The implication of inhomogeneities in $Li_7La_3Zr_2O_{12}$ ceramics

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INTRODUCTION

Portable devices such as mobile phones, cameras, tablets, as well as electric vehicles rely on the availability of energy and so far Li-ion batteries are the most used energy storage system. A limiting factor for Li-ion batteries is the ion conducting organic electrolyte because of their chemical instability and flammability. Therefore, a lot of research focuses on replacing the organic electrolyte by solid state materials. Cubic $Li_7La_3Zr_2O_{12}$ (LLZO) garnets and its variants are among the most promising candidates for future Li-battery systems [1]. They provide a very high Li-ion conductivity and combine chemical and electrochemical stability. In this contribution, we present a combined study of electrochemical impedance spectroscopy (EIS) and inductively coupled plasma mass spectrometry (ICP-MS) techniques on LLZO, to determine the effects of varying lithium and dopant content on the Li-ion conductivity. Besides overall conductivity measurements using blocking electrodes, measurements on microelectrodes of different size (20 – 300 µm) were performed to obtain information on local Li-ion conductivities. Within one and the same sample, conductivity variations up to almost one order of magnitude were found. Using laser ablation ICP-MS the local distribution of elements like Li, Zr, La, Al, *etc.* can be measured and correlated with variations in local conductivities.

EXPERIMENTAL

Impedance Spectroscopy

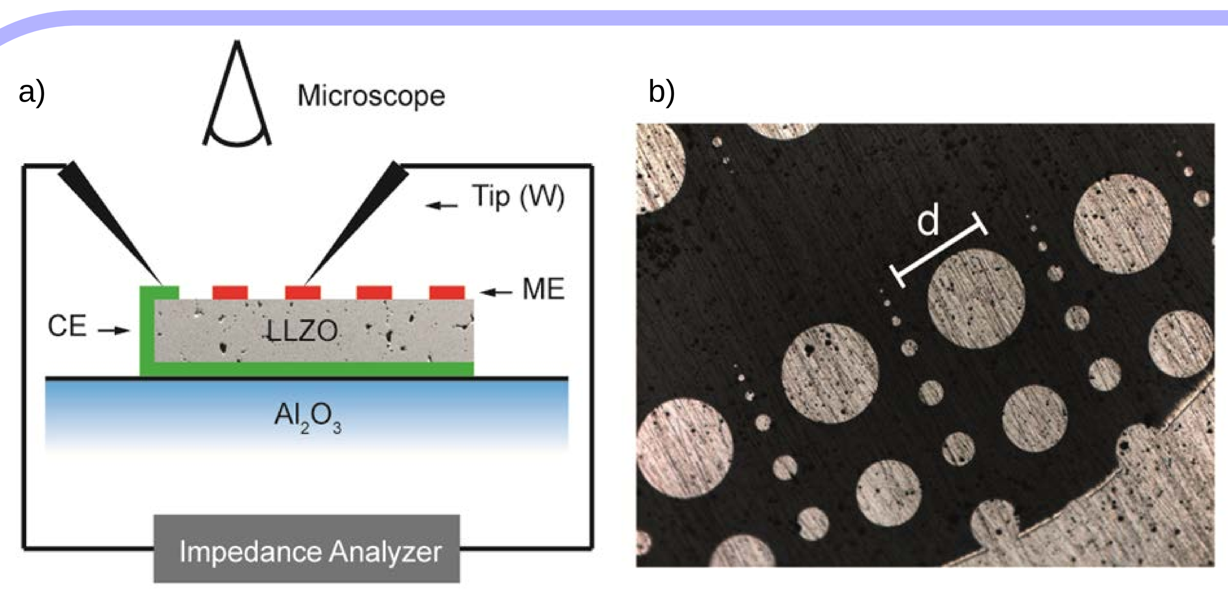
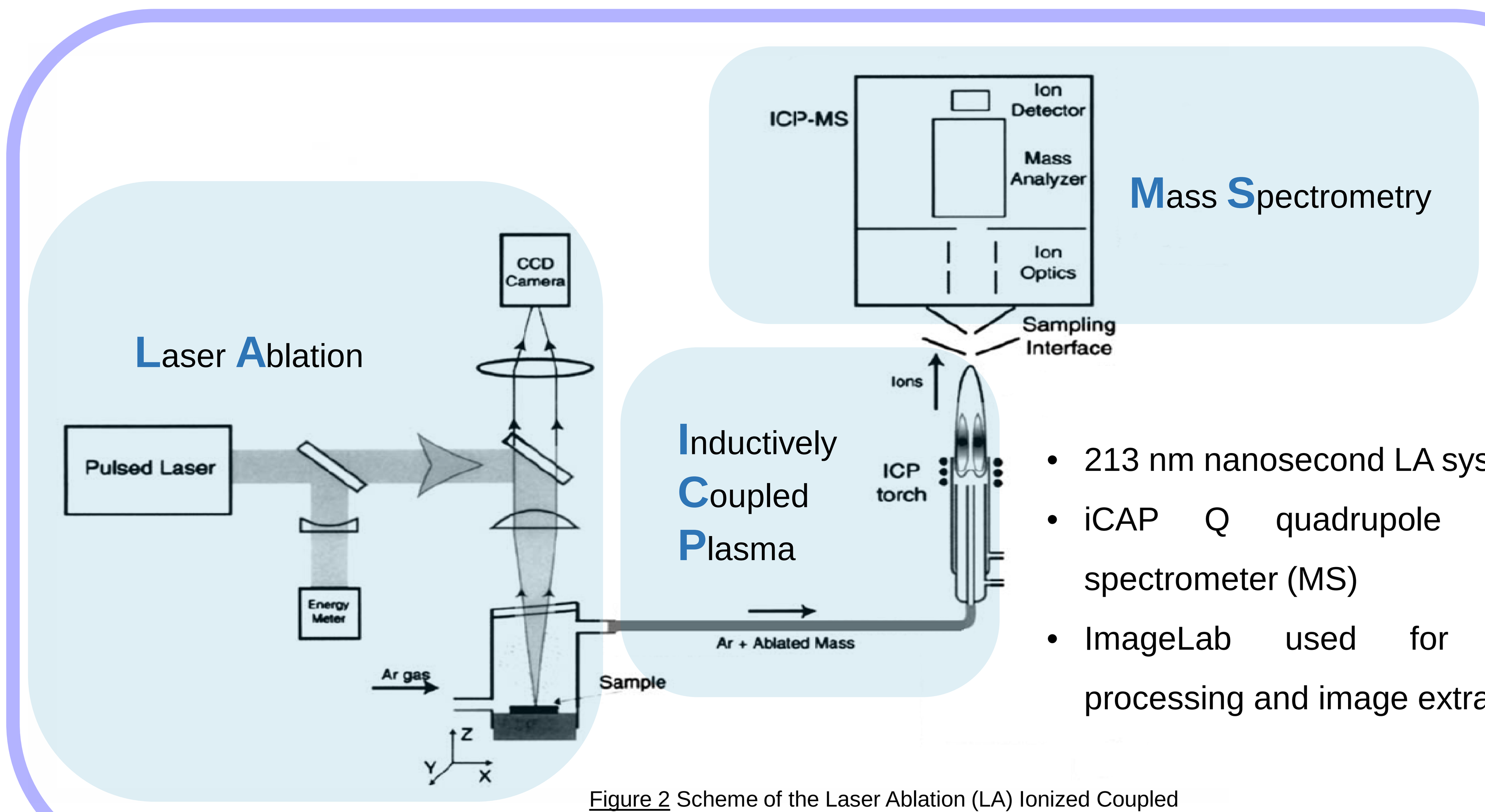


