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

SPONSORED BY THE Federal Ministry of Education and Research

JÜLICH Forschungszentrum

Oxide ceramic all-solid-state Li batteries with NCM-LLZO based composite cathodes

Christoph Roitzheim[a], Yoo Jung Sohn[a], Martin Finsterbusch[a,b], Sven Uhlenbruck[a,b], Olivier Guillon[a,b], Dina Fattakhova-Rohlfing[a,b,c]

[a]Institute of Energy and Climate Research – Materials Synthesis and Processing (IEK-1), Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Str., 52425 Jülich, Germany

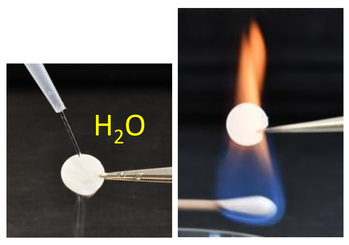
[b]Helmholtz Institute Münster: Ionics in Energy Storage (IEK-12), Corrensstr. 46, 48149 Münster, Germany

[c]Faculty of Engineering and Center for Nanointegration Duisburg-Essen (CENIDE), Universität Duisburg-Essen, Lotharstraße 1, 47057 Duisburg, Germany

Oxide based all-solid state batteries

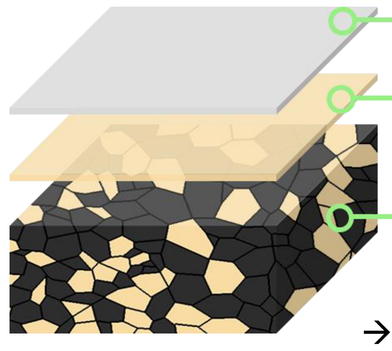
Oxides provide extremely high safety during production as well as on cell level

- NO formation of volatile compounds (no HF or H_2S)
- NO irreversible chemical reaction with water enables sustainable, water based processing
- NO toxic metals in the electrolyte/separator
- Good thermal stability and heat dissipation
- Enable variable operation temperatures:
  25-40 °C (aimed) ← **60 °C** (currently) → up to 150 °C for special applications
- Quasi pressure-free operation possible (0 bar in the case of porous LLZO anode)
- Room temperature ionic conductivity of up to 1.5 mS/cm (LLZO:Ga) [1]



Thin sintered LLZO separator

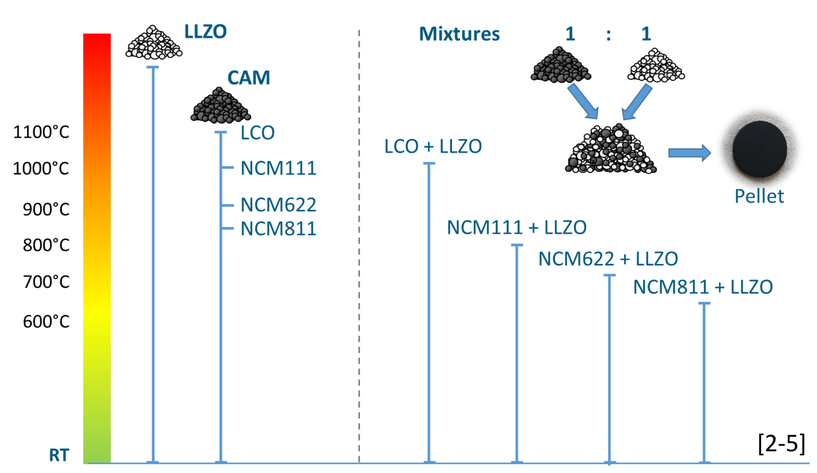
Garnet-type fully inorganic all-solid state battery (ASB)



→ High energy density cells enabled by LLZO stable in contact with a Li metal anode

