MATERIAL DEVELOPMENT AND PROCESSING ASPECTS OF CO-SINTERED CERAMIC ELECTRODES FOR ALL SOLID-STATE BATTERIES

Katja Waetzig, Jochen Schilm, B. Matthey, St. Barth, K. Nikolowski, M. Wolter

Dresden, 20th of September 2017

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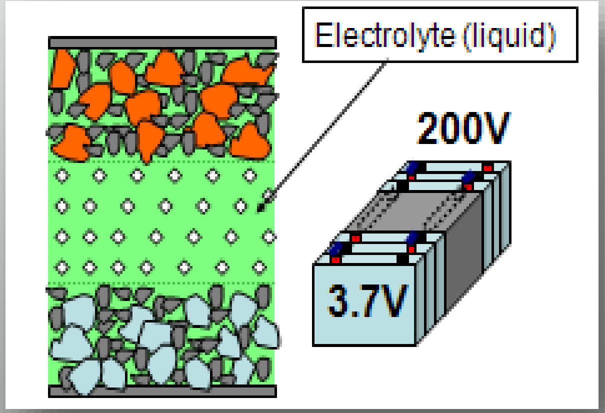
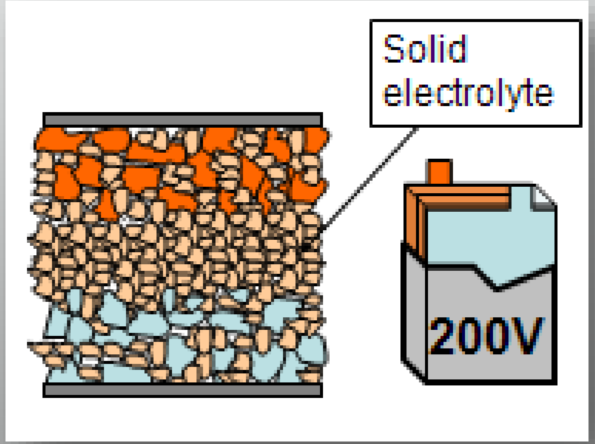
Motivation
All-Solid-State Lithium Batteries



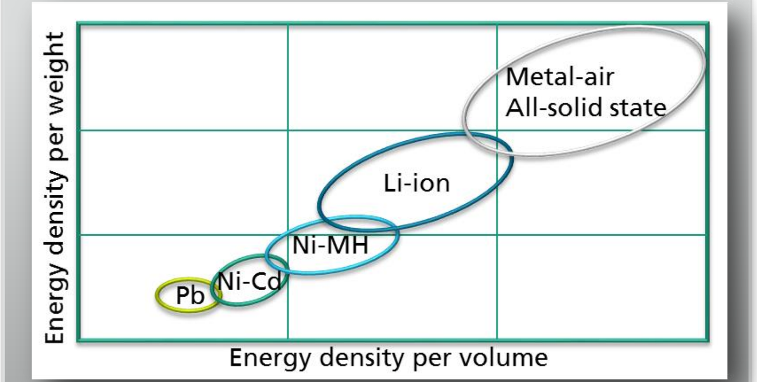
Conventional Liquid Electrolyte Li-Ion Battery

+ high voltage and high energy density
- flammable liquid electrolyte



All-Solid-State Lithium Battery

+ higher energy density
+ high-capacity active materials usable
+ safe Li-ion conductive ceramic
  (non flammable, mechanical stable)
- high internal resistance



The **solid electrolyte**

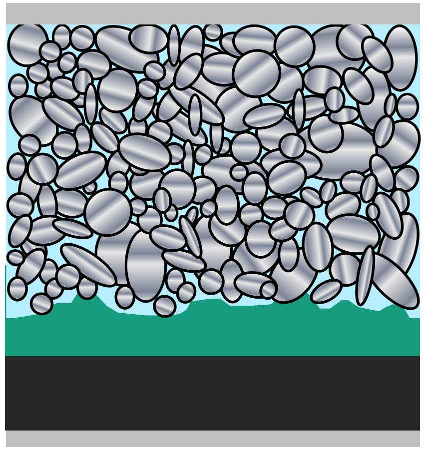
is

a key material !

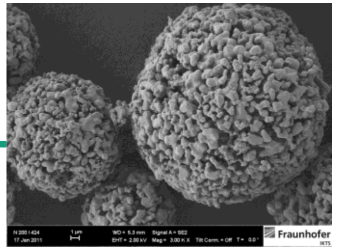
M. Ogawa, K. Yoshida, K. Harada, SEI Technical Review 74, 88-90 (2012).

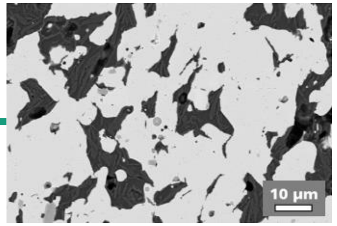
National Institute of Advanced Industrial Science and Technology (AIST), press release (2010).

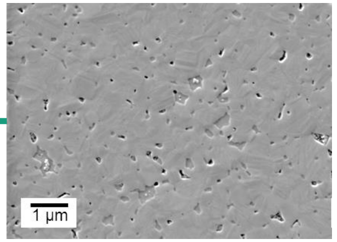
All-Solid-State Battery
Principal Concept

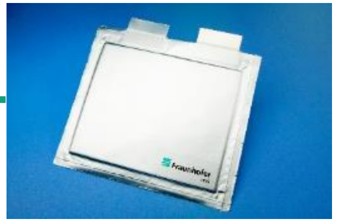


contacts	aluminum
composite cathode	high energy cathode materials (NCM, LNMO) electronic conducting phase: graphite ionic conducting electrolyte phase
all solid state electrolyte	particle filled polymer, ceramic all solid state
anode	lithium metal, composite anode
contacts	nickel









Material Development

Process technology

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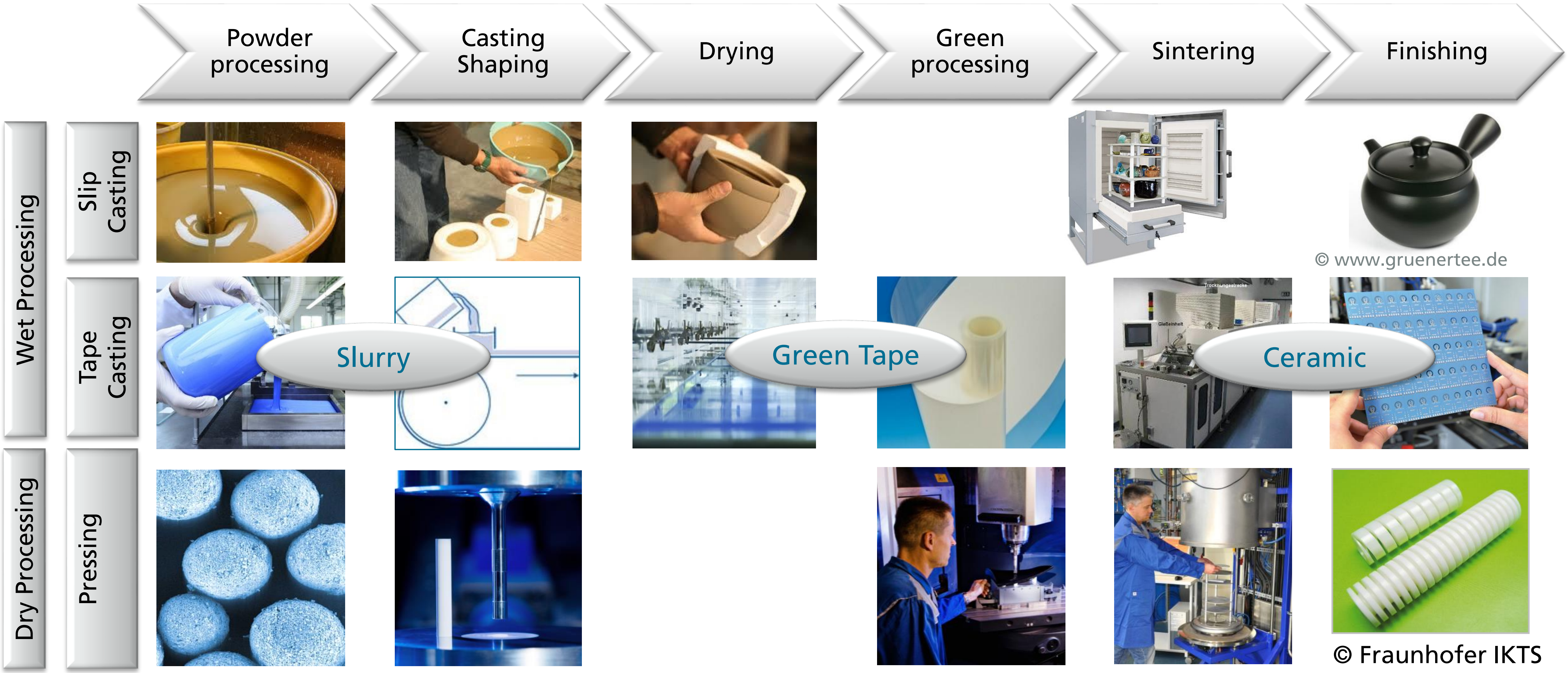
Process Technologies

