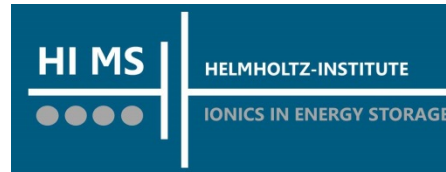




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Famous quote about safety:

*"It will never happen to me"*

Captain E.J. Smith (1850 – 1912), Captain of the Titanic

# Acknowledgements



Federal Ministry of Economics and Technology (BMWFi)

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Federal Ministry of Education and Research (BMBWF)

Economy and Science Ministries of North-Rhine-Westphalia (NRW)

University of Muenster (WWU)

Helmholtz Association and Forschungszentrum Jülich GmbH



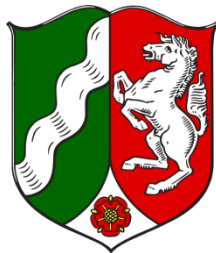
Bundesministerium  
für Wirtschaft  
und Technologie



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für Umwelt, Naturschutz  
und Reaktorsicherheit



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HELMHOLTZ  
| GEMEINSCHAFT



JÜLICH  
FORSCHUNGSZENTRUM

## Acknowledgements

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German Ministry of Education and Research (BMBF)  
within the project “Electrolyte Lab <sup>4</sup>E”



Bundesministerium  
für Bildung  
und Forschung

**81. Annual Meeting of DPG and Spring Meeting, Münster, 27 - 31 March 2017**

## **Energy Density, Lifetime and Safety – Not Only an Issue of Lithium Ion Batteries**

A. Friesen<sup>#</sup>, Falko Schappacher<sup>#</sup> and Martin Winter<sup># x</sup>



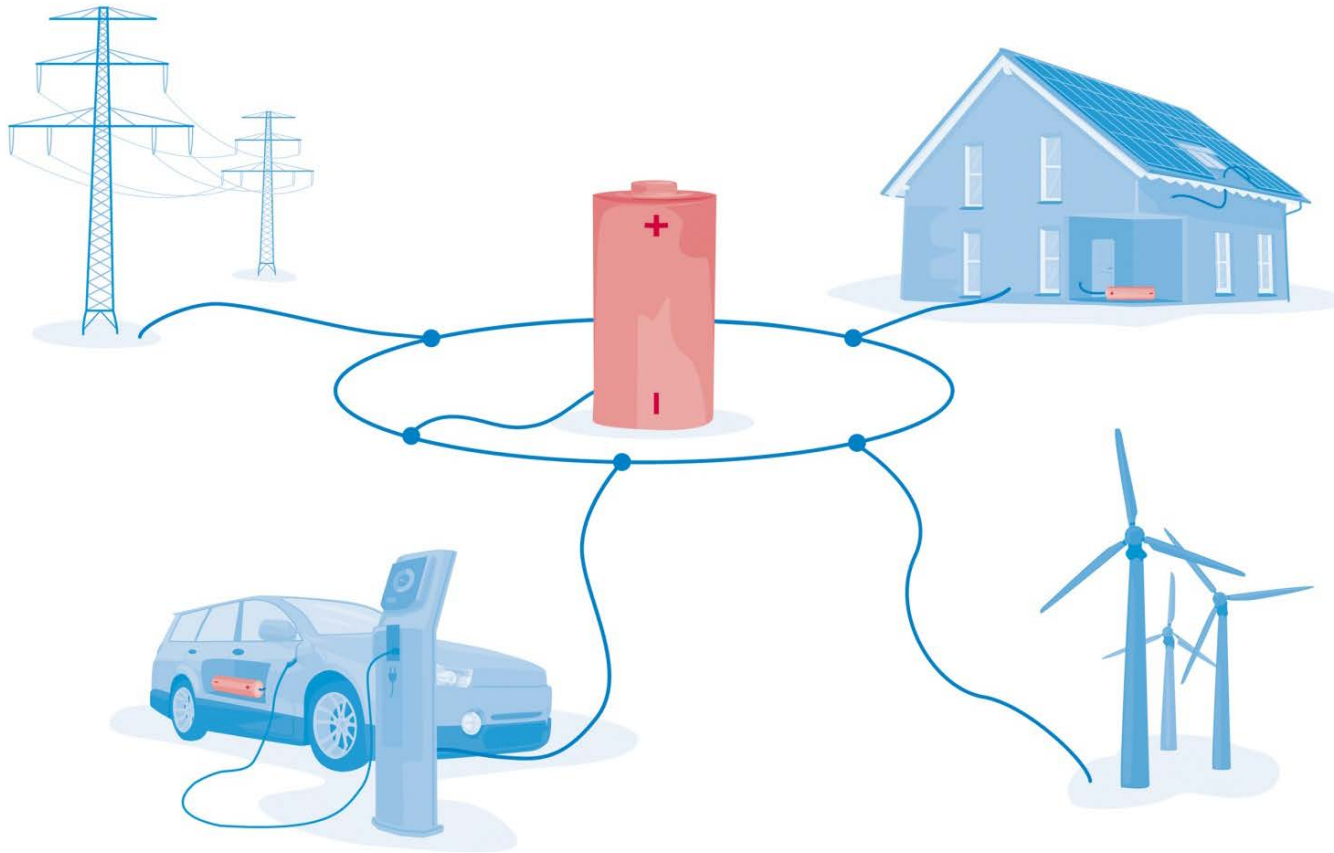
<sup>x</sup>Helmholtz-Institut Münster (HI MS)

<sup>#</sup>MEET Battery Research Center,  
Institute for Physical Chemistry,  
University of Münster

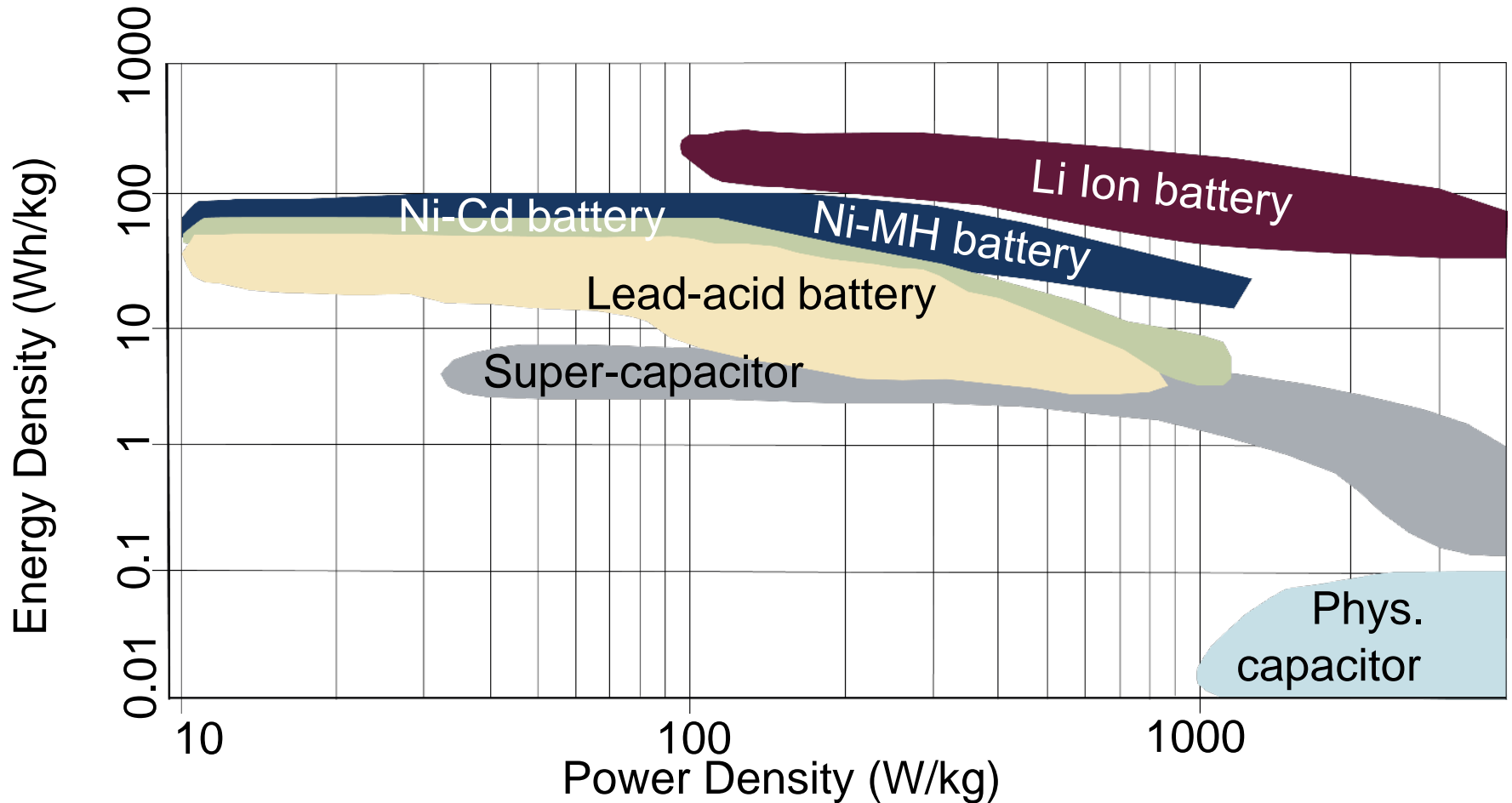
E-mail: [m.winter@fz-juelich.de](mailto:m.winter@fz-juelich.de)

E-mail: [martin.winter@uni-muenster.de](mailto:martin.winter@uni-muenster.de)

# Batteries in the Center of a Sustainable Energy Scenario

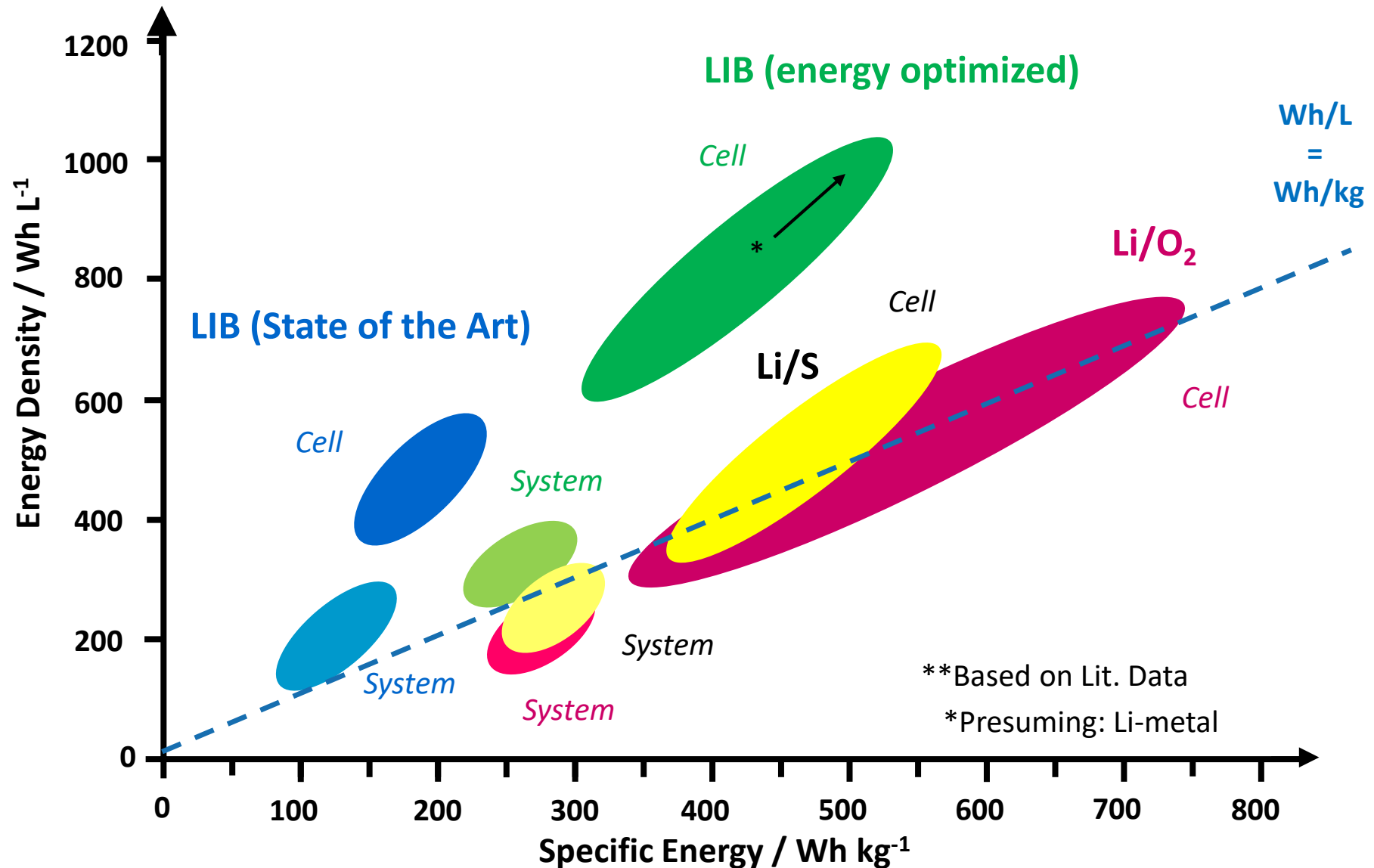


# The Lithium Ion Advantage: High Energy and/or High Power Densities in Comparison to “Conventional” Energy Storage Systems