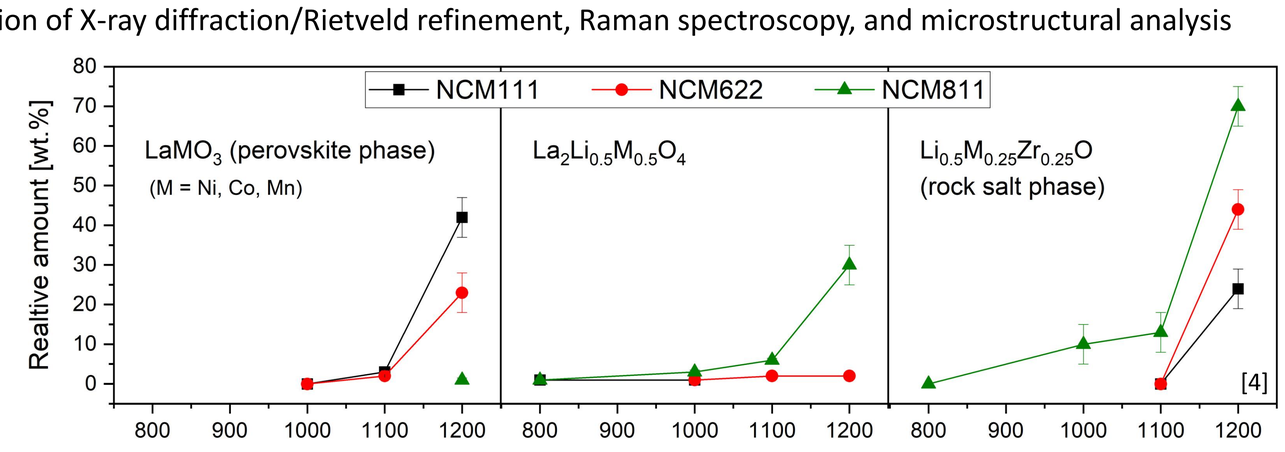
Secondary phase formation during co-sintering NCM and LLZO

- High processing temperatures required for the fabrication of dense ceramic composite cathodes lead to material compatibility issues
- The thermal stability of **$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NCM111), $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NCM622),** and **$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NCM811)** in combination with the garnet solid-state electrolyte **$Li_{6.45}La_3Zr_{1.6}Ta_{0.4}Al_{0.05}O_{12}$ (LLZO:Ta)** was studied
- 1:1 mixtures of NCM and cubic LLZO:Ta were prepared and sintered at various temperatures between 25 °C and 1200 °C in air
- The formed secondary phases were identified by a combination of X-ray diffraction/Rietveld refinement, Raman spectroscopy, and microstructural analysis



Temperature of reaction onset

- Mixtures of CAM and LLZO show significant lower thermal stability compared to their single components
- Temperature of reaction onset for LLZO/CAM mixtures depends strongly on used CAM
- Reactivity of the different NCM compositions towards LLZO increases with increasing Ni content



→ No complete decomposition: up to 1000 °C, cubic LLZO and NCM are the main phases

→ Nature and amount of formed secondary phases depend on NCM composition

→ In general, **three secondary phases** were identified

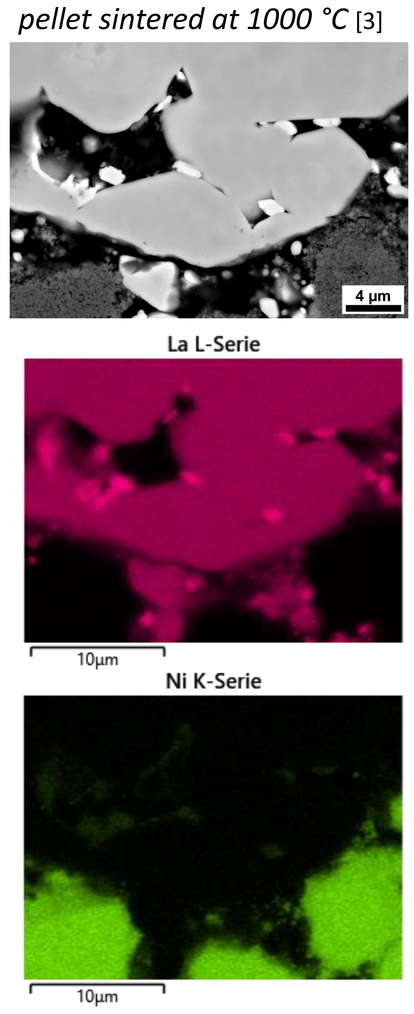
(M = Ni, Co, Mn)

