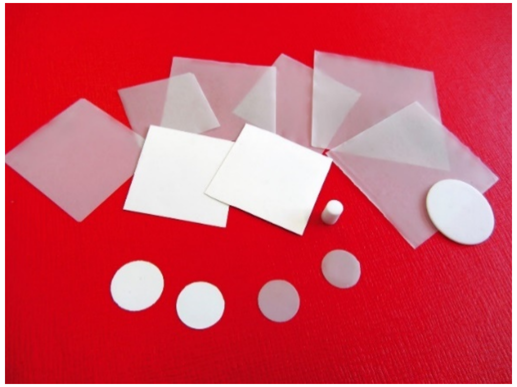
PROGRESS IN CERAMIC SOLID STATE BATTERIES

DRESDEN BATTERY DAYS 2019

Kristian Nikolowski, Mareike Wolter, Juliane Hüttl, Katja Wätzig, Marco Fritsch, Jochen Schilm, Stefan Barth, Michael Arnold, Arno Görne



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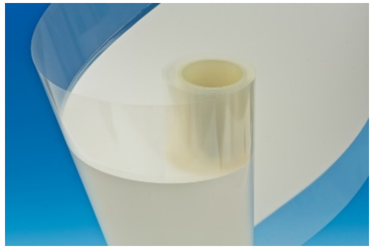
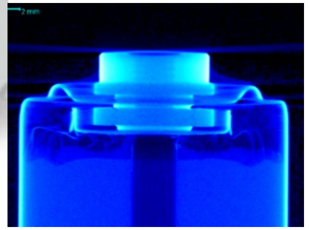
ARTEMYS

FEST BATT Cluster of Competence for Solid-state Batteries



Sites of IKTS working together in the field of ASSB

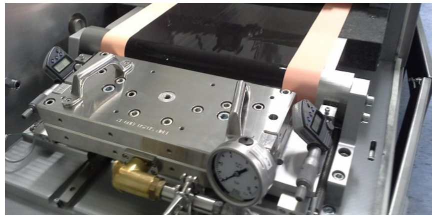


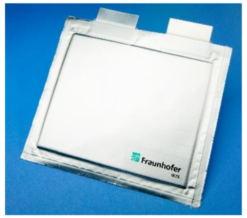
IKTS-HD
Technology Center ‚Tape Casting'
Roll-to-roll technology development

Application Center ‚Battery Technology'
Production Development
Cooperation with thyssenkrupp
System Engineering

Headquarter IKTS-DD
Li-Ion Battery Material Development &
Battery Testing
Material Diagnostics

Mobile Energy Storage Systems and Electrochemistry




Solid state electrolytes

properties

Organic electrolytes		Inorganic electrolytes		
semi-solid	**polymer**	**sulfides**	**oxides**	**phosphates**
Gel-polymer electrolytes Solid-like dispersions of nanoparticles	PEO …	$Li_{10}GeP_2S_{12}$, $Li_2S\text{-}P_2S_5$ …	Garnet($Li_7La_3Zr_2O_{12}$) Perovskite …	LATP ($Li_{1+x}Al_xTi_{2-x}(PO_4)_3$) LAGP ($Li_{1+x}Al_xGe_{2-x}(PO_4)_3$) …
	✓ flexible → compensation of volume changes ✓ stable with Li metal (?) ? low ion conductivity at RT ? limited rate capability ? limited oxidation stability at high cathode potentials (> 4 V) ? transference number	✓ high ion conductivity at RT ✓ ductile → easy to densify ? moisture sensitive ? low thermodynamic stability → reduction at low potentials → oxidation at medium potentials	✓ high ion conductivity at RT ✓ high chemical and electrochemical stability ✓ safety ? brittle ? sintering of electrolyte(s) ? large scale production	

Solid state electrolytes

properties

Organic electrolytes

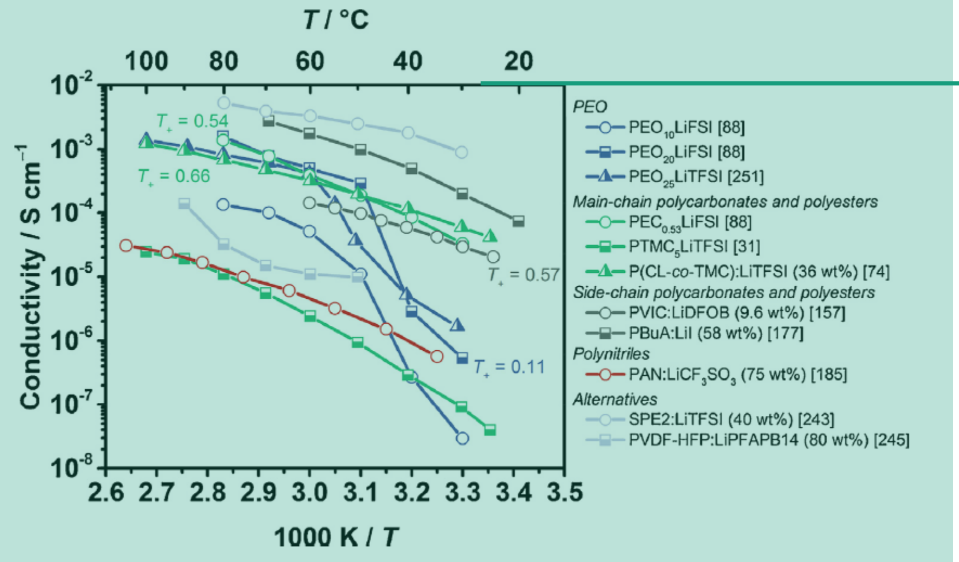
semi-solid

Gel-polymer electrolytes

Solid-like dispersions of nanoparticles

polymer

PEO



J. Mindemark, M.J. Lacey, T. Bowden, D. Brandell, Beyond PEO—Alternative host materials for Li + -conducting solid polymer electrolytes, Progress in Polymer Science 81 (2018) 114–143.

Inorganic electrolytes

sulfides

$Li_{10}GeP_2S_{12}$, Li_2S-P_2S_5

oxides

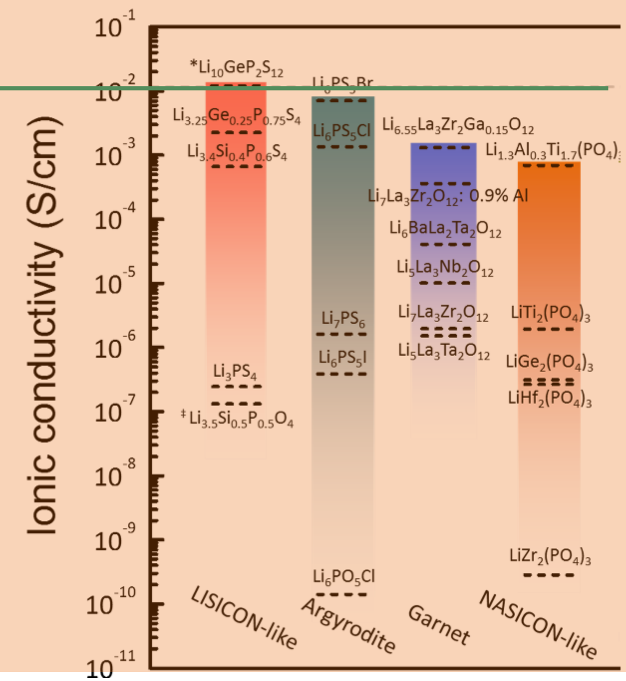
Garnet ($Li_7La_3Zr_2O_{12}$)

Perovskite

phosphates

LATP ($Li_{1+x}Al_xTi_{2-x}(PO_4)_3$)

LAGP ($Li_{1+x}Al_xGe_{2-x}(PO_4)_3$)



J.C. Bachman, S. Muy, A. Grimaud, H.-H. Chang, N. Pour, S.F. Lux, O. Paschos, F. Maglia, S. Lupart, P. Lamp, L. Giordano, Y. Shao-Horn, Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction, Chem. Rev. 116 (2016) 140–162.