Ceramic Technology - A Short Introduction



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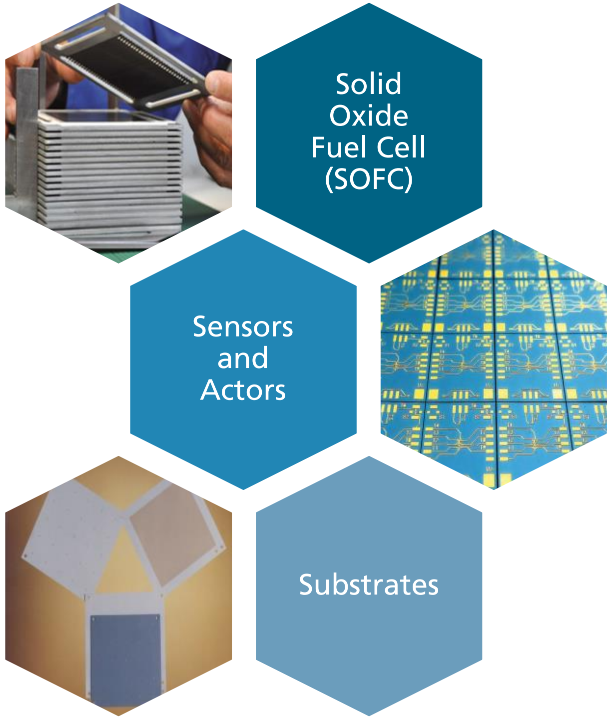
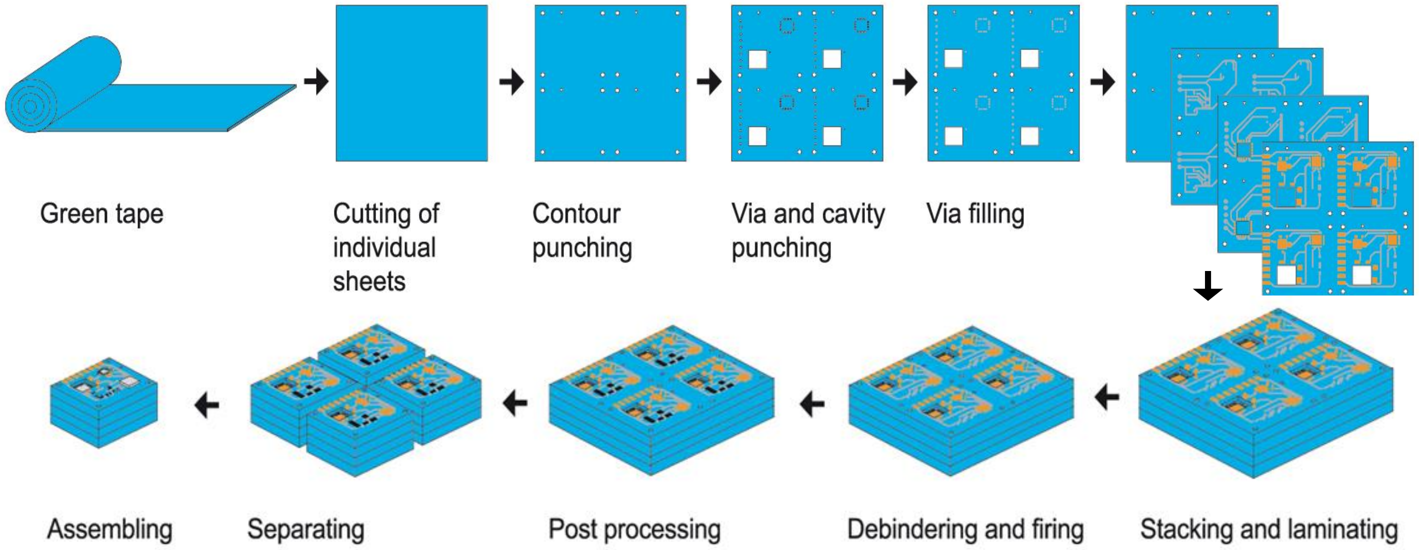
Processing of All-Solid-State Batteries

Multilayer as Established Ceramic Technology





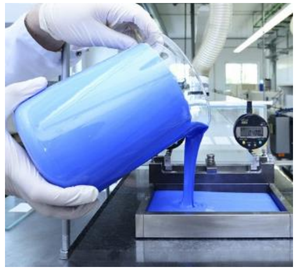
Technology	Thickness before Sintering (µm)	Thickness after Sintering (µm)
Tape Casting	50 - 500	40 - 400
Screen Printing	10 - 100	8 - 80
Other Printing Techniques	< 10	< 8

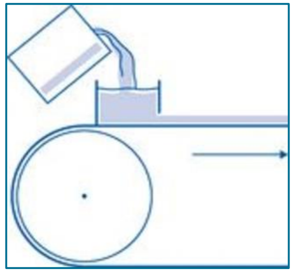
Is it possible to process All-Solid-State Batteries as multilayered ceramic?

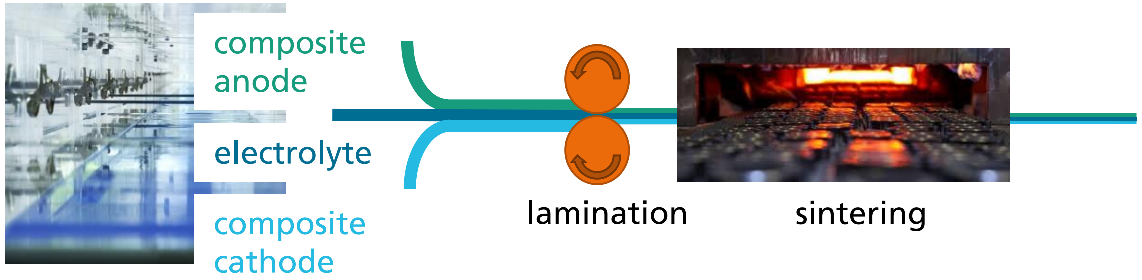
Processing of All-Solid-State Batteries

Roll-to-Roll - Challenges

Powder processing → Casting Shaping → Drying → Green processing → Sintering → Finishing







cutting
contacting
stacking

Tape casting / Lamination

- Compatibility with organic additives and solvents
- Homogeneity of inorganic and organic components
- Optimized content of solid

Co-Sintering

- Compatibility of electrolyte and active materials
- Reduced sintering temperatures to inhibit chemical reactions

Addition of anode / collectors

- Low ohmic resistance between electrodes and metal foils
- Compatibility between Lithiu electrolyte

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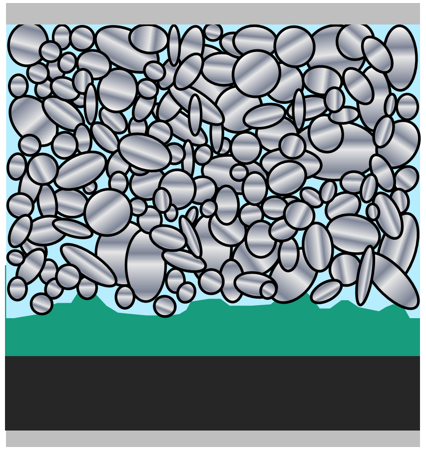
All-Solid-State Battery
Principal Concept



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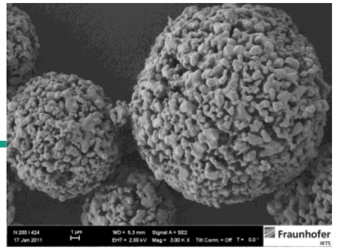
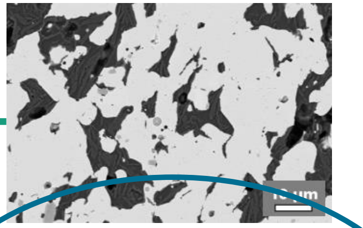
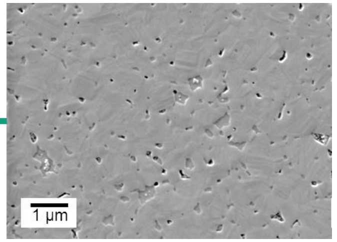


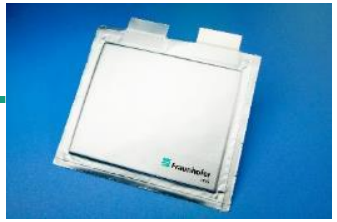

Material Development

Process technology



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Material Development

Li-Ion Conductive Separators and Solid Electrolytes

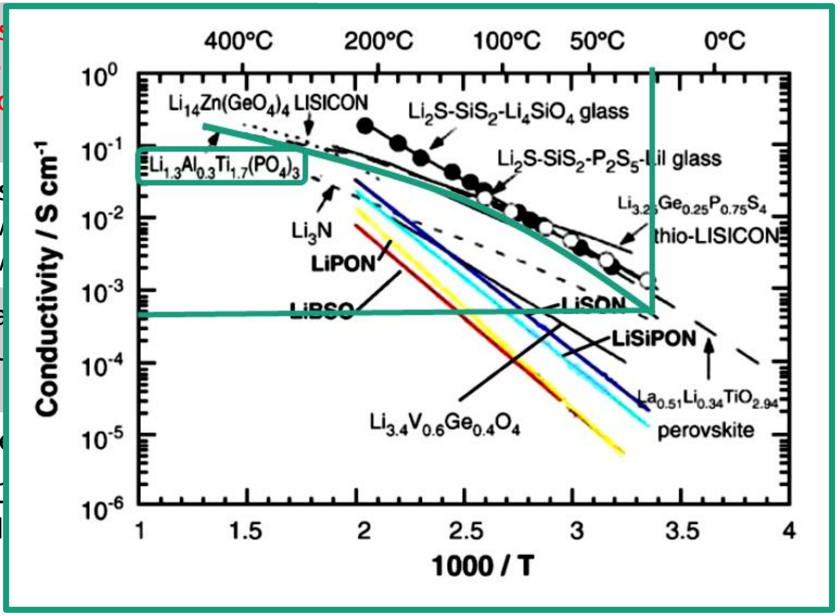
Type	Materials	Conductivity (S cm−1)	Advantages	Disadvantages
Oxide	Perovskite $Li_{3.3}La_{0.56}TiO_3$, NASICON $LiTi_2(PO_4)_3$, LISICON $Li_{14}Zn(GeO_4)_4$ and garnet $Li_7La_3Zr_2O_{12}$	10^{-5}–10^{-3}	• High chemical and electrochemical stability • High mechanical strength • High electrochemical oxidation voltage	• Non-flexible • Expensive large-scale production
Sulfides	Li_2S–P_2S_5, Li_2S–P_2S_5–MS_x	10^{-7}–10^{-3}	• High conductivity • Good mechanical strength and mechanical flexibility • Low grain-boundary resistance	• Low oxidation stability • Sensitive to moisture • Poor compatibility with cathode materials
Hydrides	$LiBH_4$, $LiBH_4$–LiX (X = Cl, Br or I), $LiBH_4$– $LiNH_2$, $LiNH_2$, Li_3AlH_6 and Li_2NH	10^{-7}–10^{-4}	• Low grain-boundary resistance • Stable with lithium metal • Good mechanical strength and mechanical flexibility	• Sens • Poo with c
Halide	LiI, spinel Li_2ZnI_4 and anti-perovskite Li_3OCl	10^{-8}–10^{-5}	• Stable with lithium metal • Good mechanical strength and mechanical flexibility	• Sens • Low • Low
Borate or Phophate	$Li_2B_4O_7$, Li_3PO_4 and Li_2O–B_2O_3–P_2O_5	10^{-7}–10^{-6}	• Facile manufacturing process • Good manufacturing reproducibility • Good durability	• Rela condu
Thin film	LiPON	10^{-6}	• Stable with lithium metal • Stable with cathode materials	• Expe produ

LiPON, lithium phosphorus oxynitride; LISICON, lithium superionic conductor; NASICON, sodium superionic cond

PEO, poly(ethylene oxide).