$LaMO_3$
- Perovskite phase
- **$LaCo_{1-x}Mn_xO_3$** ($x < 0.4$) is the most likely composition [6]

$La_2Li_{0.5}M_{0.5}O_4$
- M = Ni was identified → **$La_2Li_{0.5}Ni_{0.5}O_4$**
- Forms as isolated particles (see SEM/EDS)

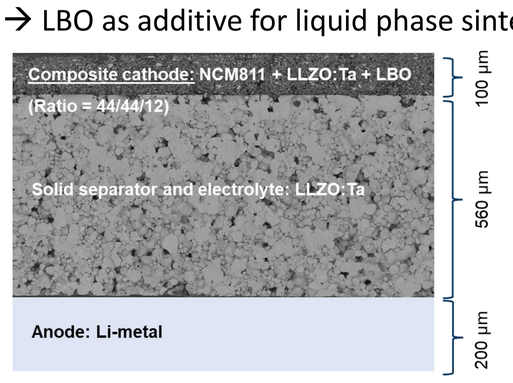
$Li_{0.5}M_{0.25}Zr_{0.25}O$
- Rock salt phase
- Zr-containing
- e.g. **$Li_{0.5}Co_{0.25}Zr_{0.25}O_2$** in the case of NCM111/LLZO

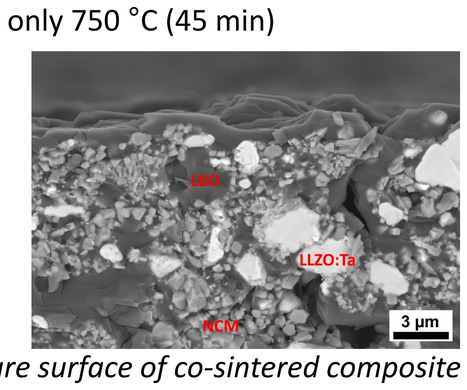
Cross-section of NCM811/LLZO:Ta pellet sintered at 1000 °C [3]



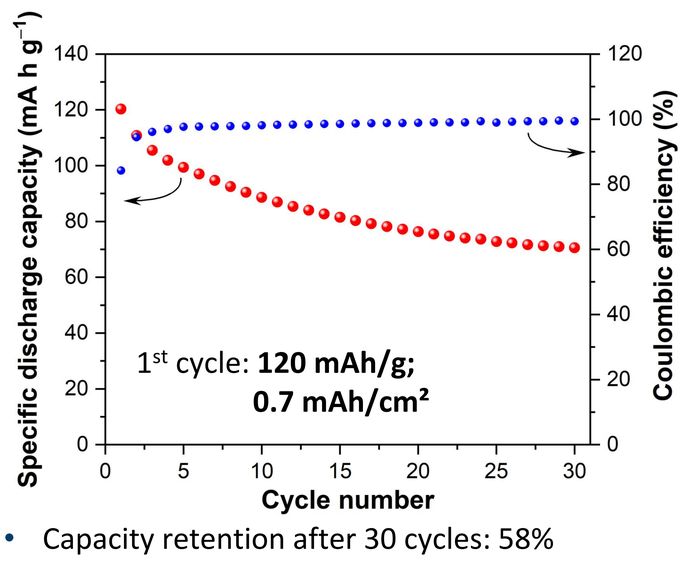
Fully inorganic cell

- Co-sintered composite cathode: **NCM811**, Li_3BO_3 (LBO), and LLZO:Ta (44:12:44)
  → LBO as additive for liquid phase sintering at only 750 °C (45 min)