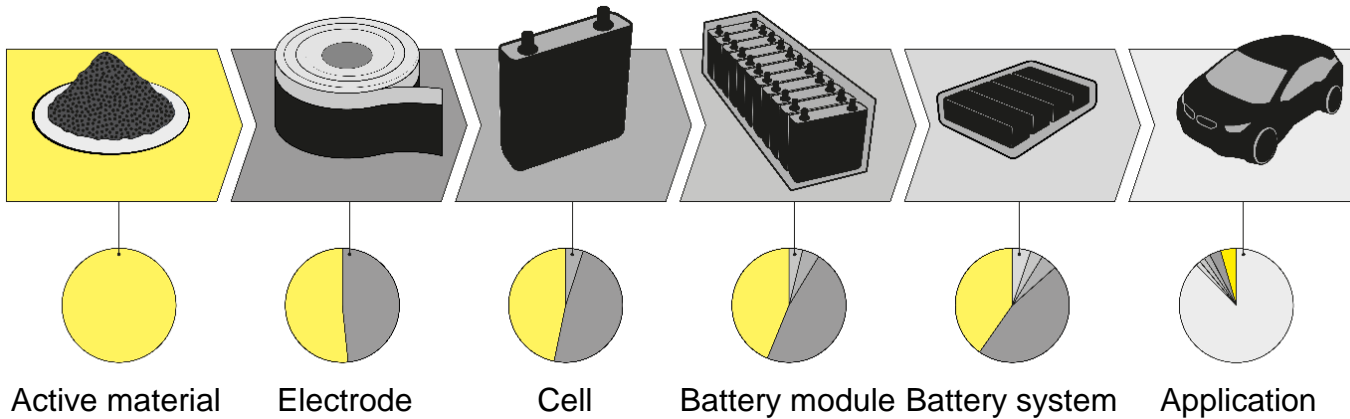




# The Lithium Ion Advantage: High Energy Density per Volume in Comparison to Eventual Future Electrochemical Energy Storage Systems\*\*



# Active and Inactive Materials: From Material Level to Battery Level



Increasing amount of inactive components  
→ Decreasing energy density

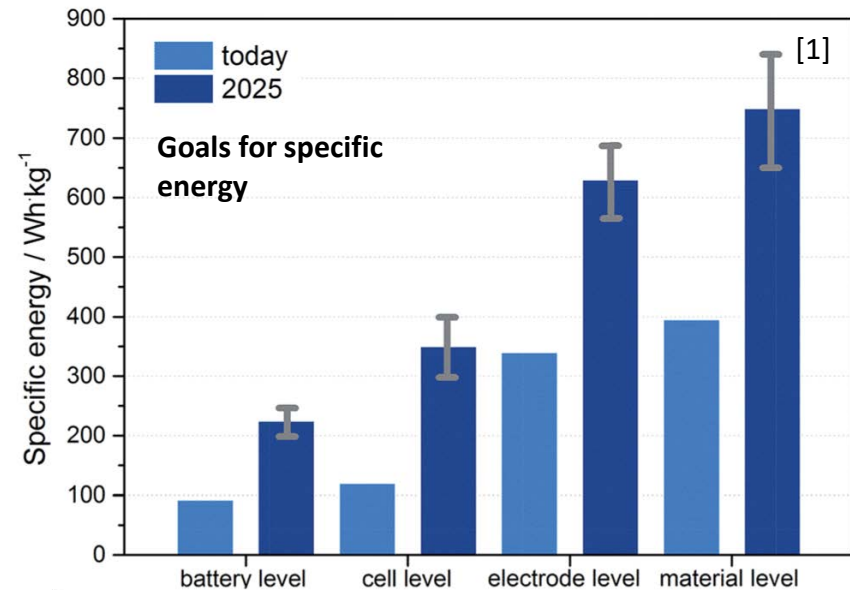
## Specific energy/energy density of LIBs:

$$\text{Specific energy} \left[ \frac{\text{Wh}}{\text{kg}} \right] = \frac{\text{Capacity (Cell)} * \text{Cell voltage}}{\text{Mass active \& inactive materials}}$$

$$\text{Energy density} \left[ \frac{\text{Wh}}{\text{L}} \right] = \frac{\text{Capacity (Cell)} * \text{Cell voltage}}{\text{Volumen active \& inactive materials}}$$

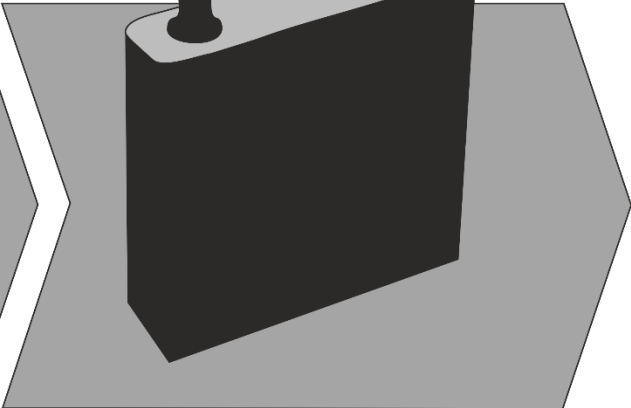
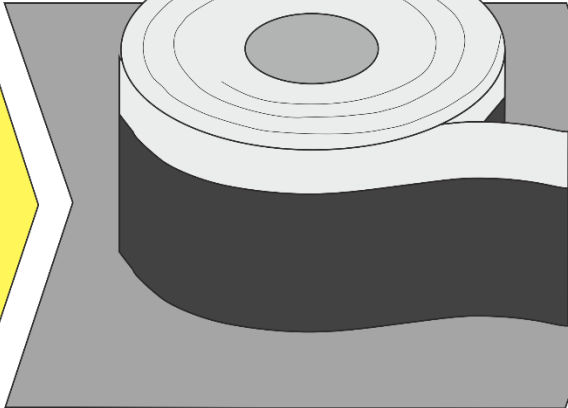
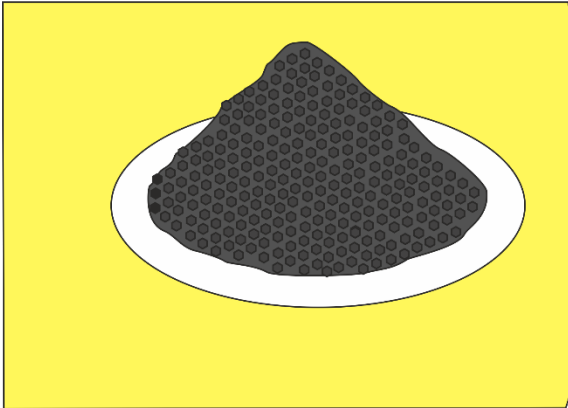


