APPLICATION OF CERAMIC TECHNOLOGIES IN ALL SOLID STATE BATTERIES

Mareike Wolter, Kristian Nikolowski, Katja Wätzig, Jochen Schilm, Uwe Partsch

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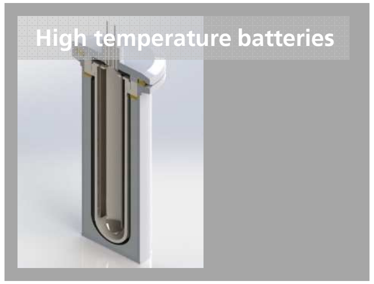
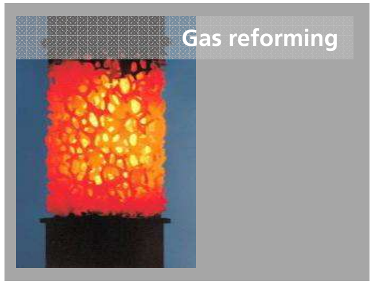
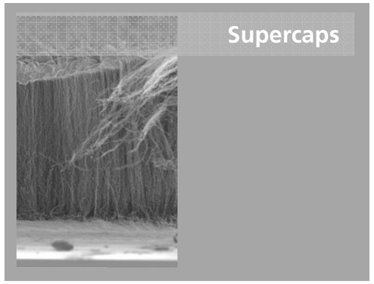
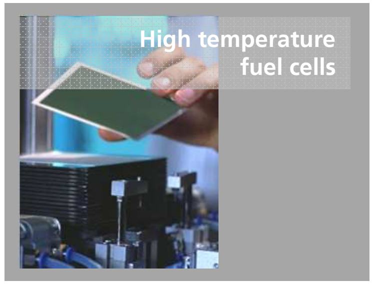
IKTS

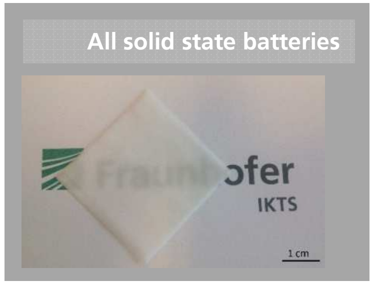
Expertise in ceramics
Energy and Environmental Technologies

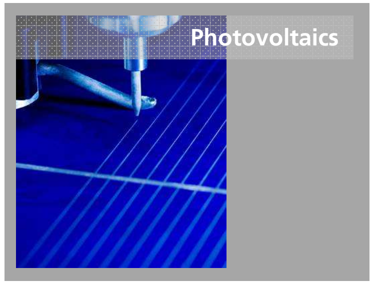


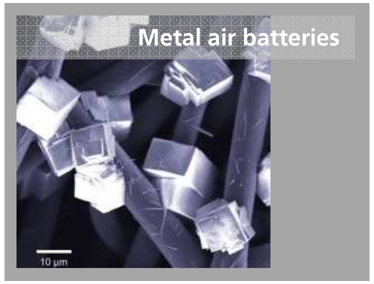


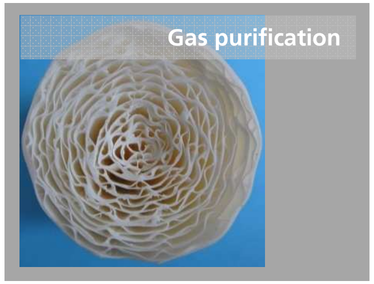


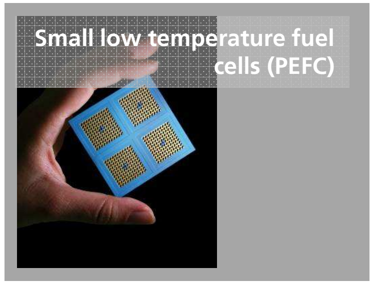


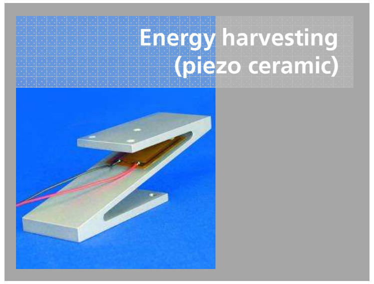


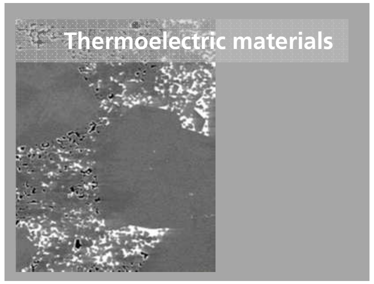












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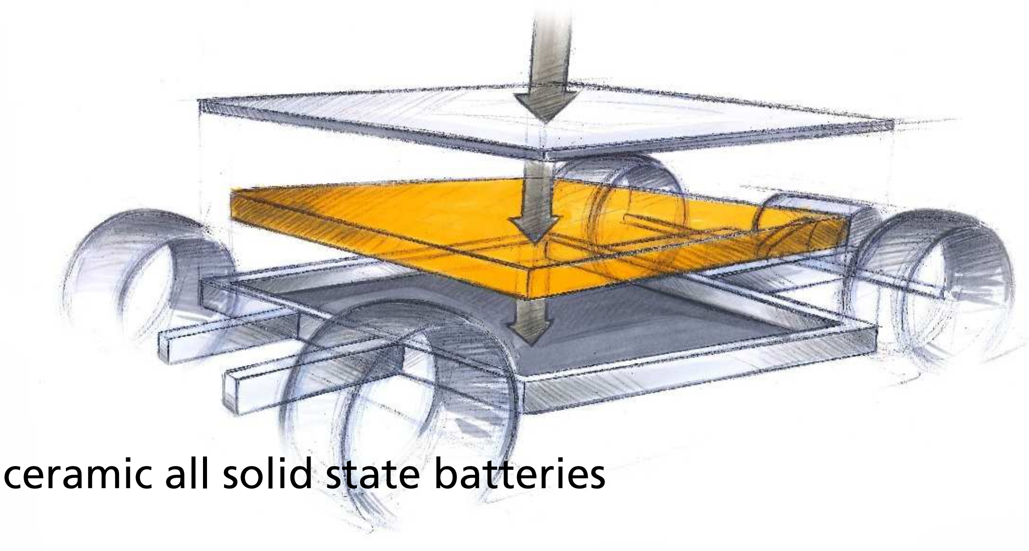
AGENDA

- EMBATT Bipolar battery concept
- Material and process innovation in EMBATT development
  → towards bipolar all solid state battery
- Ceramic technologies for all solid state batteries: preliminary results
- Conclusion

Bipolar Battery

- Significant increase of energy density on system level due to reduced system complexity
  - Stack of single cells in series
  - Integration of cell stack in one housing
    → elimination of module boundaries
  - Reduced contacting effort,
    extremely reduced internal resistance



- Promising approach for implementation of full ceramic all solid state batteries
  → high energy density + improved safety