Fracture surface of co-sintered composite cathode



- LLZO and NCM811 are the main phases
- $La_2Li_{0.5}Ni_{0.5}O_4$ as secondary phase and $Li_{2.3}C_{0.7}B_{0.3}O_3$ (LCBO) as Li-ion conducting phase (~ 10^{-5} S/cm at 100 °C)
- Active material loading: 5.7 mg/cm²

T / °C	60
P /MPa	~ 0.2
Φ_{CAM} / wt.%	44
q_A /mAh cm^{-2}	1.1
j_{chg}/j_{dschg} / mA cm^{-2}	0.04
E / V vs. Li$^+$/Li	3.0 – 4.2

- Capacity retention after 30 cycles: 58%

[3]

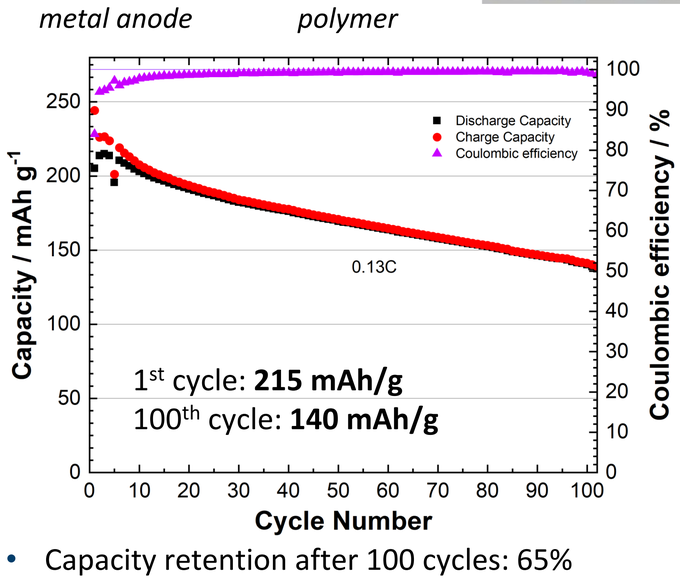
Dry, polymer-ceramic hybrid cell

- Composite cathode (**$LiNi_{0.83}Mn_{0.6}Co_{0.11}O_2$**, LLZO:Ta, carbon black, PVDF, and LiTFSI) prepared by tape casting at room temperature (not sintered)
- Cathode is infiltrated with polymer electrolyte and glued to a sintered LLZO separator

LLZO:Ta separator attached to Li metal anode

Cathode tape infiltrated with polymer

Cross-section of hybrid composite cathode



- Outstanding high initial discharge capacity > 200 mAh/g
- Higher cathode material utilization and improved cycling stability compared to fully inorganic cell

T / °C	60
P /MPa	~ 0.2
Φ_{CAM} / wt.%	60
q_A /mAh cm^{-2}	0.3
j_{chg}/j_{dschg} / mA cm^{-2}	0.04
E / V vs. Li$^+$/Li	3.0 – 4.3

- Capacity retention after 100 cycles: 65%

[5]

Member of the Helmholtz Association

[1] C. Schwab, C. Roitzheim, et al., *Journal of Materials Chemistry A* **2023,** 11, 5670-5680.
[2] S. Uhlenbruck, et al., *Journal of Electroceramics* **2017,** 38, (2), 197-206.
[3] C. Roitzheim, et al., *ACS Applied Energy Materials* **2022**, *5*, 6913-6926.
[4] A. Bauer, C. Roitzheim, et al., *Chemistry of Materials* **2023**, 35, 8958-8968.
[5] T. Demuth, et al., *Matter* **2023.**
[6] Y. Ren, et al., *Journal of Materiomics* **2016**, 2, 256-264.