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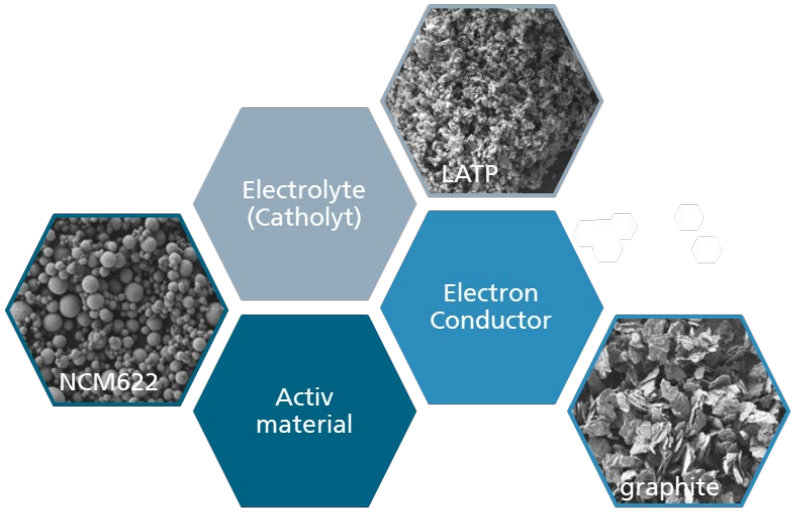
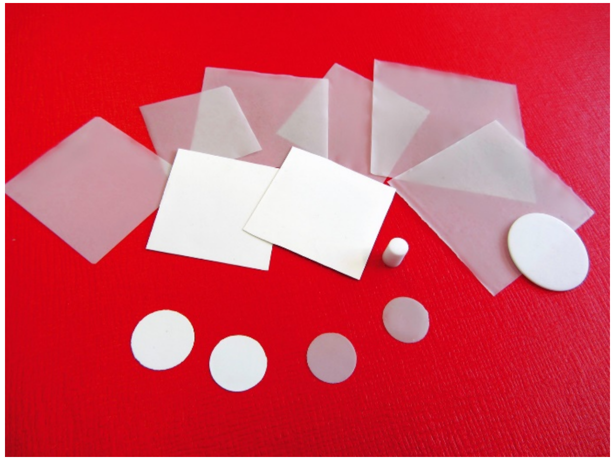
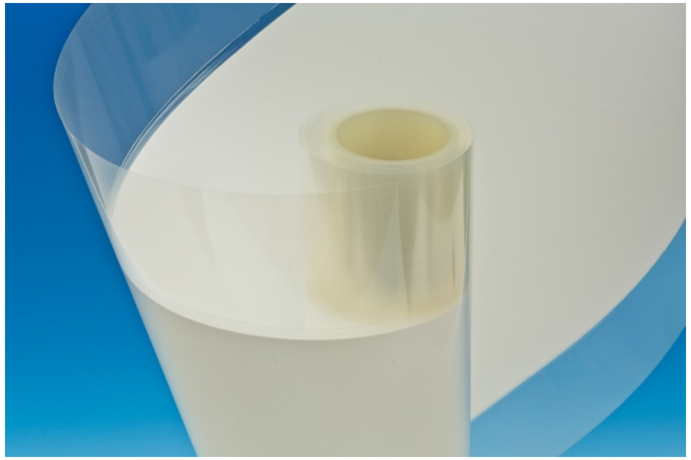
Ceramic Materials for ASSB

Great potential of all ceramic batteries

- High electrochemical and chemical stability of ceramic electrolytes
- High energy density using metallic lithium
- Potentially higher safety compared to other electrolytes







Cell concept for ceramic ASSB

Composite cathode

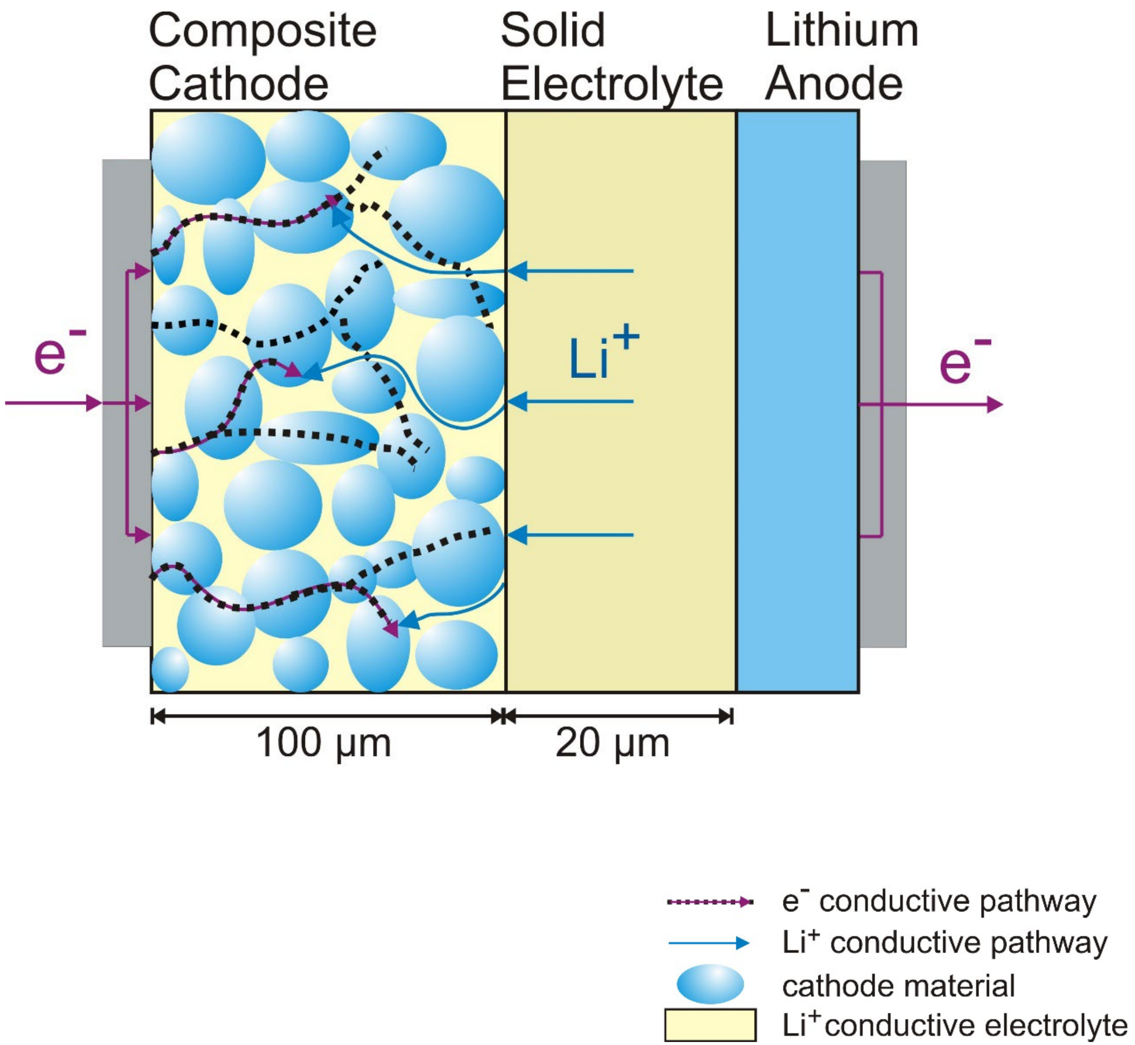
- Active material: NCM622 cathode
- Electrolyte: LATP-type
- Conductive additive: carbon

Electrolyte

- Garnet type LLZO $Li_{6.16}La_3Al_{0.28}Zr_2O_{12}$

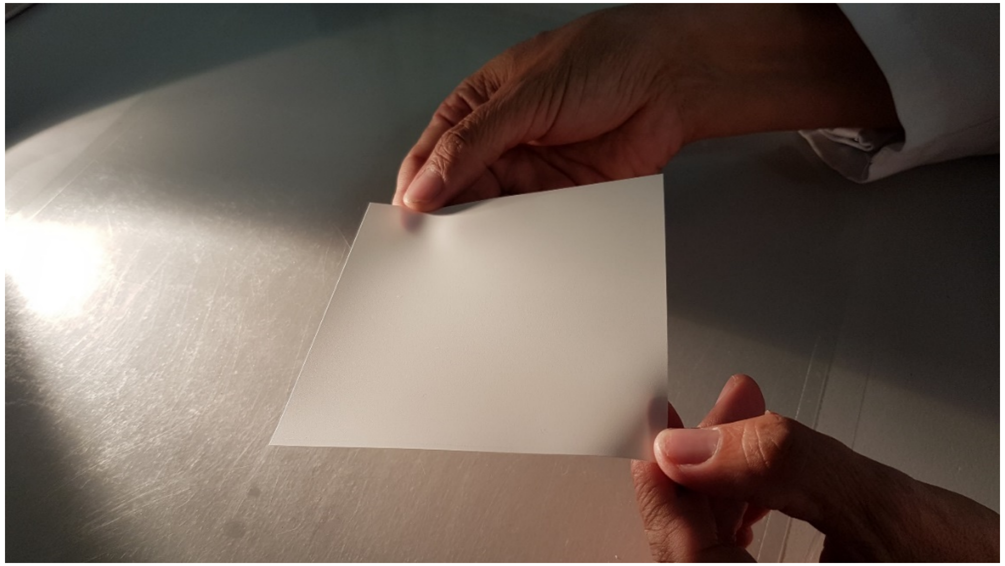
Challenges

- Availability of suitable materials in significant amounts and quality
- Adaption of processing parameters
- Full cells with components made using scalable technologies



Processes for manufacturing of LLZO ceramic electrolytes

- Two types of LLZO materials used in ARTEMYS
  - IKTS: solid state synthesis
  - Glatt: APPTec (Advanced Pulse Powder technology)
- Main tasks in the project:
  - Development of slurry based coating process for LLZO
  - Development of sintering regime for LLZO green tapes
  - Characterization of the electrochemical properties



