolved Problems

- Slow kinetics in electrodes
- Ionic conductivity in electrodes
- Volume changes in electrodes
- „Dendrite“ formation
- Interfacial resistances
- Interfacial delaminations
- Enhanced deterioration during cycling
- Higher cost
- Battery design

Taken from: (1) Dr. Frank Tietz, IEK-1, FZ Jülich, Batterieforum Deutschland, Berlin, **2018**.

Estimated Electrode Stack Energy Density



Amount of excess Li should be minimized for:

- high energy density [Wh/L]
- minimal costs [$/kWh]

TSE=Thiophosphate-based solid electrolyte | LMR-NMC = Li/Mn-rich NMC cathode

(1) Schmuch, R.; Wagner, R.; Hörpel, G.; Placke, T.; Winter, M. *Nature Energy* **2018**, *3,* 267.

Conclusion

- Roadmaps have identified the **dominant technology** for the next decade(s): The **lithium ion technology** (with or without solid electrolyte).
- There will be **no universal LIB technology** for all application purposes, but rather a variety of chemistries and configurations for specialized applications.
- The highest potential to improve key performance indicators (energy, cost, *etc*.) of LIBs is on the **material level**.
- Most promising strategies for **energy density improvements of LIBs** are the implementation of higher Si-contents in high-energy anodes as well as to increase the Ni-content of layered cathode materials.
- Li-metal based chemistries, in particular **all-solid-state-batteries** can further enhance the *energy content*. However, it will be **challenging to be cost competitive** to further improved LIBs.
- Novel **sustainable technologies "beyond lithium"** have been explored, such as batteries based on monovalent (Na^+, K^+) and multivalent (Mg^{2+}, Ca^{2+}, Al^{3+}) ions. However, it will be challenging to compete with advanced LIBs in terms of energy content and/or cost per energy.
- Foreseen 10% yearly increase in the number of batteries produced will inevitably need recycling to recover metals/materials whose abundance is limited: **efficient recycling of materials** is mandatory.

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"Nothing great was ever achieved without enthusiasm."
Ralph Waldo Emerson, American Philosopher

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DFG Deutsche Forschungsgemeinschaft

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