Figure 1 a) Sketch of the microelectrode (ME) measurement setup. b) The optical microscope image shows a part of the microelectrode array on top of a sample.

Parameters

Intended composition:	$Li_{6.4}Al_{0.2}La_3Zr_2O_{12}$	Frequency:	$3 \times 10^6 – 10^4$ Hz
Electrode material:	Ti (10 nm)/Pt (200 nm)	Grain Size:	~150 µm
Temperature:	23°C		

LA – ICP - MS



- 213 nm nanosecond LA system
- iCAP Q quadrupole mass spectrometer (MS)
- ImageLab used for data processing and image extraction

Figure 2 Scheme of the Laser Ablation (LA) Ionized Coupled Plasma (ICP) Mass Spectrometry (MS) setup [2]

RESULTS

Microelectrode measurements

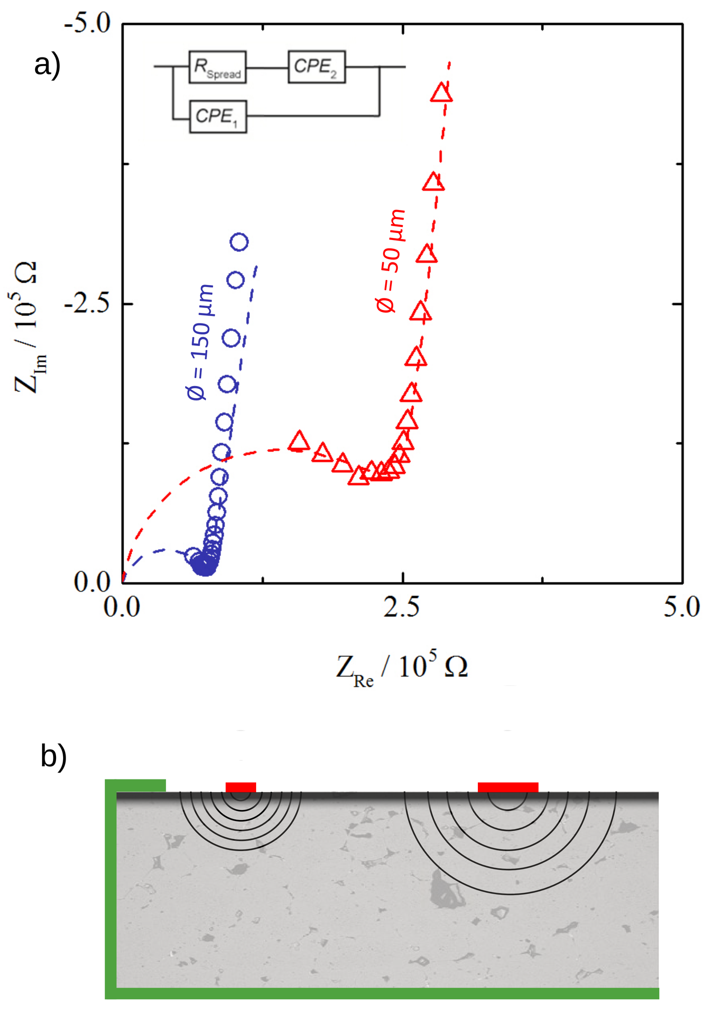


Figure 3 a) Impedance spectra obtained on microelectrodes with two different diameters (Ø), and the corresponding fits (dashed lines). b) Sketch of the potential distribution in LLZO.

- High frequency semicircle corresponds to charge transport of lithium
- Differently sized microelectrodes investigate different volumes
- Small microelectrodes are more sensible to near surface phenomena

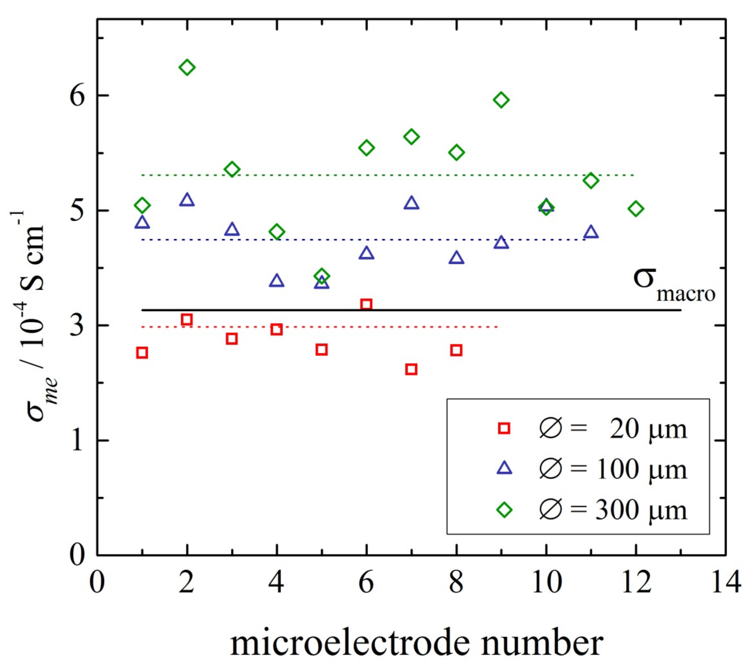


Figure 4 Local conductivities found for differently sized microelectrodes (σ_{me}) compared to the overall effective performance of the sample (σ_{macro}).

- Difference between σ_{me} and σ_{macro} is a factor two
- σ_{me} depends on the microelectrode diameter indicating surface near phenomena (degradation)