Effect on specific energy/energy density

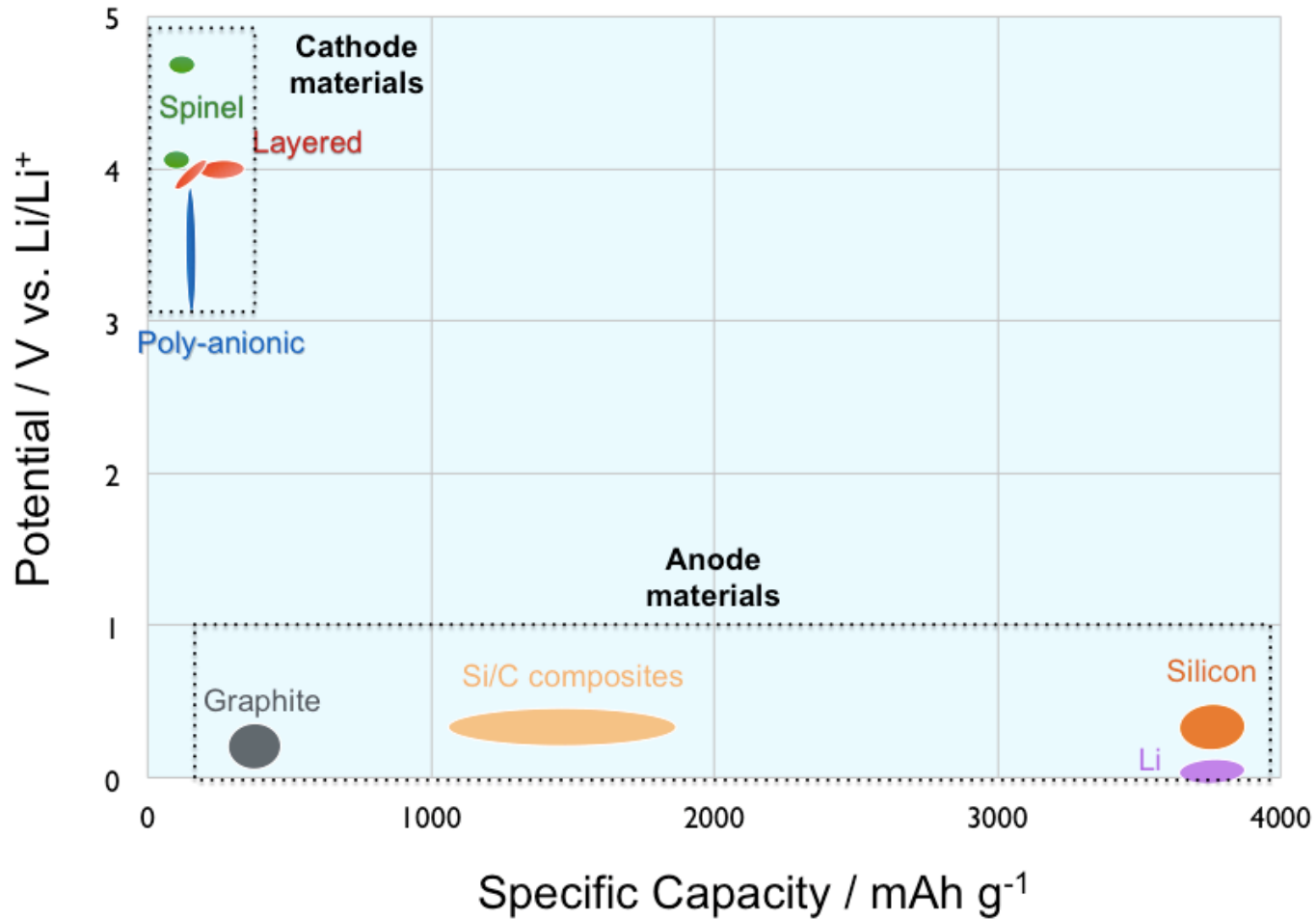




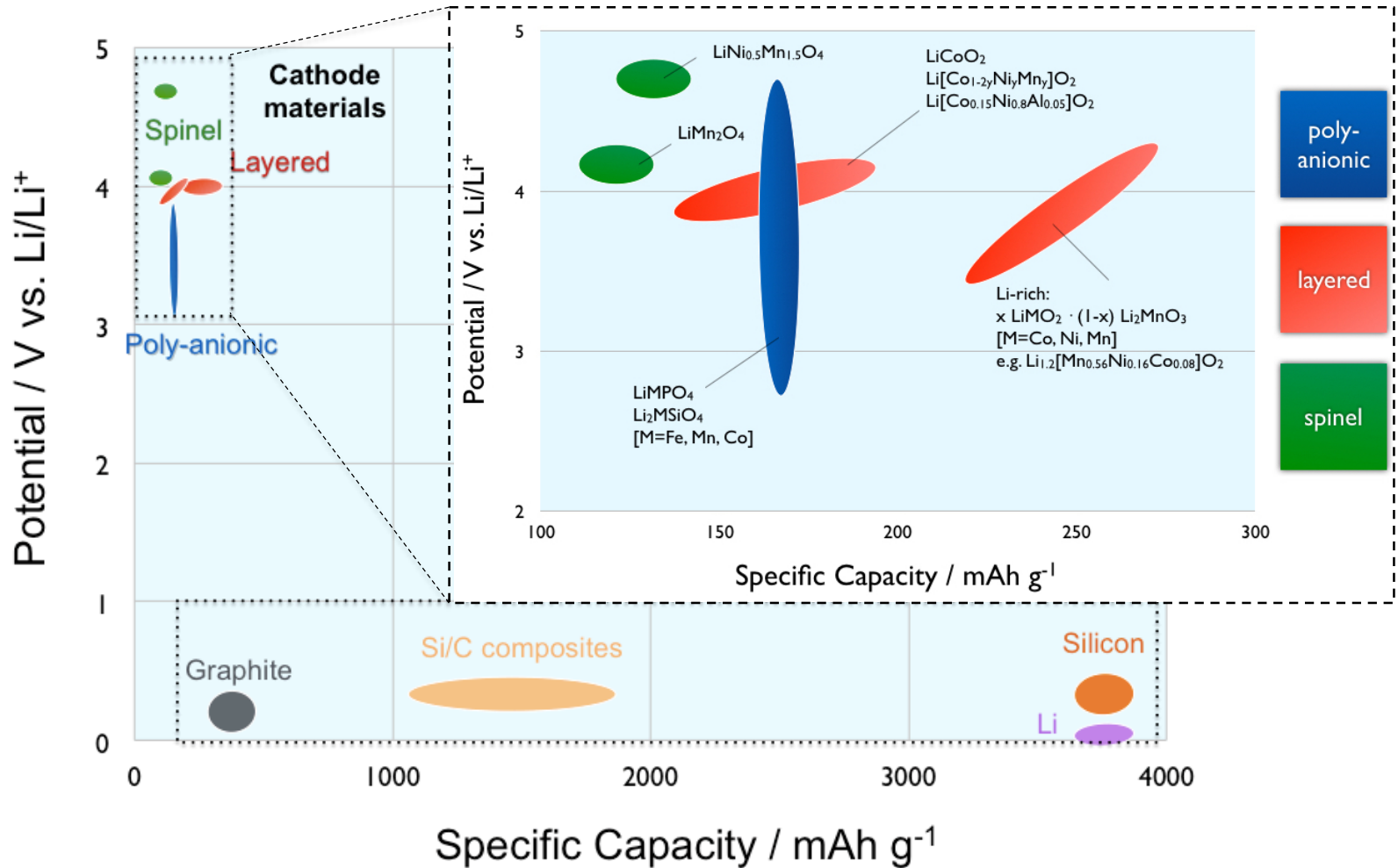
# Material



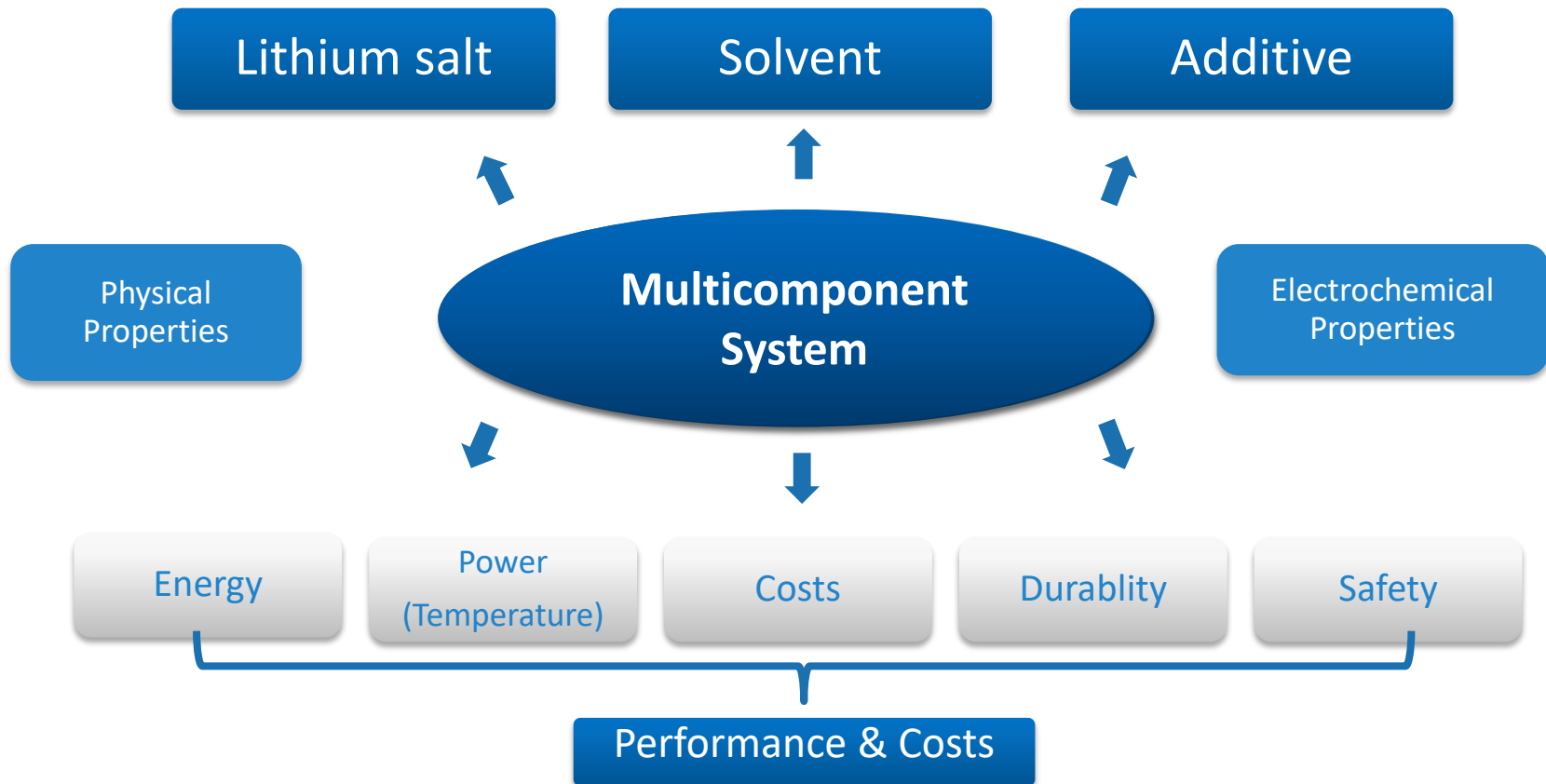
# LIB: State of the Art and Near Future



# LIB: State of the Art and Near Future

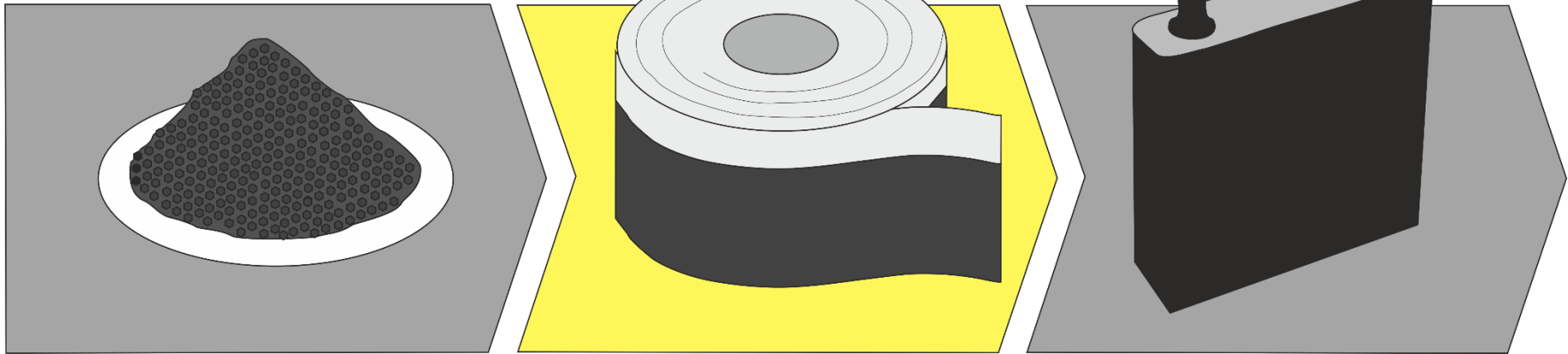


# Electrolyte as Key Component of the Battery Cell

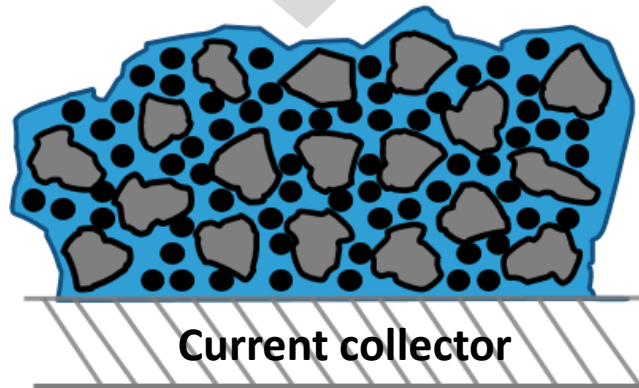
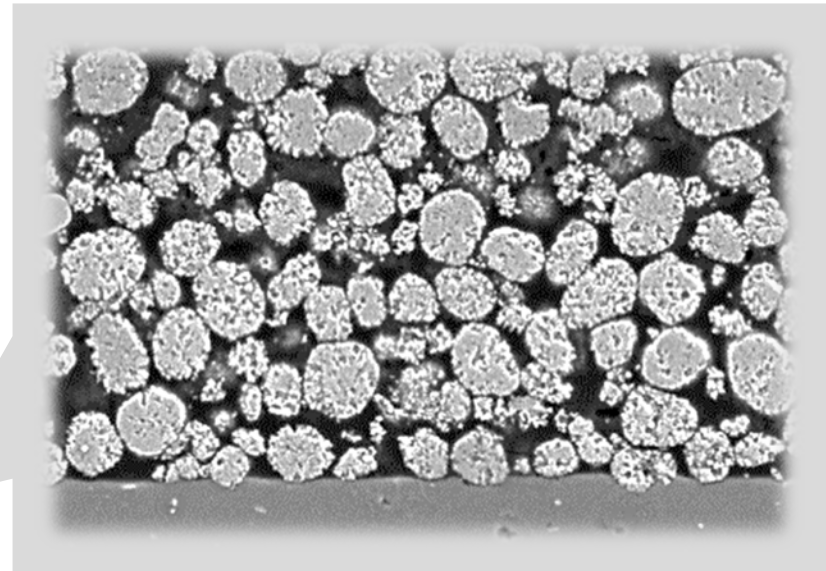
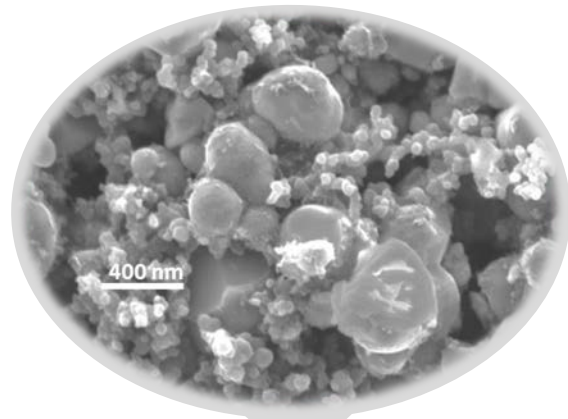