Tape casted LLZO green tape

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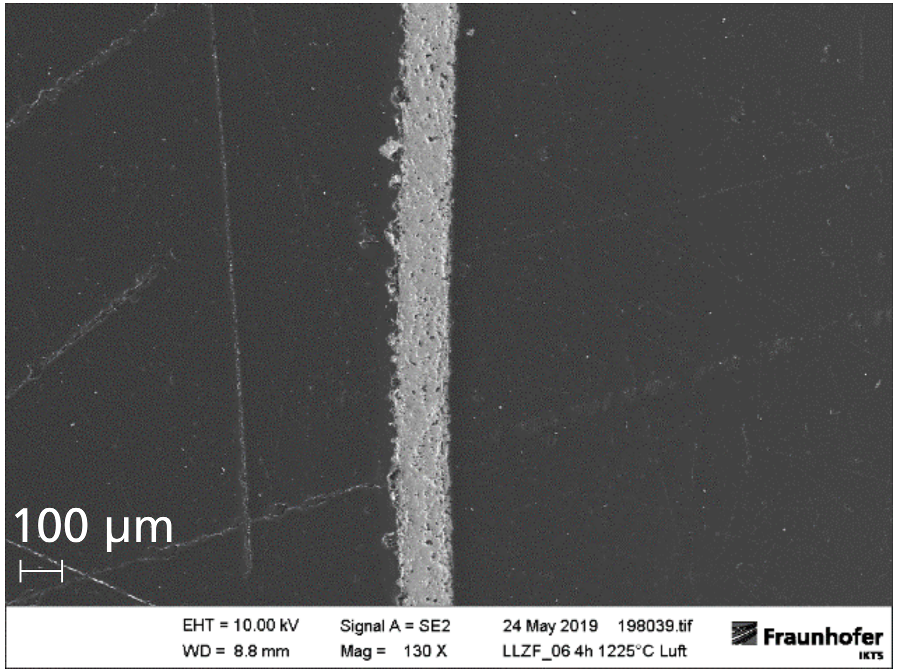

SEM image of the cross section of a sintered 2-fold laminate of LLZO green tapes

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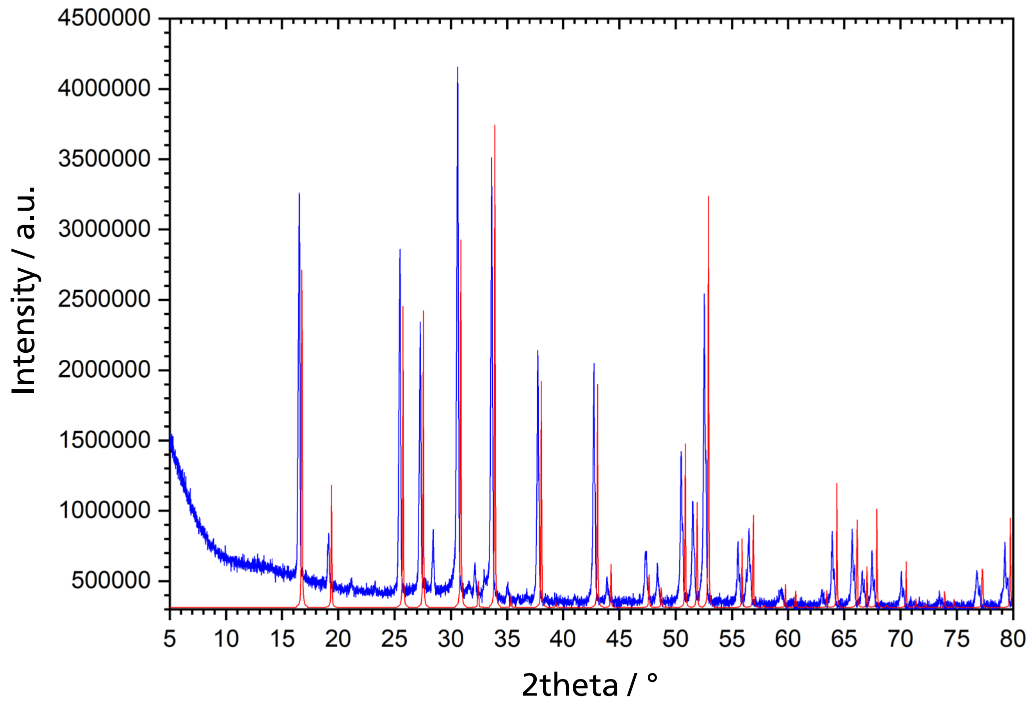
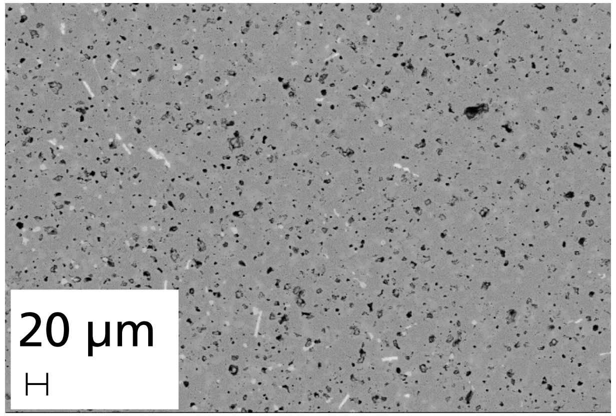


X-ray diffraction pattern of debindered and sintered LLZO green tape

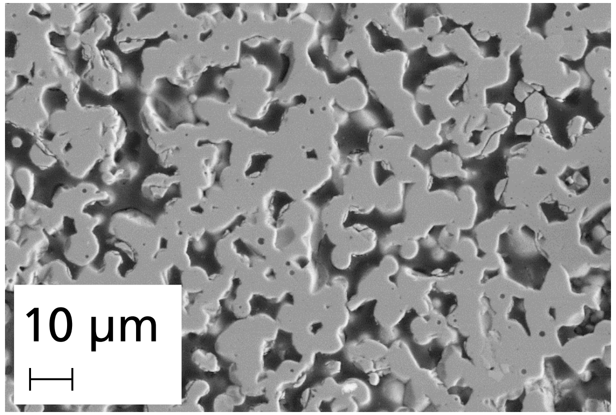
Processes for manufacturing of LLZO ceramic electrolytes

