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# Tape casting of oxide-ceramic electrolyte layers for all-solid-state lithium batteries


*T. Reppert, C.-L. Tsai, M. Finsterbusch, S. Uhlenbruck, O. Guillon, M. Bram.*

Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), 52425 Jülich, Germany and Jülich Aachen Research Alliance: JARA-Energy


## Introduction

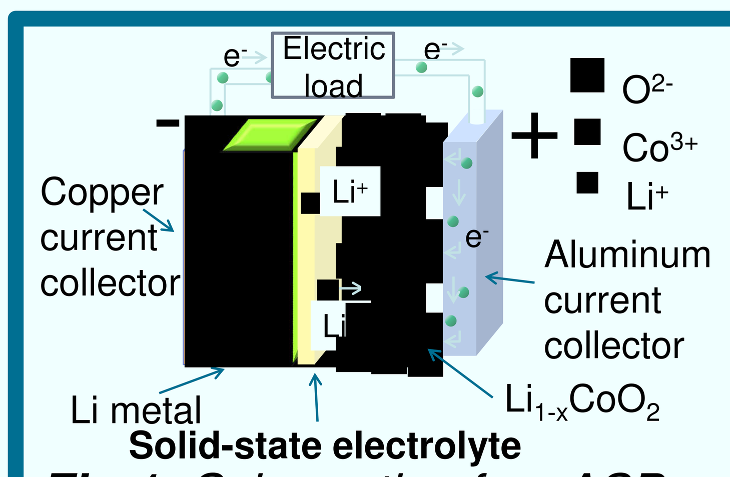


***Fig.1:*** *Schematic of an ASB.*

All-solid-state lithium batteries (ASB) have better safety properties due to the incombustible solid electrolyte than commercial lithium ion batteries (LIB), which use flammable organic liquid as electrolyte. As an alternative one of the most promising oxide materials, $Li_7La_3Zr_2O_{12}$ (LLZ), are investigated. LLZ is an ionic conductor with a good thermal and electrochemical stability. Its potential of using high voltage cathode materials and its chemical compatibility with metallic lithium enables a higher energy density.

## Motivation

- **Proof of concept exists:**
  Prototype all-solid-state cell from bulk Ta-LLZ (LCO|Ta-LLZ|Li) that was able to light up an LED at 22℃.
- **Current tasks:**
  Bridging between lab scale and industrial application by large size LLZ functional layers, fabricated using established technologies.

## Methods

### Material preparation:

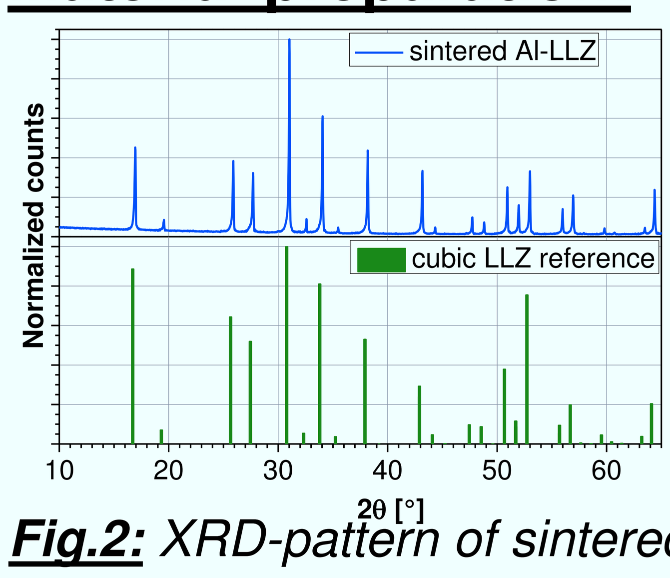


***Fig.2:*** *XRD-pattern of sintered Al-LLZ and ICSD reference.*

- **Solid-state reaction**
  - Stoichiometric composition out of oxide starting materials
  - Heat treatment to form highly conductive cubic LLZ phase
  - Structure stabilization and conductivity increased by Al-, Ta- and Y-substitution
- **Spray pyrolysis technique**
  - Al-LLZ were synthesized in scale of kilograms from solution of starting materials
  - subsequently ball milling and heat treatment to form cubic LLZ phase.