→ Good processability

$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP)



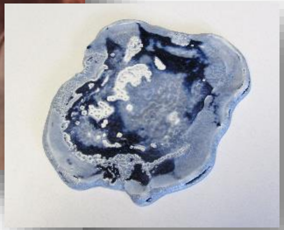
A. Manthiram, X. Yu, S. Wang, NATURE Reviews, Materials 2 (2017) 16103.

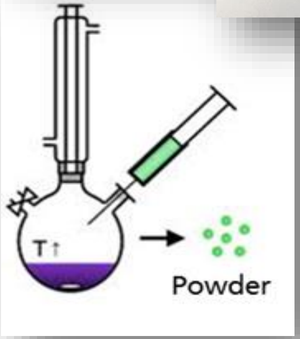
P. Knauth, Solid State Ionics 180 (2009) 911–916.

Material Development

Synthesis of LATP Electrolyte Ceramic

melting and quenching
(top-down)





sol-gel synthesis
(bottom-up)

Attritor
Netzsch

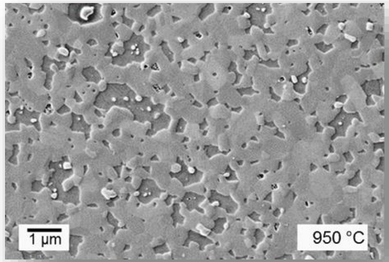
milling

milled powder

spark plasma
sintering (SPS)

sintering under
pressure

characterization



microstructure of ceramic

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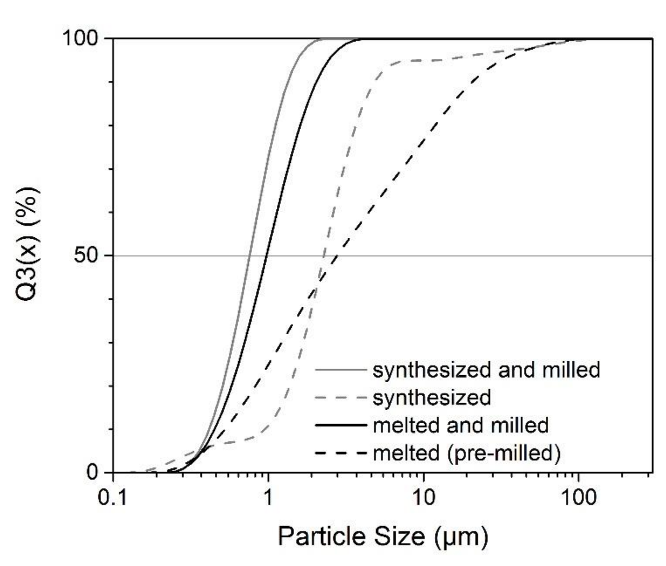
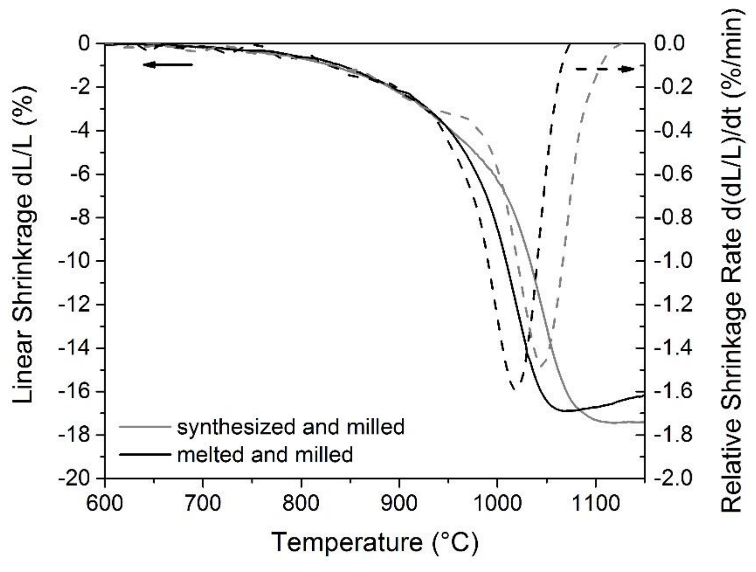
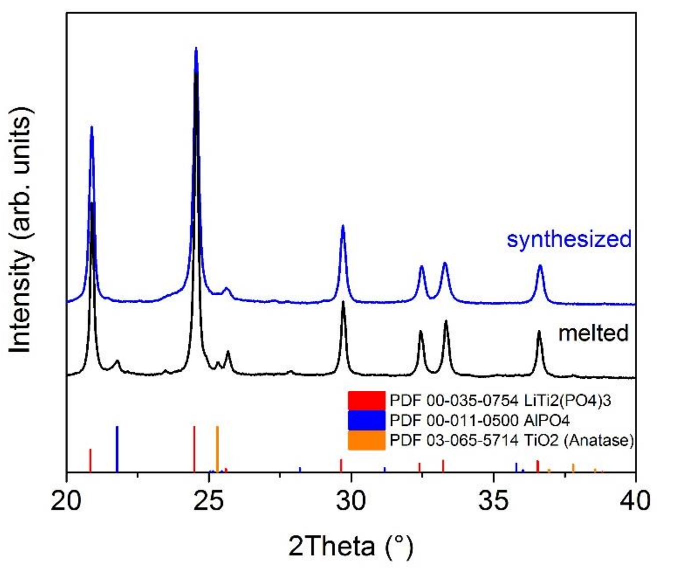
Material Development

Characterization of LATP Powder







Particle size distribution

- comparable particle size of both powders after intense milling

Sintering shrinkage

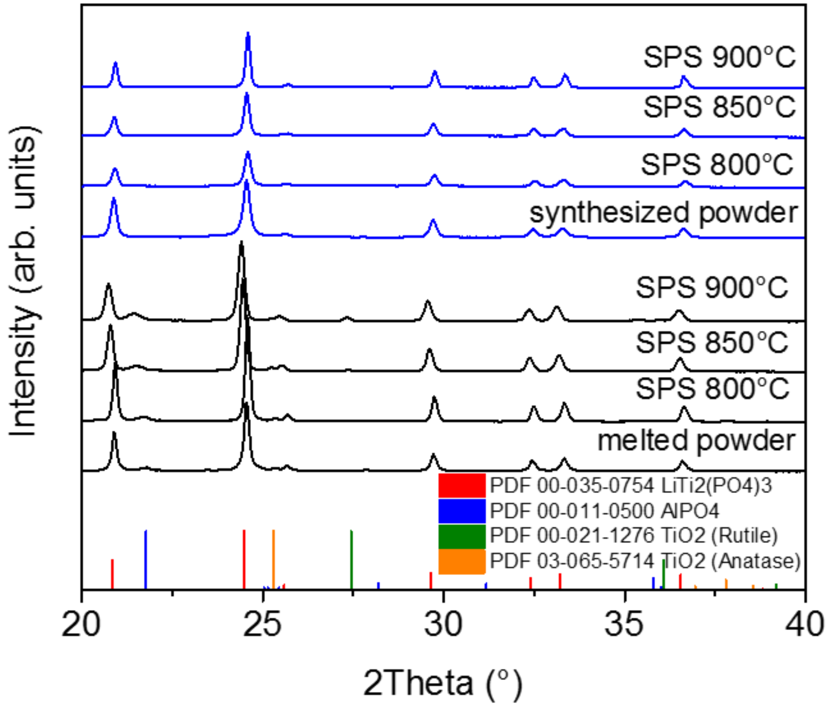
- comparable sintering shrinkage of both powders

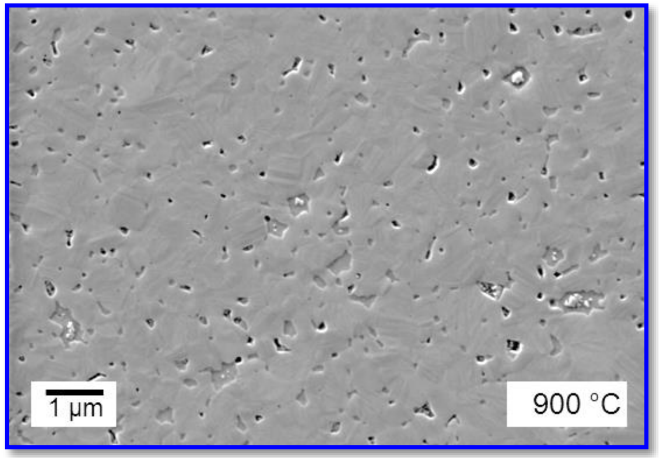
Phase analysis

- phase purity of synthesized powder
- secondary phases after melting and quenching

Material Development

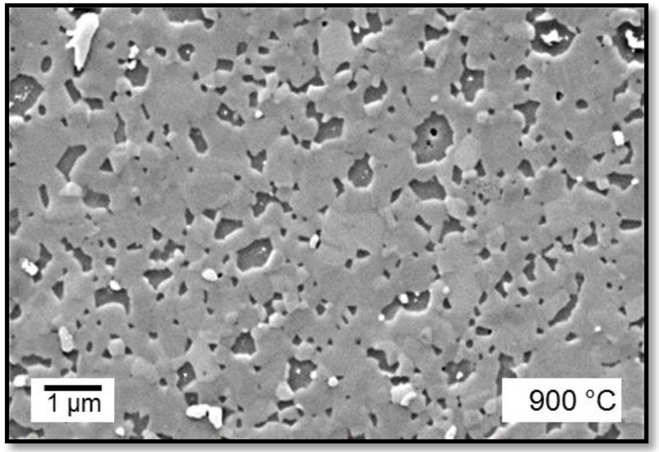
Characterization of LATP Ceramic





Ceramic made of **synthesized and milled powder**:

- fine grains
- less porosity
- reduced content of secondary phases



Ceramic made of **melted, quenched and milled powder**:

- fine grains
- less porosity
- high content of secondary phases

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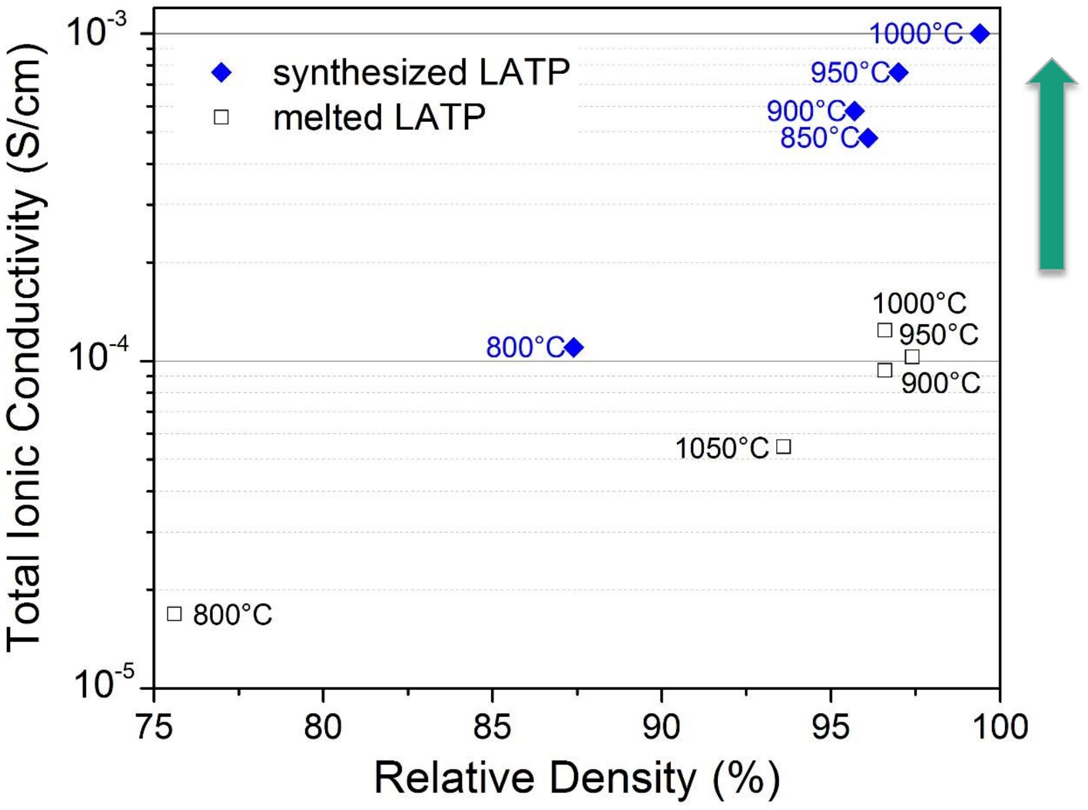
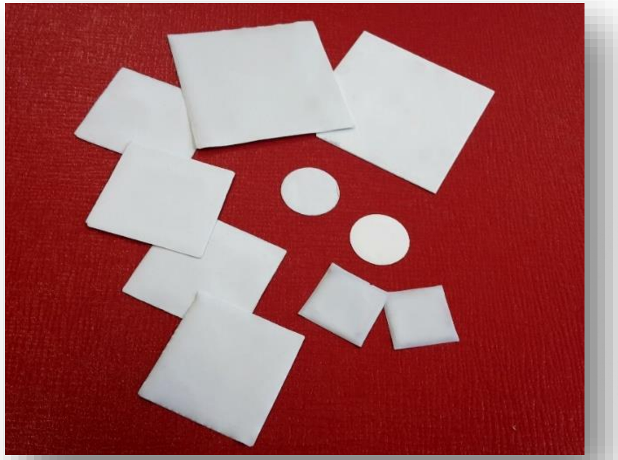
Material Development

Characterization of LATP Ceramic



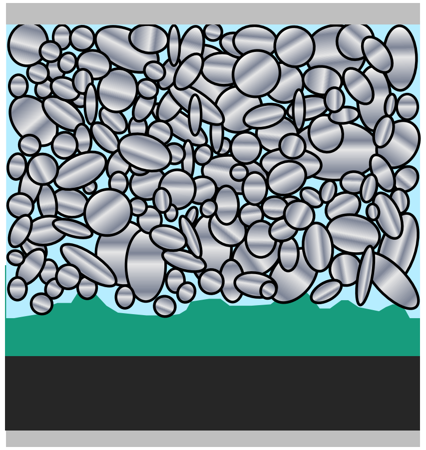
Material Development



Li conductive tapes made of LATP ceramic

Highest total ionic conductivity of ceramic made of synthesized and milled LATP powder $1 \cdot 10^{-3}$ S/cm

All-Solid-State Battery
Principal Concept



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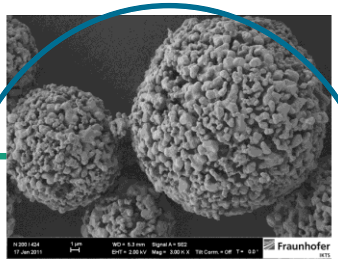

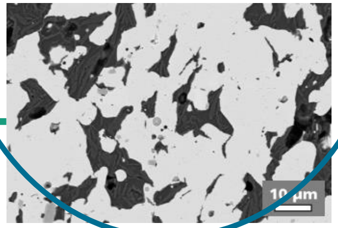

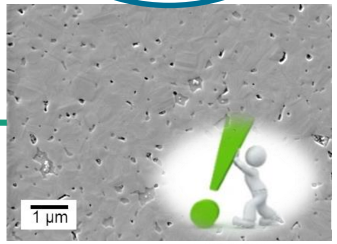

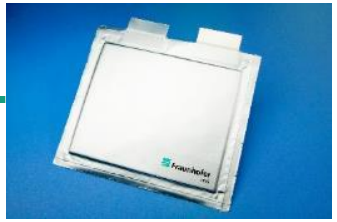

Material Development

Process technology

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Material Development

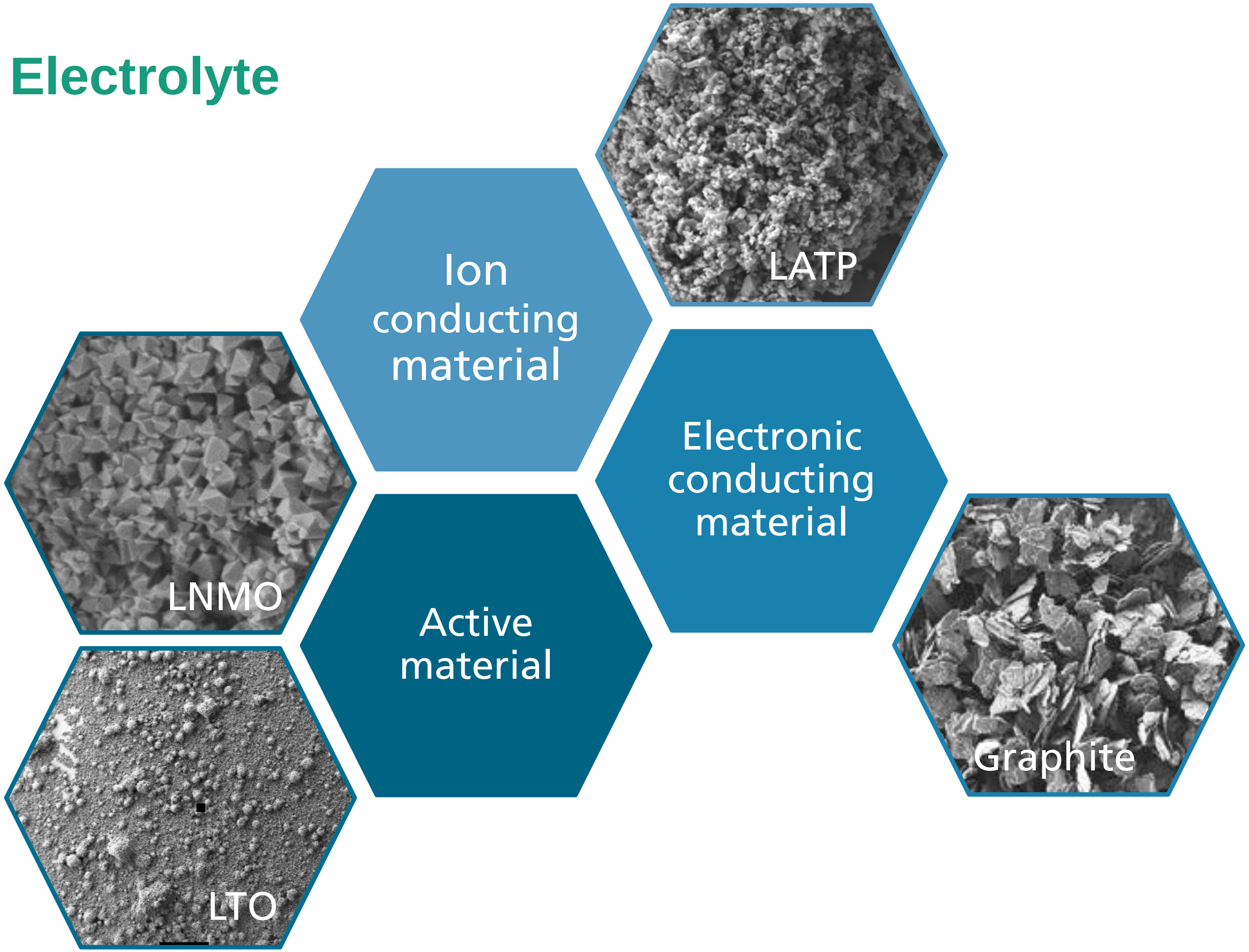
Active Materials and Solid Electrolyte

Co-Sintering:

Active Material + Electrolyte

→ Composite Cathode

→ Composite Anode



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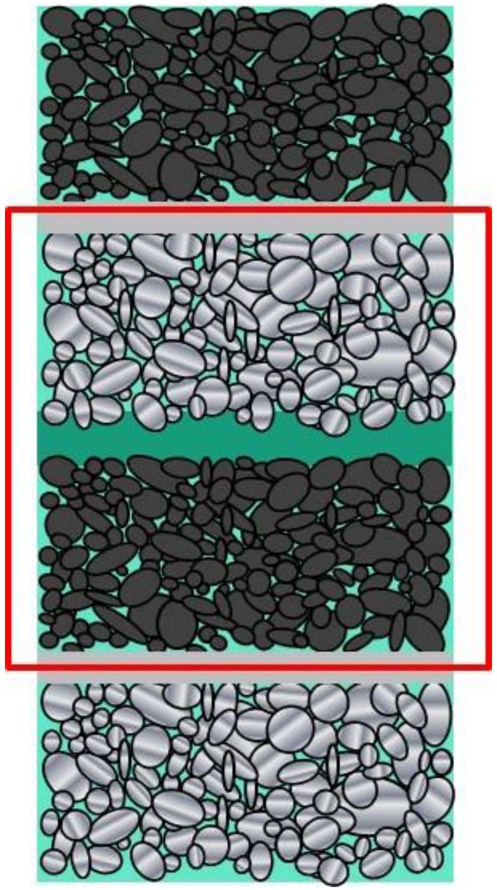
Cell concept based on LATP electrolyte