Liquid electrolytes need separator: organic and/or ceramic

# Electrode



# Powdery Materials → Composite Electrode Structures



Amount in the composite electrode:  
Binder: ~ 1-5 wt.%  
Conductive agent: ~ 1-5 wt.%



Active material



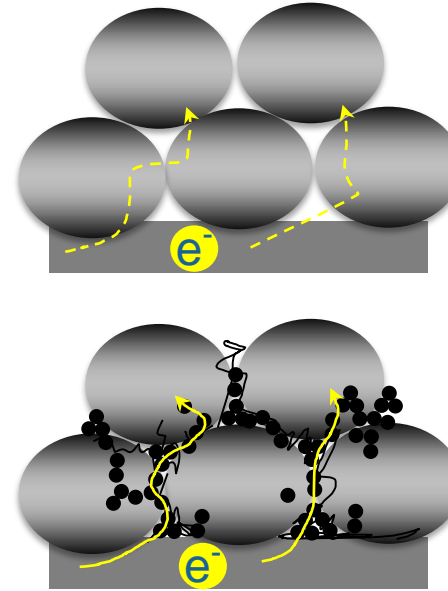
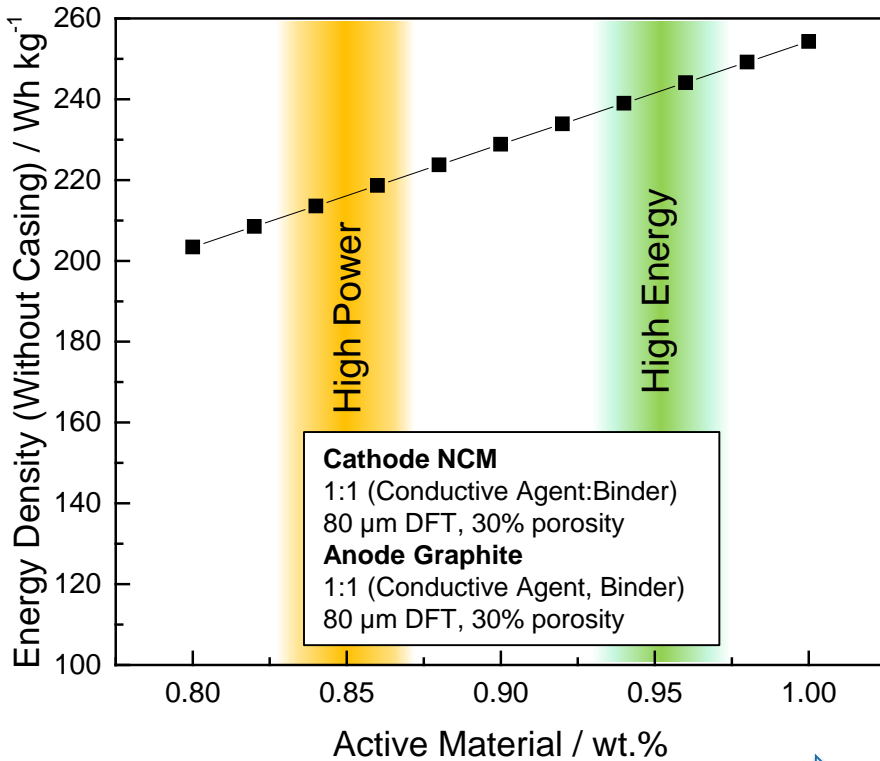
Conductive agent



Binder / Porosity / Electrolyte



# Performance of LIB: Electrode Level – Active Material



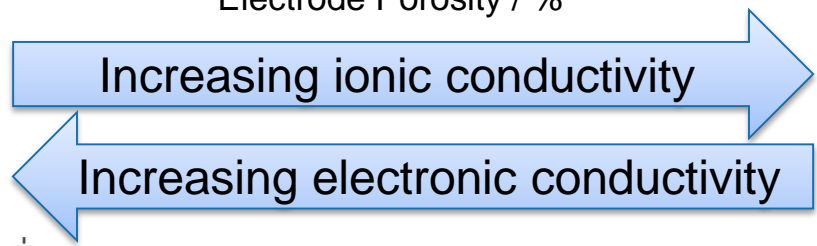
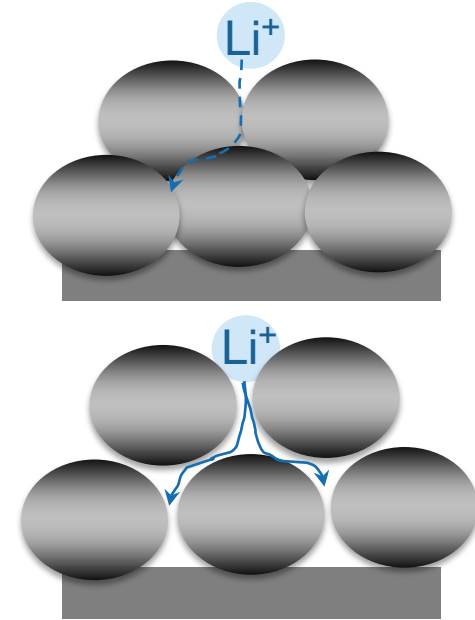
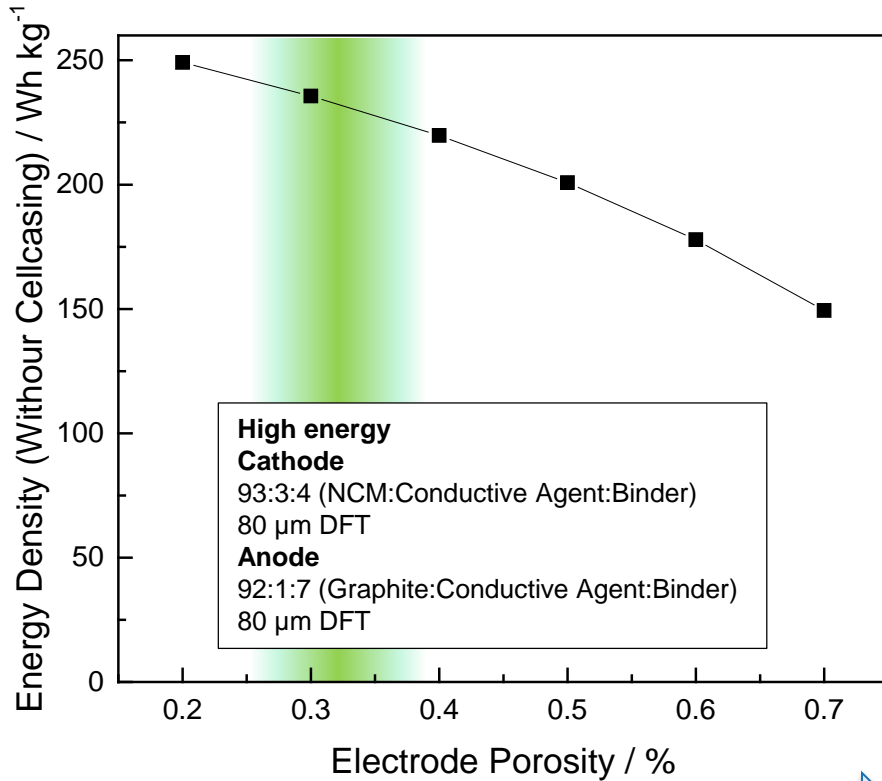
High content of active material increases energy density at the expense of power capability