LA – ICP - MS

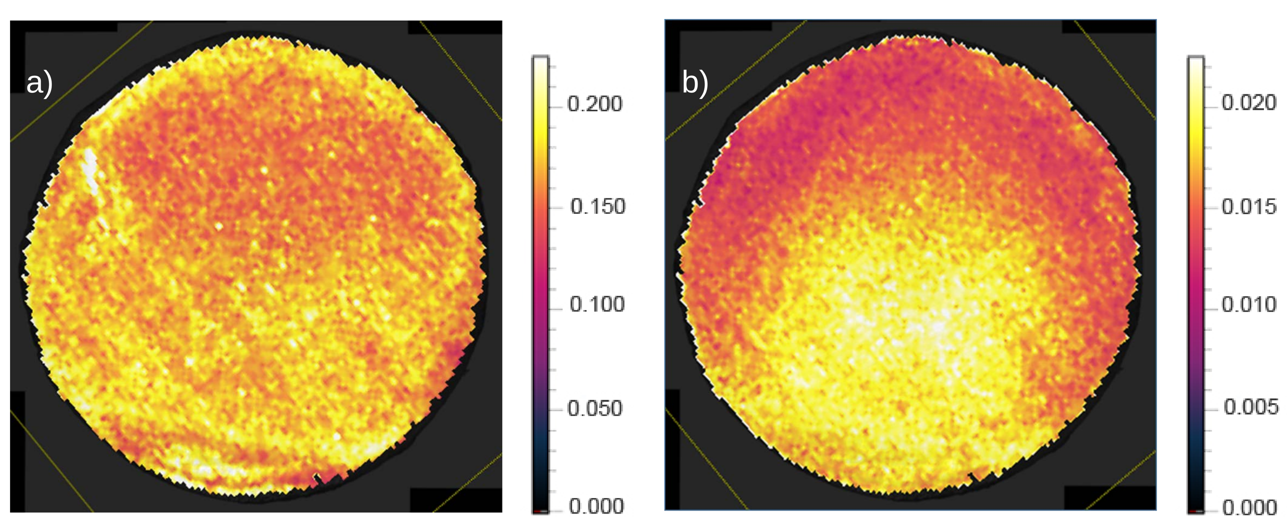


Figure 5 a) Intensity distribution, normalized to the zirconium signal, of the element a) lithium $\left(\frac{Li}{Zr}\right)$ and b) aluminium $\left(\frac{Al}{Zr}\right)$.

- Normalization to zirconium in order to diminish artefacts caused by the ablation
- Lithium distribution appears to be homogeneous
- Amount of aluminium decreases towards the outer rim

CONCLUSION

- **Local conductivity measurements using micro-electrodes were successfully achieved on LLZO**
- **Conductivity of microelectrodes depends on the diameter**
- **Local impedance measurements reveal the existence of conductivity variations (higher conductivities near the outer rim)**
- **ICP measurements show inhomogeneous aluminium distribution, indicating that variations in local conductivity are related to stoichiometric changes**

OUTLOOK

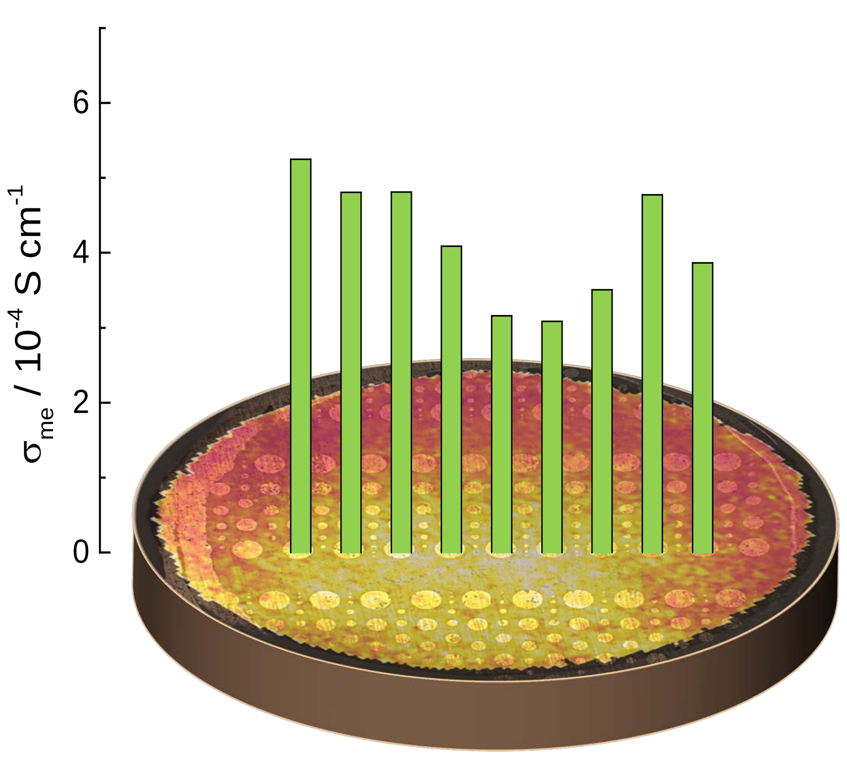


Figure 6 Sketch of measurement results when combining LA-ICP-MS and microelectrode measurements

→ Combining quantitative LA-ICP-MS and microelectrode measurements will allow to find the stoichiometry with the optimal ionic conductivity

→ Depth profiling will give further information on the overall distribution of elements

→ accurate analysis of the composition will help to improve preparation routes

References

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