Kathode	Anode	[V]	electrolyte	[Wh/l]	[Wh/kg]	
LNMO	LTO	3.2	liquid	479	180	
LNMO	LTO	3.2	LATP	702	199	8 % LATP
LNMO	LTO	3.2	LATP	588	174	20 % LATP
LNMO	Lithium	4.7	LATP	1094	411	8 % LATP
LNMO	Lithium	4.7	LATP	926	348	20 % LATP



- Cathode: 2.9 mAh/cm², 90% LNMO, 8 % LATP, 2% graphite; //
  77% LNMO, 20 % LATP, 3% graphite
- Anode: 2.9 mAh/cm², 90% LTO, 8 % LATP, 2% graphite//
  77% LTO, 20 % LATP, 3% graphite
- LATP electrolyte: 5 µm thickness

- **Significant influence of ion conducting phase on specific energy density**
  → object of process development

Fraunhofer IKTS

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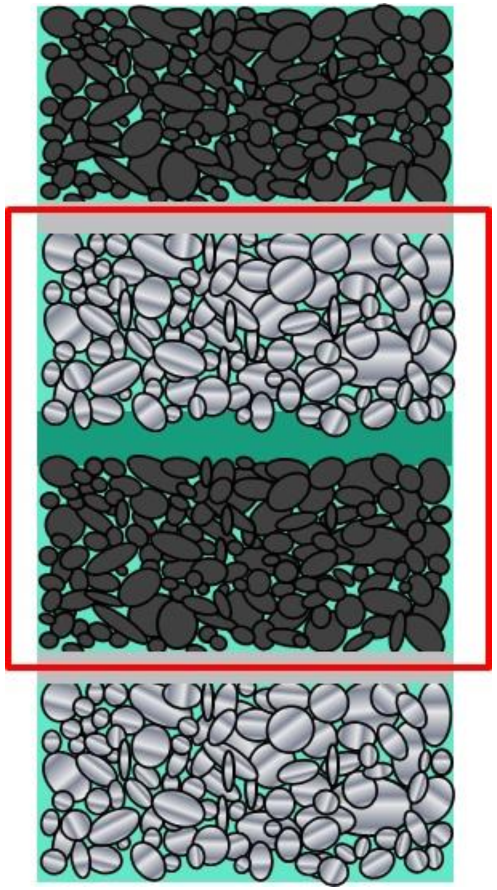

Lithium Anode	Composite Anode made of LTO / LATP
+ higher potential difference (4.7 V) + increased energy density per volume / weight	+ processing with conventional technologies + no safety risk + no dendrite growth + high rate capability
- Processing under inert atmosphere - higher safety risk - dendrite growth	- lower potential difference (3.2 V) - moderate energy density per volume / weight

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Material Development – Composite Cathode

Powder synthesis of cathode material $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)

- Investigation of synthesis parameters for material properties adapted to solid state battery application

- Scale up spray drying process, granulate particles

Precursor composition	→ nucleation, morphology
Pre-Calcination (T, t)	→ homogeneity
Calcination (T, t)	→ phase, crystallite size

parameters for LNMO-synthesis

→ acetate-salts

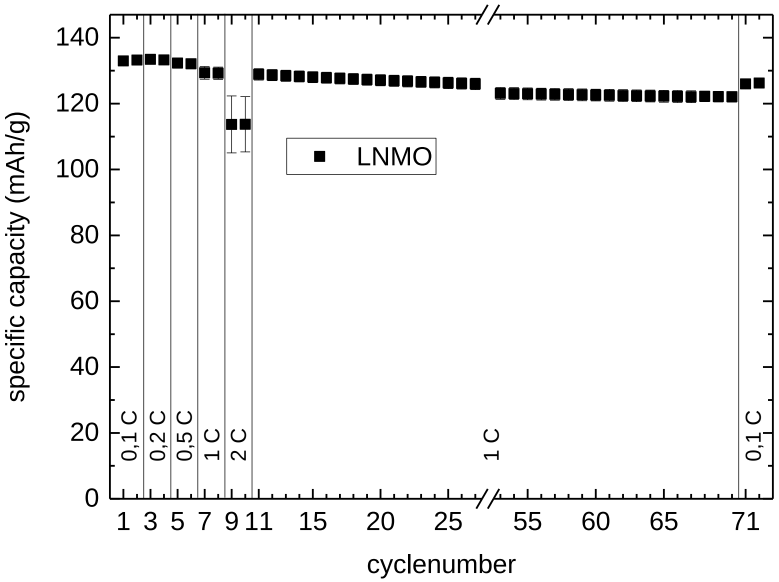
→ 5 h at 800 °C followed by grinding

→ additional 5 h at 800 °C

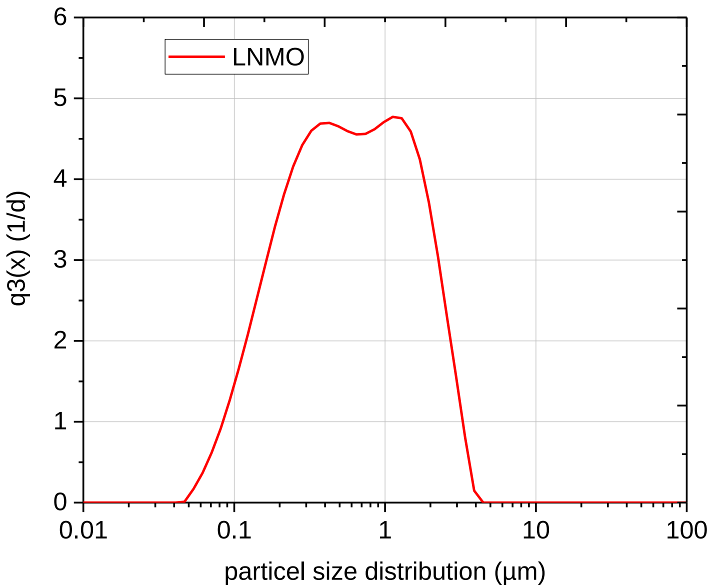
Material Development – Composite Cathode

Powder synthesis of cathode material $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO)

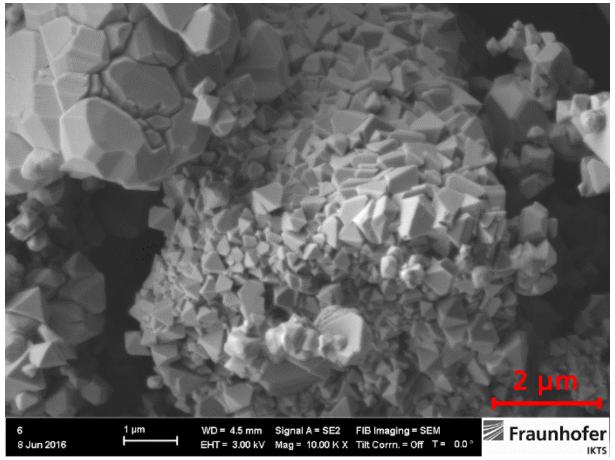
- The as descripted synthesized LNMO shows defined particles - and good electrochemical properties
  - Octahedral crystals, crystal size below 4 µm
  - 133 mAh/g at 0.1 C, 94 % capacity lost over 60 cycles



