New Solid-State Electrolytes for Lithium Batteries

Investigations on High-Entropy Li-Garnets

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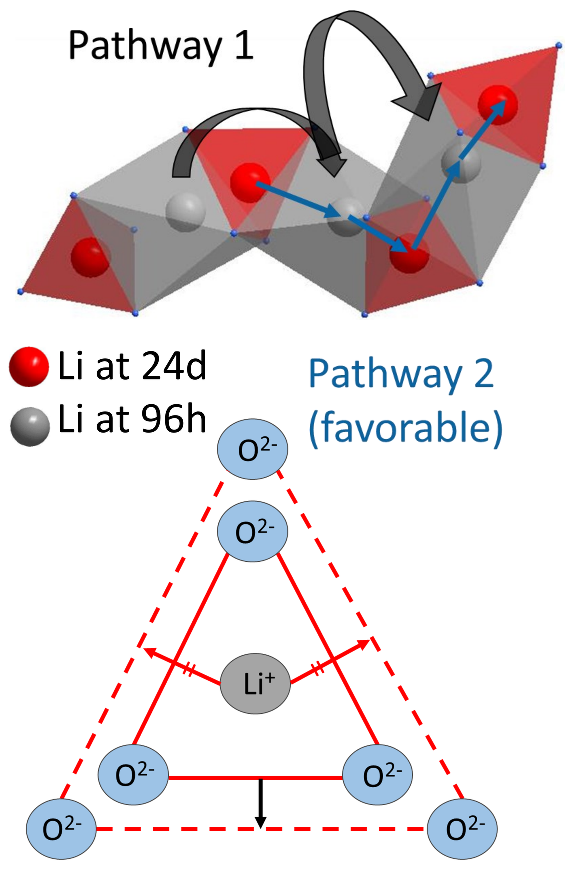
Motivation and Introduction

1

- New high-performance materials are needed to achieve higher levels of energy and power density, longer cycle life and improved safety of lithium (ion) batteries
- Solid electrolytes are promising, as they appear to allow safe operation of batteries with lithium metal anodes
- Li-garnets ($Li_7La_3Zr_2O_{12}$) offer many advantages compared to common organic liquid electrolytes [1,2]
  - Compatibility with lithium metal
  - High Li-ion conductivity ($\sigma = 10^{-4} - 10^{-3}$ S · cm^{-1})
  - Wide electrochemical window (> 6 V vs. Li/Li^+)
- Li^+ ions can conduct via two pathways [3]
  - 1: 96h ⟶ 96h ⟶ 96h
  - 2: 24d ⟶ 96h ⟶ 24d
  - Li^+ vacancies are needed to enable ion mobility
- Li^+ migration hindered by triangular O^{2-} faces [4]

⟶ Increasing the lattice size by inserting larger cations



High-Entropy Garnets

- High-entropy approach has been shown to be beneficial for ionic conductivity [5]
- High-entropy approach enables finetuning of properties
- Selection of suitable cation combination via atomic size factor δ [6]

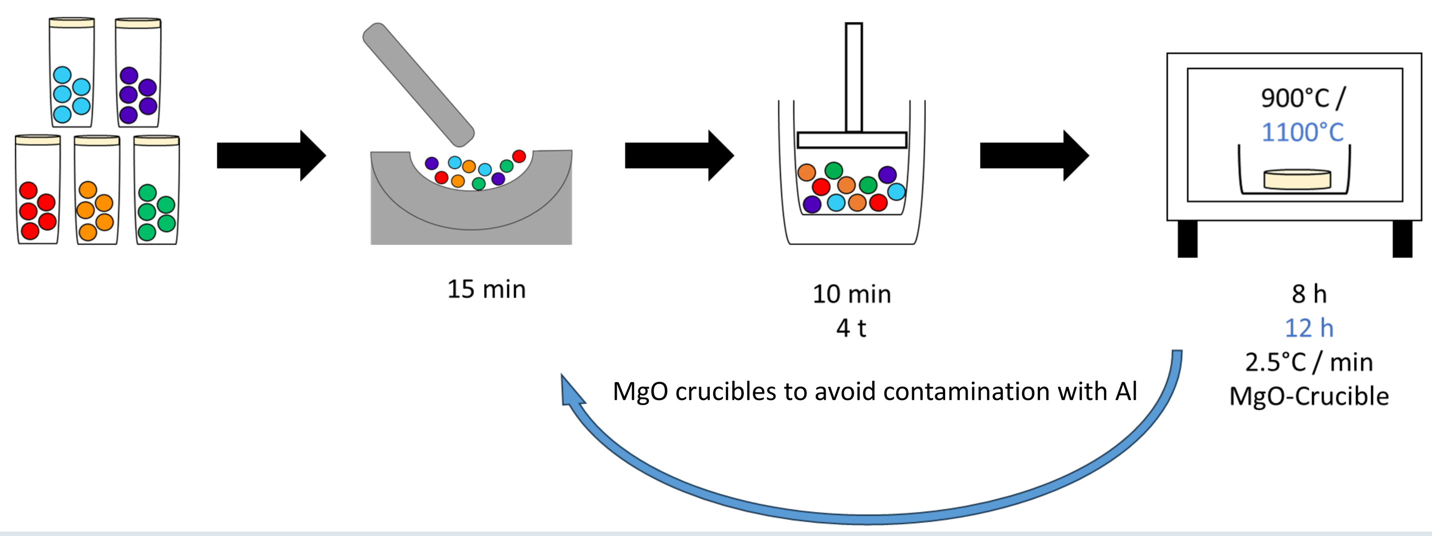
$$\delta = \sqrt{\sum_{i=1}^{N} c_i \left(1 - \frac{r_i}{\sum_{i=1}^{N} c_i r_i}\right)^2}$$