1. Powder optimization with pressed and sintered pellets



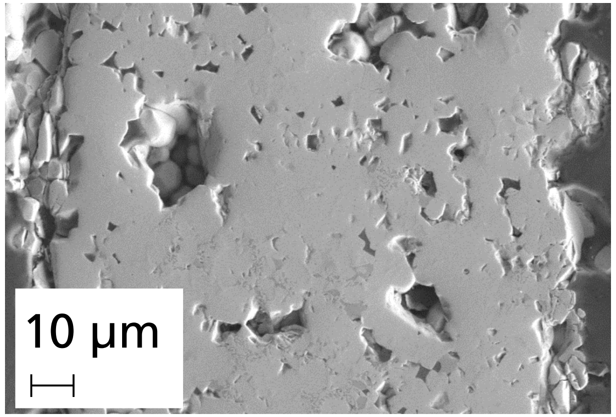
$\sigma_{Ion} = 2 \cdot 10^{-4}$ S/cm

2. Transfer to tape casting manufacturing



$\sigma_{Ion} = 6 \cdot 10^{-7}$ S/cm

3. Recipe and process optimization to obtain homogenous tapes



$\sigma_{Ion} = 3 \cdot 10^{-5}$ S/cm

4. Further parameter optimization

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Electrolyte

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Challenges

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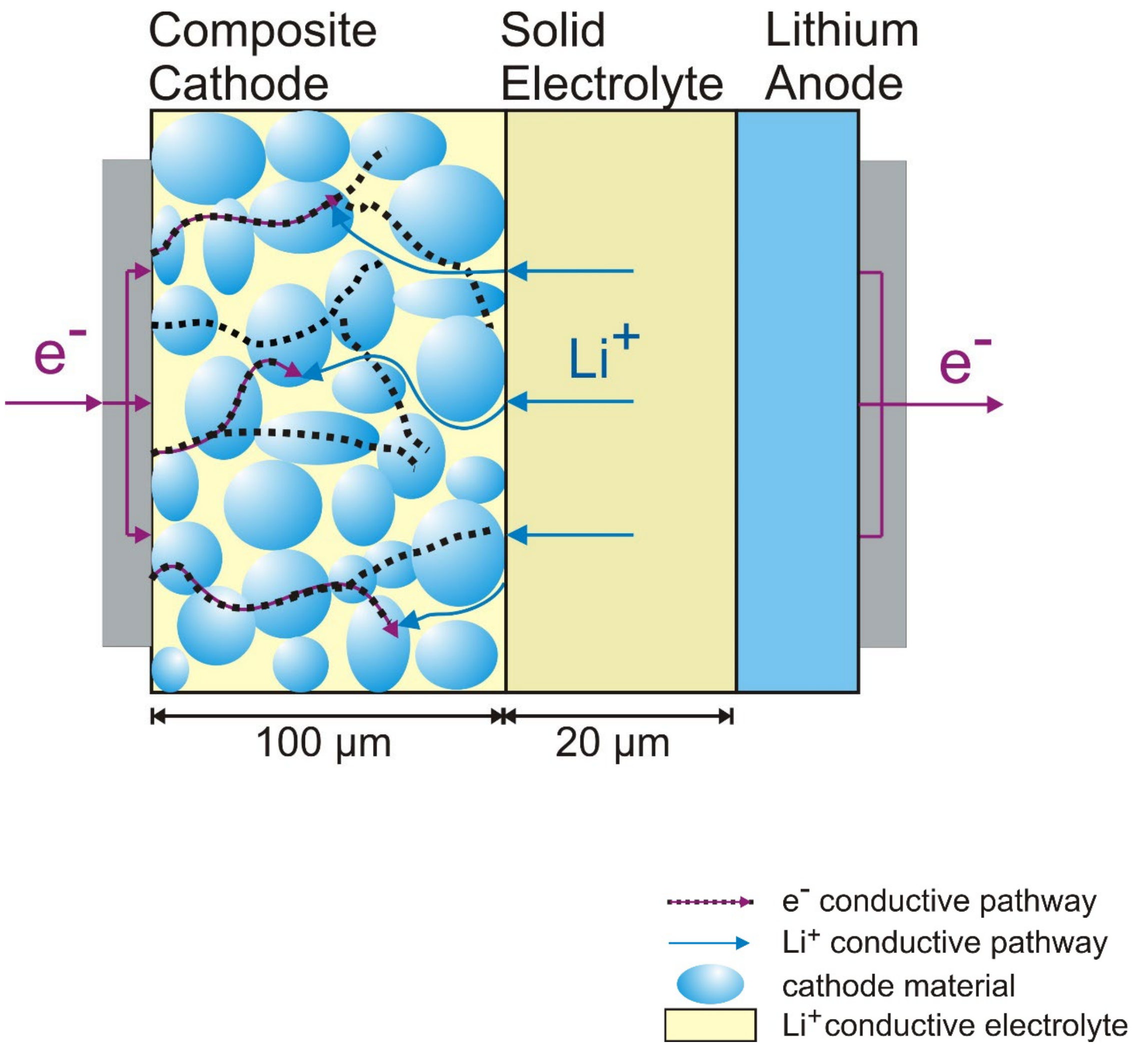
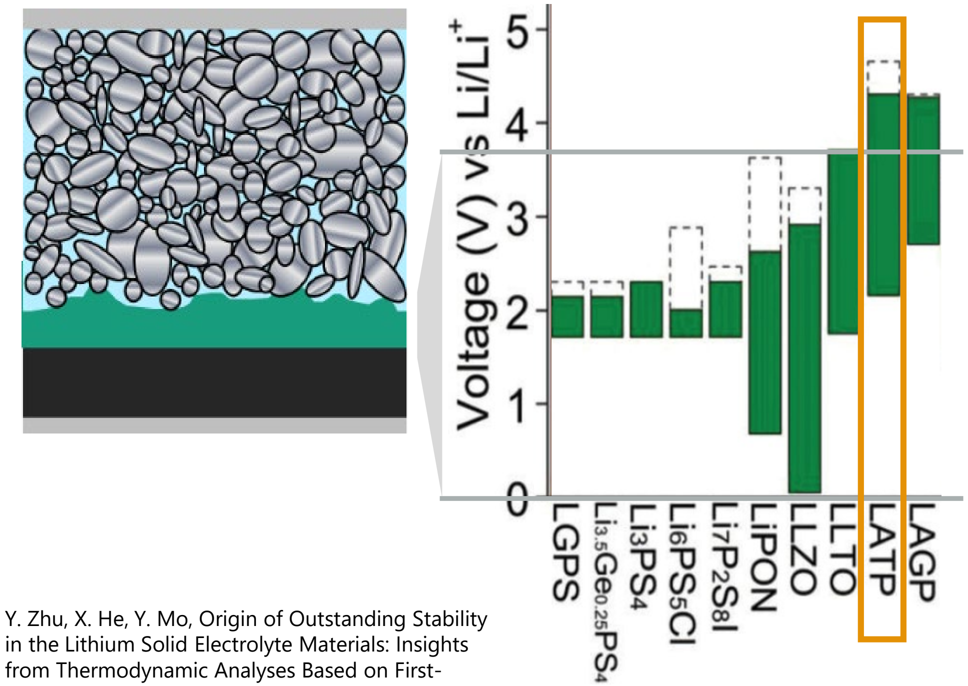
- Adaption of processing parameters
- Full cells with components made using scalable technologies

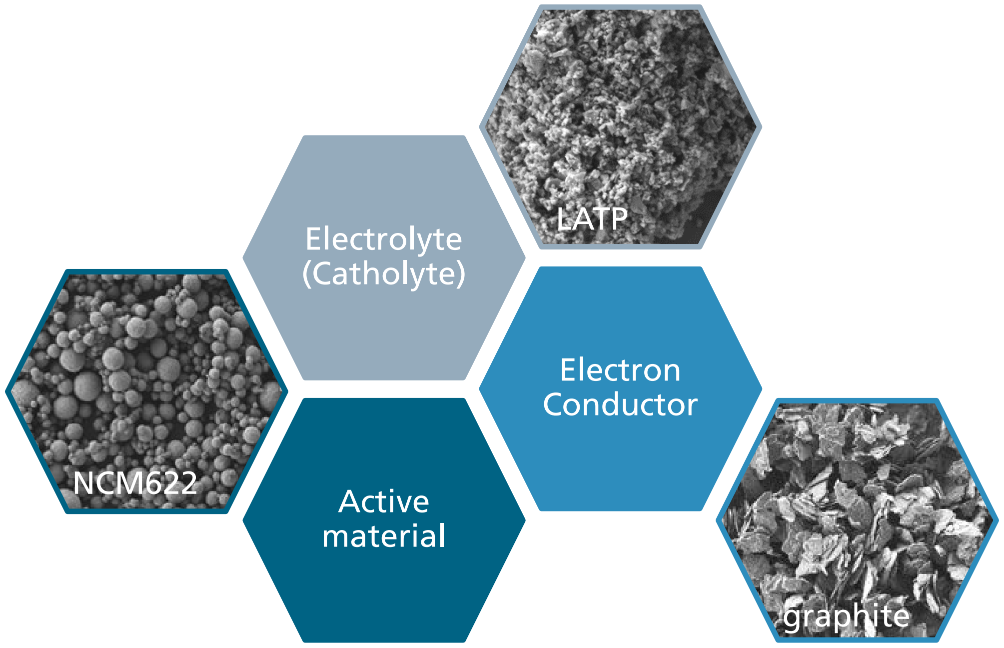


Development of composite cathode with phosphatic solid electrolyte

- Electrochemical stability vs. NCM 622



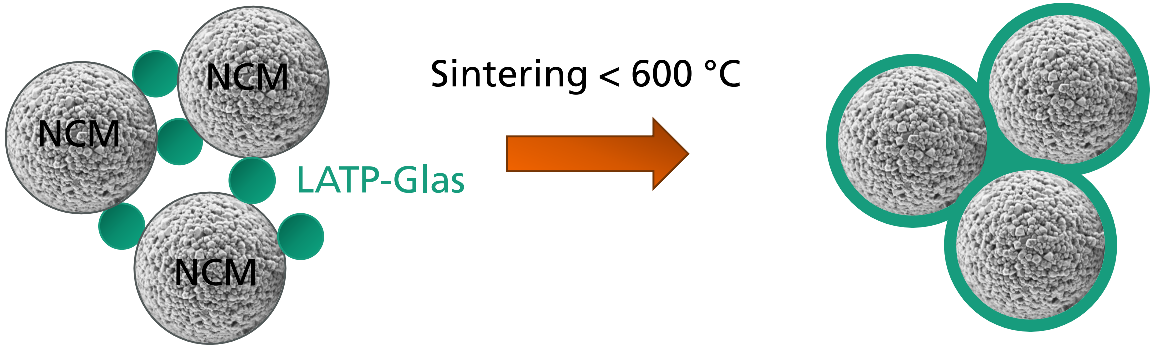
Y. Zhu, X. He, Y. Mo, Origin of Outstanding Stability in the Lithium Solid Electrolyte Materials: Insights from Thermodynamic Analyses Based on First-Principles Calculations, ACS applied materials & interfaces 7 (2015) 23685–23693.c