Performance and aging test of LNMO



particle size distribution of LNMO



FESEM of LNMO

electrode foil production: al-foil, 80% LNMO, 10% PVDF, 10% graphite

coin cell production: vs lithium, 1M $LiPF_6$ in EC:DEC (1:1), whatman separator

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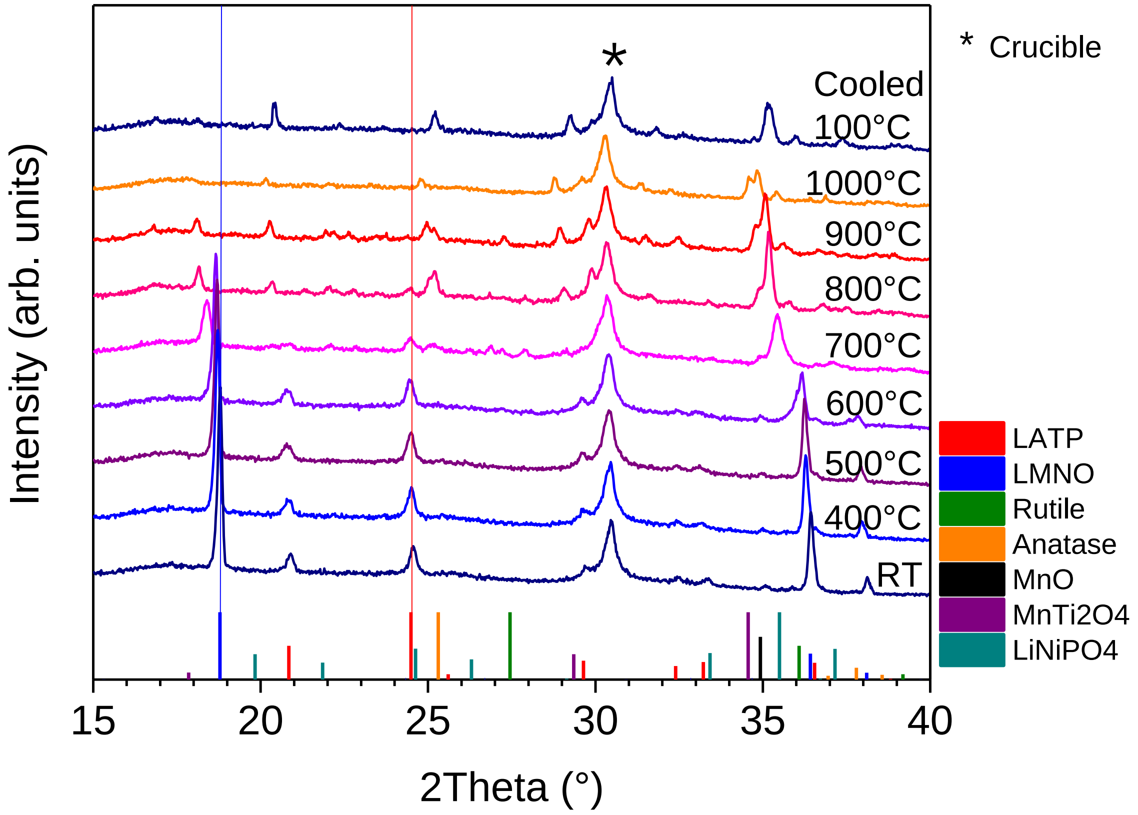
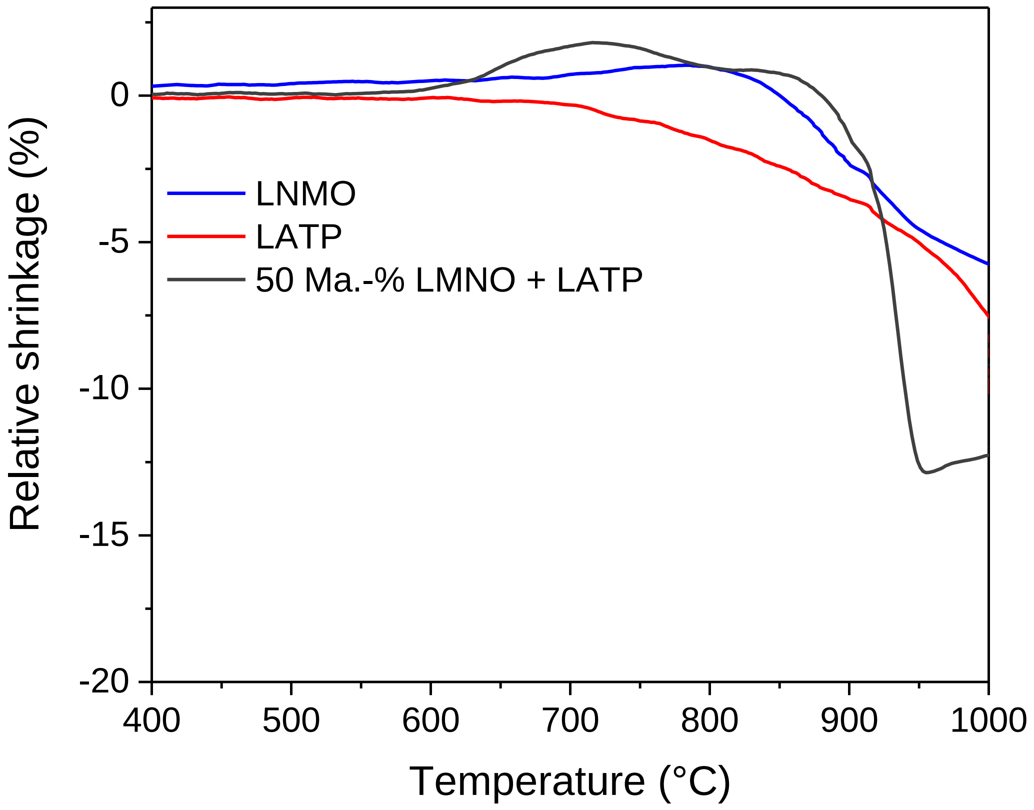
Material Development – Composite Cathode

Co-Sintering of LMNO and LATP (50 wt%)





Transformation of Phases

- Decomposition of LATP and LMNO (600 - 700 °C)
- Formation of MnO, MnO_2 and $LiNiPO_4$ (> 600 °C)
- Completed reaction between LATP and LMNO at 800 °C

Increased shrinkage > 900 °C by reaction of both components

Sintering temperature of LATP have to be reduced!

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Material Development

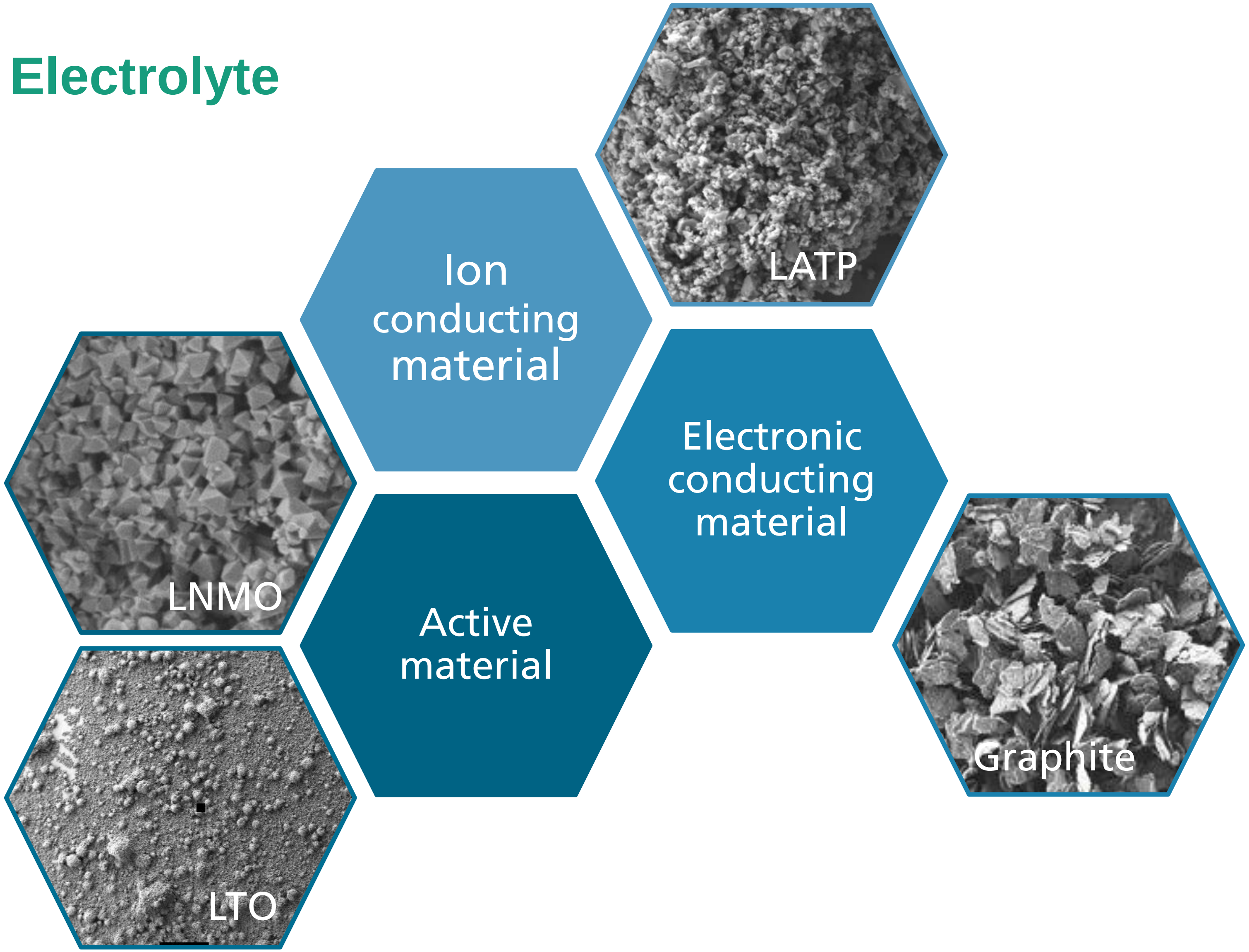
Active Materials and Solid Electrolyte

Co-Sintering:

Active Material + Electrolyte

→ Composite Cathode

→ Composite Anode



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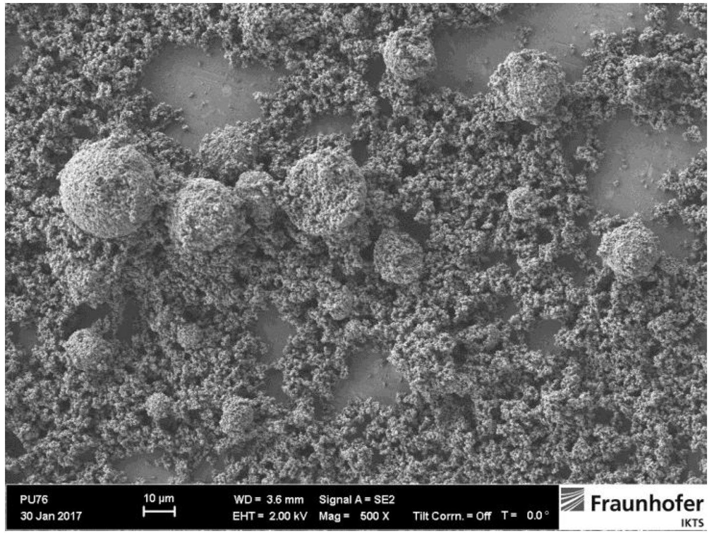
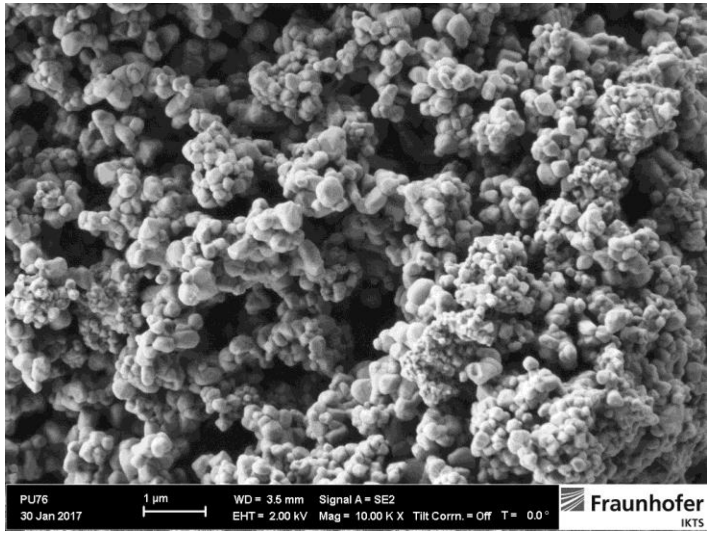
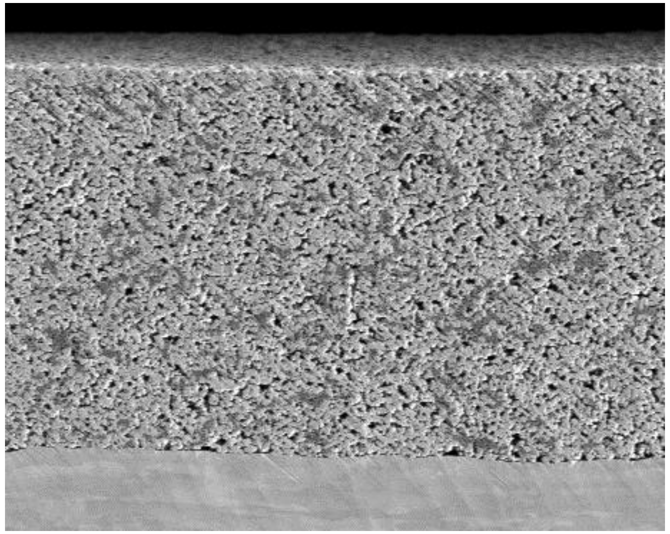
Material Development – Composite Anode