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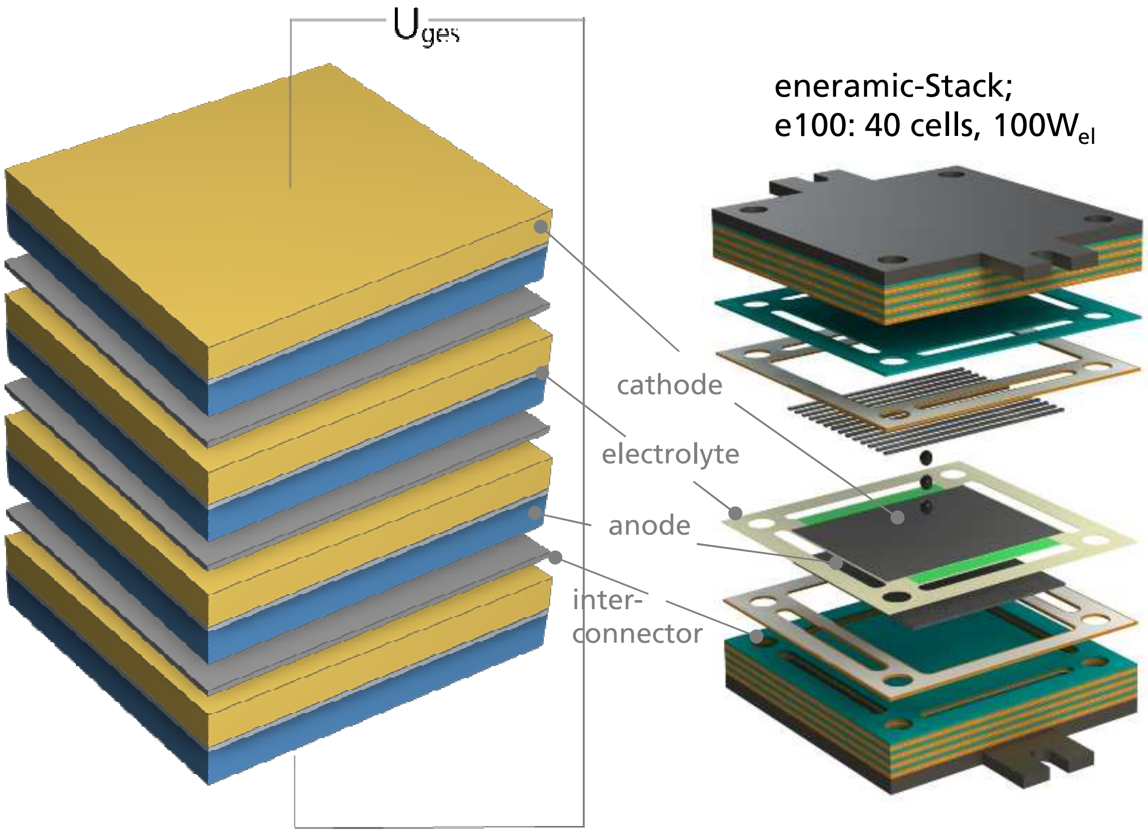
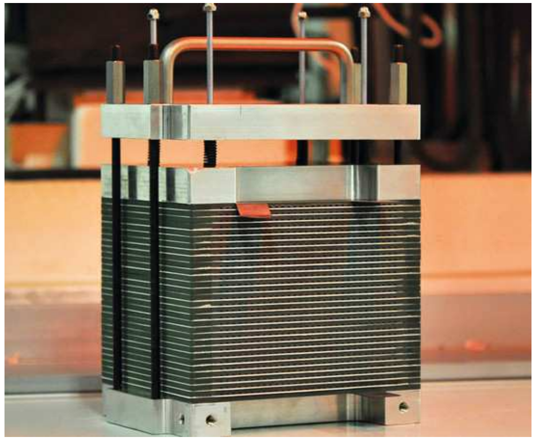
Bipolar concept

IKTS solid oxide fuel cell (SOFC) stack technology





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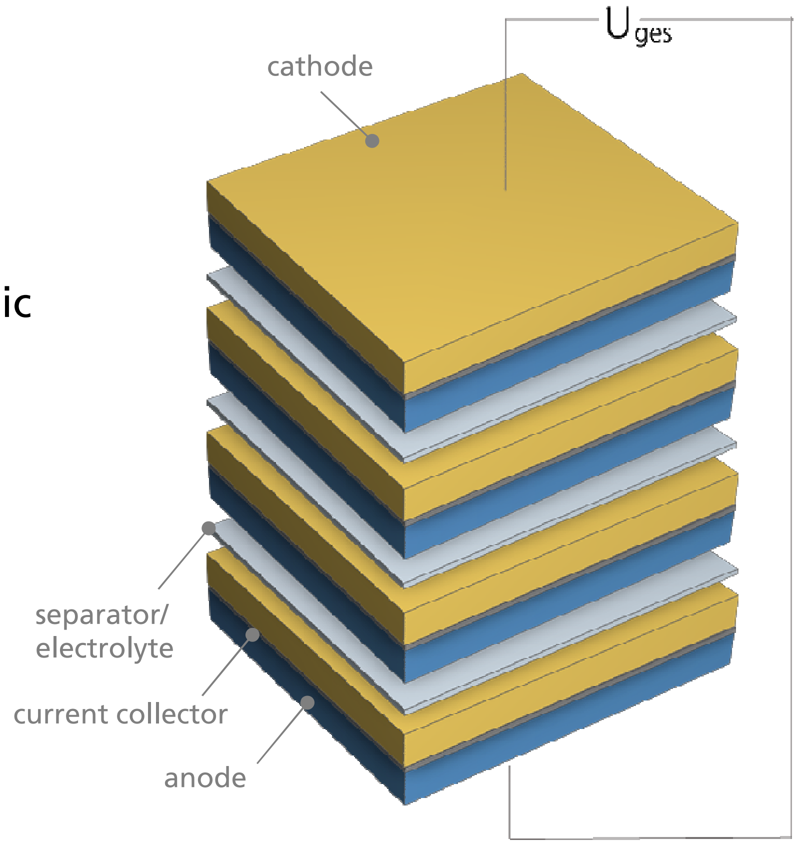
EMBATT Bipolar Battery

Chassis-embedded Energy

- IKTS research focus:
  - cell concept
  - development and optimization of active material, ceramic separator and electrolyte
  - process development regarding cell manufacturing (electrodes, …)

- Manufacturing and system integration are part of collaborative projects with industrial partners (projects: EMBATT1.0; EMBATT2.0)



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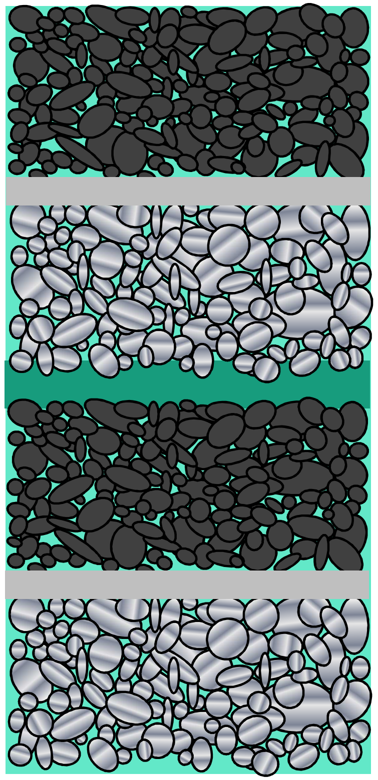
Material and process innovation in EMBATT development

EMBATT1.0



cathode
cathode materials (**NCM, LFP,** …)
electronic conducting phase: carbon black
ion conducting electrolyte phase: liquid electrolyte

contacts
aluminum

anode
anode material (**LTO**)
electronic conducting phase: carbon black
ion conducting electrolyte phase: liquid electrolyte

separator
ceramic coating, **liquid electrolyte**

- State of the art lithium ion battery chemistry
- Manufacturing innovations for high load electrodes and ceramic separator
- Stack assembly: electrolyte filling and sealing

200 Wh/l

Battery energy density

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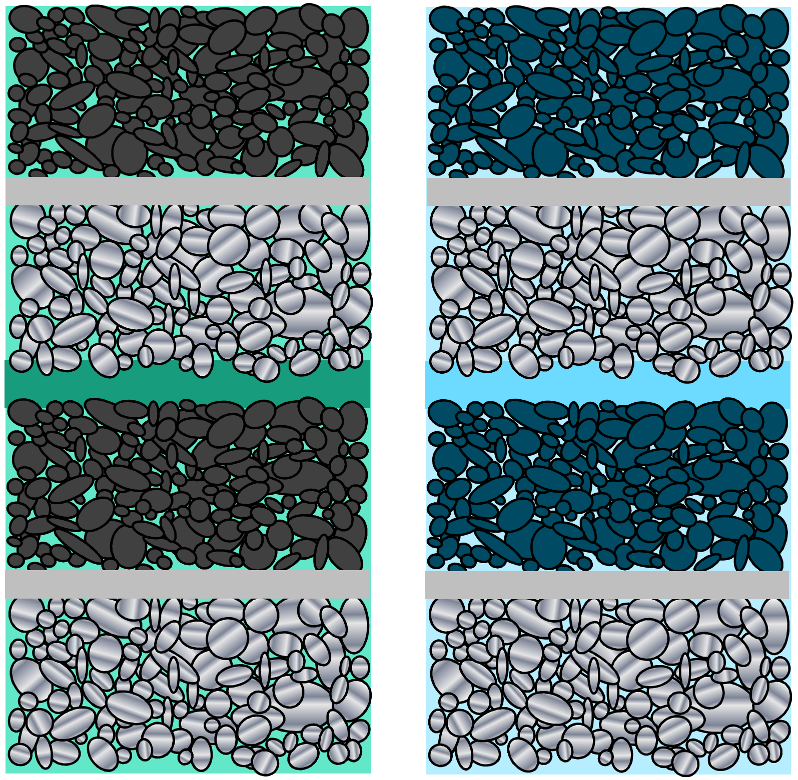
Material and process innovation in EMBATT development