Development of composite cathode with phosphatic solid electrolyte

- Main task: reduction of the sintering temperature < 600 °C

1. Co-sintering of NCM and LATP-glas



Composite cathode with LATP cathodic electrolyte

2. Reaction sintering of LAP-Glas + TiO_2 → LATP

Composite cathode with LATP cathodic electrolyte

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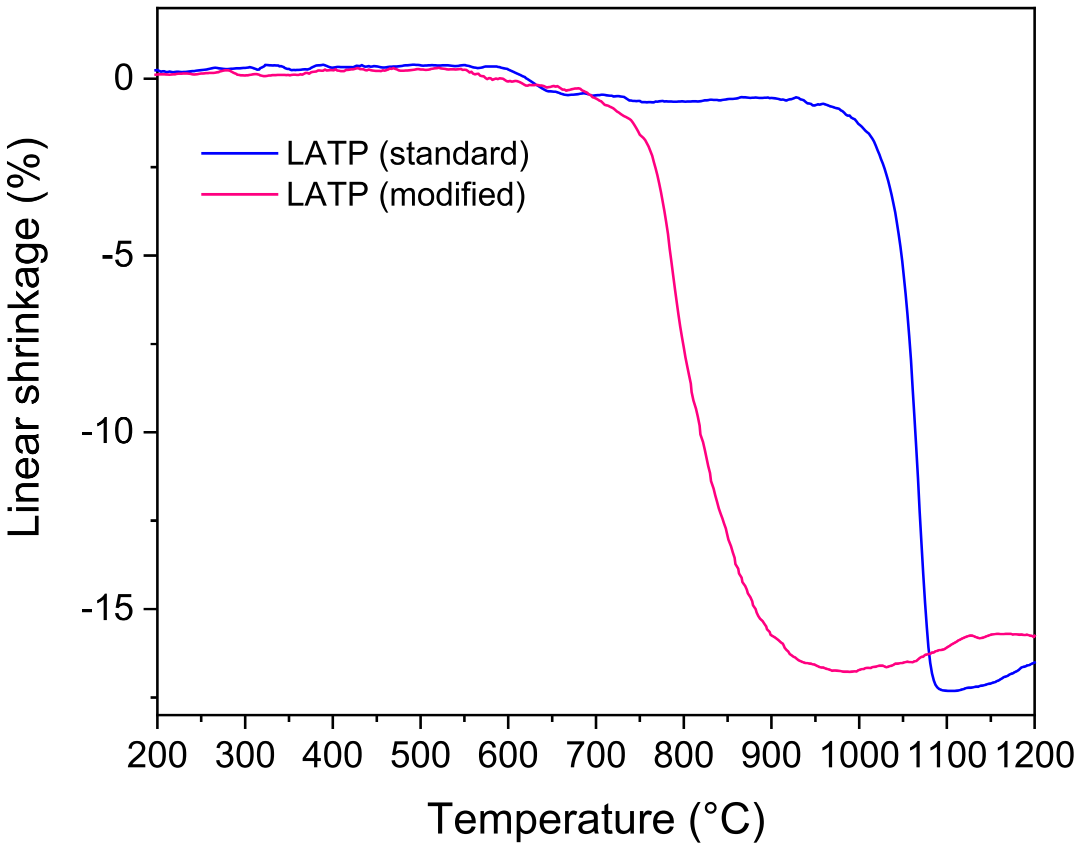
Development of composite cathode with phosphatic solid electrolyte

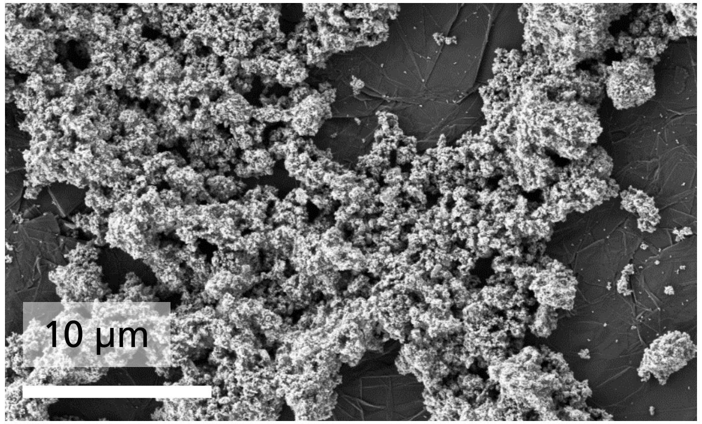


Reduction of crystallization temperatur by modification of LATP

Together with Ferro, Project ARTEMYS

Development of composite cathode with phosphatic solid electrolyte

- Mixture of 50:50 wt.-% LATP and NCM622
- Shrinkage behavior by optical dilatometry
- Dry pressing of cylindrical discs
- Co-sintering at different temperatures in air with 30 min dwell time
- Phase analysis
- Microstructure

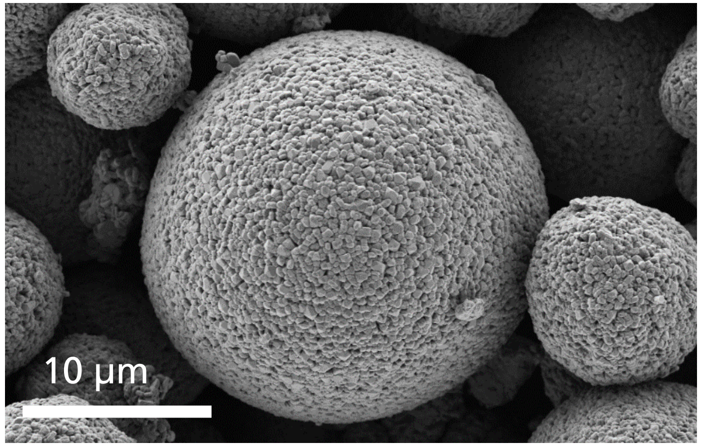


$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$

Li-Ion Conductivity: 10^{-4}-10^{-3} S/cm

NCM 622: $Li_{1+x}(Ni_{0.6}Co_{0.2}Mn_{0.2})_{1-x}O_2$

Discharge Capacity: 178 Ah/kg @ 0.1C



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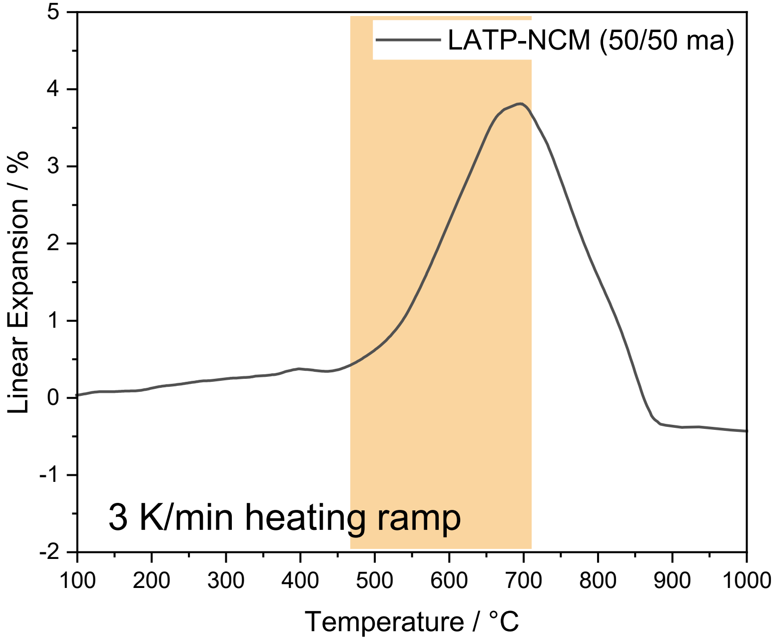

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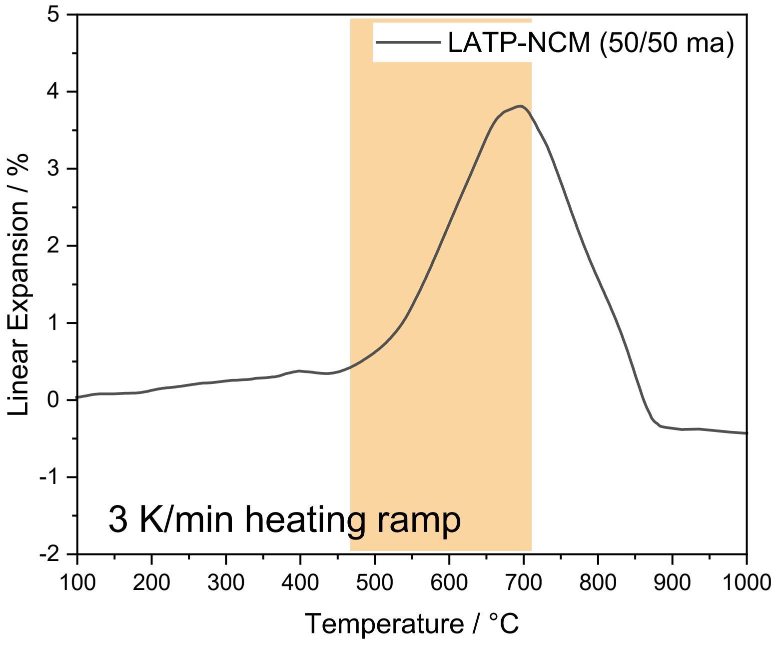

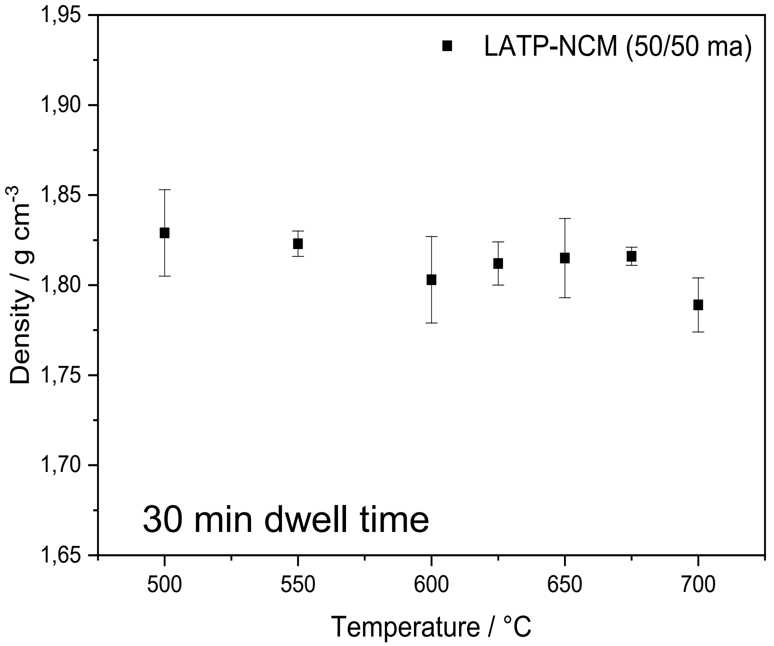

- ➢ Volume expansion at T > 450 °C
  → Start of reaction to secondary phases
- ➢ Volume reduction between 700 and 850 °C
  → Sintering of the secondary phases, rest porosity

