ELECTROCHEMICAL ENERGY STORAGE BASED ON LATEST GENERATION OF LITHIUM BATTERIES AND SODIUM/NICKEL-CHLORIDE BATTERIES

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www.ikts.fraunhofer.de

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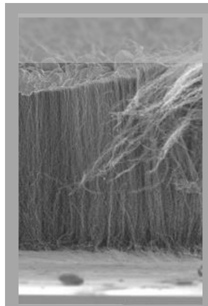
Fraunhofer IKTS in Profile

Energy and Environmental Technologies at IKTS

High temperature batteries

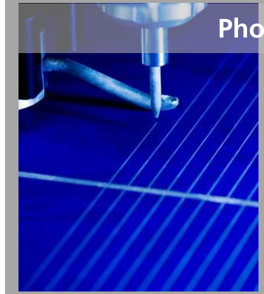
Gas reforming

Supercaps

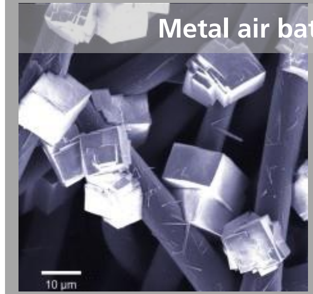


Lithium batteries

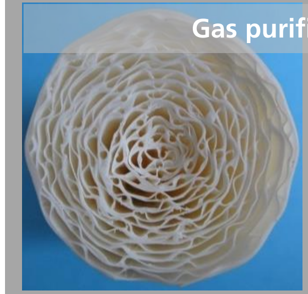
Photovoltaics



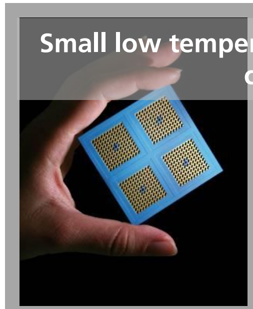
Metal air batteries



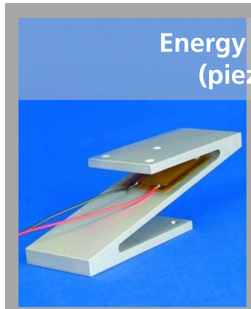
Gas purification



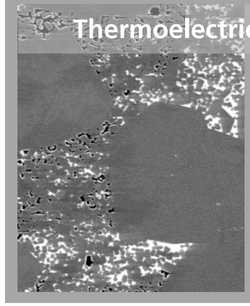
Small low temperature fuel cells (PEFC)



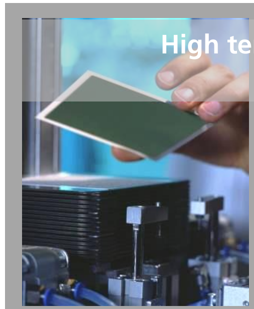
Energy harvesting (piezo ceramic)



Thermoelectric materials



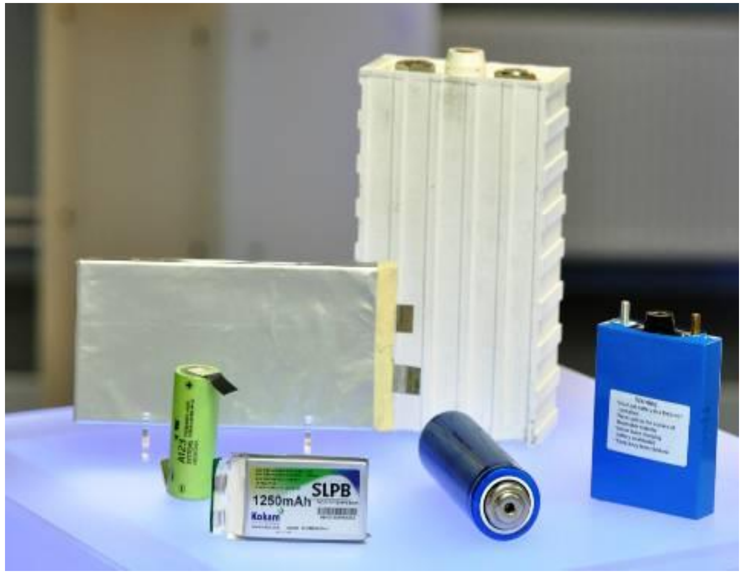
High temperature fuel cells



All solid state batteries

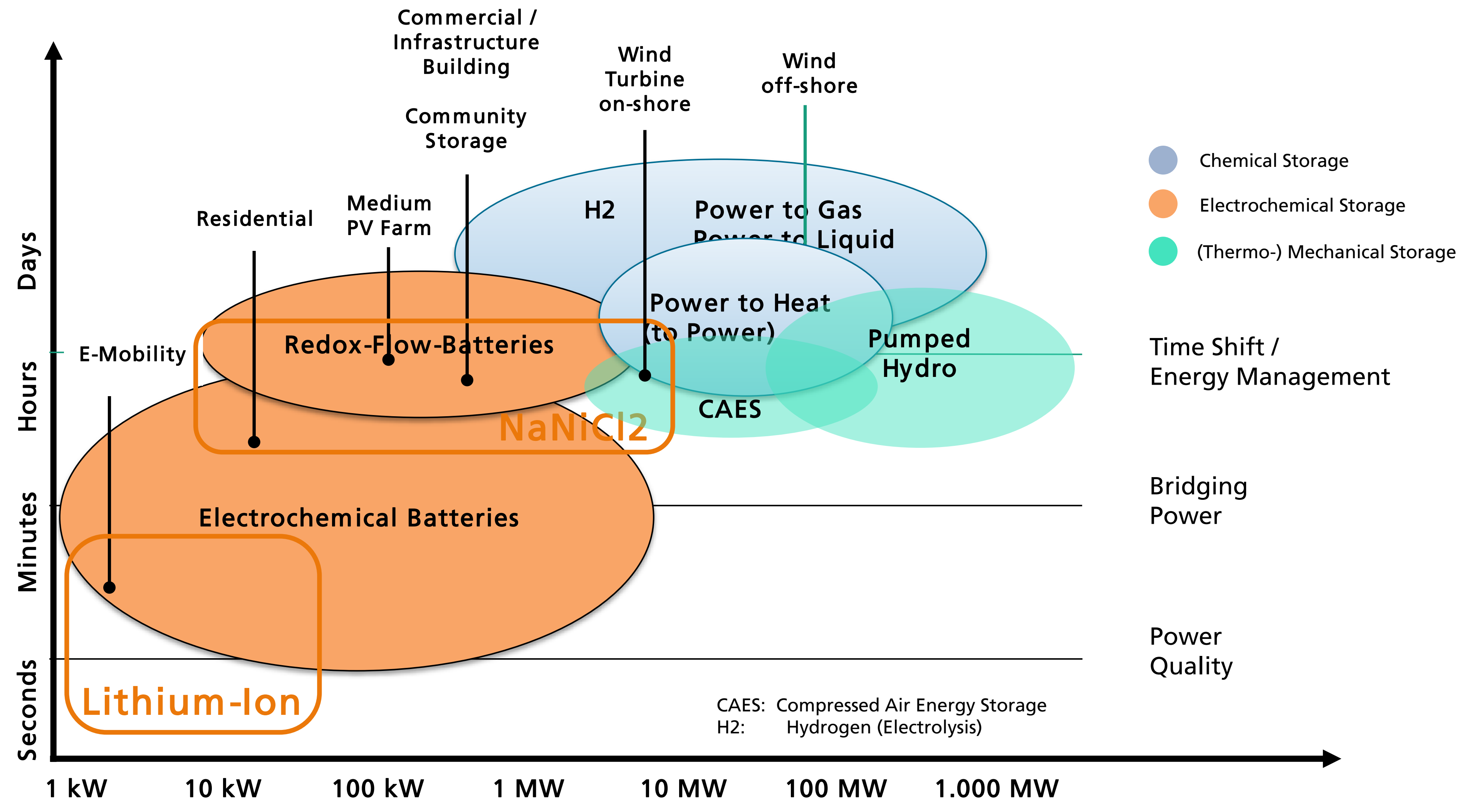
Motivation

Energy storage for stationary and mobile application



Sources: NGK Insulators, Younicos

Electrochemical energy storage devices - application fields addressed



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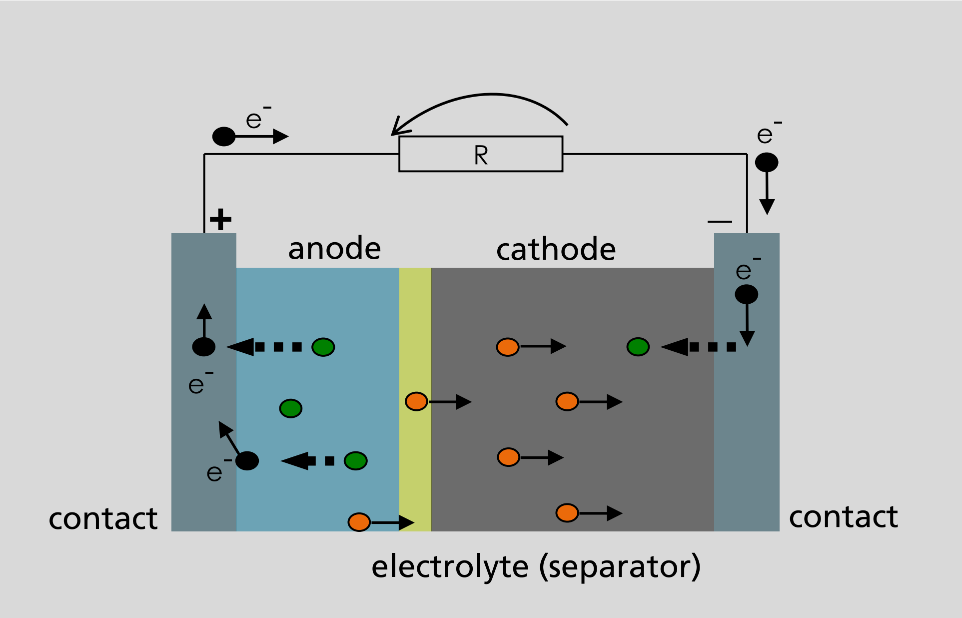
Electrochemical energy storage devices

Galvanic cell

Electrochemical cell that derives electrical energy from spontaneous redox reactions

Primary cell	Secondary cell	Tertiary cell
non-rechargeable batteries	Rechargeable batteries, accumulator	Fuel cells → require a constant flow of reactants from outside source



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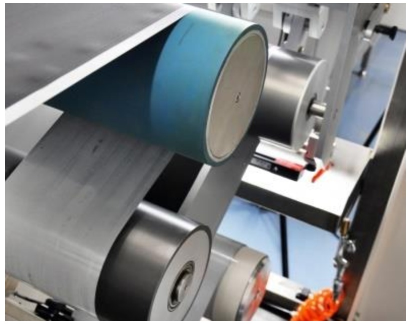
Electrochemical energy storage devices – IKTS Approach



