APPLICATION OF CERAMIC TECHNOLOGIES IN ALL SOLID STATE BATTERIES

Mareike Wolter, Kristian Nikolowski, Katja Wätzig, Jochen Schilm, Uwe Partsch
Expertise in ceramics
Energy and Environmental Technologies

- High temperature batteries
- Gas reforming
- Supercaps
- High temperature fuel cells
- All solid state batteries
- Lithium batteries
- Photovoltaics
- Metal air batteries
- Gas purification
- Small low temperature fuel cells (PEFC)
- Energy harvesting (piezo ceramic)
- Thermoelectric materials
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
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
Bipolar concept

IKTS solid oxide fuel cell (SOFC) stack technology

eneramic-Stack; e100: 40 cells, 100W\textsubscript{el}
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)
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
Material and process innovation in EMBATT development

- **EMBATT1.0**
  - **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

- **EMBATT2.0**

  - **200 Wh/l**
  - **450 Wh/l**

- **Battery energy density**

- **Polymer electrolyte based all solid state battery**
- **High voltage LNMO cathode material with adapted particle morphology**
- **Manufacturing of composite electrodes**
Manufacturing process – ‘organic’ bipolar battery (EMBATT1.0, EMBATT2.0)

- 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

EMBATT1.0

EMBATT2.0

EMBATT3.0

cathode: cathode materials (LNMO)
electronic conducting phase: carbon black
ion conducting electrolyte phase: glas-ceramic electrolyte
electronic conducting barrier

anode: lithium metal

separator: ceramic coating, glas-ceramic electrolyte

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

<table>
<thead>
<tr>
<th>200 Wh/l</th>
<th>450 Wh/l</th>
<th>...</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery energy density</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Solide state electrolytes

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Sulfides</th>
<th>Oxides</th>
</tr>
</thead>
</table>
| + 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 |

**Polymers**

![PEO polymer chain](image.png)

**Sulfides**

![LiCoO₂](image.png)

**Oxides**

![Graphite](image.png)

---


### Solide state electrolytes

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Sulfides</th>
<th>Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO polymer chain</td>
<td><img src="image" alt="Sulfide Diagram" /> LiCoO₂ Li⁺ LiCoO₂ LiS·P₂S₅ Li⁺ LiCoO₂ Li⁺ 5 µm</td>
<td>Lithium Aluminium Titanium Phosphate Li₁₁₃Al₀₃Ti₁₇(PO₄)₃ → NASICON structure → [M₂(PO₄)₃]- framework stabilized with Li⁺</td>
</tr>
</tbody>
</table>
| + good processibility and flexibility | + high ionic conductivity (10⁻³-10⁻² S/cm at RT)  
- low ionic conductivity (10⁻⁵-10⁻⁴ S/cm)  
- low mechanical stability |  


Manufacturing of components - composite electrode, solid electrolyte

Casting, Printing

Thermal processing

Al$_2$O$_3$

LiFePO

LTCC

NiZn-Ferrit

LTCC

NiZn-Ferrit

LTCC
Manufacturing of components - composite electrode, solid electrolyte

Cathode supported

Li$_3$Fe$_2$(PO$_4$)$_3$/LATP interface sintered at 1000°C

Electrolyte supported

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

LiCoO$_2$-cathode active material and Li$_3$BO$_3$ solid electrolyte

LiLaZrNbO-Solid electrolyte

10 μm


S. Ohta et al.: All-solid-state lithium ion battery using garnet-type oxide and Li$_3$BO$_3$ solid electrolytes fabricated by screen-printing, Journal of Power Sources 238 (2013) 53e56
Manufacturing process – ‘full ceramic’ bipolar battery

- Thermal treatment $\rightarrow$ batch process
- Stacked package design of sintered components:
  - Thermal mismatch $\rightarrow$ cracks
  - Evaporation of lithium
  - Loss of flexibility
  - Reactivity with other phases (e.g. cathode materials)
  - Conductive material interfaces
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
- 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
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
Powder synthesis of high energy cathode material LiNi_{0.5}Mn_{1.5}O_4