### Solid-electrolyte processing:

- **Tape casting**
  - Established, reproducible and up-scalable technology.
  - Slurry development and subsequent sintering studies of tape casted LLZ-films.

***Fig.3:*** ***(l.)****A tape casting line at IEK-1 can be used for large scale tape casting.* ***(m.)****Al-LLZ tapes were successfully processed by tape casting with a gap size of 250 µm and 500 µm.* ***(r.)*** *Solid electrolytes with a green tape thickness of 90 µm and 180 µm were used for further sintering studies.*

## Results

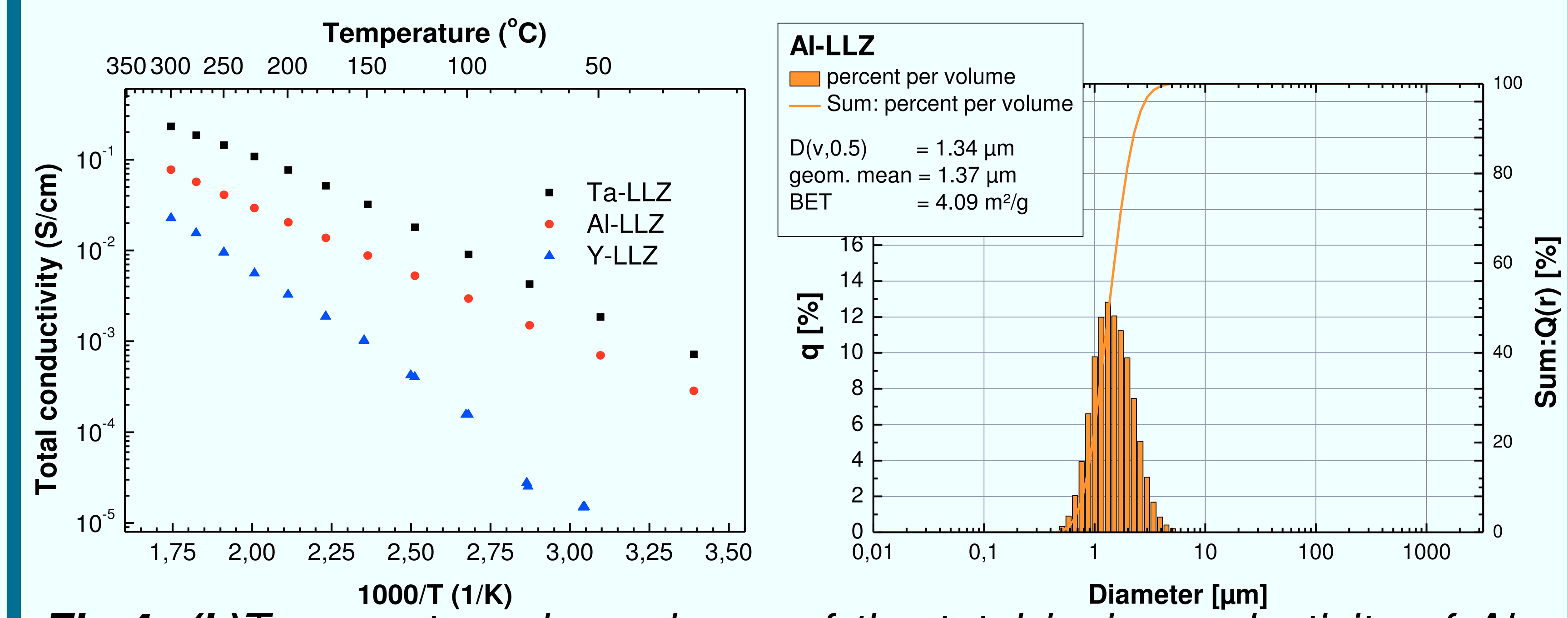


***Fig.4:*** ***(l.)****Temperature dependence of the total ionic conductivity of Al-, Ta- and Y-substituted LLZ. The total conductivity was derived from impedance spectroscopy (1MHz-1Hz, amplitude: 20 mV/mm, temperature range: 22-300°C).* ***(r)*** *1.6 kg of Al-LLZ were synthesized by spray pyrolysis and subsequently ball milled. The obtained powder has a mono-modal particle size distribution.*