Material

Technology

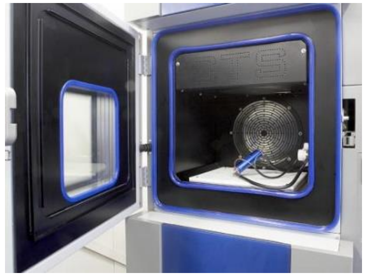
Electrode

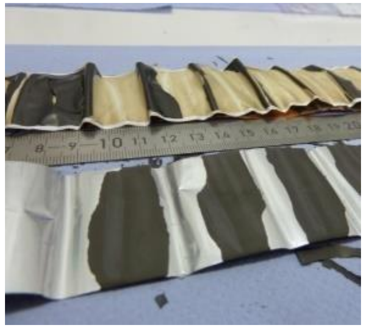
Manufacturing

Battery Cell

Ceramic Expertise

Battery Expertise





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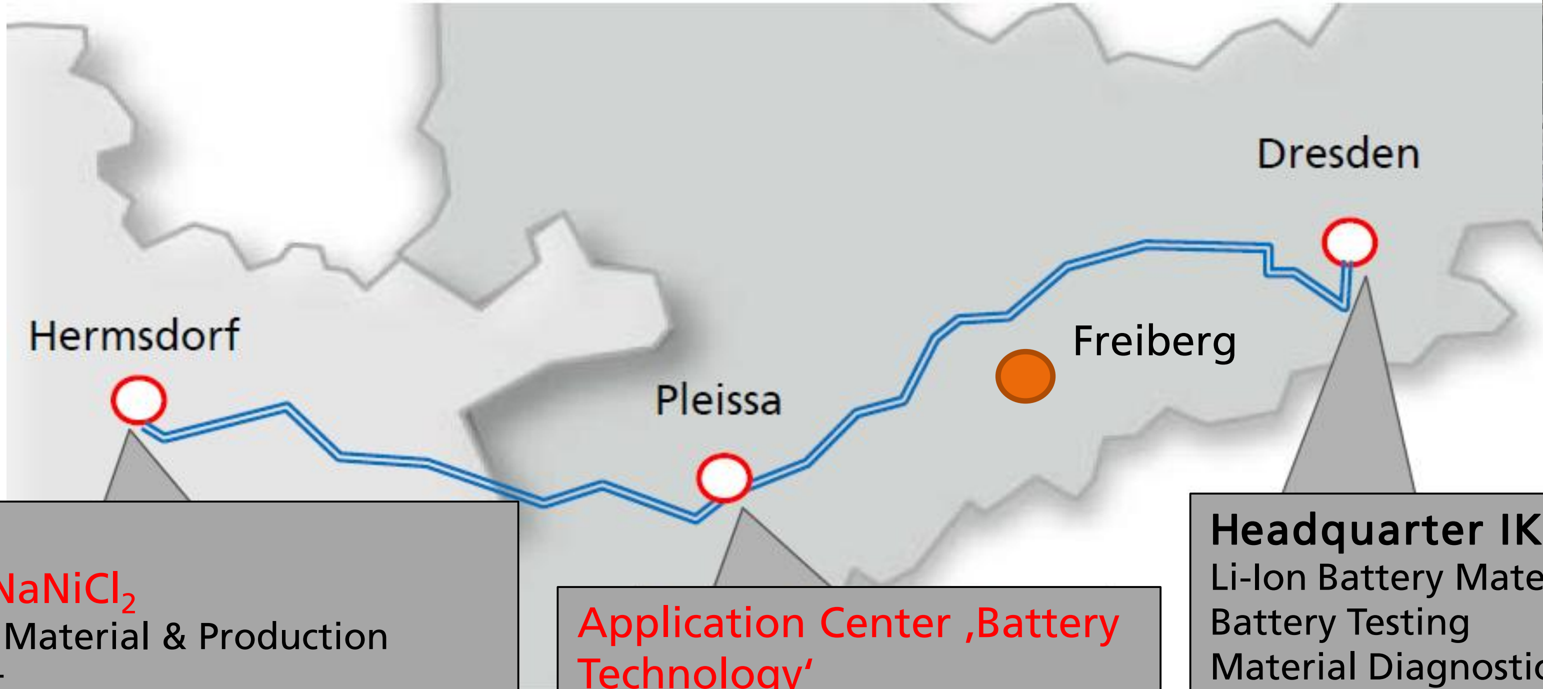
Sites of IKTS & Battery Pilot Plants



IKTS-HD

Pilot Plant $NaNiCl_2$

(Cerenergy®) Material & Production Development

Technology Center ‚Tape Casting‘

Roll-to-roll technology development

Application Center ‚Battery Technology‘

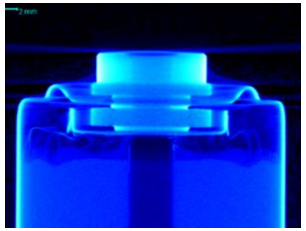
Production Development

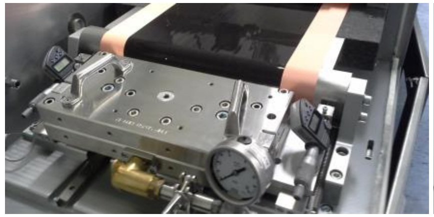
Cooperation with ThyssenKrupp System Engineering

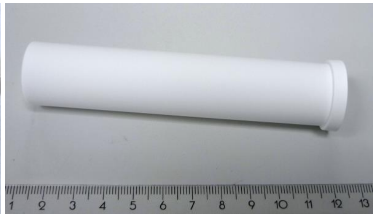
Headquarter IKTS-DD & IKTS-MD

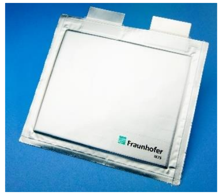
Li-Ion Battery Material Development & Battery Testing

Material Diagnostics









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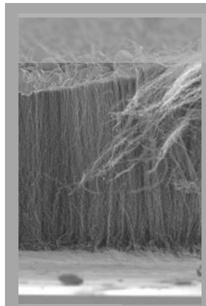

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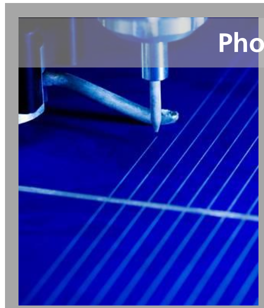

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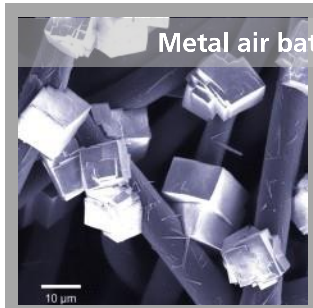

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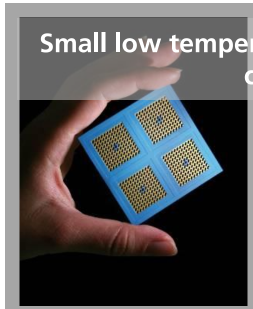

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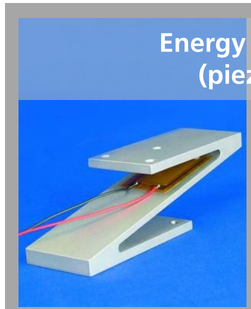

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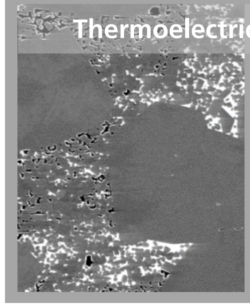
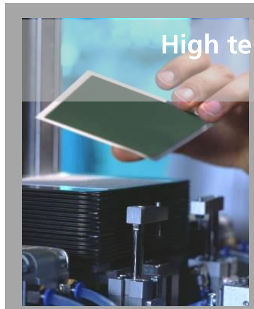


High temperature fuel cells



All solid state batteries

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Lithium-Ion-Batteries

Applications:

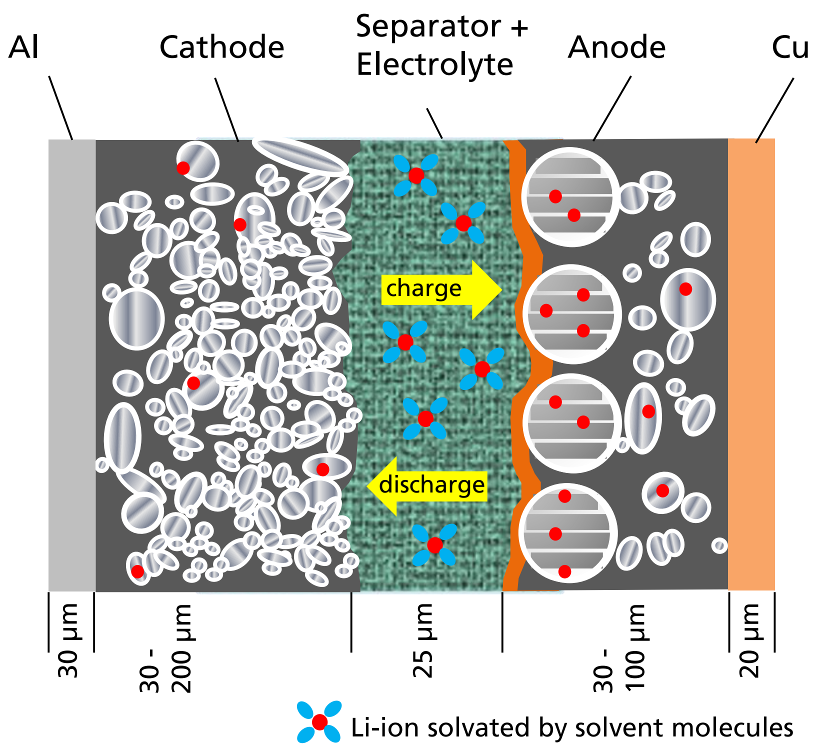
- E-Mobility
- Small stationary power systems

Advantages

- High energy density
- High performance dynamics

Development topics

- Reduction of manufacturing costs
- Improvement of durability and costs



- Li-Ions are intercalated into and extracted from host materials (active masses)
- Voltage is defined by combination of active masses
- Capacity is partially defined by active masses but strongly influenced by electrode and cell design