Development of composite cathode with phosphatic solid electrolyte

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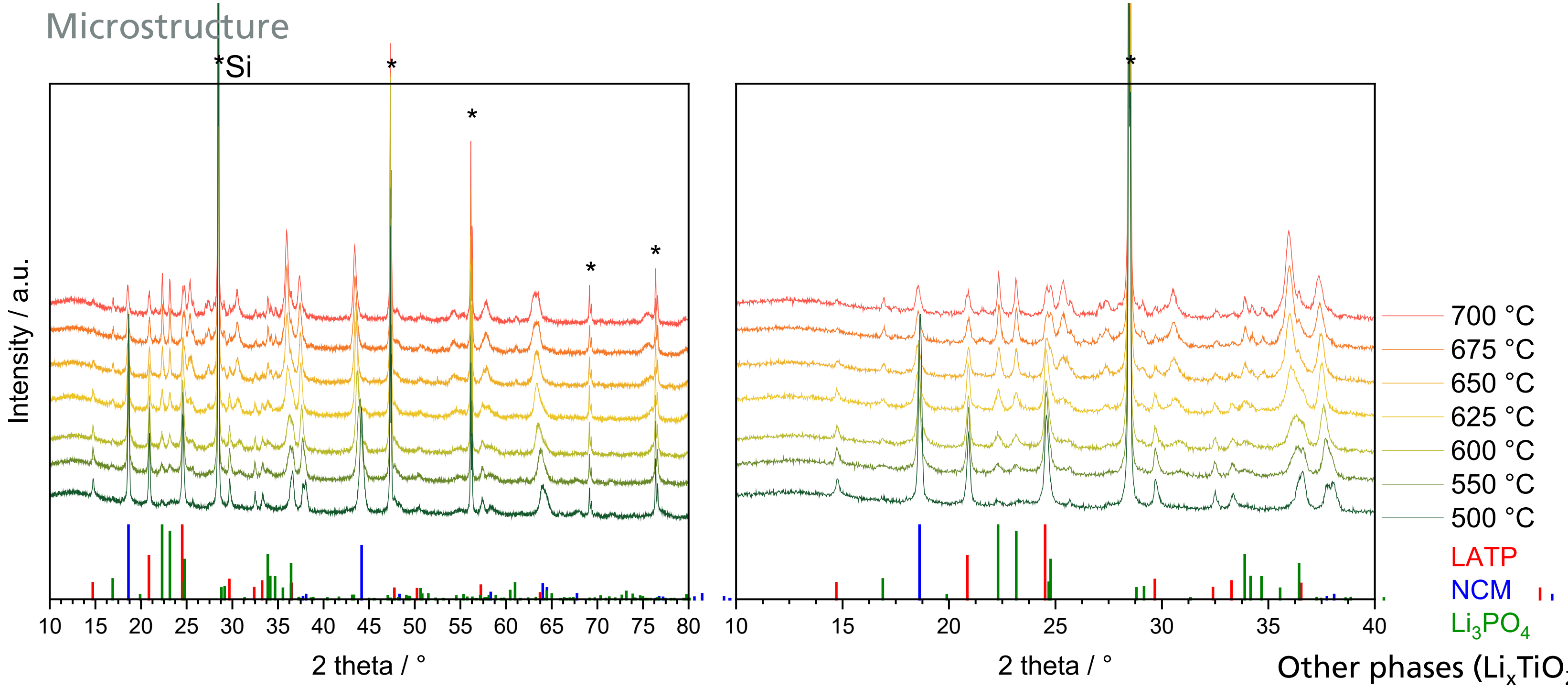

Other phases (Li_xTiO_2, $LiTiOPO_4$, $MnCo_2O_4$, NiO) are not indexed.

> ➢ Starting temperature for secondary phases formation at T ~ 550 °C
>
> ➢ Main reaction products:
>
> Li_3PO_4, Li_xTiO_2, $LiTiOPO_4$, $MnCo_2O_4$, NiO

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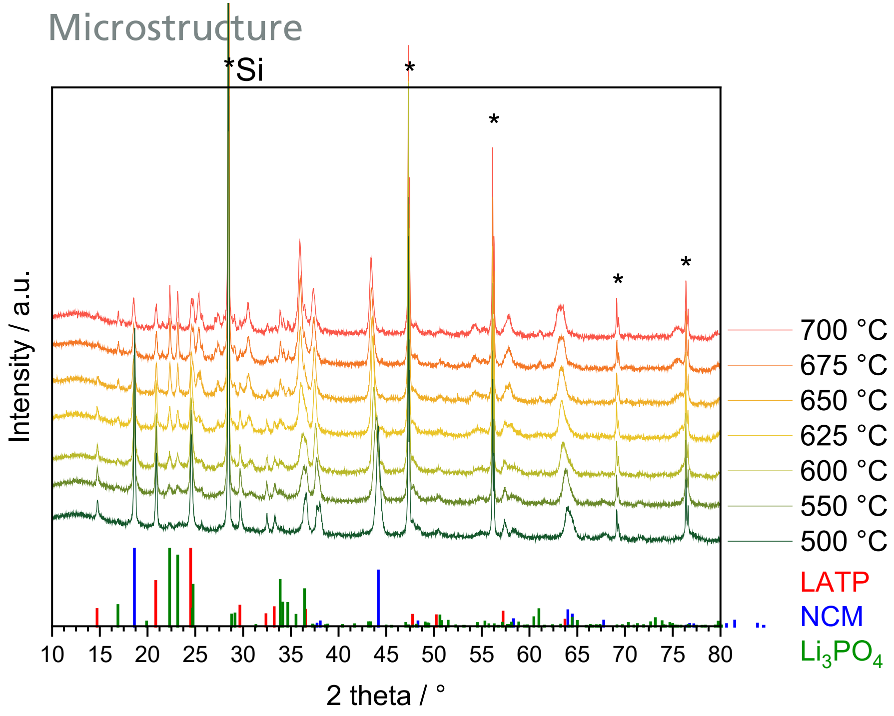

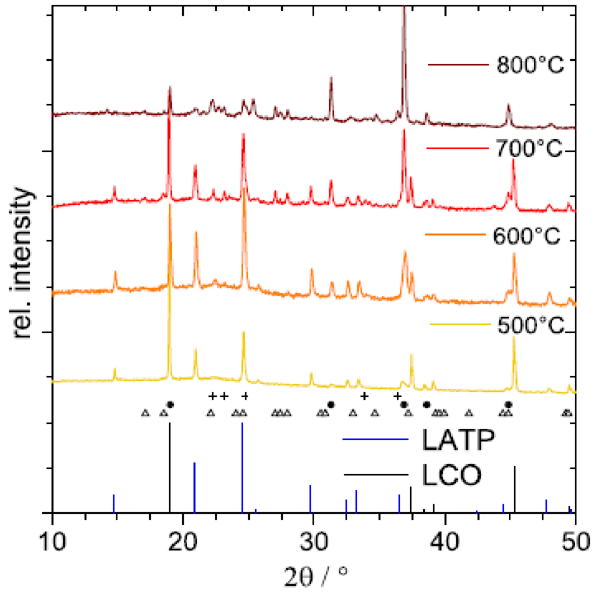

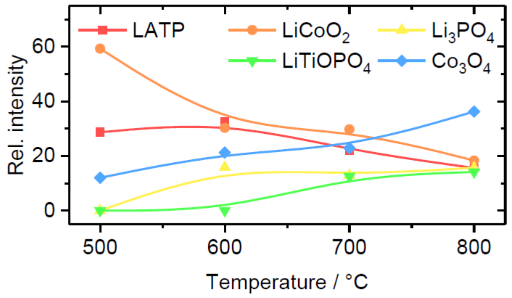

M. Gellert, E. Dashjav, D. Grüner, Q. Ma, F. Tietz, International Journal of Ionics 24 [4] (2018) 1001-1006.

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Development of composite cathode with phosphatic solid electrolyte