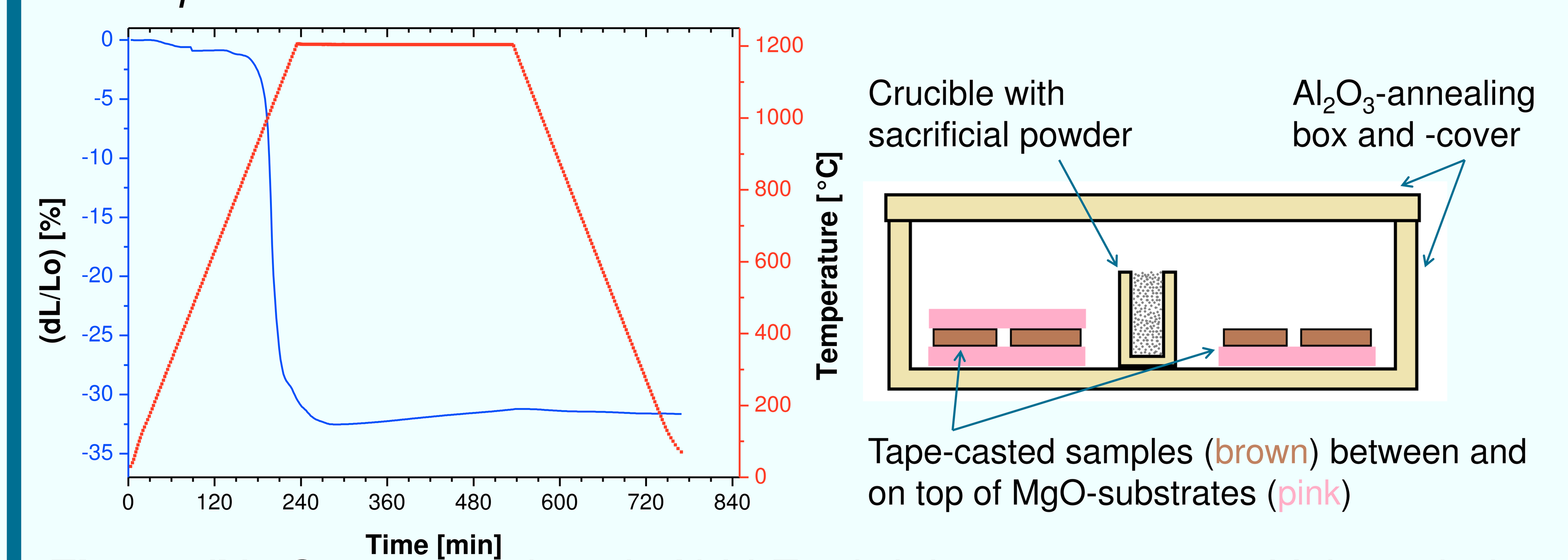


***Fig.5:*** ***(l.)*** *Spray pyrolyzed Al-LLZ shrinks approx. 30 Vol-% during sintering at 1000℃,* ***(r.)*** *Sintering set-up for casted Al-LLZ green tapes.*