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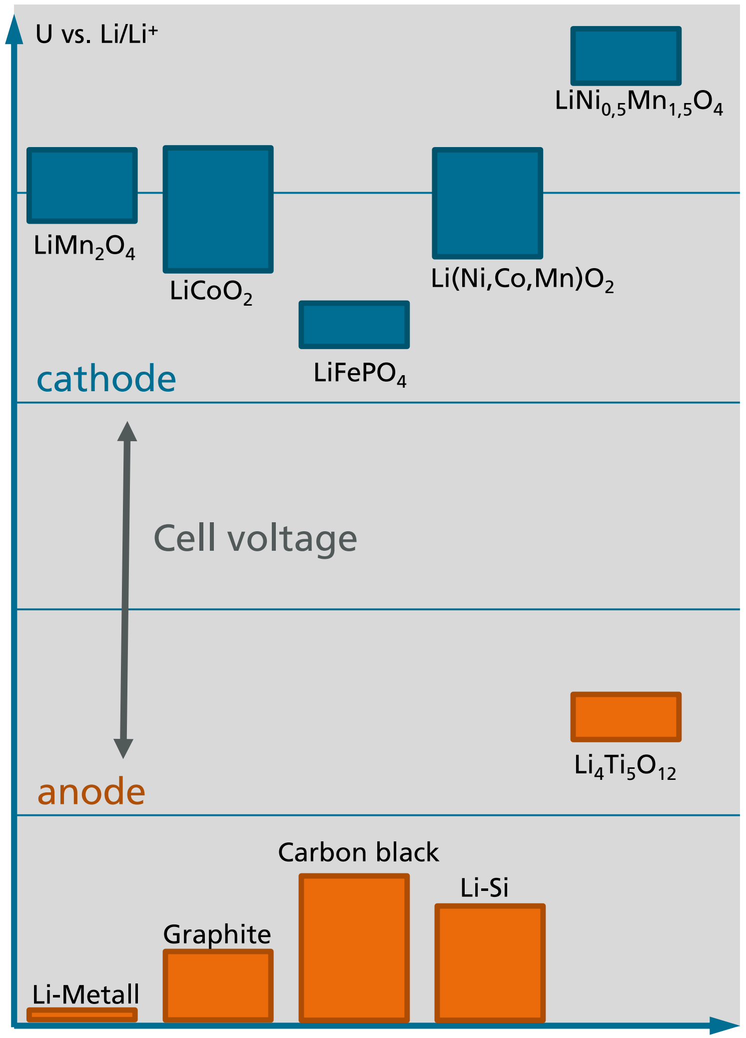
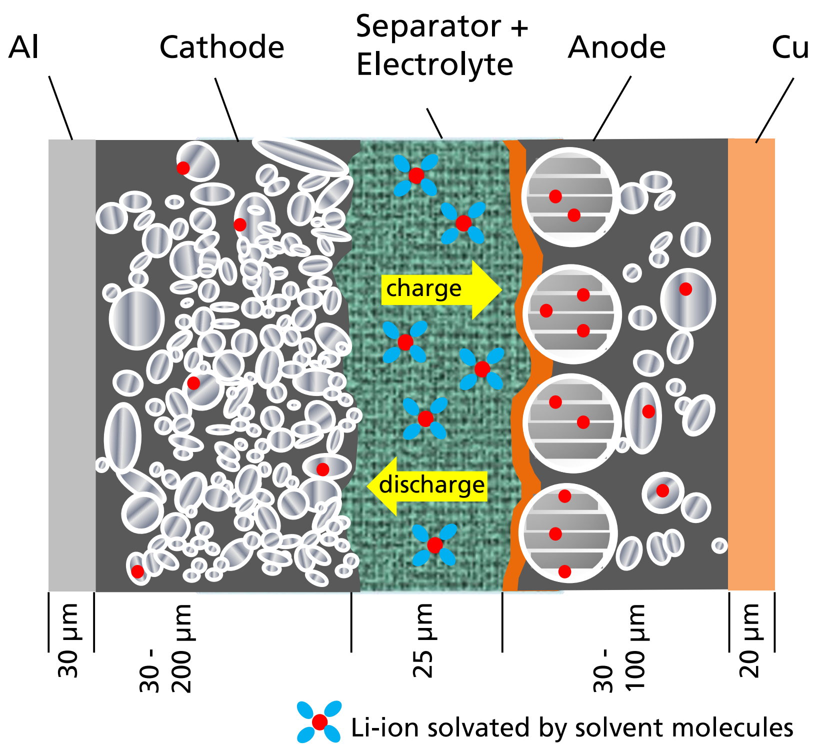
Lithium-Ion-Batteries





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Manufacturing process of Lithium-Ion battery cells

Optimum battery performance and lifetime relies on optimized battery manufacture

- State of the art process was developed for small consumer cells
- Automotive and large stationary application require
  4x lifetime; 10x cycle number; 20x larger electrode areas

→ **significant higher requirements on production processes**

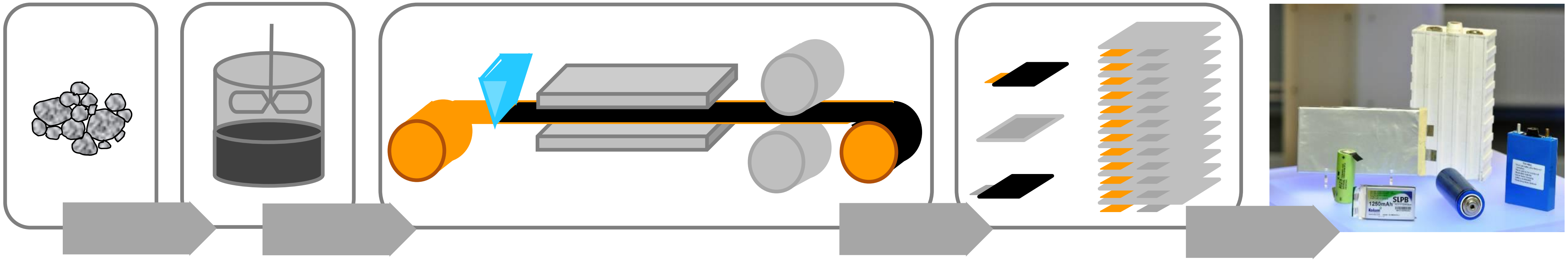
Material synthesis
active materials, separator

Slurry preparation
mixing

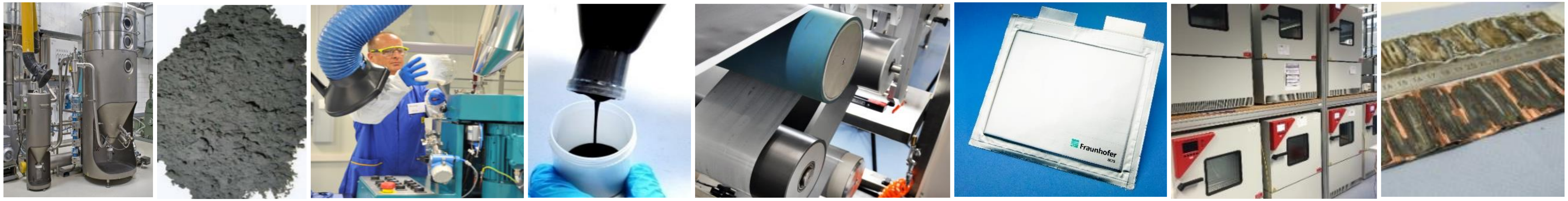
Electrode manufacturing
casting, drying, calendering

Cell assembly
slitting, stacking, electrolyte filling, packaging

Testing
formation, aging, test



Manufacturing process of Lithium-Ion battery cells



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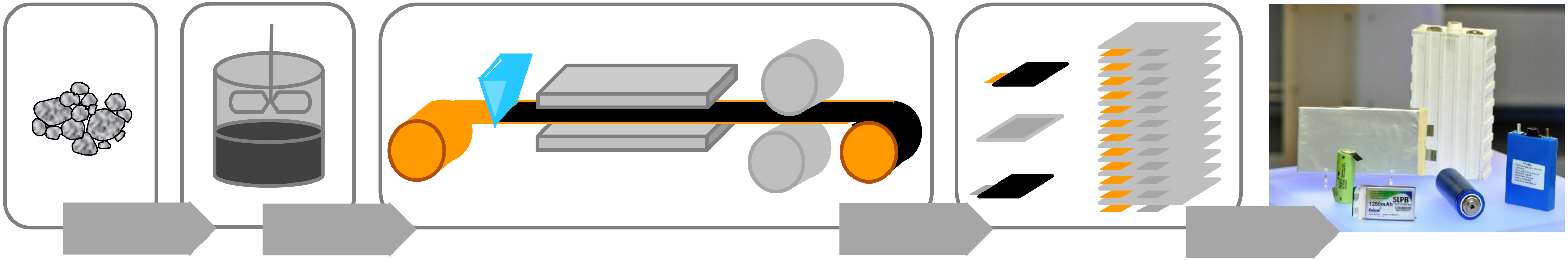

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Application Center ‚Battery Technology‘ (Fraunhofer IKTS/ThyssenKrupp)

Process development and optimization for battery production

- Optimum battery performance and lifetime relies on optimized battery production

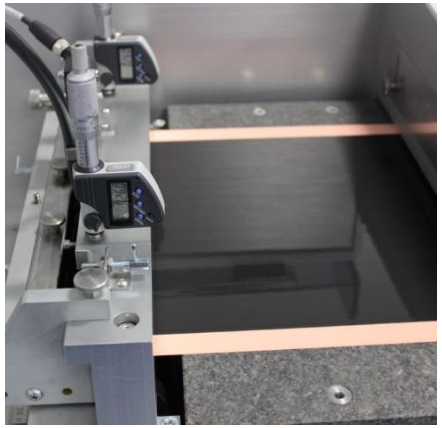
→ Development of optimized manufacturing methods along the entire value chain of lithium ion cell production

- Process optimization is the main tool to reach cost targets

→ Manufacturing methods for high-performance lithium ion battery cells

→ From discontinuous laboratory to (semi)continuous pilot plant processes
→ Up-Scaling to high throughput production processes





thyssenkrupp

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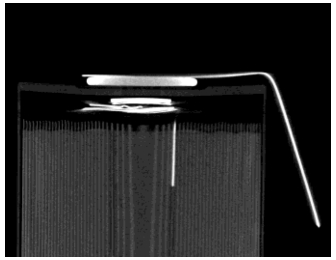
Energy density in lithium ion batteries