EMBATT1.0 EMBATT2.0



cathode cathode materials (**LNMO**)
electronic conducting phase: carbon black
ion conducting electrolyte phase: polymer electrolyte

contacts aluminum

anode anode material (**LTO**)
electronic conducting phase: carbon black
ion conducting electrolyte phase: polymer electrolyte

separator ceramic coating, **polymer electrolyte**

- Polymer electrolyte based all solid state battery
- High voltage LNMO cathode material with adapted particle morphology
- Manufacturing of composite electrodes

200 Wh/l 450 Wh/l Battery energy density

thyssenkrupp, automotive engineering iav, Glatt, IPF Leibniz-Institut für Polymerforschung Dresden e. V., isocoll Chemie GmbH, LITARION, ULT Umwelt-Lufttechnik, KMS Technologycenter, Fraunhofer IKTS

Manufacturing process – ‚organic' bipolar battery (EMBATT1.0, EMBATT2.0)

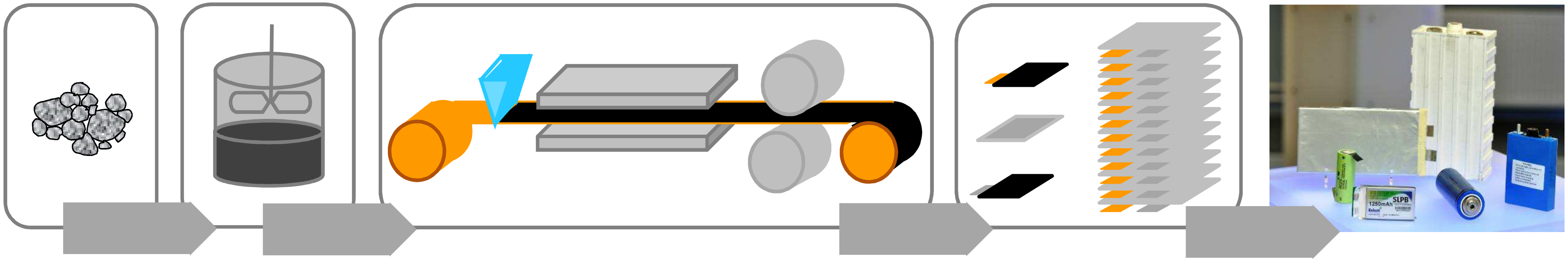
Material synthesis
active materials, separator

Slurry preparation
mixing

Electrode manufacturing
casting, drying, calendering

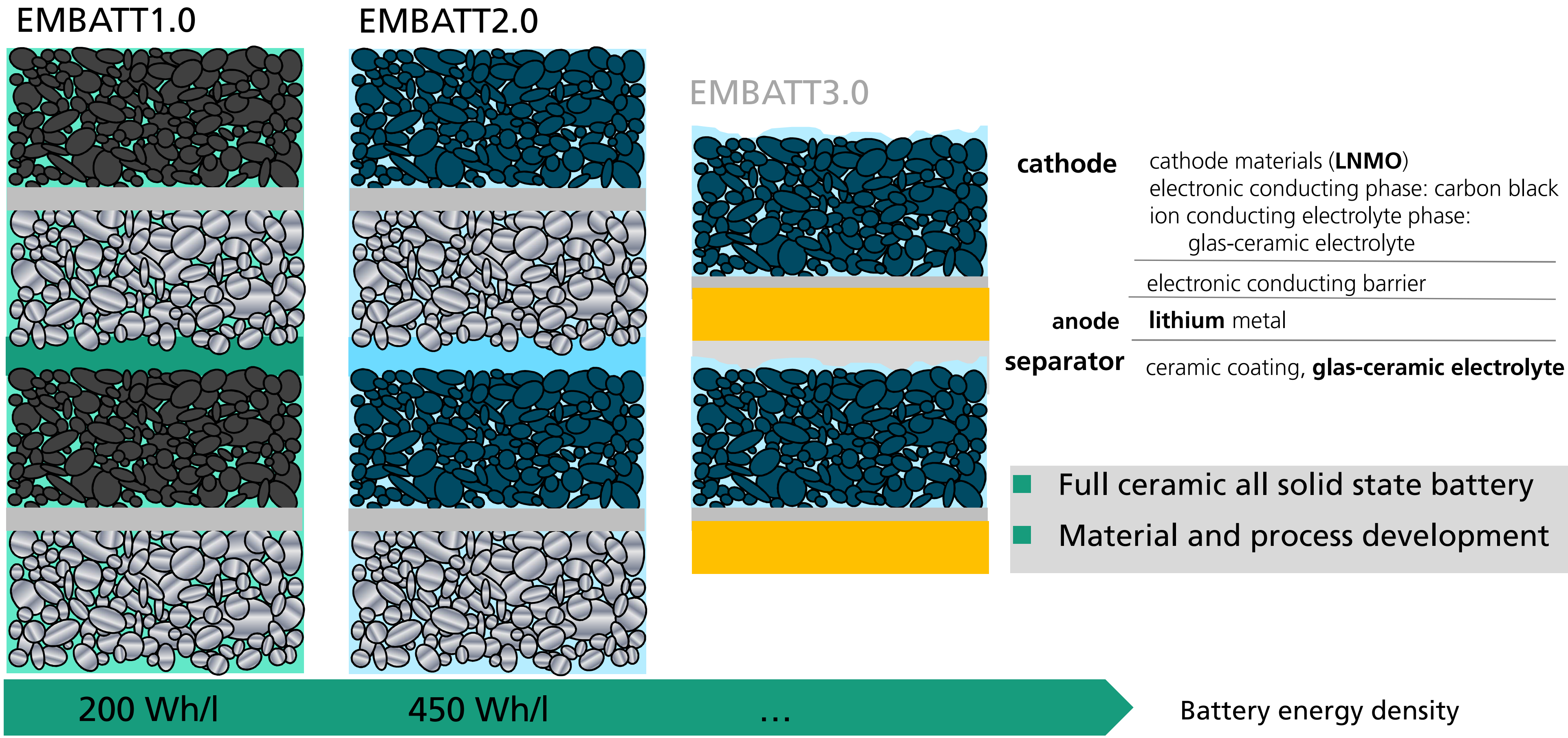
Cell assembly
slitting, stacking, electrolyte filling, packaging

Testing
formation, aging, test



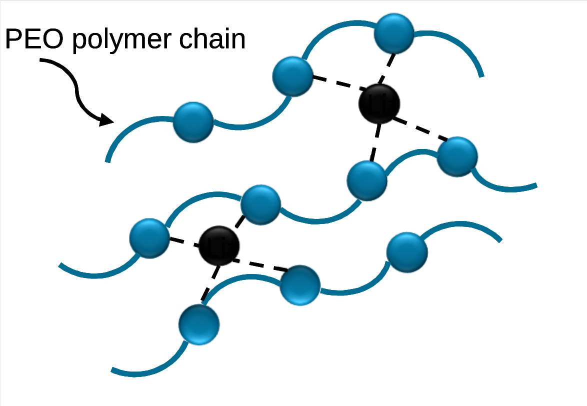
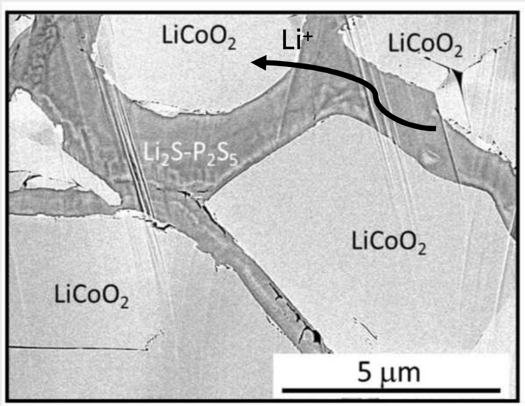
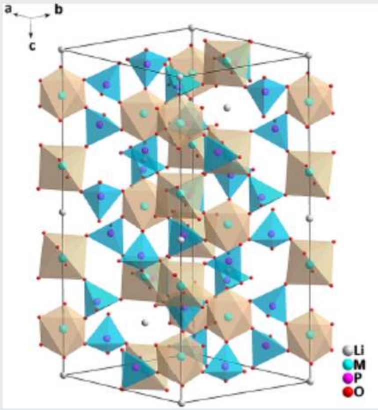
- Continuous roll-to-roll processes in electrode manufacturing
- Flexible package design
- Liquid resp. polymer electrolyte guarantees
  - high mechanical flexibility of electrodes in manufacturing and operation
  - high ionic conductivity at electrode interface