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

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

**Melting & Quenching**
- Mixing of components (Li$_2$CO$_3$, 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)
Synthesis of glass ceramic LATP materials and component manufacturing

Melting & Quenching
- Mixing of components (Li$_2$CO$_3$, 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

Tape casting
- Recipe development

Sintering
- Pressureless sintering step
- Adapted setup to avoid warping
- Minimized thickness of substrates
Synthesis of glass ceramic LATP materials and component manufacturing

Melting & Quenching

- Mixing of components (Li₂CO₃, Al(OH)₃, TiO₂ (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

Tape casting

- Recipe development

Sintering

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of green tape</td>
<td>120-300 µm</td>
</tr>
<tr>
<td>Single sintered tape</td>
<td>120 µm</td>
</tr>
<tr>
<td>Sintering temperature</td>
<td>950°C - 1150°C</td>
</tr>
<tr>
<td>CTE for RT-800°C</td>
<td>1-1.5 ·10⁻⁶ /K⁻¹</td>
</tr>
<tr>
<td>4-Point Bending strength (BB-bar)</td>
<td>55 ± 9 Mpa</td>
</tr>
<tr>
<td>Conductivity @ 25°C</td>
<td>3 ·10⁻⁴ S cm⁻¹</td>
</tr>
</tbody>
</table>
Properties of sintered LATP microstructures

- Strong anisotropy of $\text{MTi}_2(\text{PO}_4)_3$ (M = Li, Na, K) phases along the crystallographic axis
  
  $\text{M}=\text{Li}$:  
  $\alpha_a = 0,75 - 0,27 \cdot 10^{-6} \text{ K}^{-1}$  
  $\alpha_c = 30,8 \cdot 10^{-6} \text{ K}^{-1}$  
  (20°C..800°C)

- Investigation of effects during sintering process
  
  $\rightarrow$ Formation of cracks  
  $\rightarrow$ 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
Investigation of sintering properties of LATP

no He leakage

slightly increased He leakage

open porosity measureable

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$_4$ LATP ceramics”, Journal of the European Ceramic Society, Accepted (2016).
Evolution of cracks in microstructure of LATP ceramics at different sintering temperatures

1st Effect – Li loss indicated phase transition
- \( \text{AlPO}_4 \) formation
  - smaller lattice parameter
  - negative thermal expansion coefficient
- Initial microcracks in the \( \text{AlPO}_4 \) phase
- Observed at \( T = 950 \, ^\circ \text{C} \)
- Grain size ~ 0.7 µm
Evolution of cracks in microstructure of LATP ceramics at different sintering temperatures

- **900 °C**
  - Grain growth!

- **1050 °C**
  - 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

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).

Optimized sintering conditions:
- Defect free microstructures
- Maximized ionic conductivity
- Prevention of Lithium evaporation
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...
SEPTEMBER 2017
Fraunhofer-Institut für Keramische Technologien und Systeme IKTS, Dresden

TOPIC "ALL SOLID STATE BATTERIES"
- Perspectives
- Materials
- Technologies
- Application

Further information coming soon
www.ikts.fraunhofer.de
Thank you for your attention!

**Acknowledgement**
Thanks to the IKTS project team: Kristian Nikolowski, Matthias Seidel, Marco Fritsch, Stefan Börner, Beate Capraro, ...

EMBATT1.0 work is supported by funds from Europäische Fonds für regionale Entwicklung (EFRE) and the Freistaat Sachsen in frame of the "ePadFab" project.

EMBATT2.0 work is supported by funds from the German Federal Ministry of Education and Research BMBF (Bundesministerium für Bildung und Forschung) (project number 03XP0068G).

The presented work is conducted together with our partners thyssenkrupp System Engineering, GmbH IAV GmbH, Glatt Ingenieurtechnik GmbH, Leibniz-Institut für Polymerforschung Dresden e.V.