Commercial $Li_4Ti_5O_{12}$ material

- Commercial powder from Huntsman; Hombitec LTO5
- Measured capacity 169 mAh/g (at 0.1 C) in conventional electrode morphology
- Only slightly sintered agglomerates; primary particles <1µm particle size
  → good characteristics for solid state electrodes







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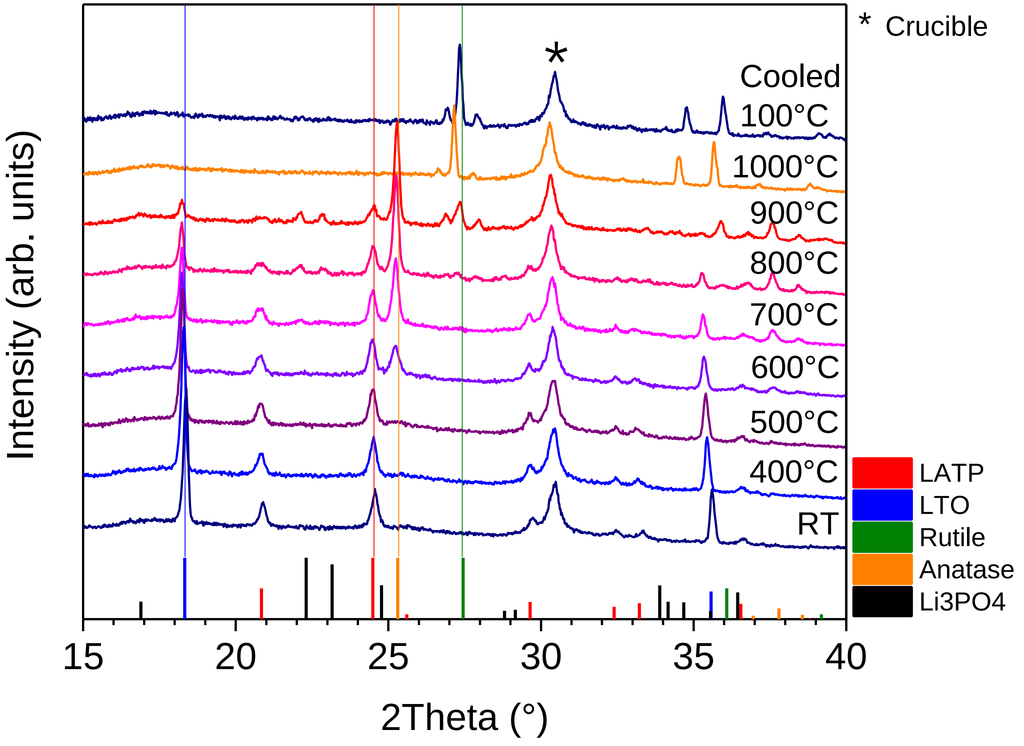
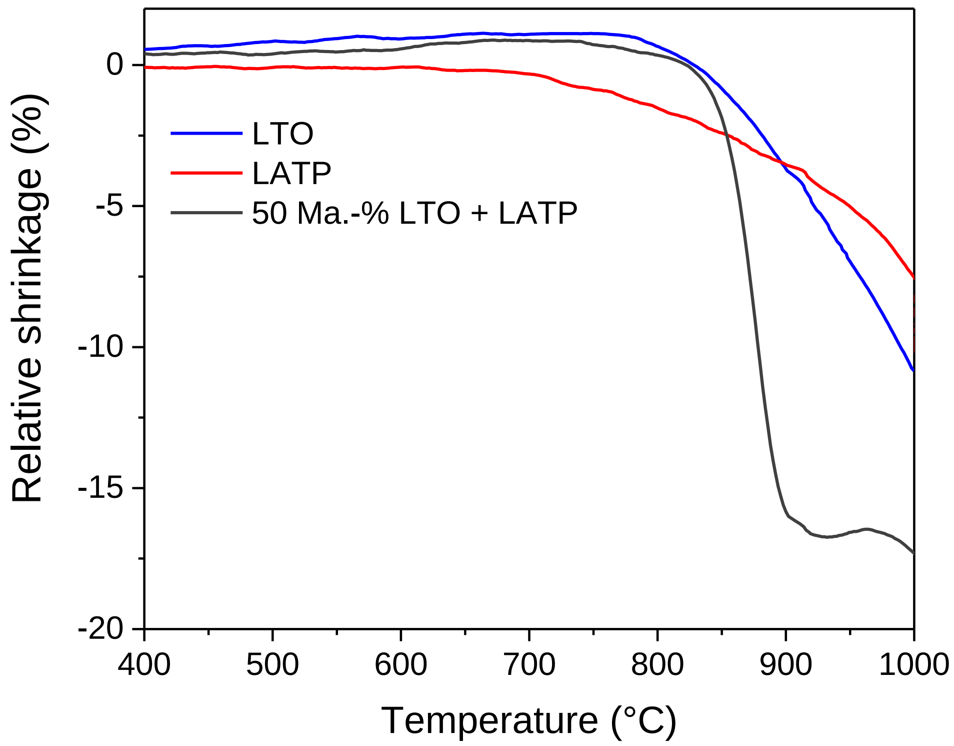
Material Development – Composite Anode

Co-Sintering of LTO and LATP (50 wt%)





Increased shrinkage > 820 °C by reaction of both components

Transformation of Phases

- Formation of Anatase (> 500 °C)
- Transformation of Anatase → Rutile (> 800 °C)
- Formation of Li_3PO_4 (> 600 °C)
- Completed reaction between LATP and LTO at 1000 °C

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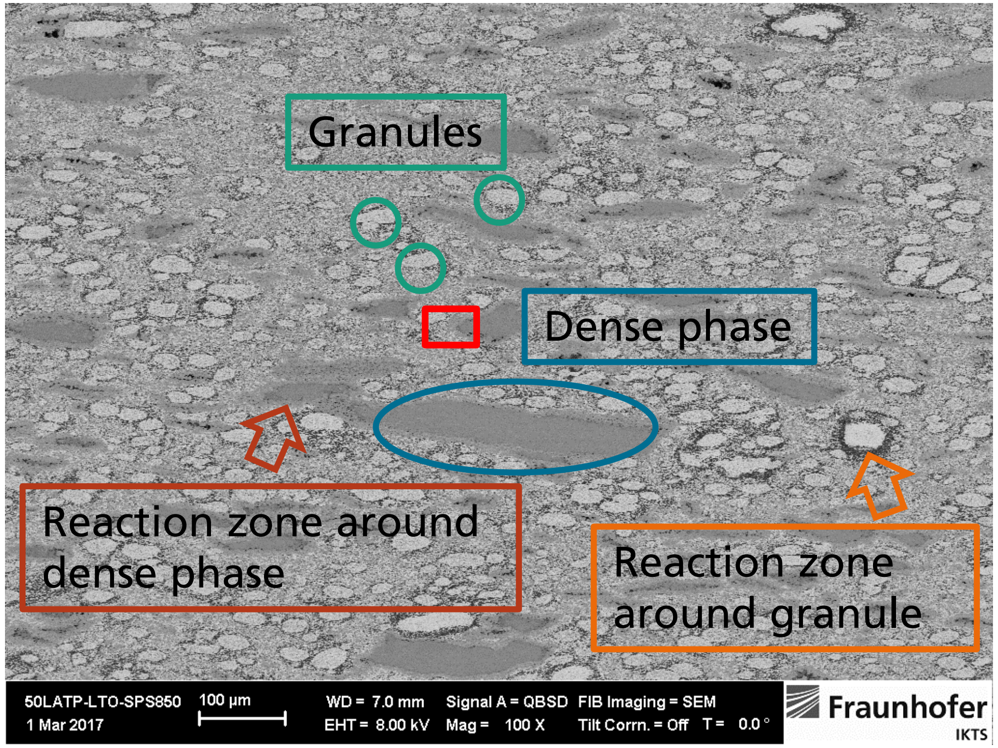
Material Development – Composite Anode

Co-Sintering of LTO and LATP (50 wt%)

	Sintering	Density g/cm³	Conductivity S/cm
LATP	SPS 850°C	2.82 (97%)	$5 * 10^{-4}$
LATP+LTO	SPS 850 °C	3.23 (~100%)	not measurable

Theoretical Densities
LATP: 2.92 g/cm³
LTO: 3.48 g/cm³
50 wt% LATP and 50 wt% LTO: 3.20 g/cm³

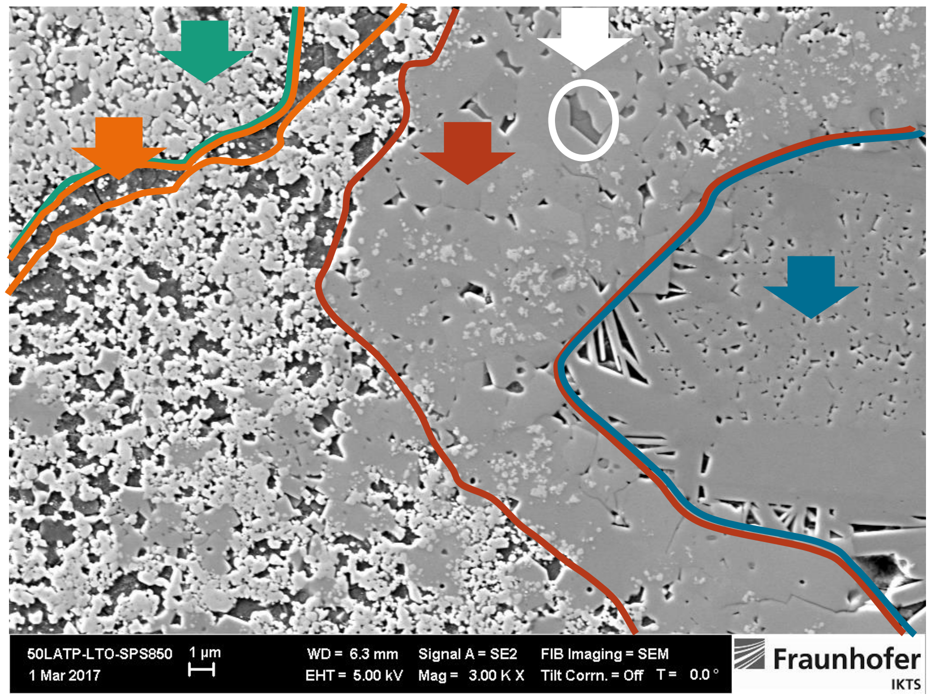


Microstructure of Spark Plasma Sintered LTO and LATP mixture (850 °C)