< 280 Wh/l



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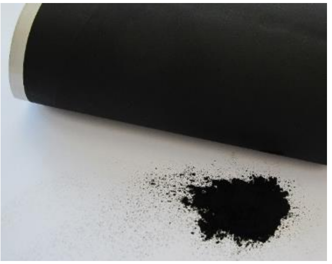
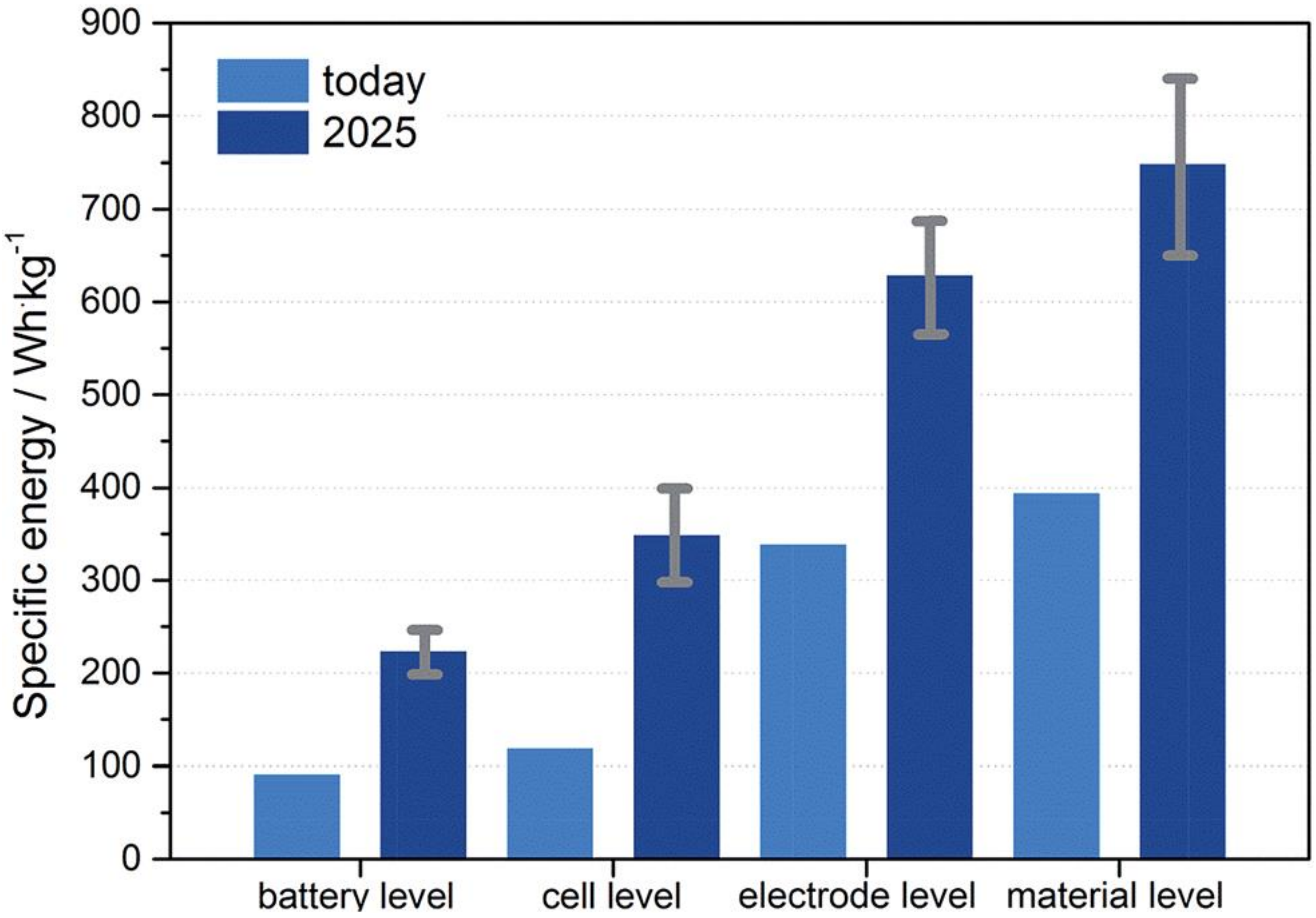


NCA: spec. 167 Ah/kg



D. Andre, S. Kim, P. Lamp, S. Franz Lux, F. Maglia, O. Paschos, B. Stiaszny, Future generations of cathode materials: an automotive industry perspective, J. Mater. Chem. A, 2015, 3, 6709

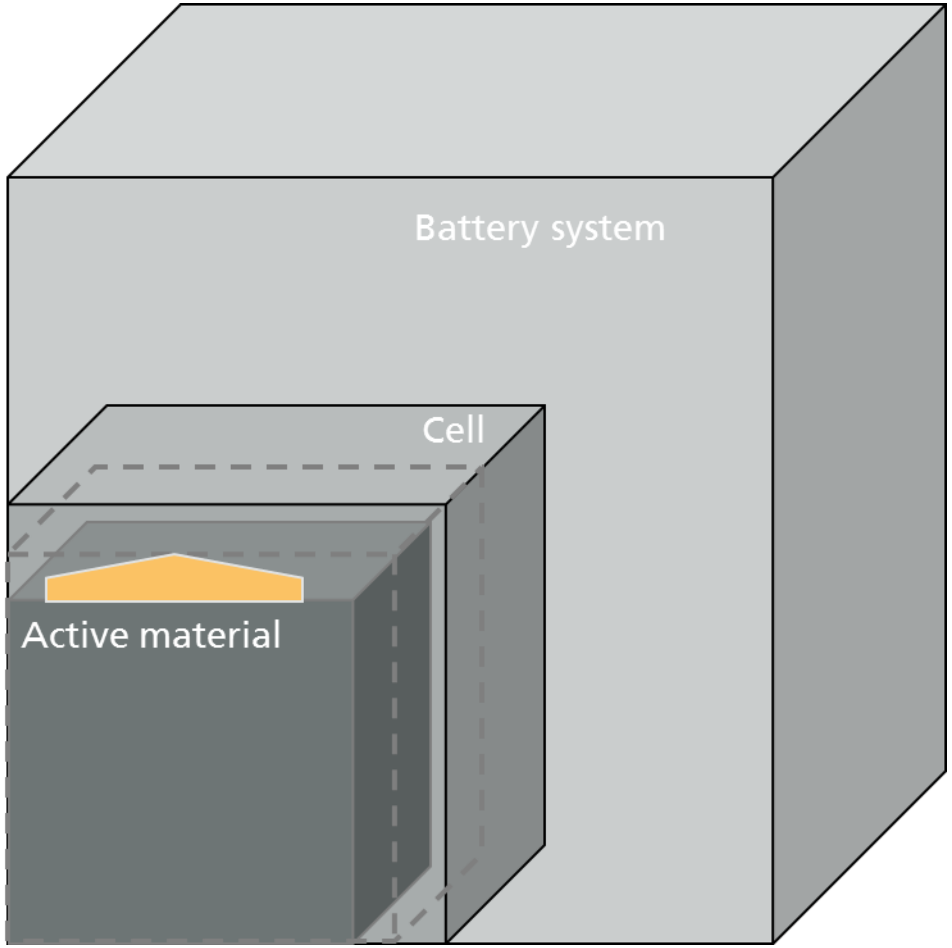
Energy density in lithium ion batteries

Cell level → approach to increase energy density

Active materials with improved storage capacity

Reduction of 'inactive' components (separator, binder,…)

Increase of packaging density in the cell



Energy density in lithium ion batteries

Cell level → approach to increase energy density

Active materials with improved storage capacity

Reduction of 'inactive' components (separator, binder,…)

Increase of packaging density in the cell

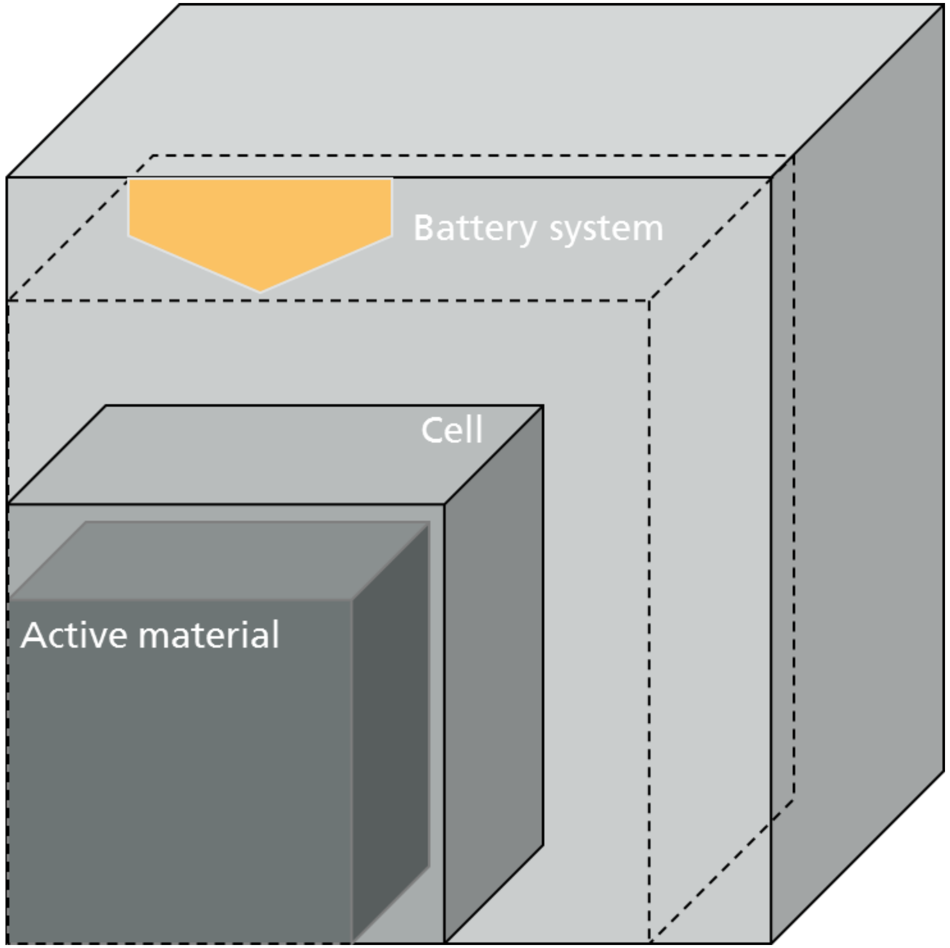
System level → approach to increase energy density

Increase of cell size

Reduction of component number → connectors, sensors

Efficient cooling

Safe cells to avoid safety devices on system level



High capacity electrodes (cell level)