Material and process innovation in EMBATT development



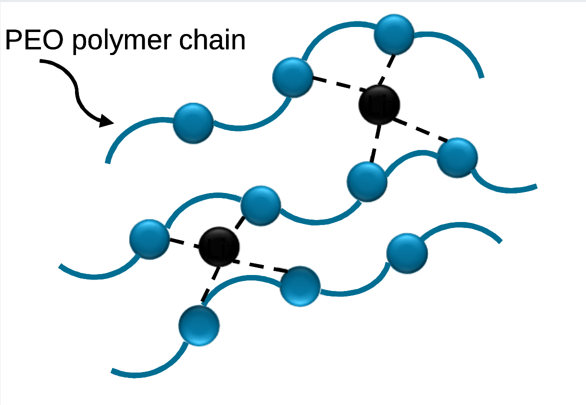
- Full ceramic all solid state battery
- Material and process development

Solide state electrolytes

Polymers	Sulfides	Oxides
		
T. Niitani, et al., Electrochemical and Solid-State Letters 8 [8] A385-A388 (2005).	*A. Sakuda, et al., Scientific Reports 3, 2261 (2013).*	*Y. Ren et al., J. Am. Ceram. Soc. 98 [12] 3603-3623 (2015).*
+ good processibility and flexibility - low ionic conductivity (10^{-5}-10^{-4} S/cm) - low mechanical stability	+ high ionic conductivity (10^{-3}-10^{-2} S/cm at RT) - highly hygroscopic - low mechanical stability	+ good ionic conductivity (< 10^{-3} S/cm at RT) + stable against air and high temperatures

Solide state electrolytes

Polymers



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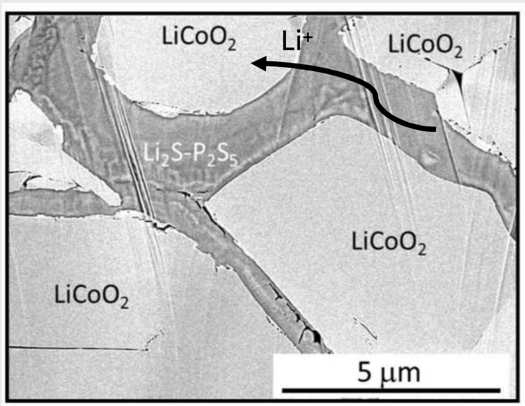
- low ionic conductivity (10^{-5}-10^{-4} S/cm)
- low mechanical stability

Sulfides



A. Sakuda, et al., Scientific Reports 3, 2261 (2013).

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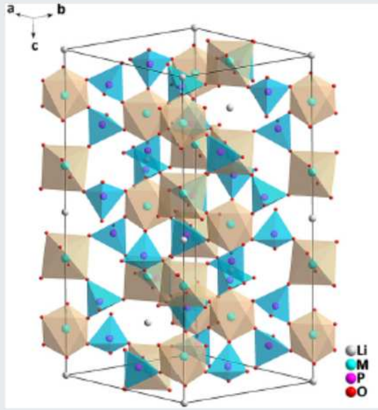
Oxides



Y. Ren et al., J. Am. Ceram. Soc. 98 [12] 3603-3623 (2015).

Lithium Aluminium Titanium Phosphate $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$
→ NASICON structure
→ $[M_2(PO_4)_3]$- framework stabilized with Li^+

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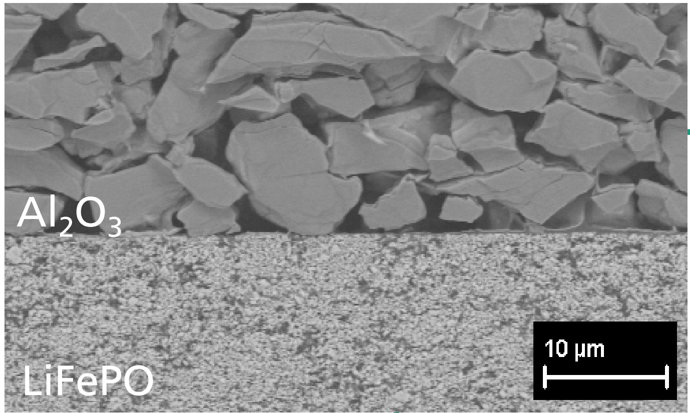
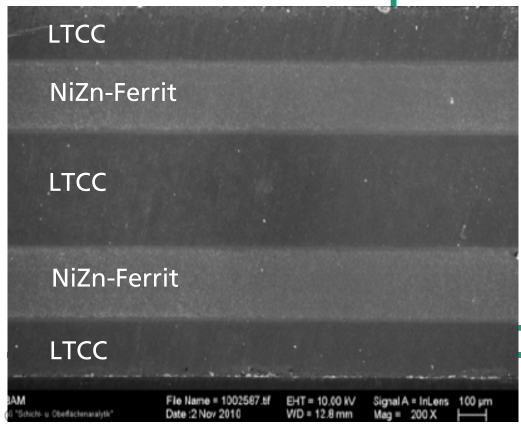
Manufacturing of components - composite electrode, solid electrolyte



Casting, Printing

Thermal processing



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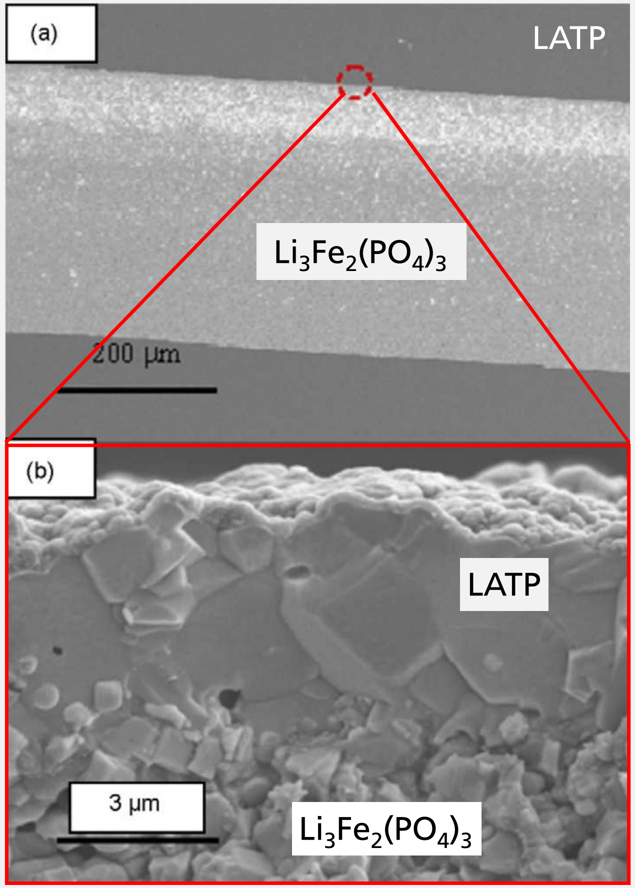
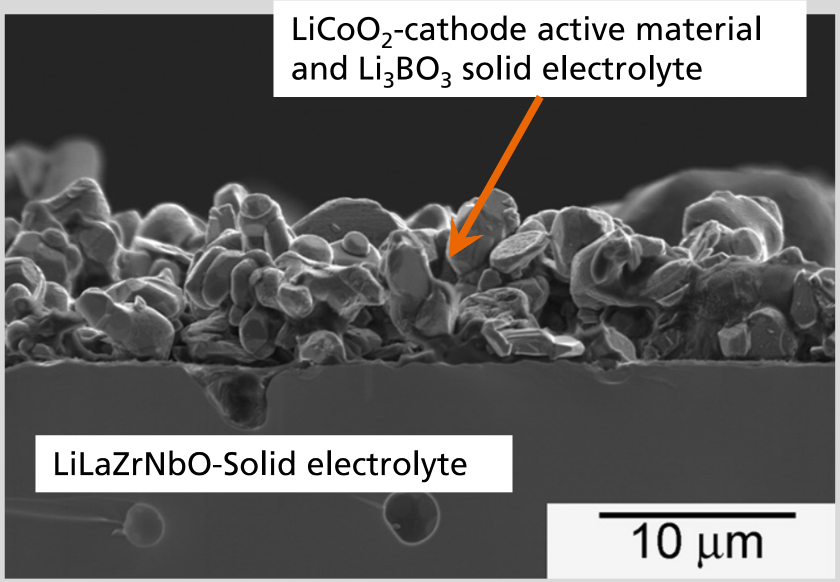
Manufacturing of components - composite electrode, solid electrolyte