Increasing energy density

Decreasing resistance

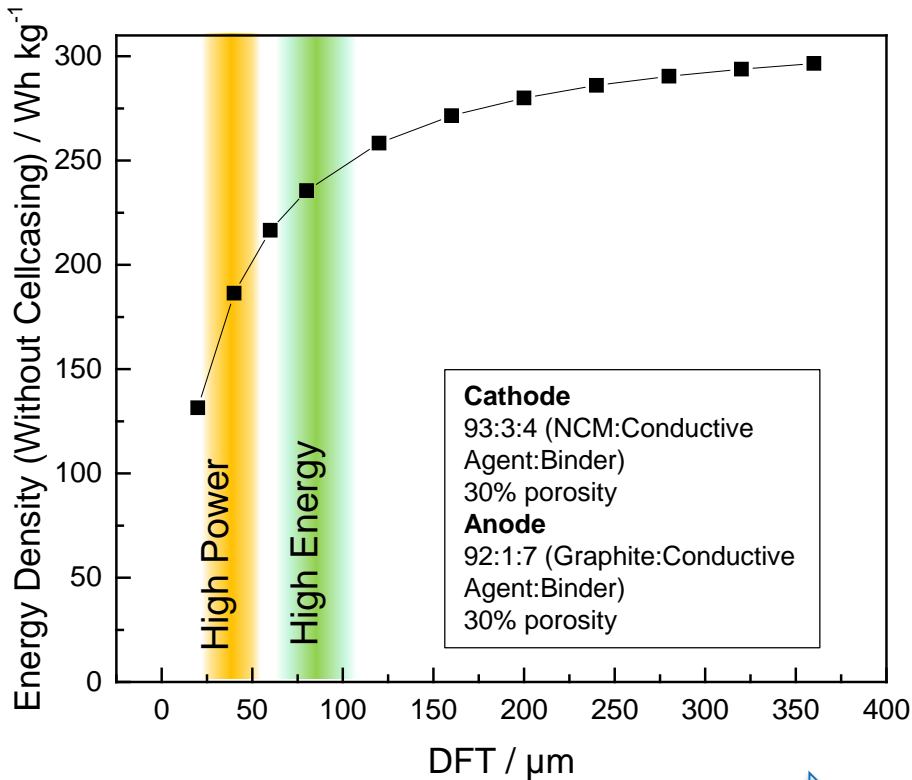
DFT: Dry Film Thickness

# Performance of LIB: Electrode Level – Electrode Porosity



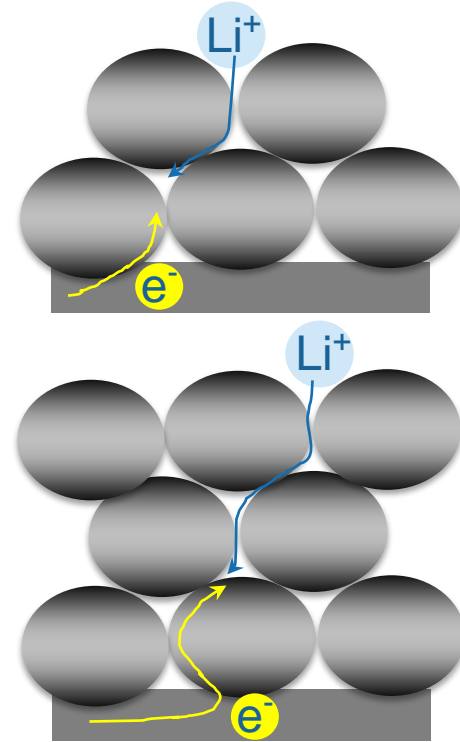
DFT: Dry Film Thickness

# Performance of LIB: Electrode Level – Dry Film Thickness



Increasing Diffusion Distance

Increasing Amount of Inactive Material

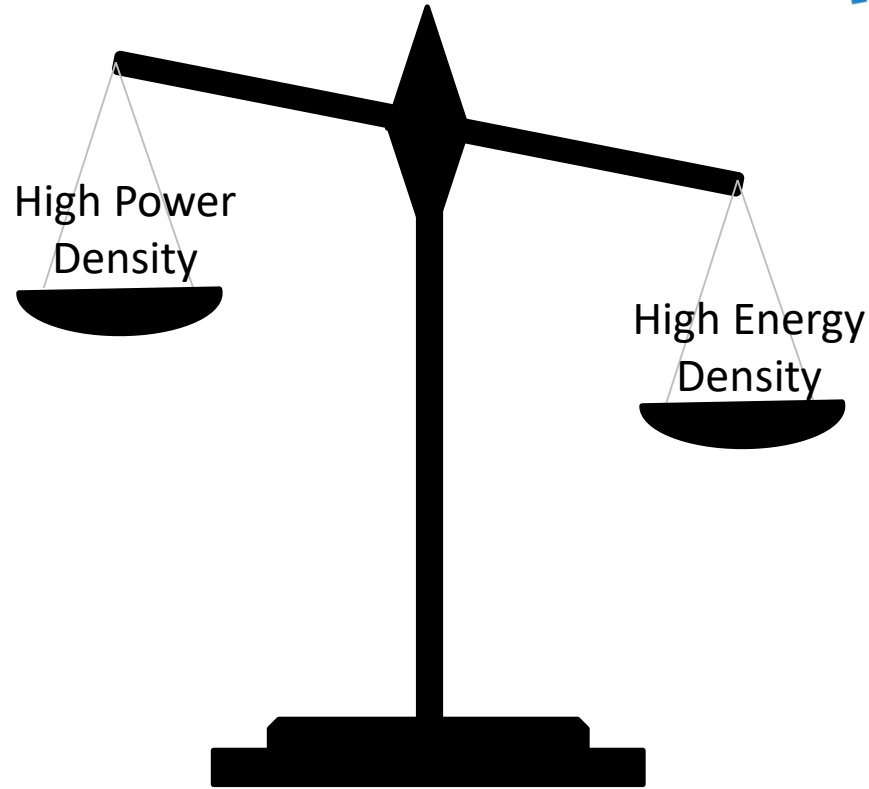
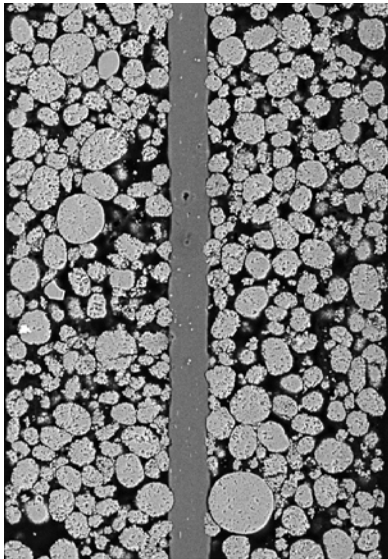


Increasing the electrode thickness increases the energy density but enlarges distances for ion and electron transport  
→ Reduced power capabilities

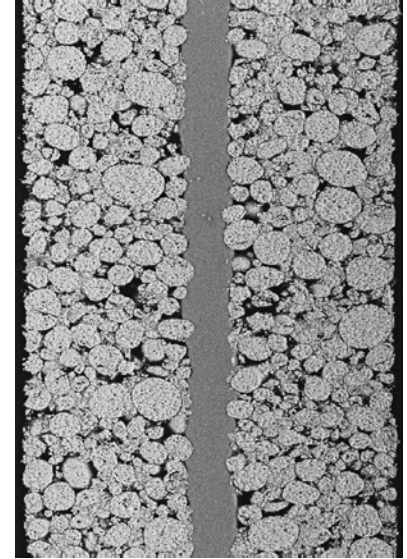
High potential to increase the energy density

# Performance of LIB: Electrode Level

High Power  
Density Electrode



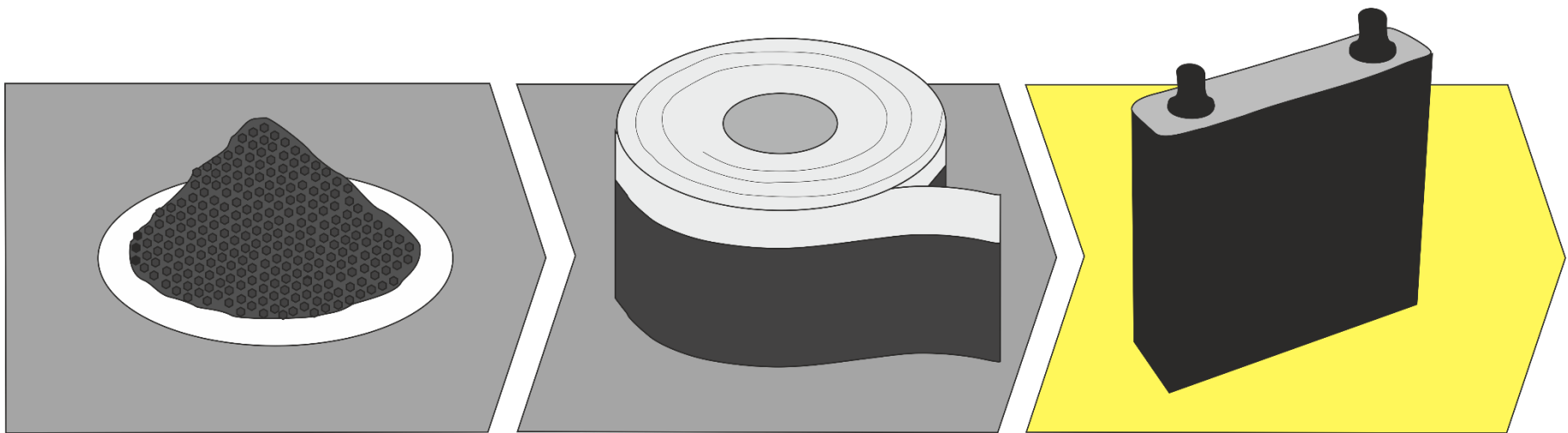
High Energy  
Density Electrode



## Variation of parameters

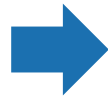
- Porosity (Calendering)
- Particle Size (primary and secondary)
- Dry Film Thickness (DFT)
- Current collector thickness
- Tab position
- Tab welding

# Cell



# Comparison of Cell Types: Advantages and Disadvantages

## Cylindrical



High energy density

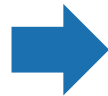
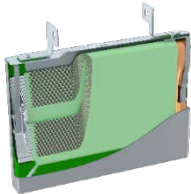


Easy and fast manufacturing



Fast heating

## Prismatic



Heat transfer



Easy packaging

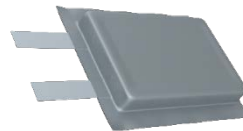
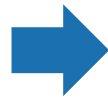
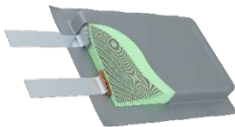