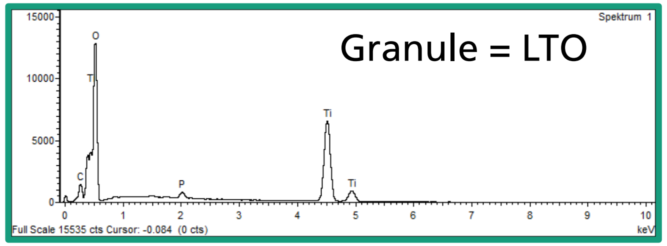
→ No continuous pathways of Li conductive LATP electrolyte through microstructure

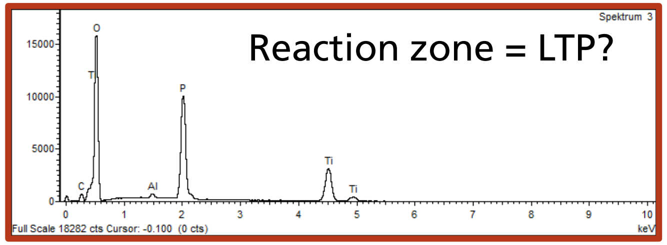
Mixture of anode material and solid electrolyte

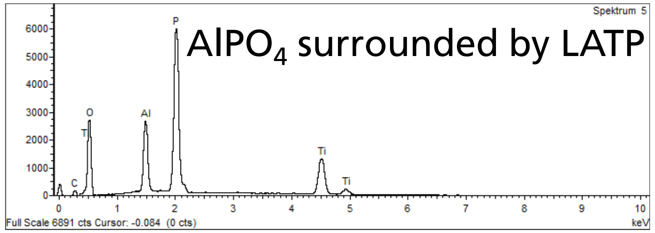
LTO and LATP (50 wt%)

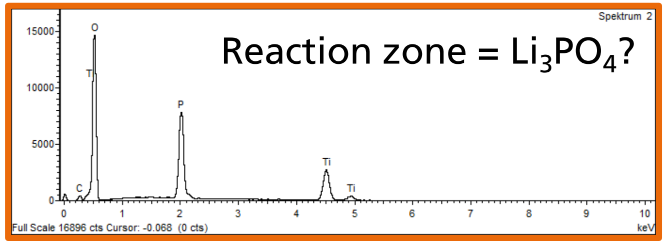


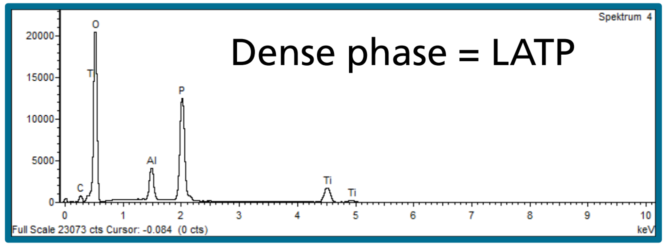
Microstructure of Spark Plasma Sintered LTO and LATP mixture (850 °C)











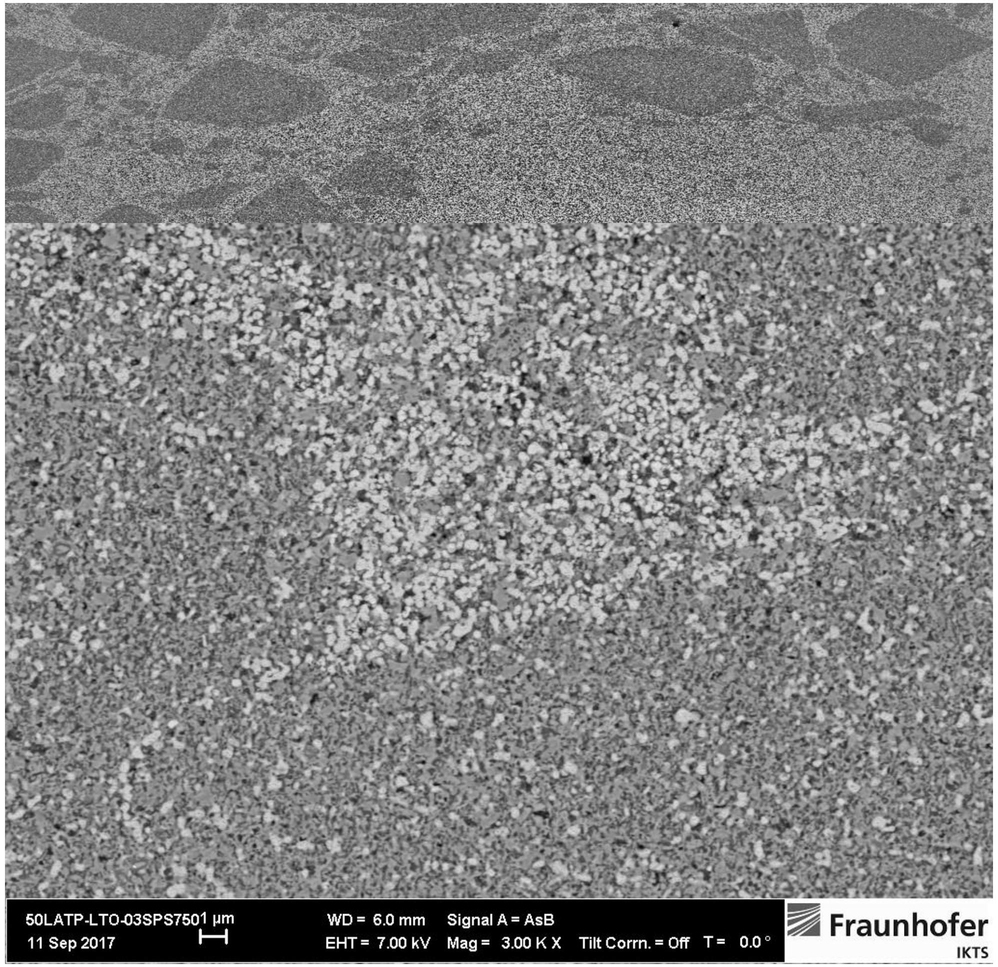
Consequences

- Optimized dispersion of particles → Homogeneous mixing of both components

Material Development – Composite Anode

Co-Sintering of LTO and LATP (50 wt%)

	Sintering	Density g/cm³	Conductivity S/cm
low intensive mixing			
LATP	SPS 850°C	2.82 (97%)	$5 * 10^{-4}$
LATP+LTO	SPS 850 °C	3.23 (~100%)	not measurable
high intensive mixing			
LATP+LTO	SPS 850°C	3.01 (81.1%)	not measurable
LATP+LTO	SPS 750°C	2.23 (69.6%)	$9 * 10^{-7}$



Microstructure of LTO and LATP mixture (SPS 750 °C)

Theoretical Densities
LATP: 2.92 g/cm³
LTO: 3.48 g/cm³
50 wt% LATP and 50 wt% LTO: 3.20 g/cm³

→ Pathway of Li conductive LATP electrolyte through microstructure
→ Inhomogeneous microstructure

Materials Development
Conclusion

- Temperatures for co-sintering should be:
  Anode < 500 ° C; Cathode < 600 ° C
- Next Steps:
  - Investigation of graphite stability in binary and ternary mixtures of electrode materials
  - Investigation of mixing parameters for optimum dispersion of the particles (percolating network of LATP and graphite)
  - Investigation of approaches to liquid phase sintering → reduction of sintering temperatures
  - Optimization of densification of the electrode microstructure (minimum porosity)

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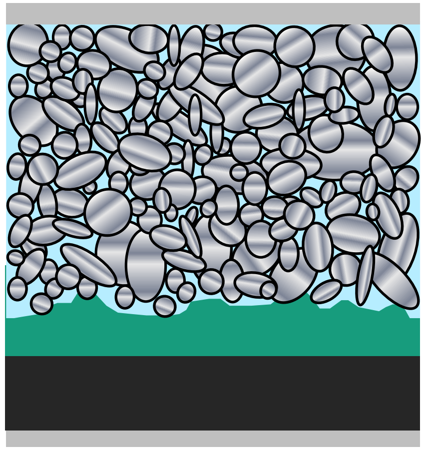
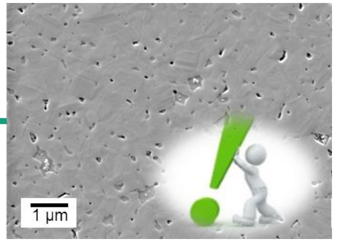
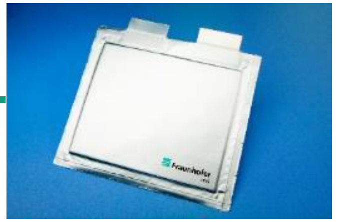
All-Solid-State Battery
Principal Concept



contacts	aluminum
composite cathode	high energy cathode materials (NCM, LNMO) electronic conducting phase: graphite ionic conducting electrolyte phase
all solid state electrolyte	particle filled polymer, ceramic all solid state
anode	lithium metal, composite anode
contacts	nickel





Material Development

Process technology

Conclusion and Outlook

- Process technology
  - Usage of conventional ceramic technologies (tape casting, screen printing, …) → Compatibility of organic and inorganic materials ?
  - Continuous fabrication possible → Co-sintering of active materials and electrolyte ?
  - Contacting with Lithium metal (anode) or other metals as current collectors ?

- Material development
  - Different Li-conductive electrolyte are known
  - Sintering of ceramic electrolyte at high temperatures (800 – 1000 °C)
  - Reaction of active materials and electrolyte during co-sintering → Reduction of sintering temperatures (< 800 °C)

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Thank you for your attention!

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