Active materials with high specific storage capacity

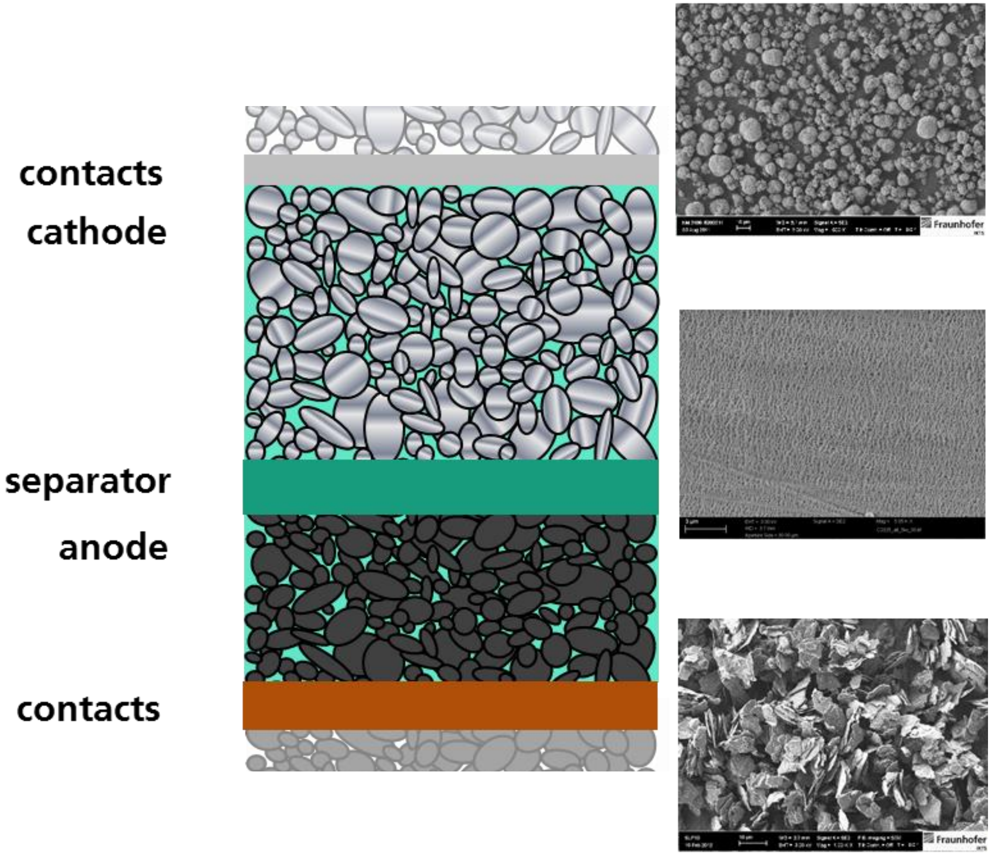
Adapted powder grain size distribution
→ maximum packaging density

Increased electrode thickness

Reduced separator thickness

Influence on

- Subsequent process steps, e.g. electrolyte filling
- Cell performance and life time



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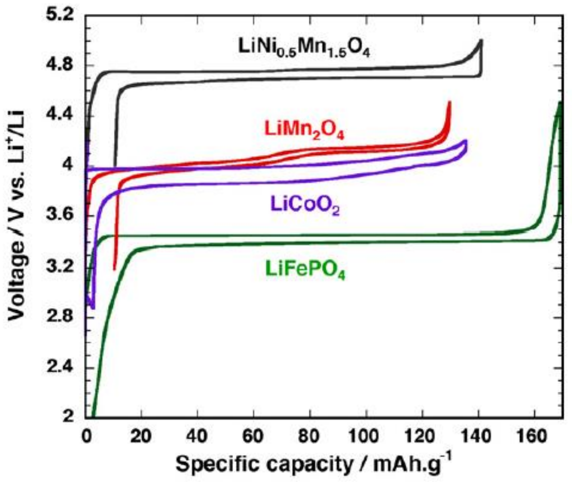
Synthesis of $LiNi_{0.5}Mn_{1.5}O_4$ high voltage spinel with adapted morphology



- High cell voltage of 4.7 V vs. Li/Li+
- Theoretical capacity of 147 mAh/g

  690 Wh/kg, 3034 Wh/l,

⇨ Full cells with high energy density possible

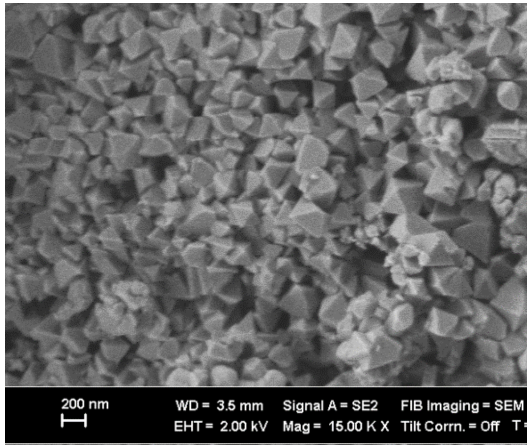
- Spinel type structure with 3D channel network

⇨ High lithium diffusivity enables high power cells

- Cobalt free
- Investigate synthesis parameters to achieve best material properties

Patoux, Sébastien et al. (2009) *Journal of Power Sources* 189 (1), 344–352.

Synthesis of $LiNi_{0.5}Mn_{1.5}O_4$ high voltage spinel with adapted morphology



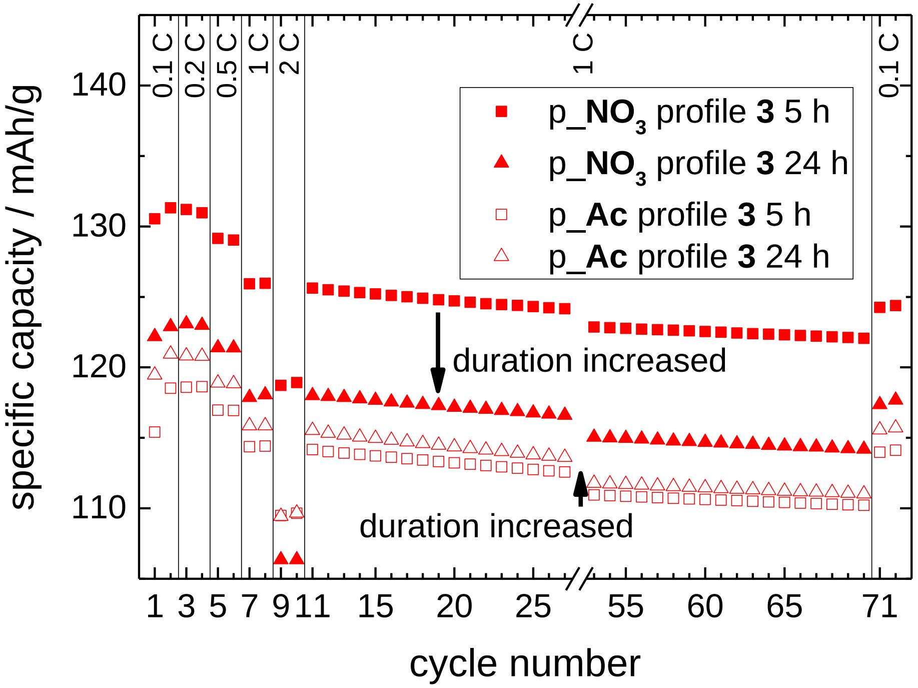
- Varied synthesis parameters and influence on material properties:

  Precursor composition → nucleation, morphology

  Pre-treatment → homogeneity

  Calcination (temp., time) → phase, crystallite size

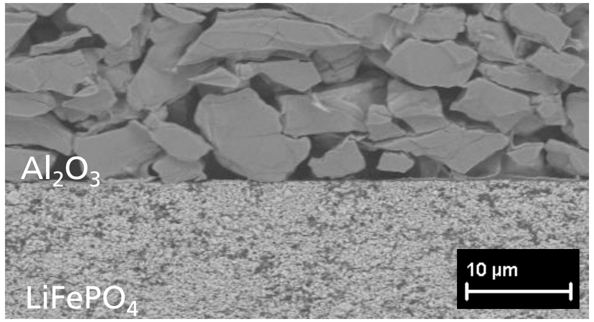
- Best samples show 131 mAh/g → in agreement with good literature results
- Highest capacity for short calcination times

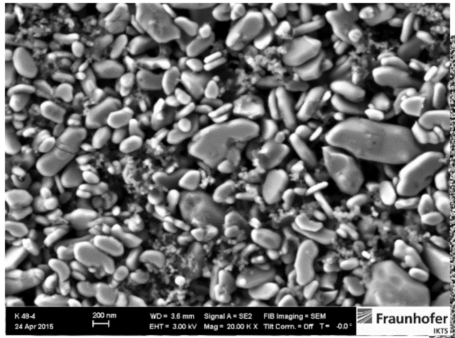


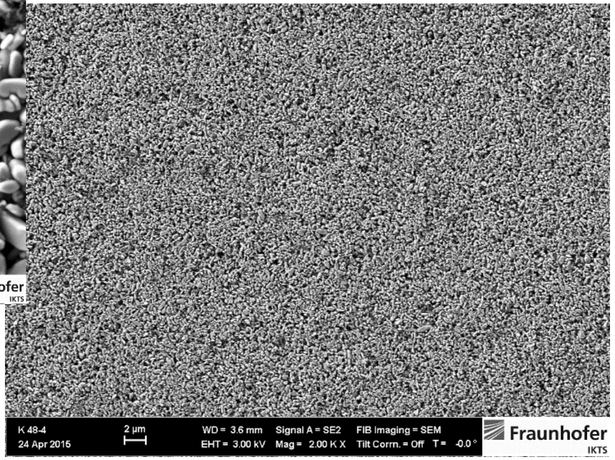
Electrodes: 80 % $LiNi_{0.5}Mn_{1.5}O_4$, 10 % PVDF, 10 % carbon on Al-foil; dried for 20 h at 60 °C.
Coin cells vs. metallic lithium, electrolyte: LP40 (1M $LiPF_6$ in EC:DEC 1:1)

Manufacturing of high capacity electrodes

- Cost efficient, environmentally friendly manufacturing processes (e.g. aqueous processing)
- Increasing surface loading for high-energy electrode
- Realization of morphology, conductivity, wettability of the electrodes

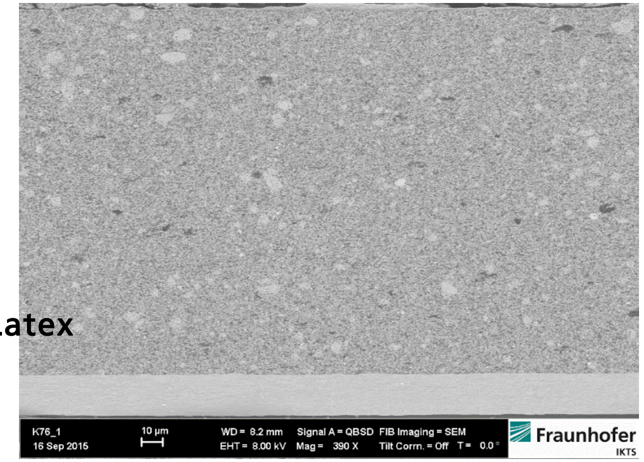






Thickness: 38 µm
SL 8,3 mg/cm²; 1,18 mAh/cm²
$LiFePO_4$ / Super P-Li / CMC / PVDF

$LiFePO_4$ / Super P-Li / CMC / Latex
Thickness; 196 µm
SL 36,5 mg/cm²; 4,05 mAh/cm²



