Inhomogeneous conductivities in Li$_7$La$_3$Zr$_2$O$_{12}$ ceramics investigated by spatially resolved impedance spectroscopy and elemental analytics

Introduction

Why should we use a solid electrolyte?

Disadvantages of organic, gel-like electrolytes:

• electrochemical stability
• chemical inertness
• Inflammability

Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) one promising material to overcome these problems!

Key messages

Material of interest: Li$_{6.4}$Al$_{0.2}$La$_3$Zr$_2$O$_{12}$ (LLZO)

Macro-measurements
• Sample thickness has crucial effect on the overall performance

Microelectrode-measurements
• Applied on LLZO for the first time
• Revealed inhomogeneities

Elemental analysis (ICP)
• Determining the amount of lithium lost during preparation
• Elemental distribution is not homogeneous
Macro-measurements

Bulk conductivity of nominally equal samples fluctuates

- $\sigma_{\text{bulk}}$ of 54 nominally equal samples
- Variation in conductivity between: $2 \times 10^{-5} - 8 \times 10^{-4}$ S cm$^{-1}$

What can be done to obtain samples with reproducible bulk conductivity?

Li$_{6.40}$Al$_{0.20}$La$_3$Zr$_2$O$_{12}$
Macro-measurements

Typical impedance spectra for macro measurements

- First semicircle $\rightarrow$ bulk
- No visible grain boundary
- Equivalent circuit used to simulate the impedance spectra
- Inductance due to wiring
Macro-measurements

Search for a reproducible sample

**Sintering conditions**

- 1100 °C for 17 h
- 1150 °C for 12 h
- 1230 °C for 6 h

**Thick & thin samples**

- h > 3 mm
- h < 2 mm

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Macro-measurements

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Thick & thin samples

Thin samples are by trend faster.

Li$_{6.40}$Al$_{0.20}$La$_3$Zr$_2$O$_{12}$

No clear trend!
Macro-measurements

Impedance measurement starts with a pristine sample

\[ \sigma_{\text{bulk}} (\text{S cm}^{-1}) = 2.2 \times 10^{-4} \]
Macro-measurements

Diameter is reduced $\rightarrow$ Impedance increases

$$\sigma_{\text{bulk}} \text{ (S cm}^{-1}\text{)}$$

- $2.2 \times 10^{-4}$
- $1.5 \times 10^{-4}$
Macro-measurements

Further reduction leads to higher impedance

\[ \sigma_{\text{bulk}} \text{ (S cm}^{-1}\text{)} \]

- $2.2 \times 10^{-4}$
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- $1.2 \times 10^{-4}$
Macro-measurements

Further reduction leads to higher impedance

<table>
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<tr>
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<td>$8.8 \times 10^{-5}$</td>
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Macro-measurements

Second phases, holes and inhomogeneities found

Diameter reduction

1230 °C

1150 °C

1100 °C

σ_{bulk} changes upon sample reduction!

Macro-measurements

- Geometric reduction leads to a variation of $\sigma_{\text{bulk}}$
- Variations are not only caused by second phases and holes
- Further investigations with microelectrodes
Micro-measurements

First time, LLZO masked with microelectrodes

Electrode: Ti (10 nm)/Pt (200 nm)
Diameter: 20 – 300 µm

Grain Size: ~150 µm

Temperature: 23°C
Frequency: 3 × 10^6 – 10^4 Hz

Diameter (d) determines the probed volume beneath!
Micro vs Macro - measurements

Impedance spectra for differently sized microelectrodes

- $R_{\text{spread}}$ – local charge transport in the bulk
- $CPE_1$ – stray capacitance required because of electrical parts
- $CPE_2$ – electrode
- No contribution from grain boundaries
Micro-measurements

Spreading resistance increases with smaller diameter

Averaged local spreading resistance of differently sized microelectrodes

- spreading resistance increases as the diameter of the electrode decreases

\[ \sigma_{me} = \frac{1}{2d R_{spread}} \]  

Micro-measurements

Bulk inhomogeneities responsible for high local conductivity

Averaged local conductivities of differently sized microelectrodes

- $\sigma_{\text{me}} > \sigma_{\text{bulk}}$
  related to bulk inhomogeneities

- $\sigma_{\text{me}}$ (300 $\mu$m) > $\sigma_{\text{me}}$ (50 $\mu$m)
  assume - low ionic conduction near the surface [2]

Micro-measurements

Local degradation observable in impedance spectrum

Impedance spectra of different microelectrodes
Cycle 1 - pristine state
Cycle 2 - three weeks exposed to ambient air

A change in the impedance spectra indicates degradational phenomena [3]

Micro-measurements

Local conductivity measurements

Local conductivities of 300 µm electrodes across the sample

Conductivity in the outer region is higher than in the centre of the sample

Reason why? -- unknown
ICP – Inductively coupled plasma

Analytical method to count the amount of cations (Li, Al, Zr, ...)

ICP-OES
chemical analysis of the hole sample

LA-ICP-MS
local elemental analysis near the surface
Laser resolution: 5 - 300 µm

ICP – Inductively Coupled Plasma
OES – Optical Emission Spectroscopy

LA – Laser Ablation
ICP – Inductively Coupled Plasma
MS – Mass Spectrometry
ICP – OES

Sample digestion for ICP-OES measurements

LLZO 50 mg  Borax 0.8 g  5 h  + HCl + HF + H₂O
ICP – OES

How much lithium do we lose during sample preparation?

the loss of lithium per formula unit (pfu) during preparation

Start: $7.10 \pm 0.26$ pfu (3.62 %)
ICP – OES

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- **End:** 6.47 ± 0.15 pfu (2.29 %)

**Loss of lithium:** ～ 9 %
LA-ICP-MS

Local line scan pattern with laser ablation

- Ø – laser beam: 60 µm
- Scan rate: 180 µm/s
- Preablation to avoid surface contamination (Li$_2$CO$_3$, ...)
- Signal normalization to correct variations of
  - material ablation
  - transport
  - instrumental drift
LA-ICP-MS

Intensity gradient in Aluminum

Lithium

Zirconia

Aluminium

Semi quantitative imaging of whole LLZO pellets

Outlook

Combination of microelectrodes and ICP

→ correlation between elemental distribution and the resulting conductivity

Summary

Macro-measurements:

• Unveiled inhomogeneities and second phases

Microelectrodes:

• Are applied on LLZO for the first time
• Revelation of local bulk inhomogeneities ($\sigma_{\text{me}} > \sigma_{\text{bulk}}$)
• Near surface related effects $\sigma_{\text{me}} (300\mu\text{m}) > \sigma_{\text{me}} (50\ \mu\text{m})$
• Observation of degradational effects by ambient air

Chemical analysis (ICP):

• Lithium loss during preparation: $\sim 9\%$
• Detection of elemental inhomogeneities
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SOLIK Li-ion conducting ceramics for all-solid state batteries
Thank you for your attention!