Cathode supported

$Li_3Fe_2(PO_4)_3$/LATP interface sintered at 1000°C





SEM image of a composite cathode sintered on a solid state electrolyte substrate

Electrolyte supported

S. Ohta et al.: All-solid-state lithium ion battery using garnet-type oxide and Li3BO3 solid electrolytes fabricated by screen-printing, Journal of Power Sources 238 (2013) 53e56

K. Nagata, T. Nanno, All solid battery with phosphate compounds made through sintering process, Journal of Power Sources 174 (2007) 832–837

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Manufacturing process – ‚full ceramic‘ bipolar battery

Material synthesis
active materials, separator

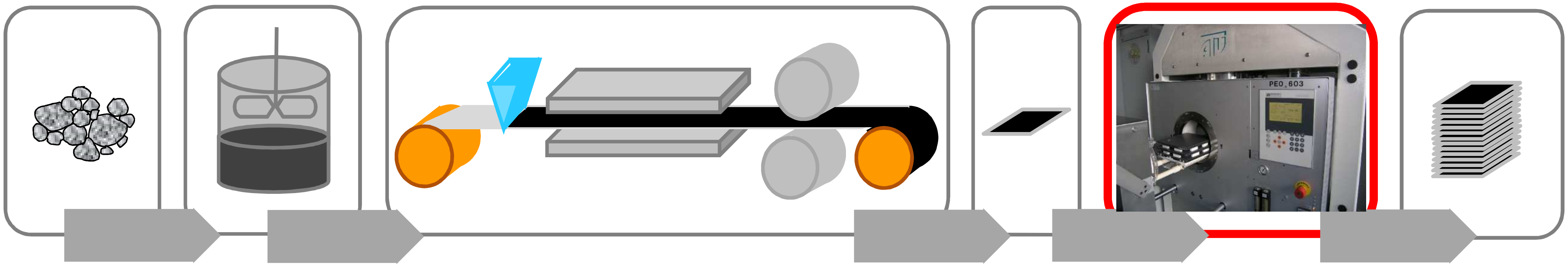
Slurry preparation
mixing

Composite electrode + solid electrolyte manufacturing
casting, drying → green tape

Sheet cutting

Thermal treatment
sintering

Implementation of lithium anode, stack assembly
stacking, packaging



- Thermal treatment → batch process
- Stacked package design of sintered components:

Thermal mismatch → cracks
Conductive material interfaces
Evaporation of lithium
Reactivity with other phases (e.g. cathode materials)
Loss of flexibility

Manufacturing of components - composite electrode, solid electrolyte

Adapted material properties:

- Primary particle size and morphology of active materials
- Sintering properties of electrolyte → adapted particle size distribution
- Surface reactivity of materials

Co-sintering of materials with similar chemical compositions:

- Similar sintering temperatures
- Low interdiffusion of elements
- No formation of undesired components at interfaces

Manufacturing of components - composite electrode, solid electrolyte

Adapted material properties:

- Primary particle size and morphology of active materials
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LNMO synthesis

Co-sintering of materials with similar chemical compositions:

- Similar sintering temperatures
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- No formation of undesired components at interfaces

Powder synthesis of high energy cathode material $LiNi_{0.5}Mn_{1.5}O_4$

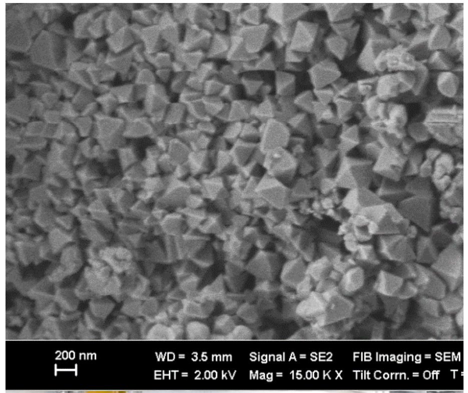
- Investigation of synthesis parameters for material properties adapted to ASSB application
- Manufacturing of primary particles with adapted morphology and high crystallinity

$LiNi_{0.5}Mn_{1.5}O_4$ → 147 Ah/kg, 4,7 V vs. Li/Li^+
→ 690 Wh/kg, 3034 Wh/l

- Lab spray drying process at IKTS

  Precursor composition, pre-treatment, phase, crystallite size

- Scale up and development of industrial processes



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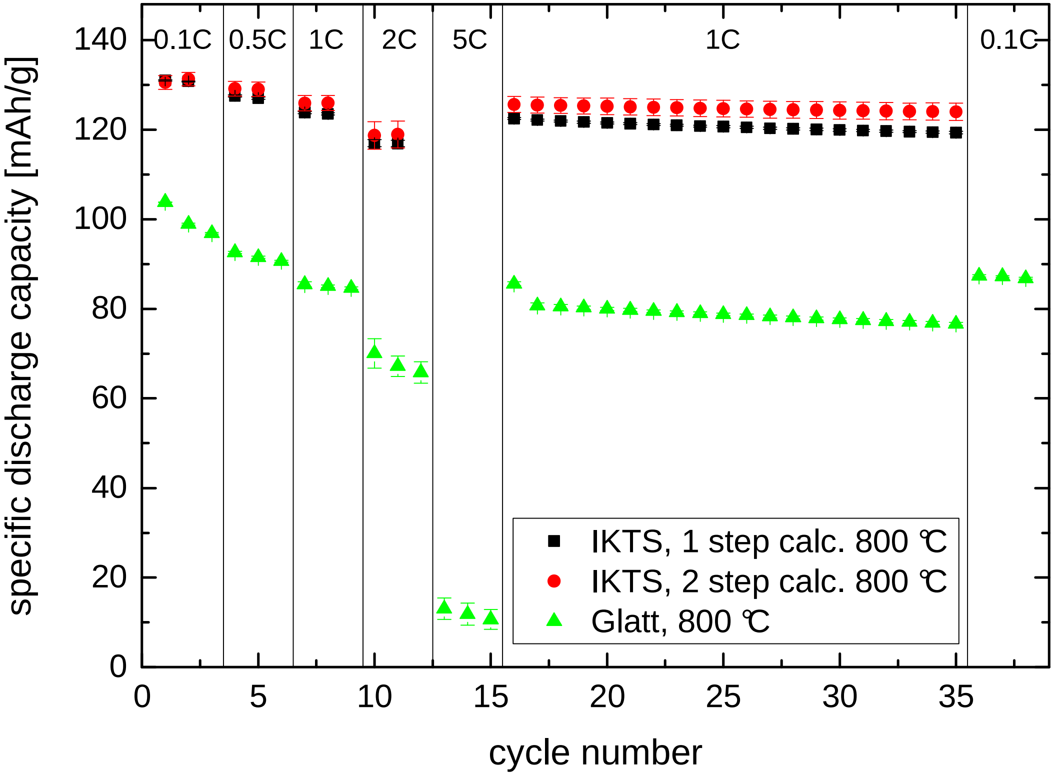