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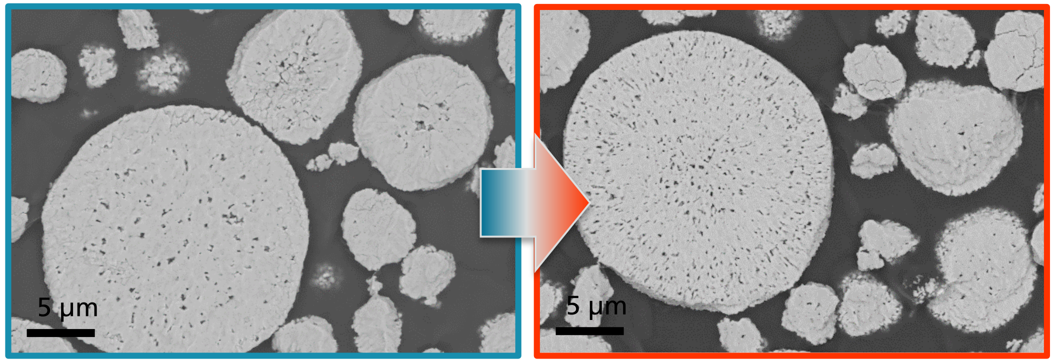
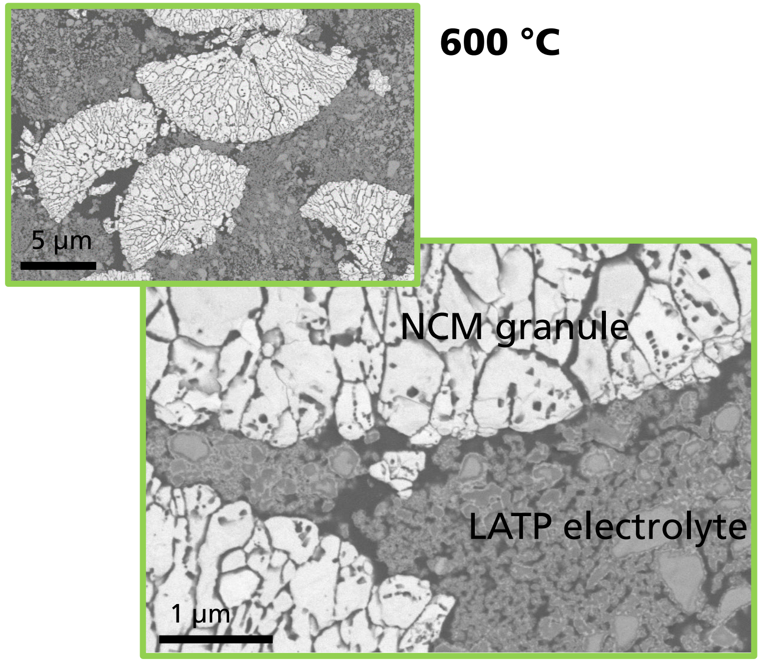
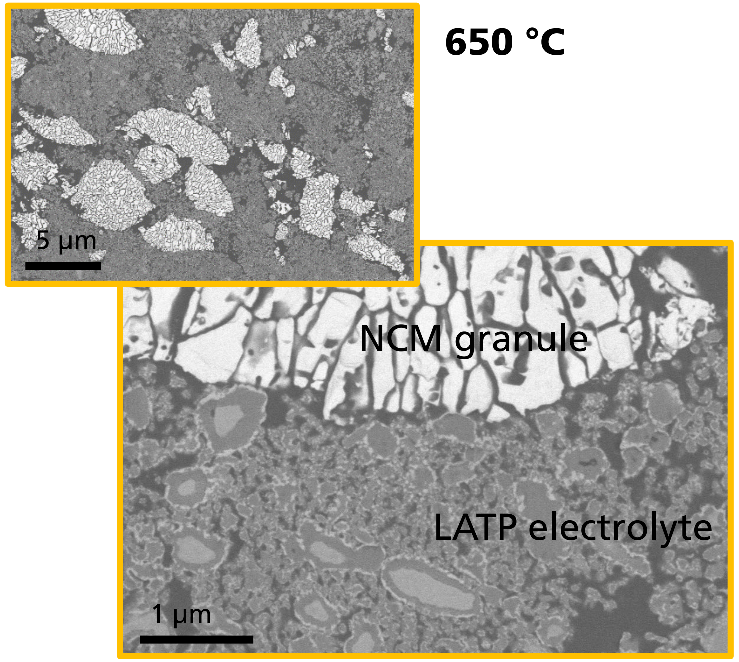


NCM622 as received NCM622 after T = 700 °C (30 min)

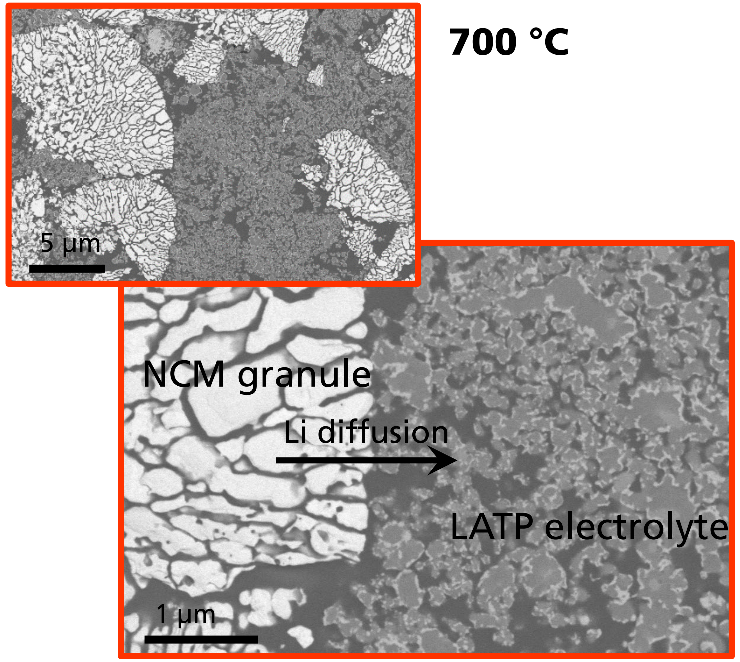
600 °C



650 °C



700 °C



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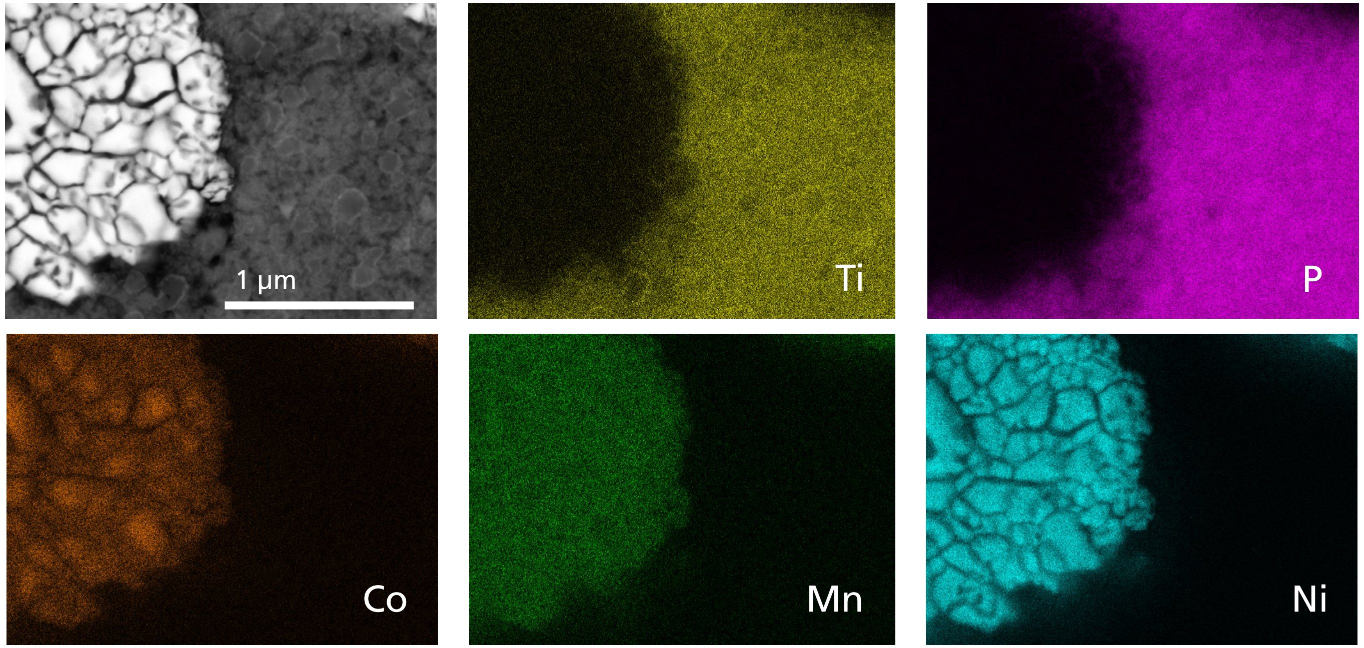