Slow and complex manufacturing



Expensive

## Pouch



Low weight



Shock- and vibration-tolerant



Design flexibility



Mechanical Stability



External pressure required



# Battery Line in MEET – 5 Ah (Pouch)

Materials



Mixing



Coating and Drying



Calandring



Slitting

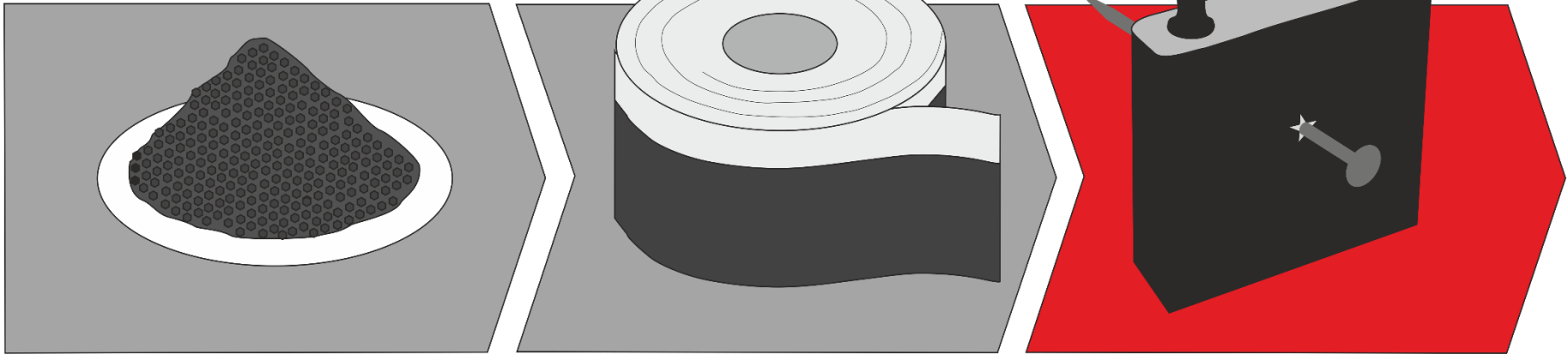


Cell Assembly

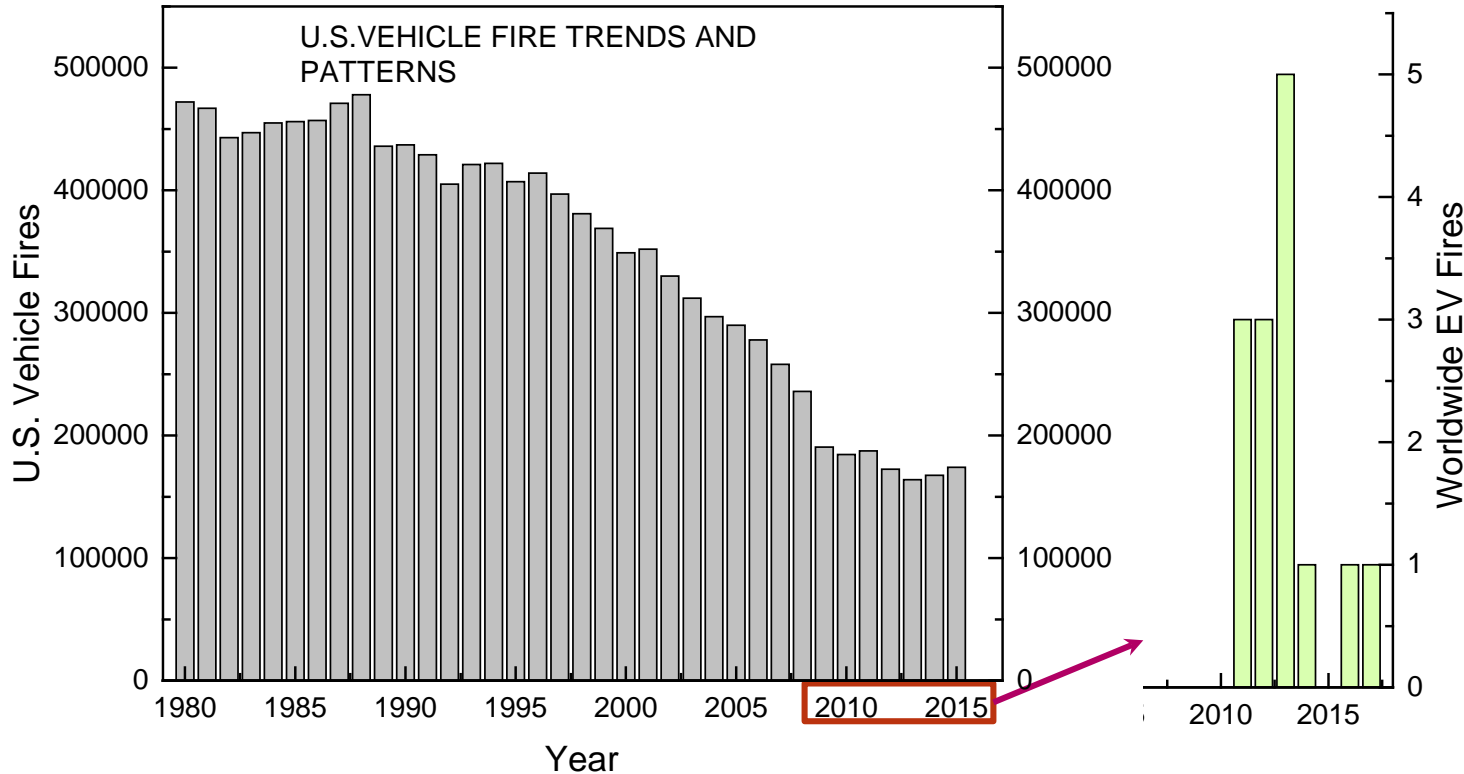


Type: 5 Ah

# Cell Safety



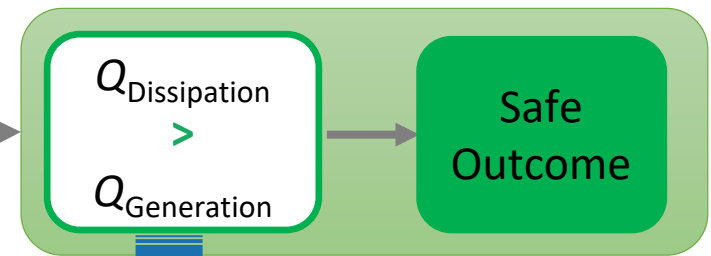
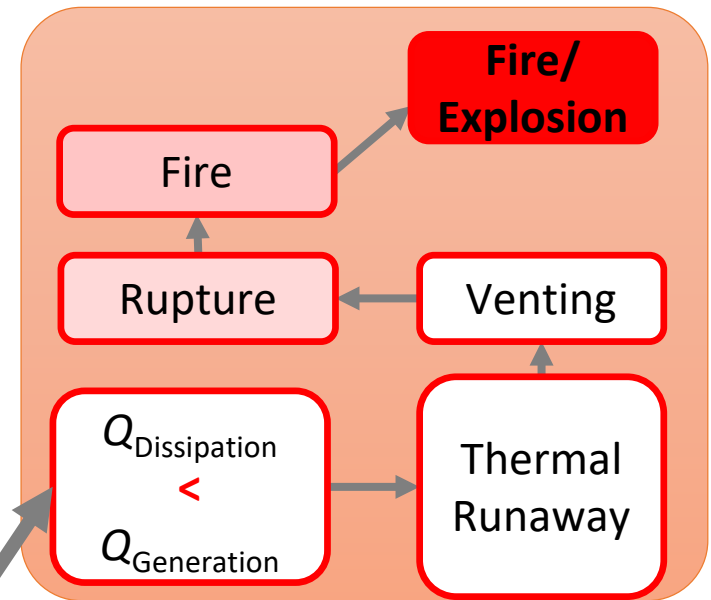
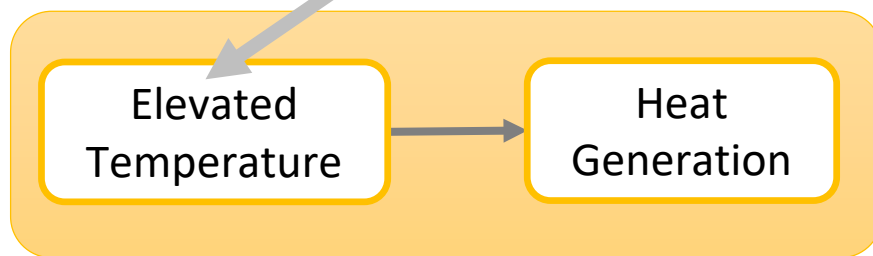
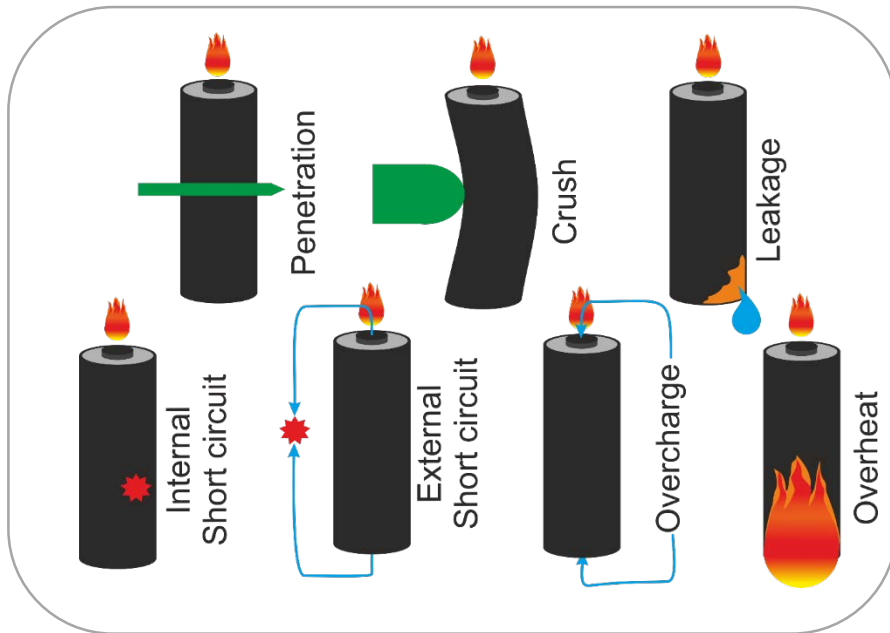
# Fire Incidents with ICE und EV



- 6x Tesla Model S
- 2x Chevrolet Volt
- 2x Fisker Karma
- 1x Zotye
- 1x BYD e6
- 2x Mitsubishi

- 90 vehicle fires per billion miles of ICE (only US data)
- 12 Total Fire Incidents with EV (Worldwide)
- 6 Tesla fires (total) and 3 billion miles driven  
 → 2 Tesla fires per billion miles

# Abuse Behavior of Lithium Ion Cells



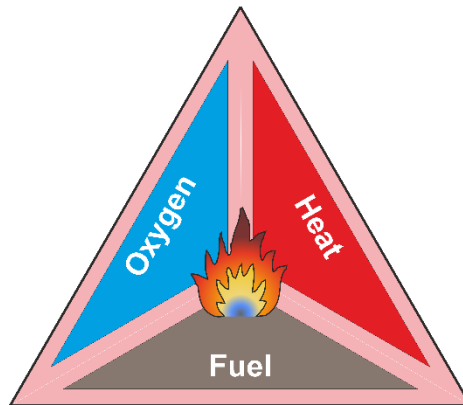
Intelligent design of battery packs  
(e.g. heat exchange with active/passive heat sink)

# Systematic Approach to Lithium Ion Material Safety

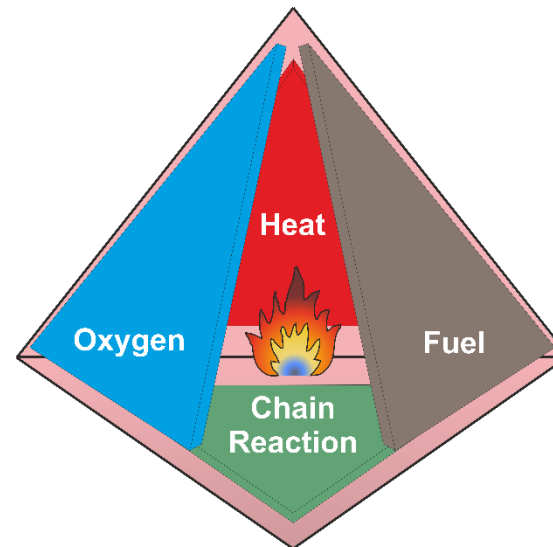


Fire is a by-product of combustion (= process of rapid oxidation of fuel). In order to ignite and burn, a fire requires three **elements**: **Heat**, **Fuel**, and **Oxygen** represented by the "**Fire Triangle**" (cf. *science of fire fighting*). The fire is prevented or extinguished by "removing" any one of them. A fire naturally occurs when the elements are combined in the right proportions (e.g., more heat is needed to ignite some fuels).

Sometimes it is useful to consider a fourth essential element of fire, the sustaining **Chemical Chain Reaction** ( $\Rightarrow$  "**Fire Tetrahedron**")



Fire Triangle



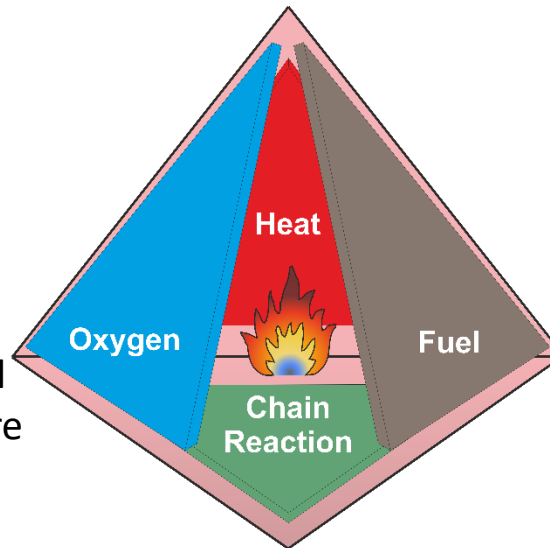
Fire Tetrahedron

# The Fire Tetrahedron in a Lithium-Ion Cell – Materials View

## Heat/Energy Release via

- Anode or cathode decomposition
- Cell short: internal/external

- **Oxygen**
- Release from layered cathodes during overcharge
- Oxygen access to cell after cell rupture/opening via gas pressure build-up or external impact



Fire Tetrahedron

## Combustibles

- Li (High surface area)
- Electrolyte solvents (and salts)
- Gases (Hydrogen-rich)



# The Fire Tetrahedron in a Lithium-Ion Cell – Materials View: Countermeasures



## Heat/Energy Release via

- Anode or cathode decomposition
- Cell short: internal external

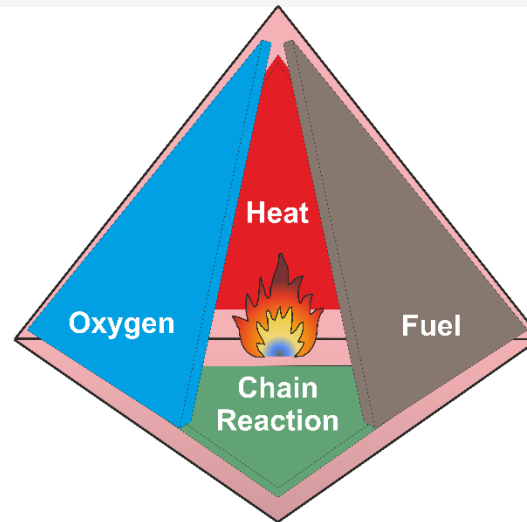
- ✓ Material Stabilization
- ✓ Cooling
- ✓ Rapid Heat Transfer

## Oxygen

- Release from layered cathodes during overcharge
- Oxygen access to cell after cell rupture/opening via gas pressure build-up or external impact

✓ Stable cathodes, e.g.,  $\text{LiFePO}_4$

✓ Suppression of gas pressure, etc.



Fire Tetrahedron

## Combustibles

- Li (Dendrites)
- Electrolyte solvents (and salts)
- Gases (Hydrogen-rich)

- ✓ No Li metal
- ✓ Non-flammable electrolytes
- ✓ Gas suppression

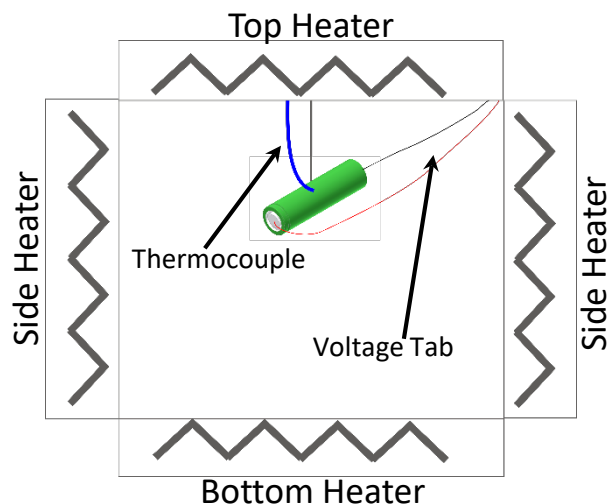
## (Radical) Chain Reaction

✓ Radical scavengers

✓ Shut-down, etc.