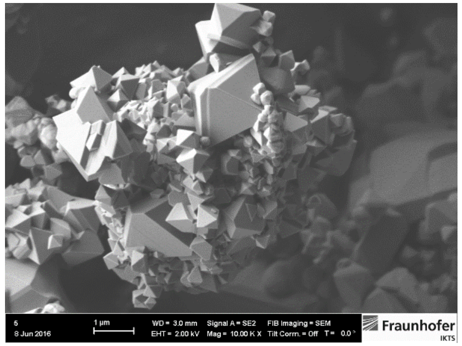

Results of IKTS lab spray drying precursor with different calcination regime ($LiNO_3$ / $Ni(NO_3)_2$ / $Mn(CH_3COO)_2$-precursor)

FIRST Results of Glatt pilot line results using APPtec technology

→ Promising electrochemical results

→ Further work on:

- Phase composition
- Reduction of Mn^{3+} amount
- Calcination regime

Glatt®

foil preparation: 80 % active material (LNMO), 10 % carbon (Super P), 10 % binder (PVDF)
coin cells: 2xWhatmann, 150 µl LP40, Ni-foam

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LATP electrolyte

Synthesis of glass ceramic LATP materials

Melting & Quenching

- Mixing of components (Li_2CO_3, $Al(OH)_3$, TiO_2 (anatase), phosphoric acid)
- Melting at 1450°C
- Quenching on a brass plate

Milling

- Vibration cup mill for rough milling
- Attritor milling (8 hours) for fine milling
- Sub micron powder

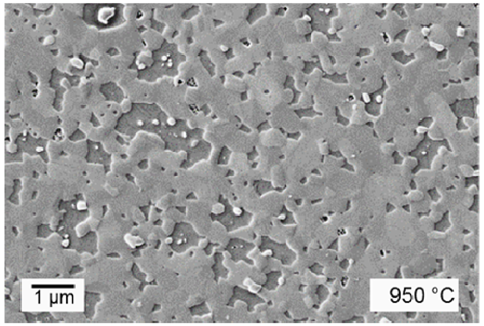
Shaping

- Powder compacts

Sintering

- Pressure less heat treatment
- SPS (100 K/min, 800 – 1050 °C)

Attritor Netzsch



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Synthesis of glass ceramic LATP materials and component manufacturing

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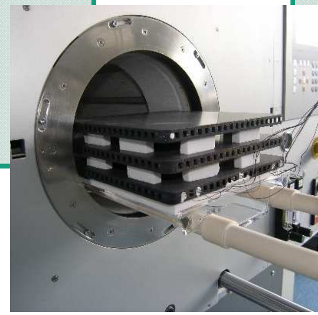
Attritor Netzsch

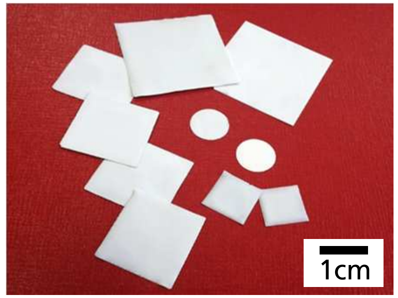
Tape casting

- Recipe development

Sintering

- Pressureless sintering step
- Adapted setup to avoid warping
- Minimized thickness of substrates





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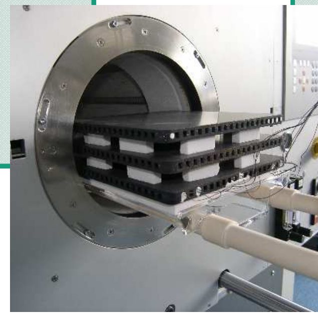
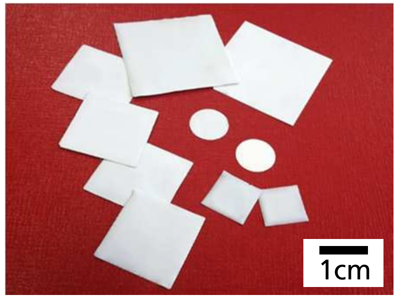


Parameter	Value
Thickness of green tape	120-300 µm
Single sintered tape	120 µm
Sintering temperature	950°C – 1150°C
CTE for RT-800°C	1-1,5 $\cdot 10^{-6}$ /K^{-1}
4-Point Bending strength (BB-bar)	55 ± 9 Mpa
Conductivity @ 25°C	3 $\cdot 10^{-4}$ S cm^{-1}



Properties of sintered LATP microstructures

- Strong anisotropy of $MTi_2(PO_4)_3$ (M = Li, Na, K) phases along the crystallographic axis

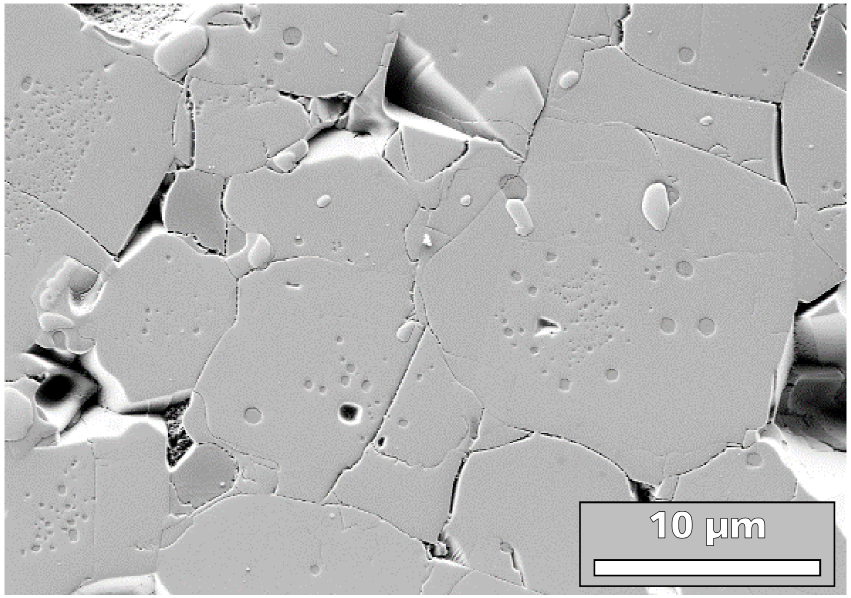
  M=Li: $\alpha_a = 0{,}75 - 0{,}27 \cdot 10^{-6}\ K^{-1}$
  $\alpha_c = 30{,}8 \cdot 10^{-6}\ K^{-1}$
  (20°C..800°C)

- Investigation of effects during sintering process

  → Formation of cracks

  → Effects from grain size and sintering process

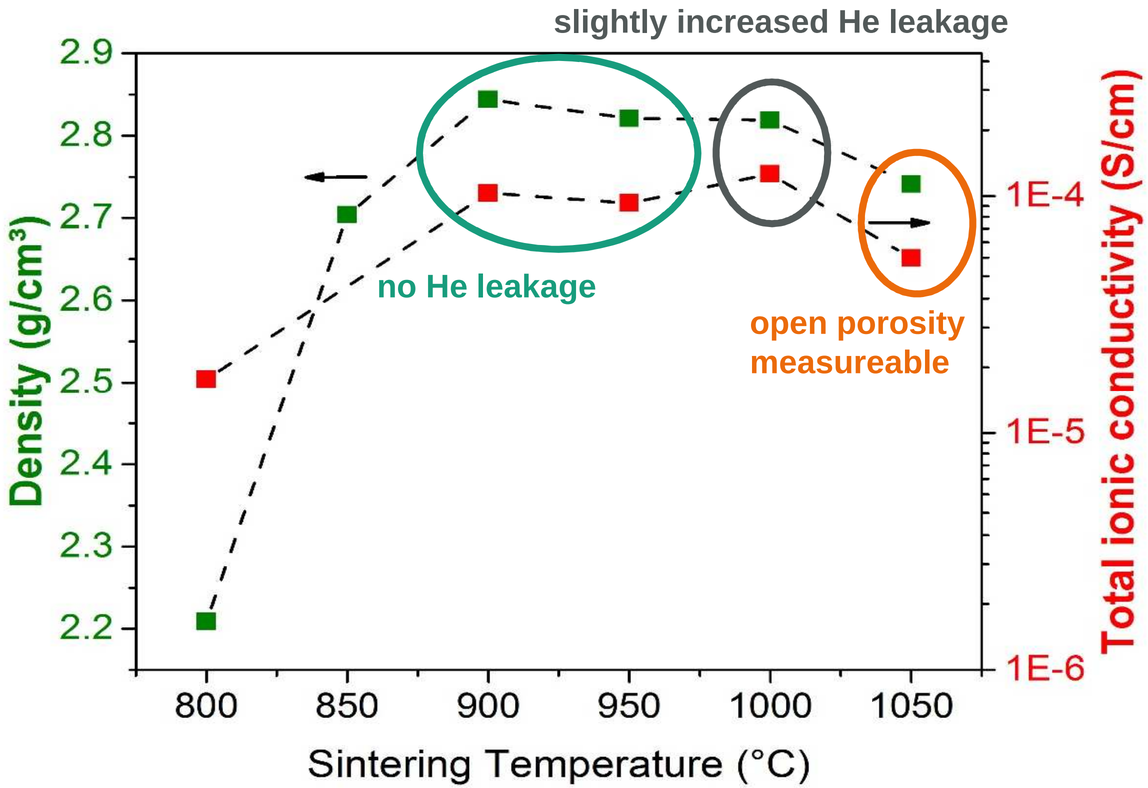
- Comprehension of the mechanism and optimization of process technology