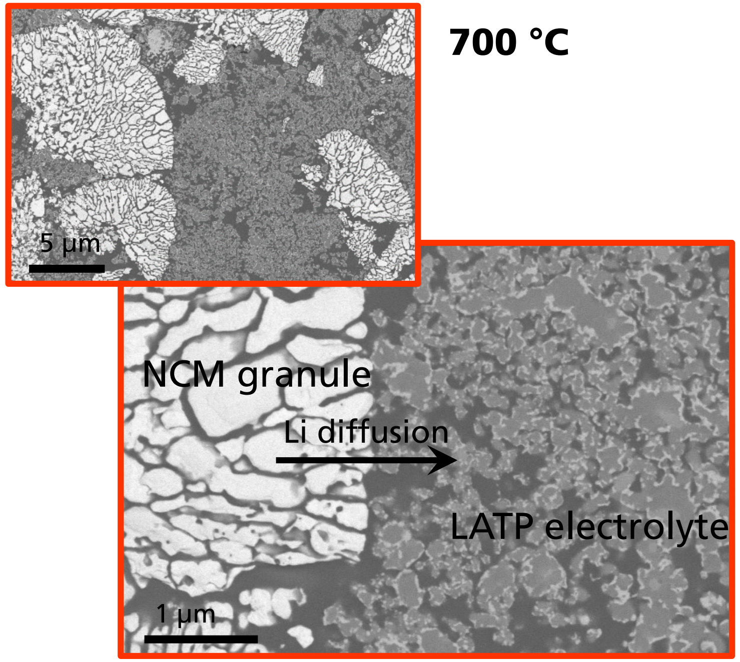

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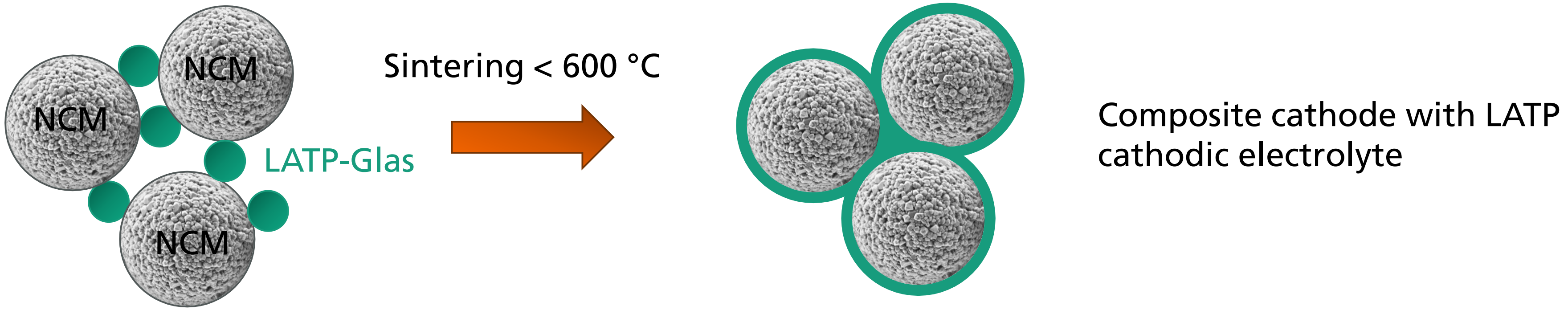
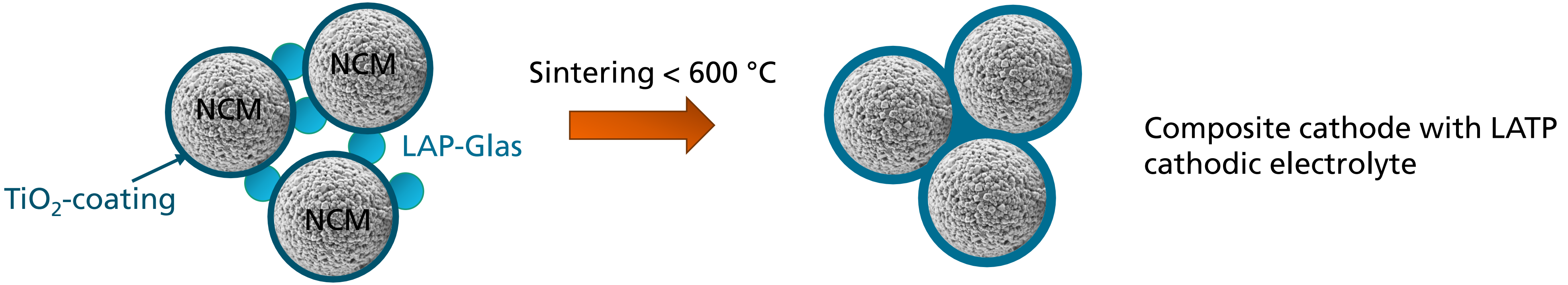
Development of composite cathode with phosphatic solid electrolyte

- Main task: reduction of the sintering temperature < 600 °C

1. Co-sintering of NCM and LATP-glas

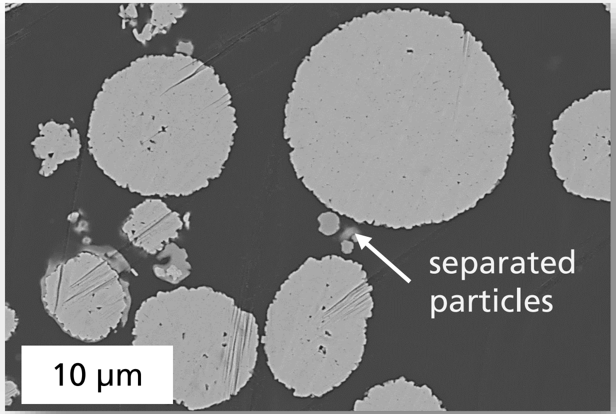


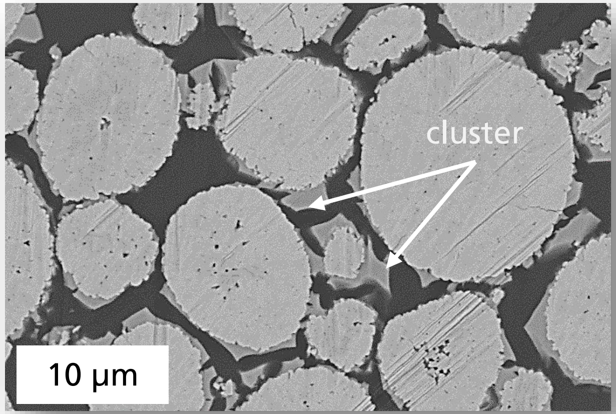
2. Reaction sintering of LAP-Glas + TiO_2 → LATP



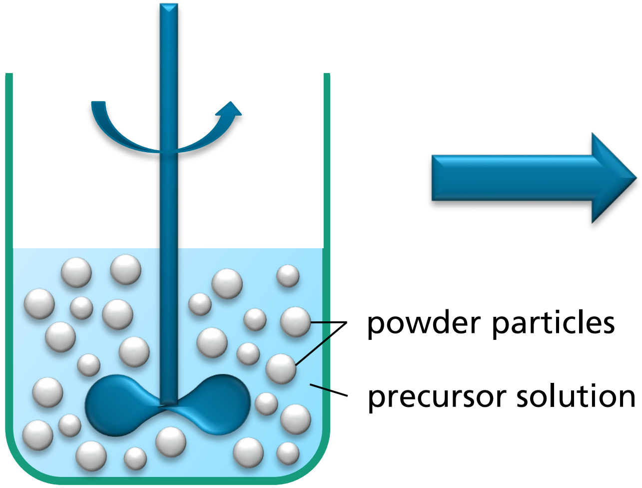
Coating of particles by spray drying

- ⇨ Preparation of precursor solution in glovebox under argon atmosphere
- ⇨ Dispersion of powder in precursor solution with stirring
- ⇨ Spray drying with optimized parameter for homogenous coating





characterization of coated particles



suspension of powder and precursor solution

spray drying in lab-scale

spray drying in technical scale

Conclusion / 1

LLZO electrolyte by tape casting

- Successful development of slurry recipe, tape casting process and sintering parameters
- Sintered electrolyte with thickness < 100 µm achieved
- Further development focuses on thinner electrolytes and increasing quality for larger area electrolytes

Reaction sintering of LAP glas + TiO_2 → LATP

- NCM particles coated with TiO_2
- First sintering experiments conducted with different LAP glasses and TiO_2
- Electrochemical characterization performed at the moment

Co-sintering of NCM and LATP-glas

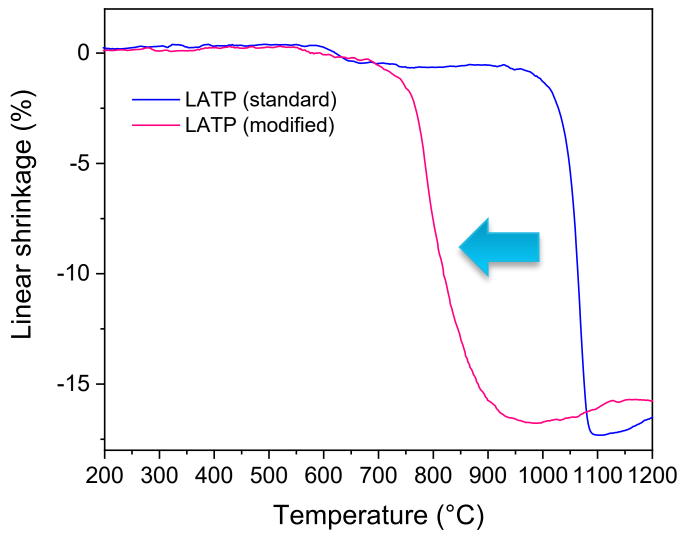
- volume expansion of the LATP-NCM mixture at T > 450 °C

⇨ start of reaction

- formation of secondary phases at T ~ 550 °C

  → finished reaction at T ~ 700 °C

- no densification of LATP electrolyte (for Li conductive pathways) below 600°C by heating rate 5 K/min



Reduction of crystallization temperatur by modification of LATP

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Conclusion / 2

Challenges – what is the status?

- Availability of suitable materials in significant amounts and quality
- ⇨ Huge point, for example processable electrolytes and tuned cathode materials

- Adaption of processing parameters
- ⇨ Tape casting process can be used for component manufacturing
- ⇨ Sintering regime: in parallel with the material development

- Full cells with components made using scalable technologies
- ⇨ Cosintering is challenging regarding the adaption of material properties
- ⇨ Additional technologies are beeing evaluated (e.g. deposition, for example aerosol or PVD)

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Acknowledgement

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ARTEMYS (03XP0114I)

FestBatt (03XP0173D)

funded by the German Federal Ministry of Education and Research.

ARTEMYS

FEST BATT *Cluster of Competence for Solid-state Batteries*

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