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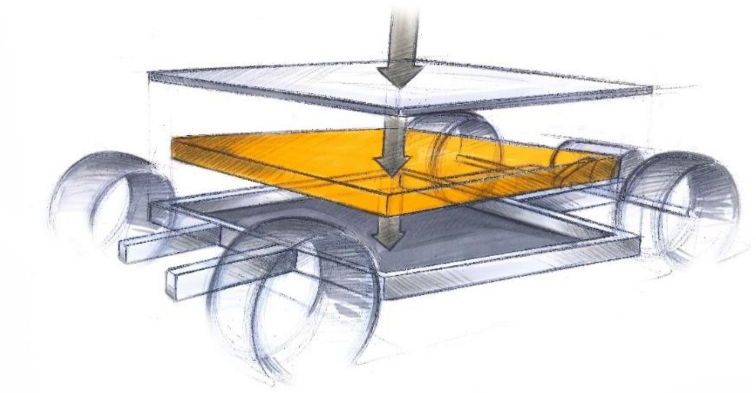
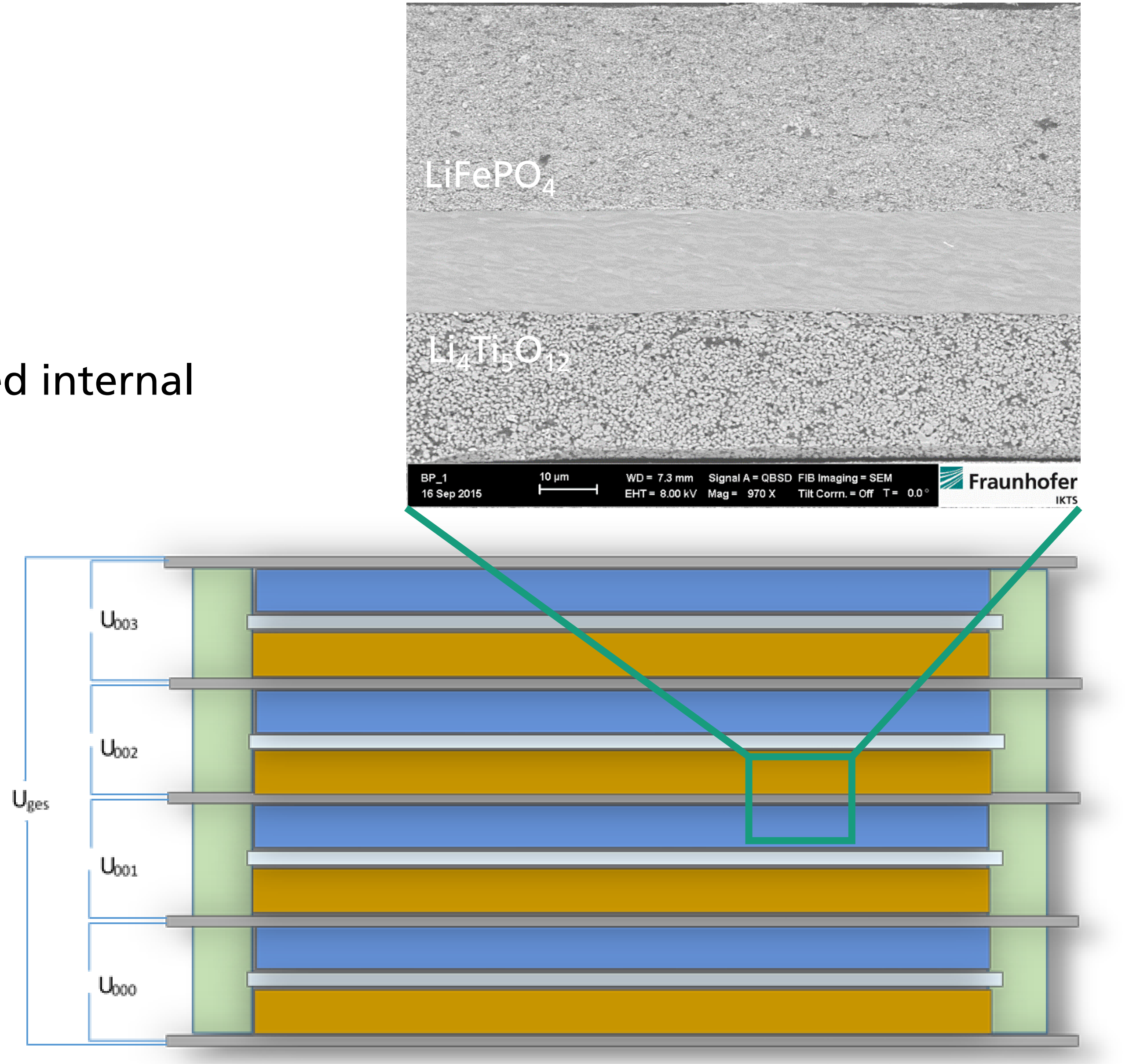
EMBATT
Chassis-embedded Energy

Bipolar Battery

- Stack of electrodes in series
- Large electrode areas
- Integration of cell stack in one housing
- Reduced contacting effort, extremely reduced internal resistance
- Elimination of module boundaries

→ 450 Wh/l on system level

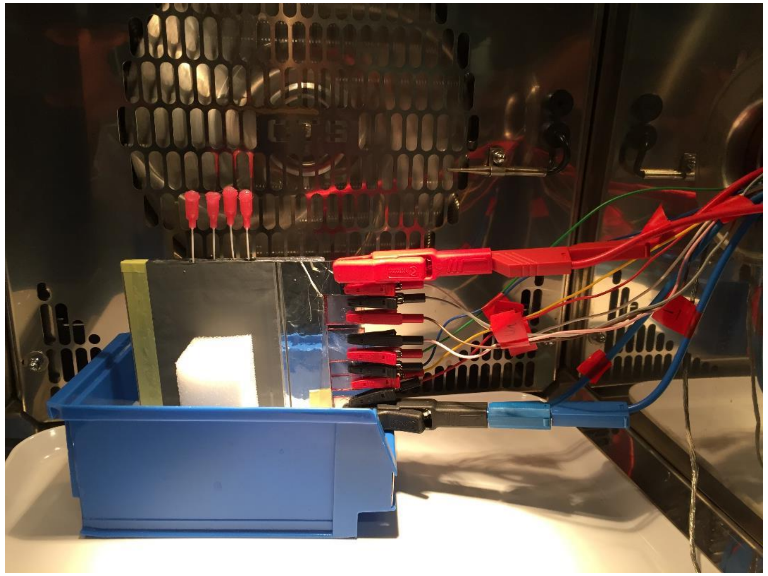


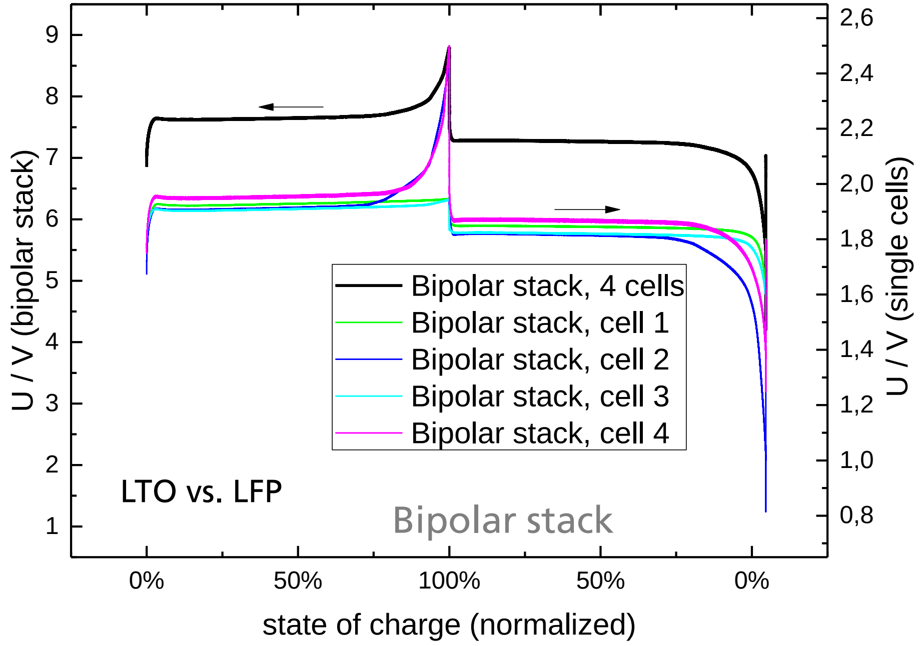


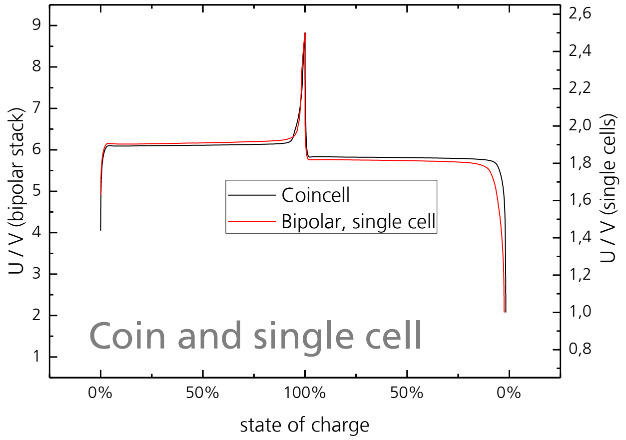
EMBATT Bipolar Battery

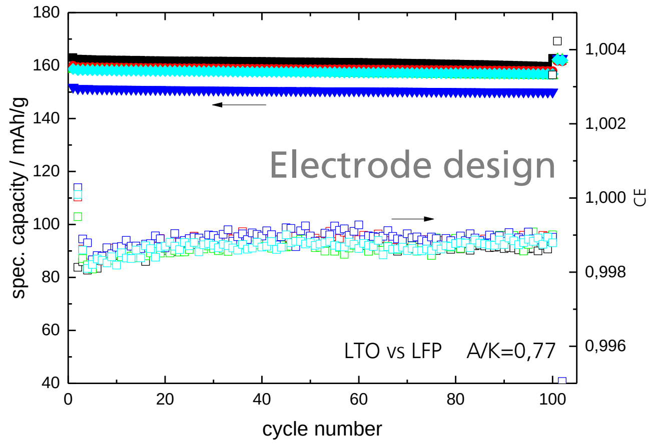
Chassis-embedded Energy

- Development of bipolar electrodes
- Design of electrodes (balancing, capacity, performance)
- Investigation of manufacturing processes









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EMBATT Chassis-embedded Energy