(additives, separators)

# Accelerating Rate Calorimetry (ARC): Thermal Stability of LIB Cells



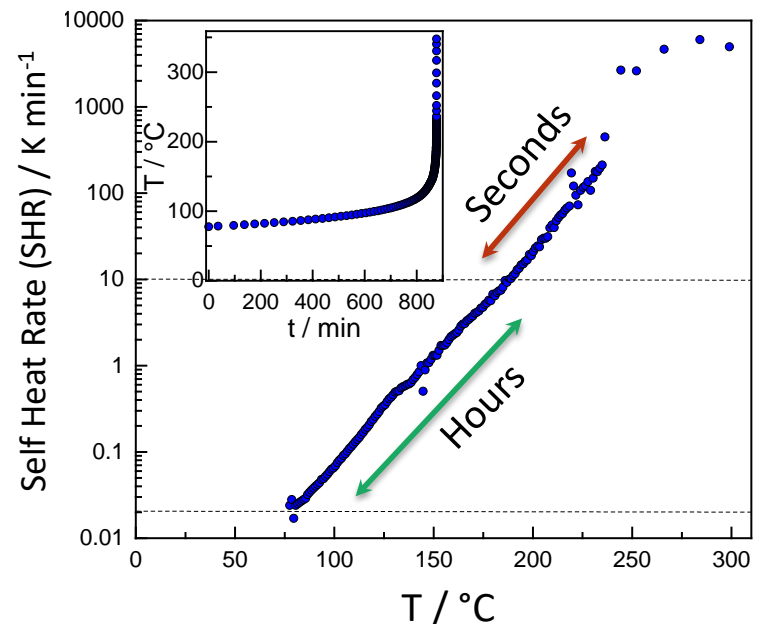
- Adiabatic environment
- No heat dissipation into surrounding

Heat Dissipation:  $Q_D = 0 J$

- Measurement of self-sustaining exothermic heat due to decomposition reactions

Heat Generation:  $Q_G \rightarrow \text{Cell Heating}$

Self-Heat Rate  $> 10 \text{ K min}^{-1}$ : Thermal runaway



High reproducibility



High precision

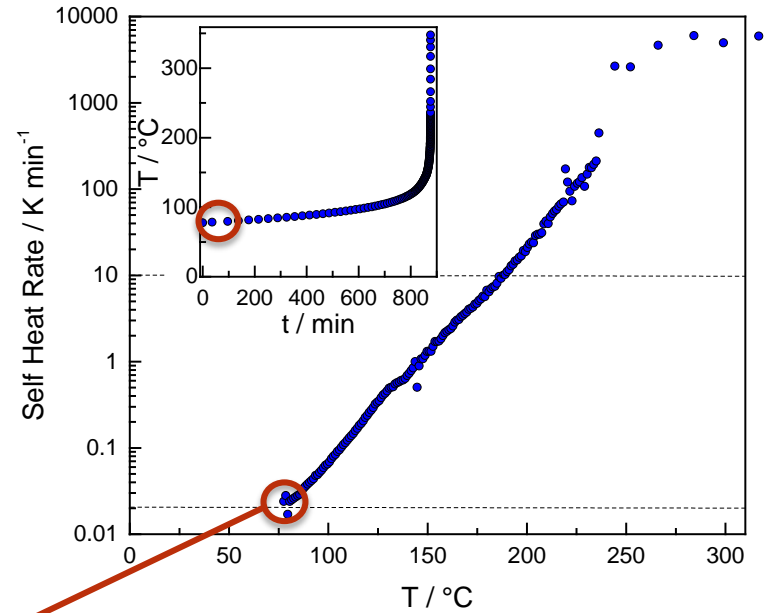
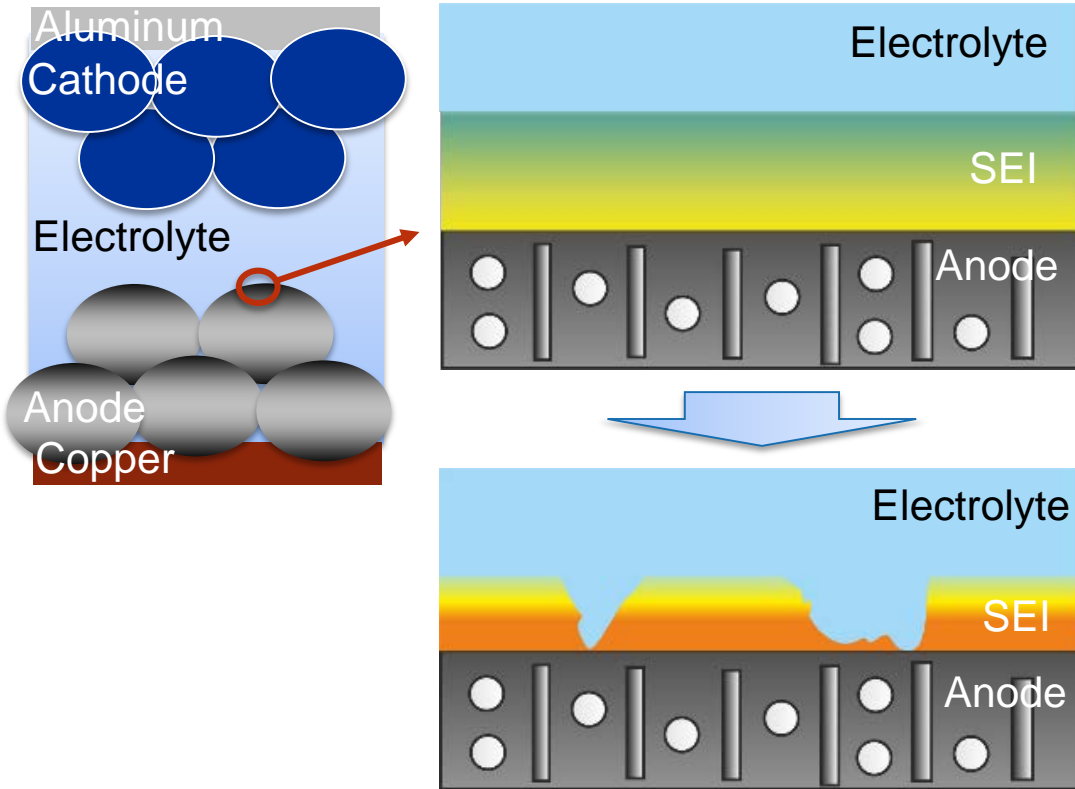


Thermal runaway



Only thermal abuse

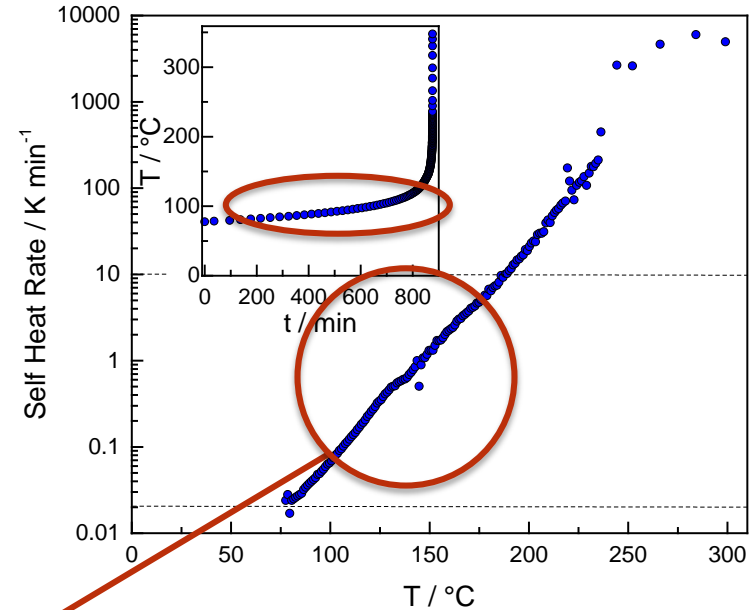
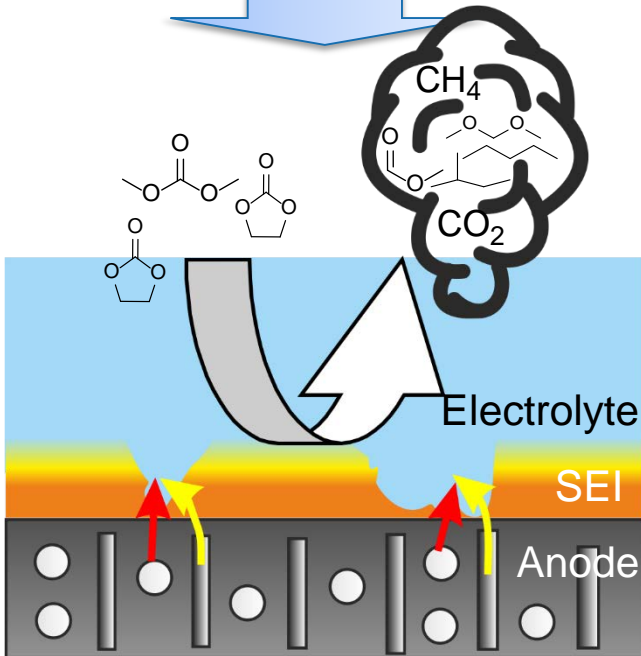
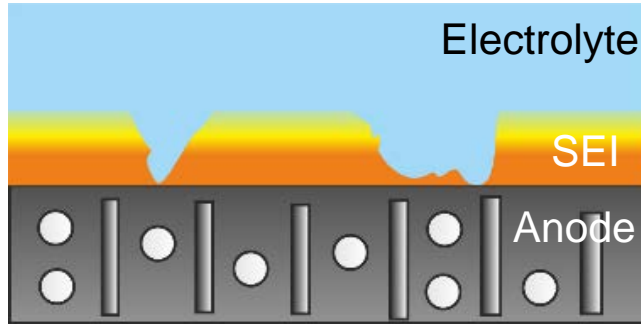
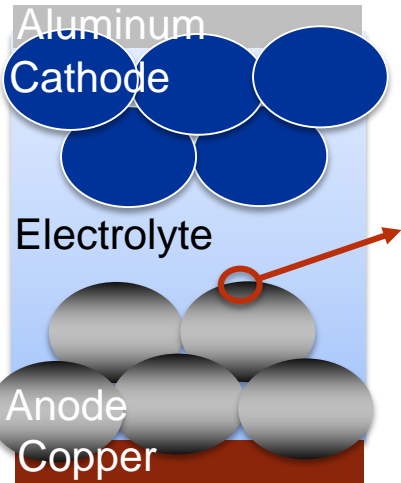
# ARC: Thermal Stability of LIB Cells Processes at Moderate Temperatures