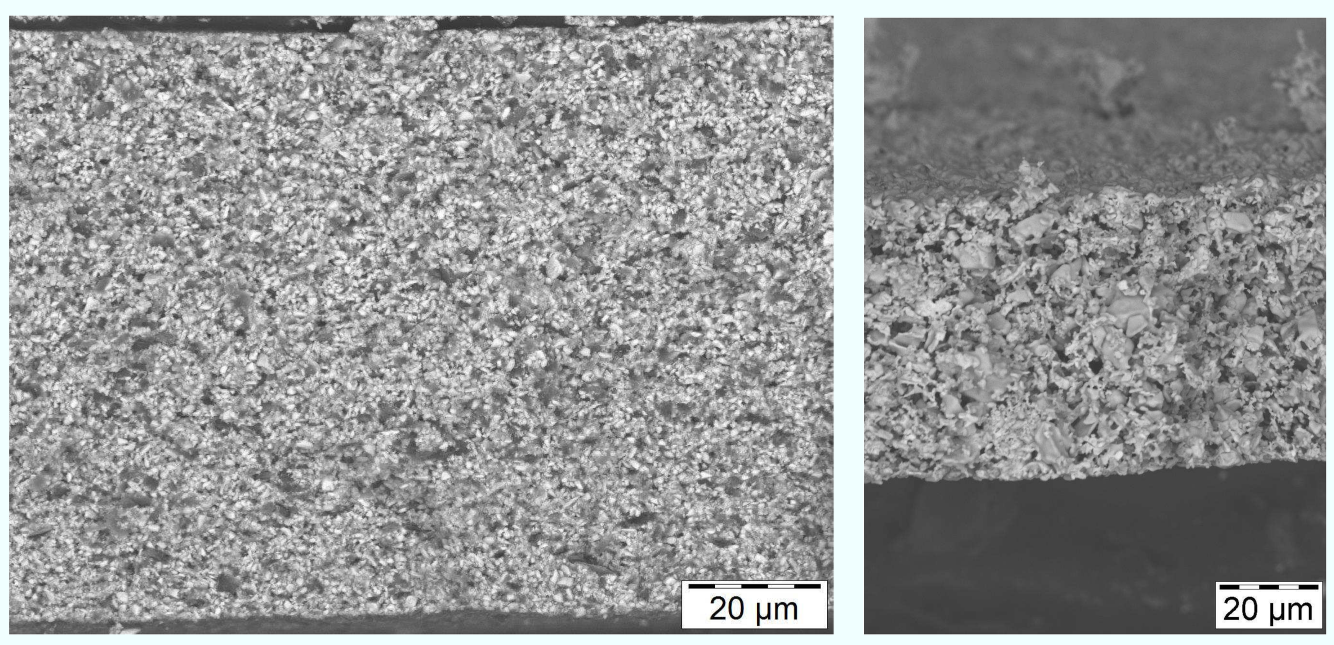


***Fig.6:*** ***(l.)*** *By evaluation of SEM images of Al-LLZ green tape (90 µm thick, 48 % organic content) and* ***(r.)*** *sintered Al-LLZ samples (57 µm thickness after sintering, 14 % calculated porosity), the densification of the solid electrolyte tape and its particle growth can be observed (2000x magnification;* $V_{acceleration}$ *= 15 kV).*

## Conclusion

- ✓ Al-, Ta- and Y-substituted LLZ were synthesized and investigated. Ta-LLZ shows the highest total conductivity ($\sigma_{ion,RT} \approx 10^{-3}$ S/cm).
- ✓ As a first step Al-LLZ was synthesized in scale of kilograms at once and can be processed by tape casting to obtain solid electrolyte tapes of 57 µm thickness and 14 % porosity.
- Further sintering studies needed to increase density and reduce deformation of sintered AL-LLZ tapes.
- Ta-LLZ will be synthesized via spray pyrolysis to obtain highly conductive solid electrolyte in the scale of kilograms for best performing oxide-ceramic solid electrolyte and mixed electrode layer in ASB application.


***Fig.7:*** *Bulk prototype all-solid-state lithium battery.*


**Contact information:** Thorsten Reppert
Forschungszentrum Jülich GmbH | 52425 Jülich
Tel.: +49/ 2461 61 8039 | Email: t.reppert@fz-juelich.de



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