Bipolar Battery

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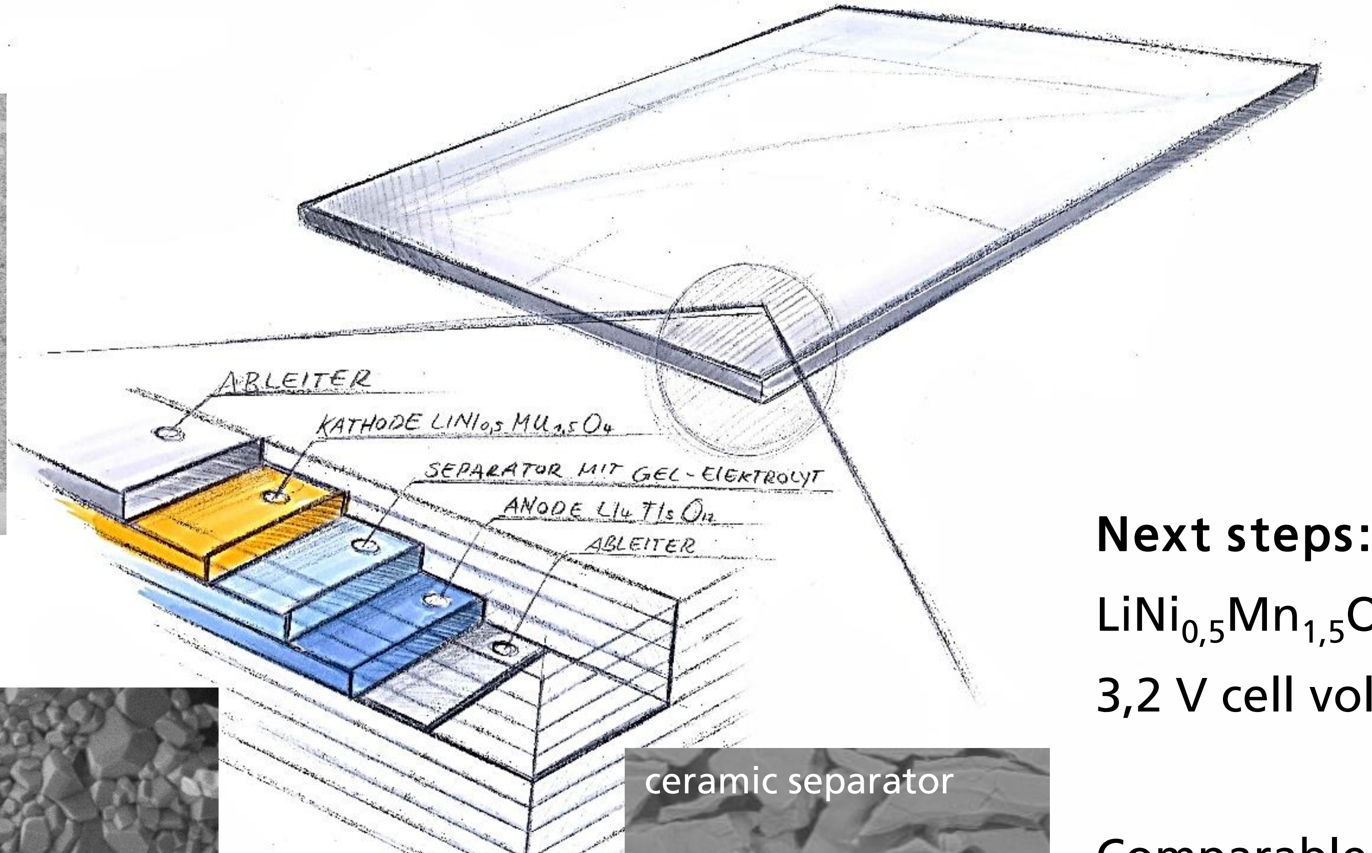

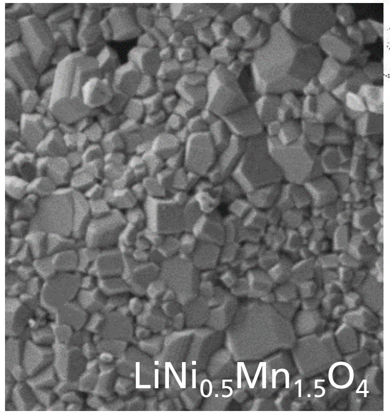

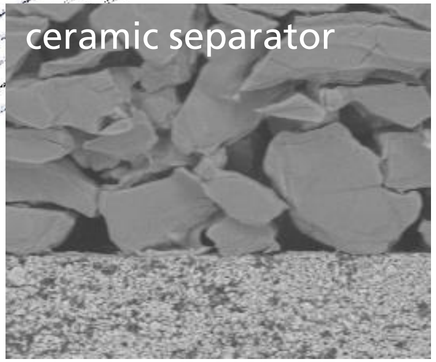

Next steps:

$LiNi_{0,5}Mn_{1,5}O_4$ / $Li_4Ti_5O_{12}$ active material

3,2 V cell voltage

Comparable processing properties of the ceramic electrode materials $LiNi_{0,5}Mn_{1,5}O_4$ and $Li_4Ti_5O_{12}$

Combination with solid electrolyte

Fraunhofer IKTS

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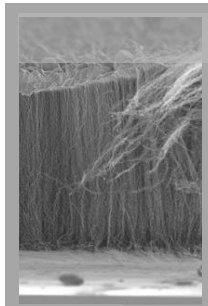
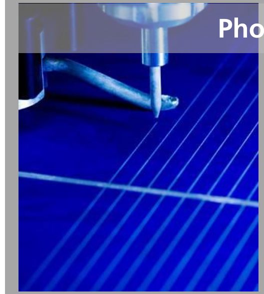
Gas reforming

Supercaps

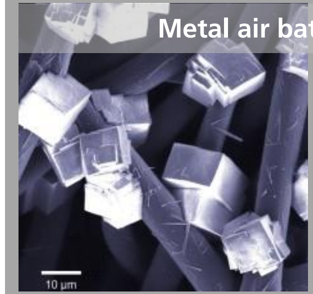


Lithium batteries

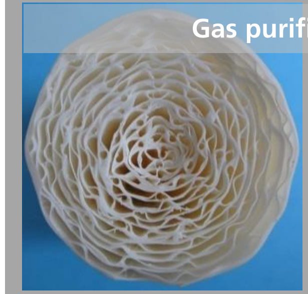
Photovoltaics



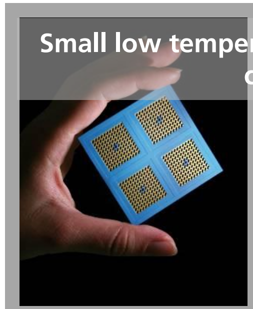
Metal air batteries



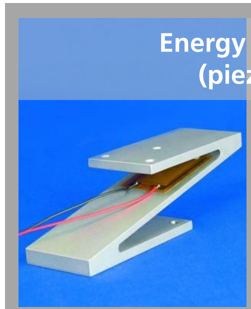
Gas purification



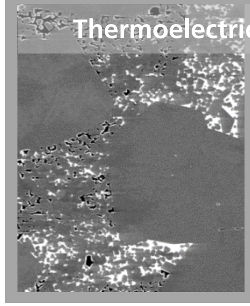
Small low temperature fuel cells (PEFC)



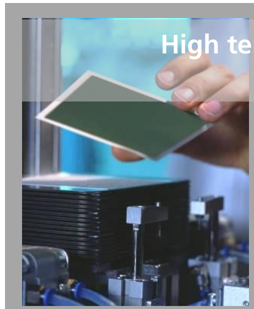
Energy harvesting (piezo ceramic)



Thermoelectric materials



High temperature fuel cells



All solid state batteries

High-Temperature-Sodium/Nickel-Chloride-Batteries

Applications:

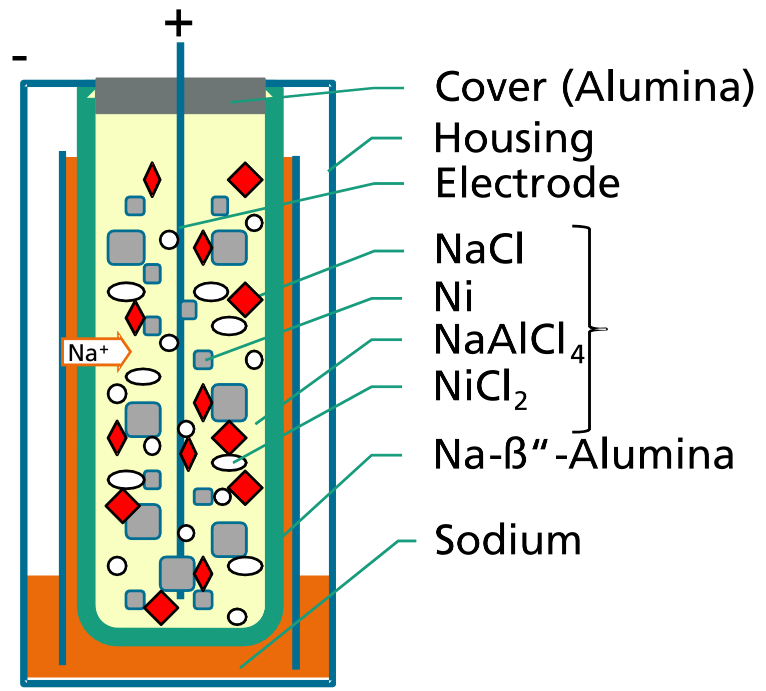
- Large stationary power systems

Advantages

- Cheap ceramic battery technology
- Cost target < 100€/kWh

Development topics

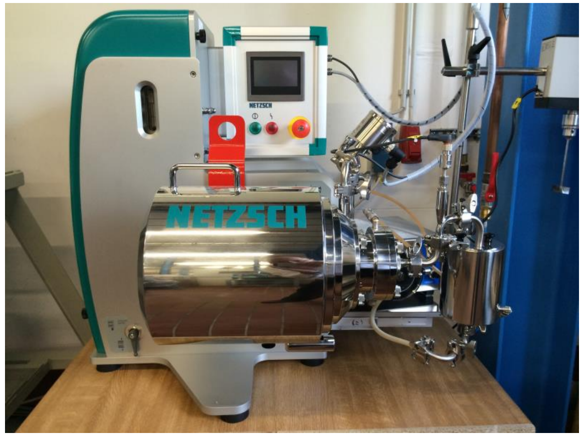
- High throughput ceramic mass production
- High quality ceramic components

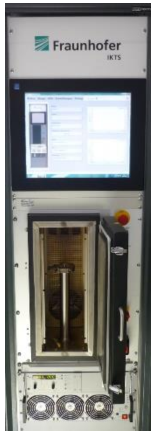


- Total cell reaction:
  $NiCl_2 + 2Na \leftrightarrow Ni + 2NaCl$, $E_0 = 2{,}58$ V
- Electrolyte: Na-ß"-Alumina **(ceramic)**
- Cathode: Nickel, NaCl, $NiCl_2$, $NaAlCl_4$
- Anode: Sodium (molten)