- SEI conversion and decomposition
- Low exothermic heat release

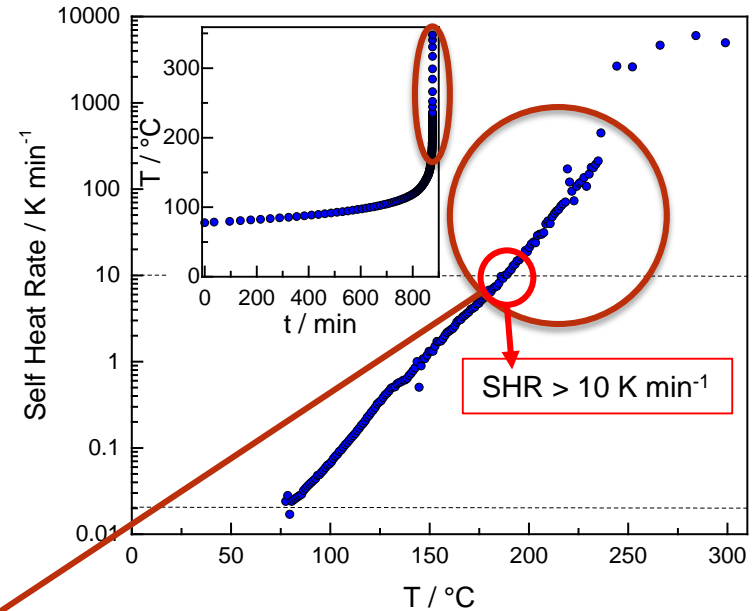
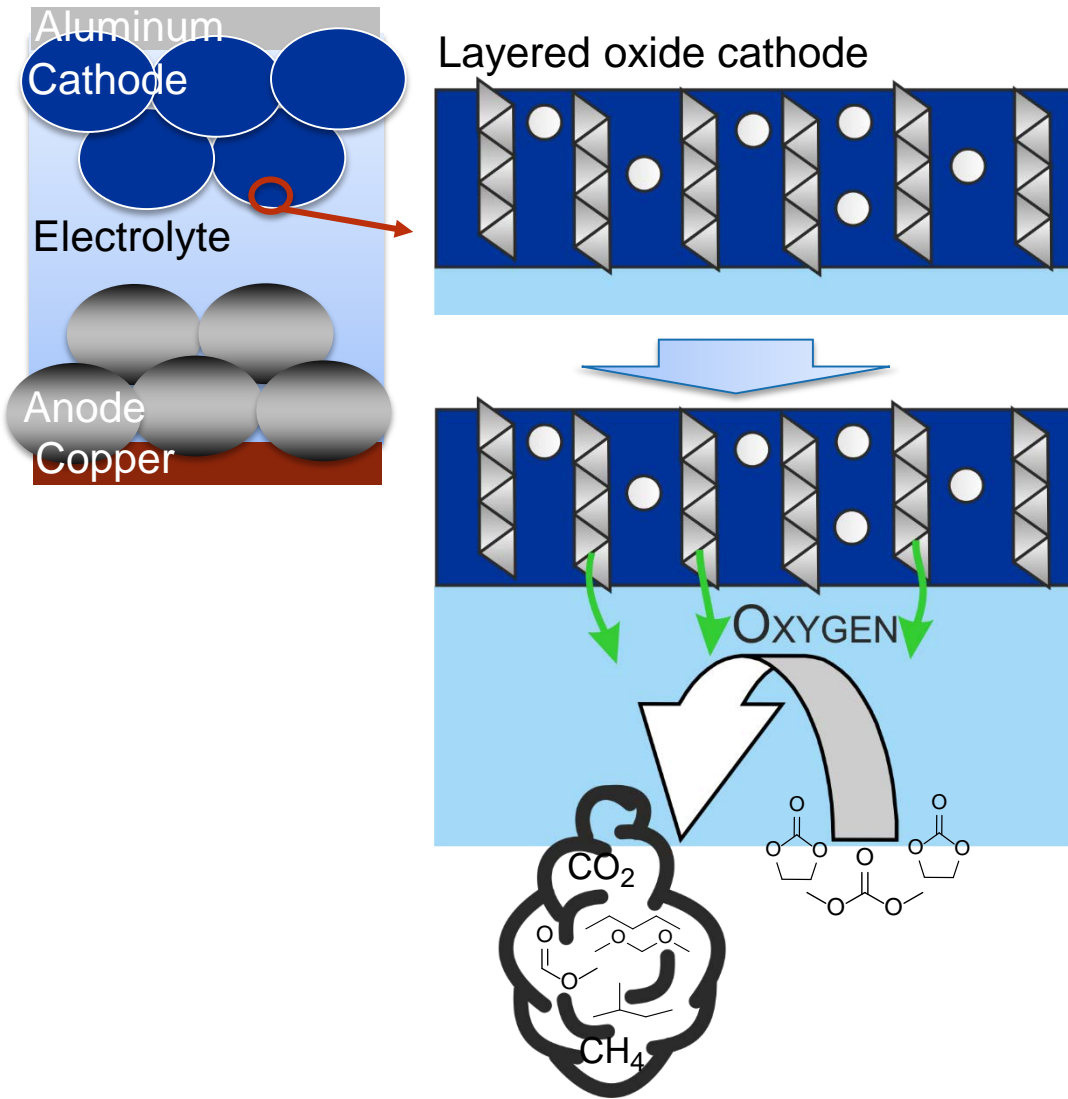
→ At a stage, where it is easy to counteract

# ARC: Thermal Stability of LIB Cells Processes at Medium Temperatures



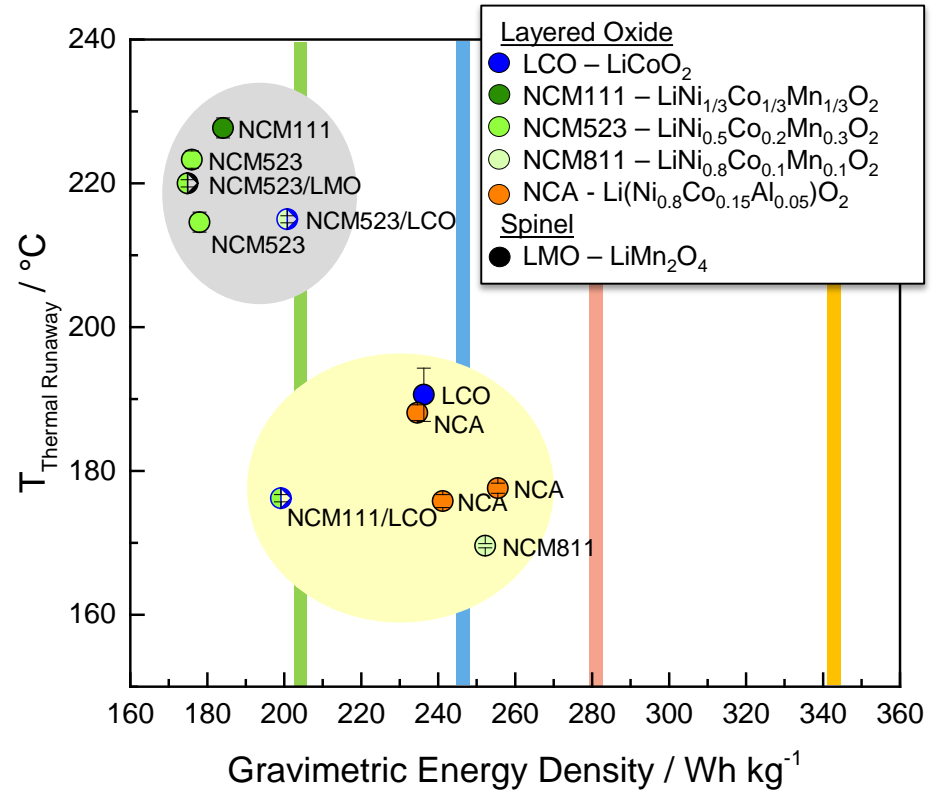
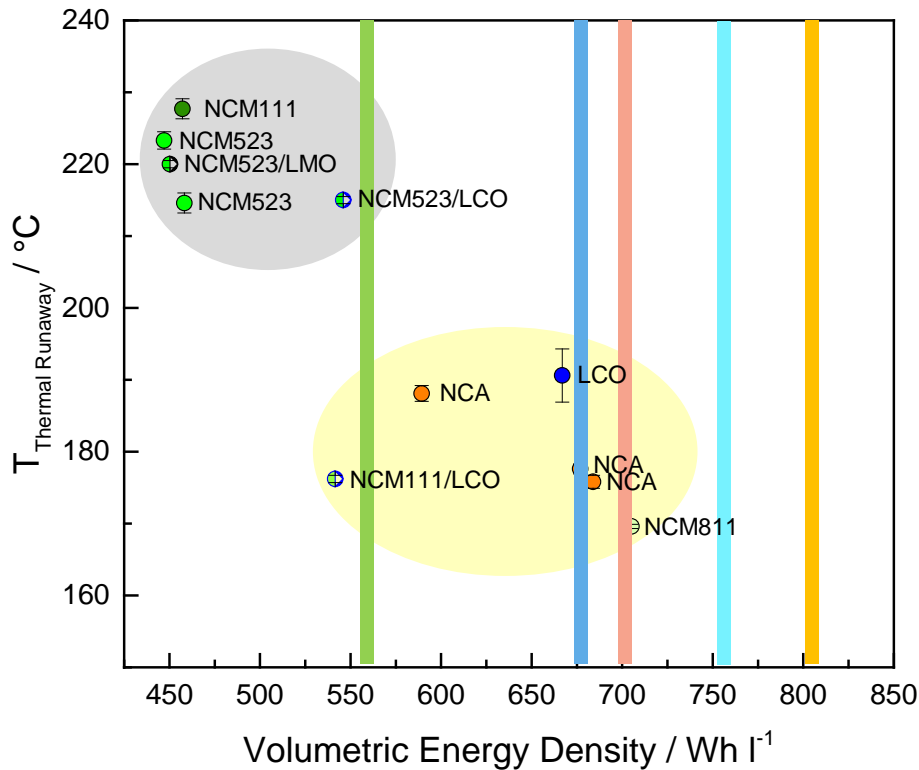
- Li (from anode) reacts with electrolyte
- Temperature dependent reaction rate
- Increased gas evolution
- Cell venting

# ARC: Thermal Stability of LIB Cells Processes at Elevated Temperatures



- Cathode decomposition
- O<sub>2</sub> evolution and electrolyte oxidation
- Highly exothermic reaction
- Generation of large amounts of gaseous products
- Cell rupture, explosion and fire (worst case)

# Case Study: Cell Safety of 18650 Cells



**Layered Oxide**

- LCO –  $\text{LiCoO}_2$
- NCM111 –  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$
- NCM523 –  $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$
- NCM811 –  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$
- NCA –  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$

**Spinel**

- LMO –  $\text{LiMn}_2\text{O}_4$

- High/middle power density cells
- High energy density cells

- Tesla Model S cell (calculation based on NCR18650B)
- Goal of Renault/Nissan alliance with LIB Tech. [1]
- LG for 2021 [2]
- CATL high power cells for 2017 [3]
- CATL high energy cells for 2017-2018 [3]

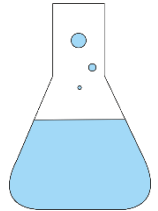
[1] ZOE Battery Durability, Field Experience and Future Vision, AABC 2017, Mainz, Germany, [2] Advances in High-Energy Density Lithium-ion Polymer Battery for EV, AABC 2016, Mainz, Germany [3] Advanced xEV Battery Development at CATL, AABC 2017, Mainz, Germany

# Summary



## 1. Material level

- Energy density determined by materials
- Large variety of materials and combinations
- High research intensity



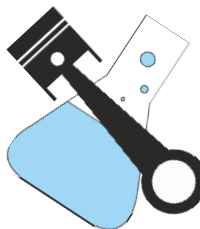
## 2. Electrode level

- Power capability determined mostly by the electrode design
- Power increase at the expense of energy density
- Many possibilities to increase both power and energy densities



## 3. Cell level

- Energy density achievable with thermally less stable materials
- More improvements needed on material and cell level for EV application (both with regard to safety and performance)





**KRAFTWERK**  
⊕ ⊖ Batterie



**BATTERIETAG**  
NRW ⊕ ⊖

**28. – 30. März 2017      Welcome in Aachen**

- Dr. Michael M. Thackeray, Argonne National Laboratory
- Dr. Kai Vuorilehto, EAS Germany GmbH
- Prof. Jeff Dahn, Dalhousie University
- Dr. Ann Laheäär, Skeleton Technologies
- Prof. Jiang Jiuchun, Beijing Jiaotong University
- Prof. Bernd Friedrich, RWTH Aachen University

<http://battery-power.eu>





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Verhandlungen

der Deutschen Physikalischen Gesellschaft e.V.

# Früher war alles besser – aber nicht die Batterien

Martin Winter , 30. März 2017

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