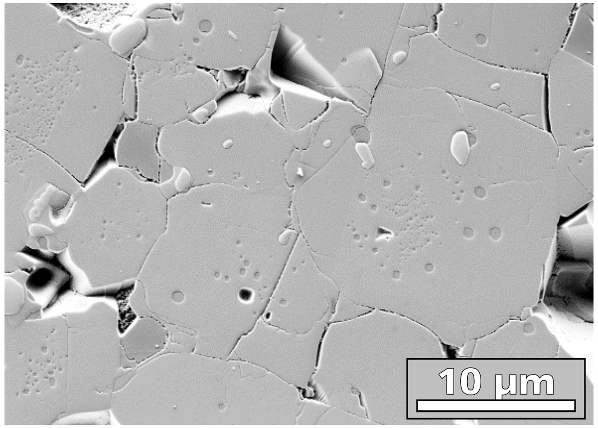


Source IKTS: SEM image of $Li0_3$ sintered at 1150°C

D. A. Woodcock and P. Lightfoot, J. Mater. Chem., 1999,9, 2907-2911

Investigation of sintering properties of LATP





K. Waetzig, A. Rost, U. Langklotz, B. Matthey, J. Schilm, “An explanation of the microcrack formation in $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ LATP ceramics”, Journal of the European Ceramic Society, Accepted (2016).

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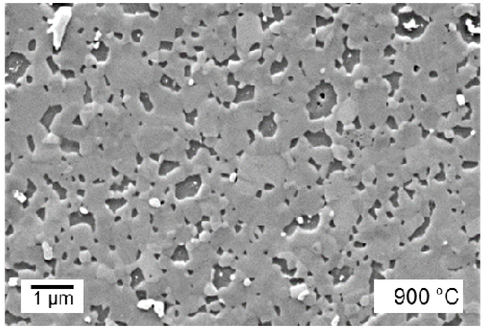
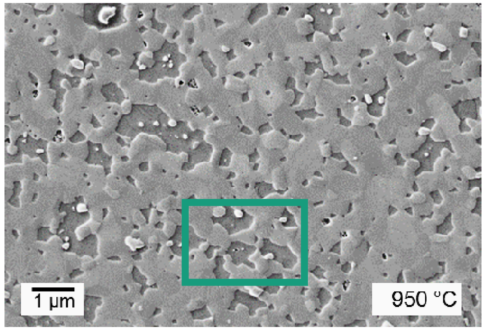
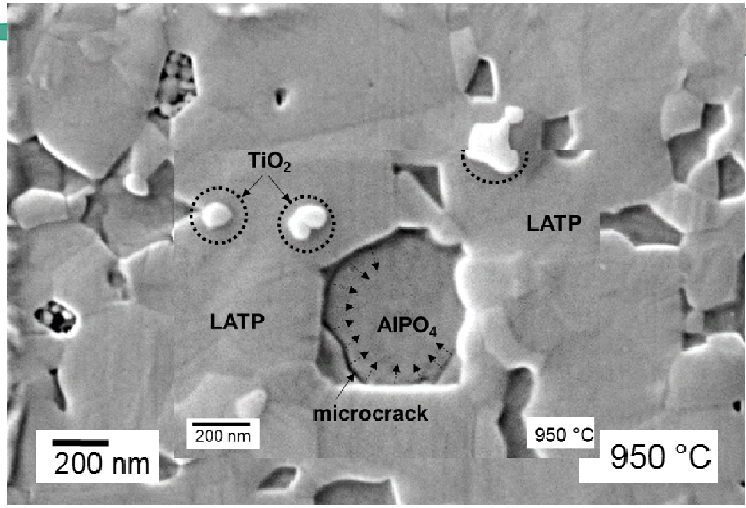
Evolution of cracks in microstructure of LATP ceramics at different sintering temperatures





900 ℃



1st Effect – Li loss indicated phase transition

- $AlPO_4$ formation
  - smaller lattice parameter
  - negative thermal expansion coefficient
- Initial microcracks in the $AlPO_4$ phase
- Observed at T = 950 °C
- Grain size ~ 0.7 µm

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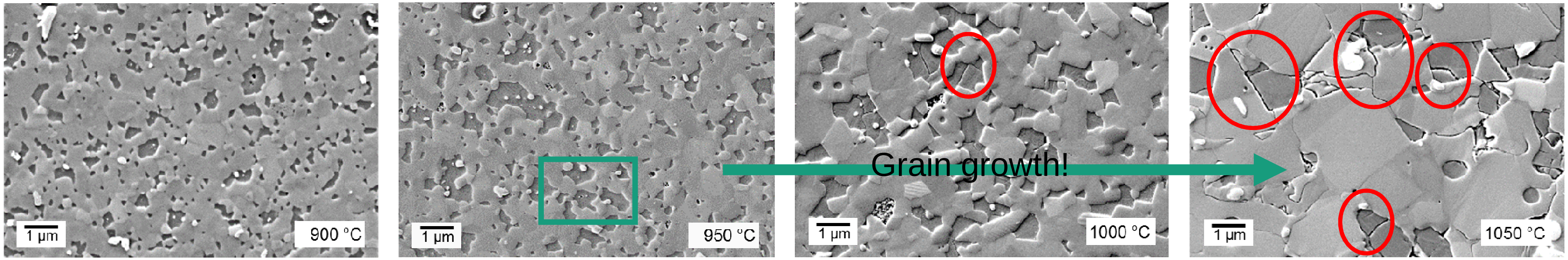
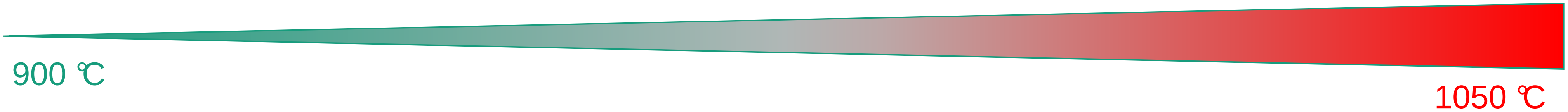
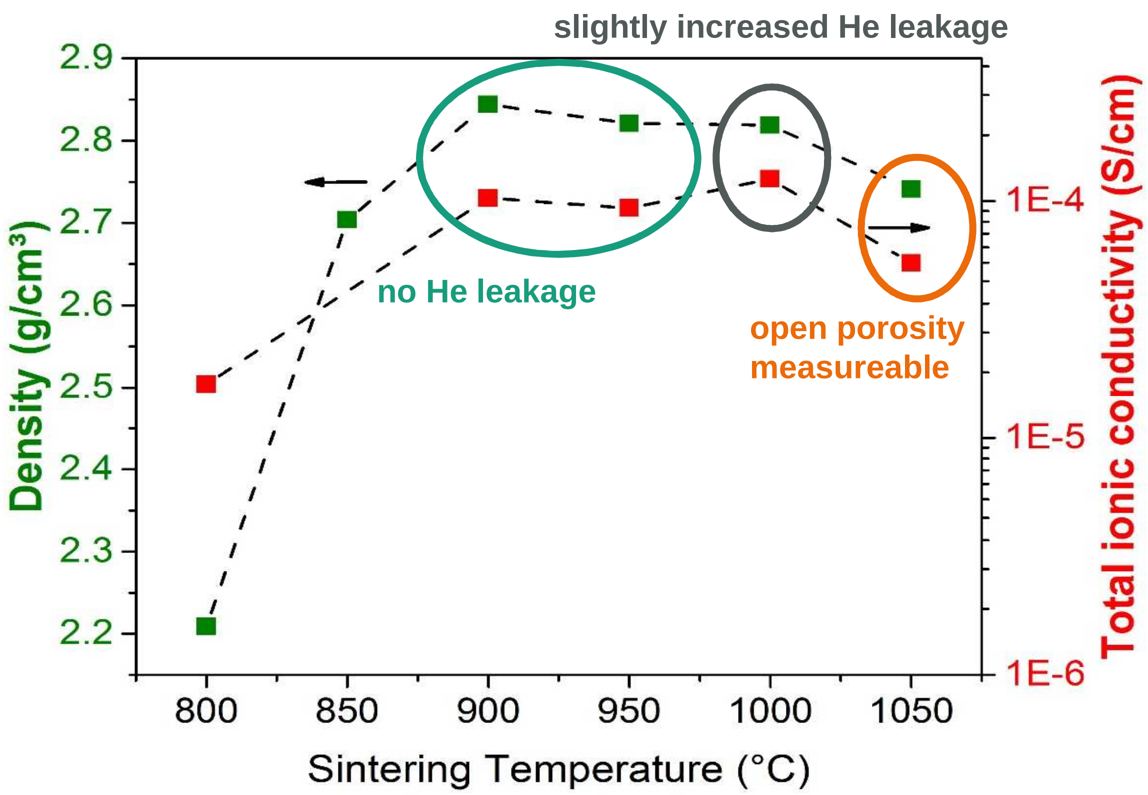