Fraunhofer IKTS

Na-β-Alumina – Electrolyte



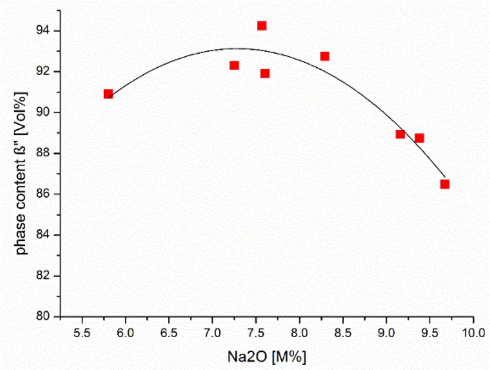


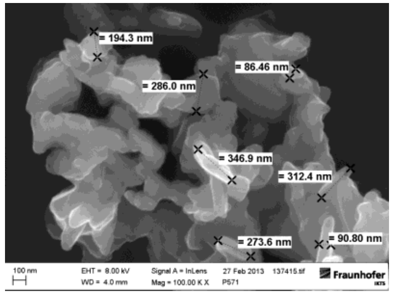
Raw materials → Milling / Homogenization → Calcination (1300°C) → Shaping (Extrusion) → Sintering (1600°C)

Targets

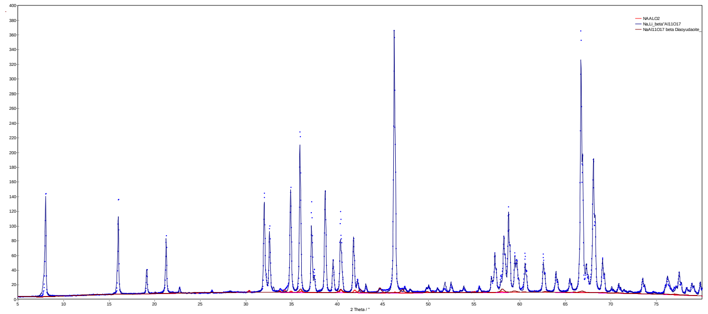
- density > 98 %
- strenth > 200 MPa
- ß“ content > 92 %
- σ = 0,22 S/cm @ 300°C

Na-β-Alumina – Electrolyte





Calcinated Li stabilized ß“-Alumina



Rietveld Analysis of IKTS ß-Alumina after Sintering

Raw materials (Boehmite, Na_2CO_3, $MgCO_3$, Li_2CO_3) → Milling / Homogenization → Calcination (1300°C) → Shaping (Extrusion) → Sintering (1600°C)

Preferred starting material: Al_2O_3 or AlO(OH) /γ-AlOOH (Boehmite)

Phase formation β“(β)-Al_2O_3

Targets
- density > 98 %
- strenth > 200 MPa
- ß“ content > 92 %
- σ = 0,22 S/cm @ 300°C

Upscaling of Na-ß-alumina batches

Laboratory synthesis

- Stoichiometry and resource variation
- Batches 1-2 kg
- Characterization, evaluation

Pilot plant synthesis

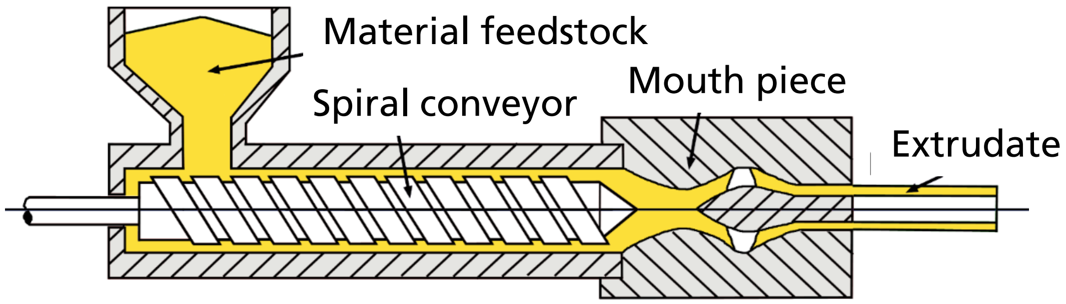
- Feasibility for upscaling by scalable aggregates
- Batches 5-20 kg
- Batches > 100 kg possible

20 kg batch synthesis (mixture of organic and aqueous material)
Experiments for resource adjustment to reach100% aqueous synthesis routes

New cost efficient production processes: extrusion of Na-ß-alumina

Why extrusion?

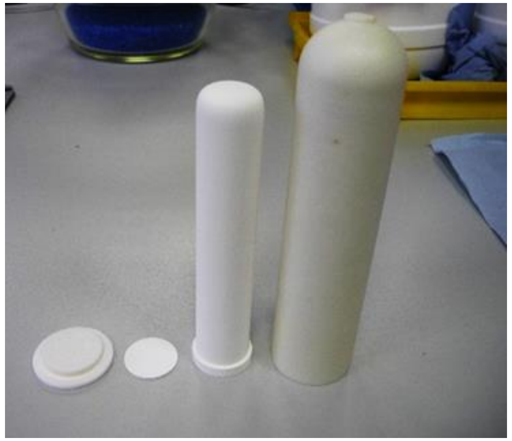
- High production rate
- Continuous process
- Tilting base (plug of a tube)
- Thinner wall thicknesses possible

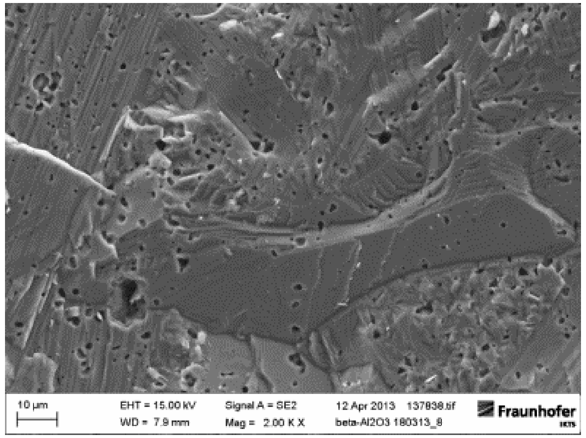


Fraunhofer IKTS

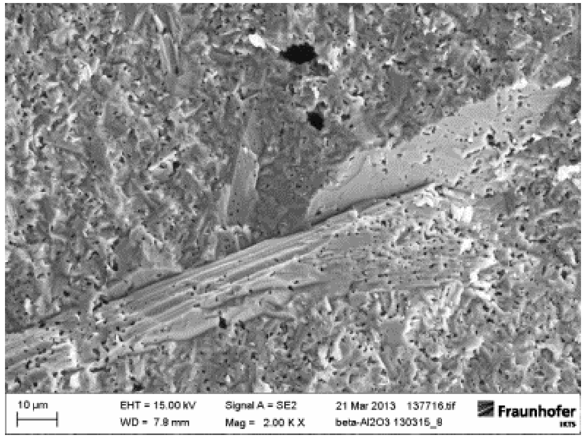
Sintering of ß-Alumina

- Na_2O sublimation starting at T > 1200 °C
  - Furnace contamination (destruction of heaters)
  - Na deficit in ß-Alumina: ↓ phase %, ↓ ρ, ↓ σ
- Na stable, gas tight kiln furniture (capsules) 1650°C
- Optimized temperature regime

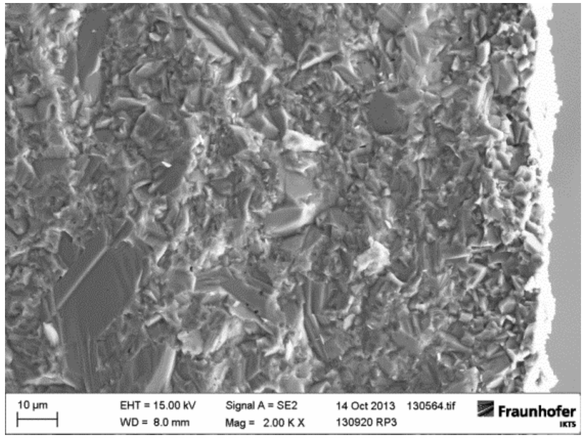




Largely giant crystallites



Giant crystallites / crystalline base structure (duplex structure)



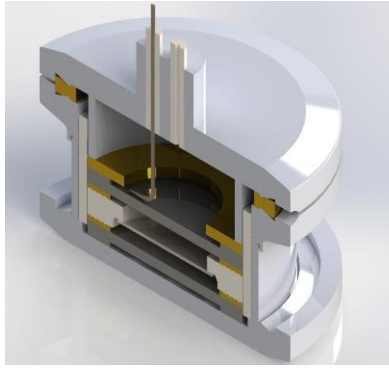
Small, uniform crystallites

Battery Development

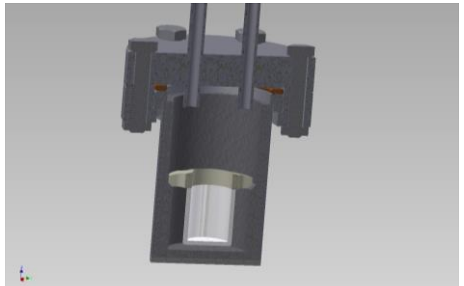
Different designs:

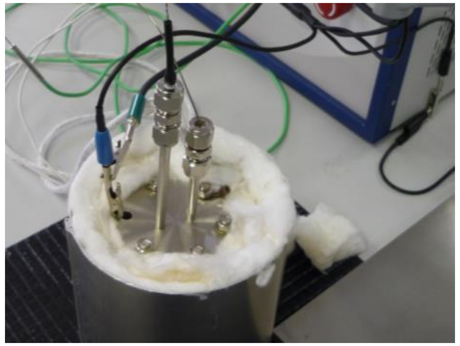
- <0.3 Ah **flat cell** for charaterizing
- **Cup cell** (cathode testing, Na/Na tests, functionalized layers of anode)
- 5 Ah **tubular cell** for design control
- 40 Ah **tubular cell „commercial“ design**

Planar cell

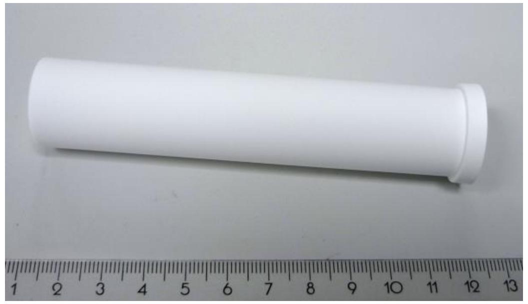


Cup cell





Laboratory cell

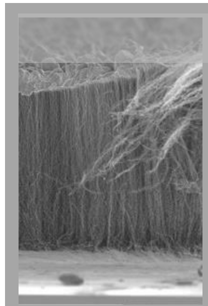


cerenergy®
intermediate cell 15 cm

Future Trends

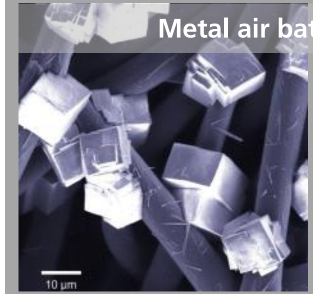
High temperature batteries

Supercaps



Lithium batteries

Metal air batteries



- Alternative battery chemistries
- Improved lifetime
- Increase in safety

- Cost reduction
  → materials and processes
- Increase in energy density

All solid state batteries

Thank you for your attention!

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Fraunhofer IKTS