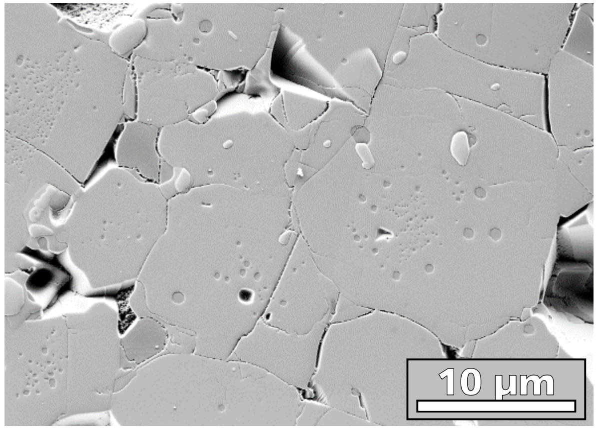


2nd Effect – Thermal expansion anisotropy of LATP

- Grain growth of LATP in direction of c
- Cracking though the main phase
- Observed at T > 1000 °C
- Grain size > 1.1 µm

Investigation of sintering properties of LATP





Optimized sintering conditions:

- Defect free microstructures
- Maximized ionic conductivity
- Prevention of Lithium evaporation

K. Waetzig, A. Rost, U. Langklotz, B. Matthey, J. Schilm, "An explanation of the microcrack formation in $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ LATP ceramics", Journal of the European Ceramic Society, Accepted (2016).

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Conclusion

- Bipolar concept
  - allows significant increase of energy density on system level
  - increase of energy and optimized safety by material and process innovations
  - represents optimal approach for assembling of a full ceramic all solid state battery
- All ceramic bipolar battery requires significant development on thermal processes
  - Compatibility of active materials and solid electrolytes for minimized interface reactions
  - Adapted sintering behavior of composite cathodes and solid electrolyte
  - Optimized thermomechanical properties (warping, cracking…)

Many open questions to discuss about…

»DRESDEN BATTERY DAYS 2017«

SEPTEMBER 2017

Fraunhofer-Institut für Keramische Technologien und Systeme IKTS, Dresden

TOPIC

‚ALL SOLID STATE BATTERIES'

- Perspectives
- Materials
- Technologies
- Application

Further information coming soon

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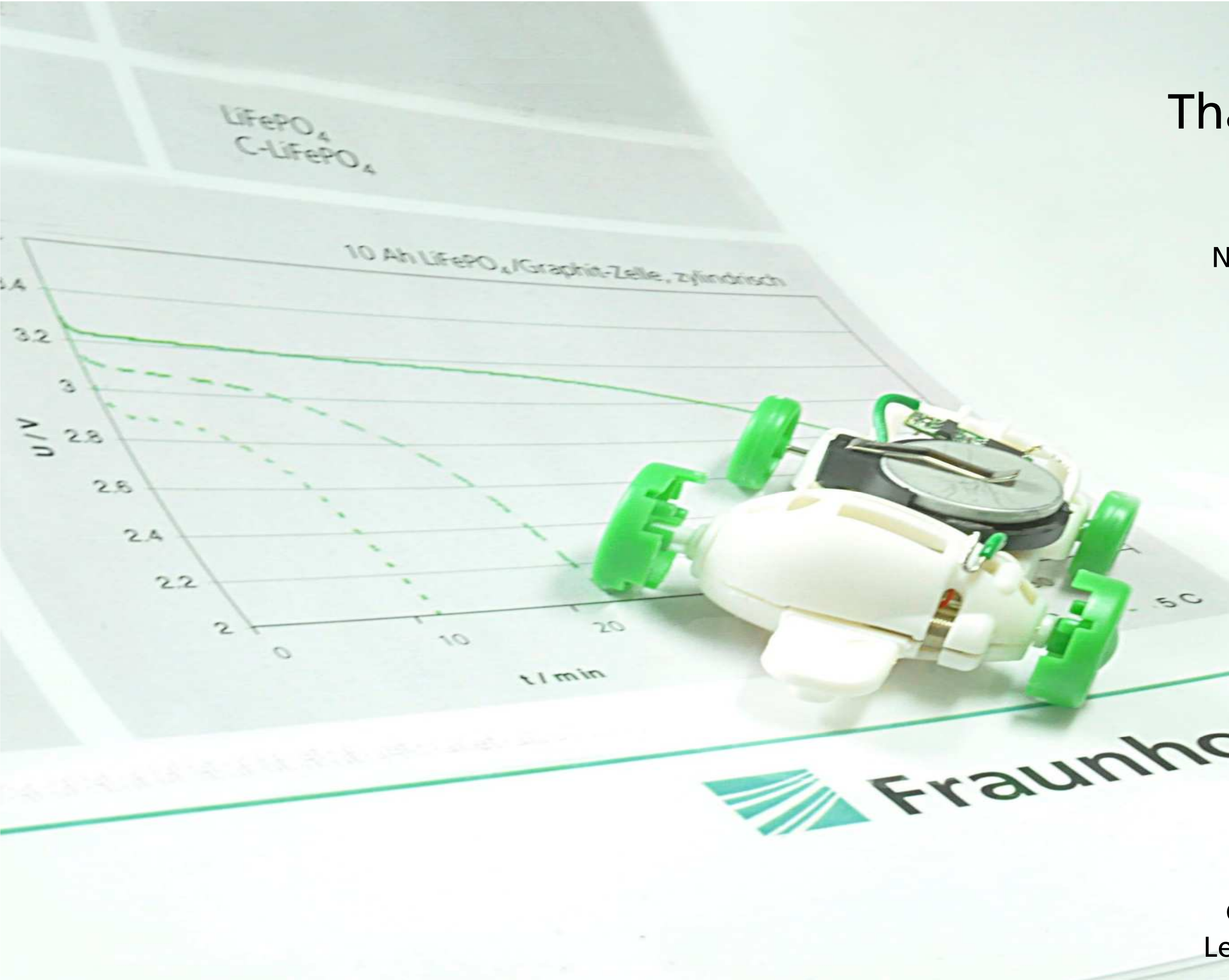

Thank you for your attention!

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