δ = atomic size factor, i = respective species, c = concentration, r = ionic radius

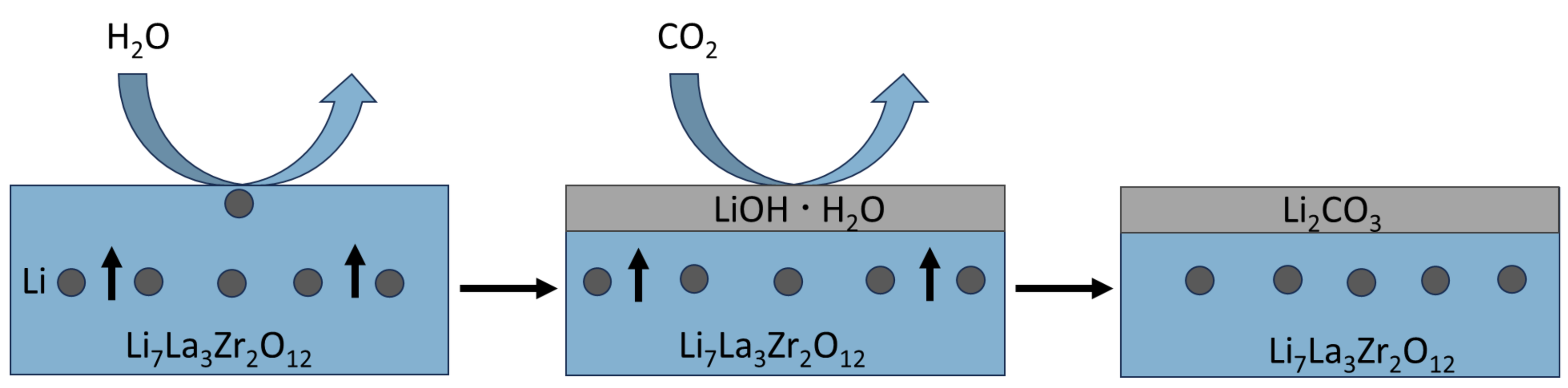
Synthesis

2

- Solid state synthesis method to prepare high-entropy Li-garnet $Li_xLa_3M_2O_{12}$ [7] (x = 6-7)
- Systematic substitution of M = Zr, Hf, Nb, Ta, Ti, Sn
- Calcination and sintering step separated (multistep)



- Li-garnets react with moisture and CO_2 in the atmosphere, which forms a Li_2CO_3 layer: [2]
  - Functions as a blocking layer between electrode and electrolyte
  - Requires samples to be stored under inert conditions

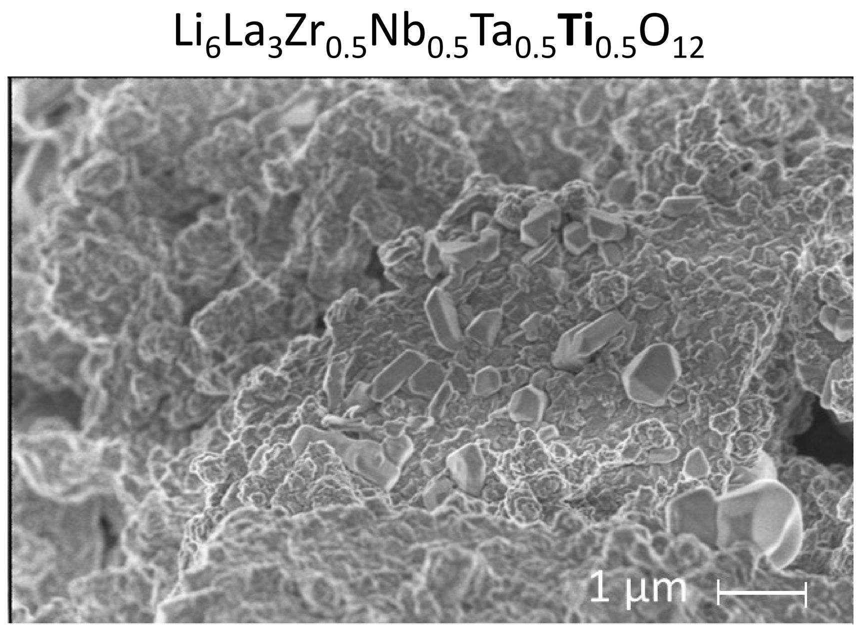


Results and Outlook

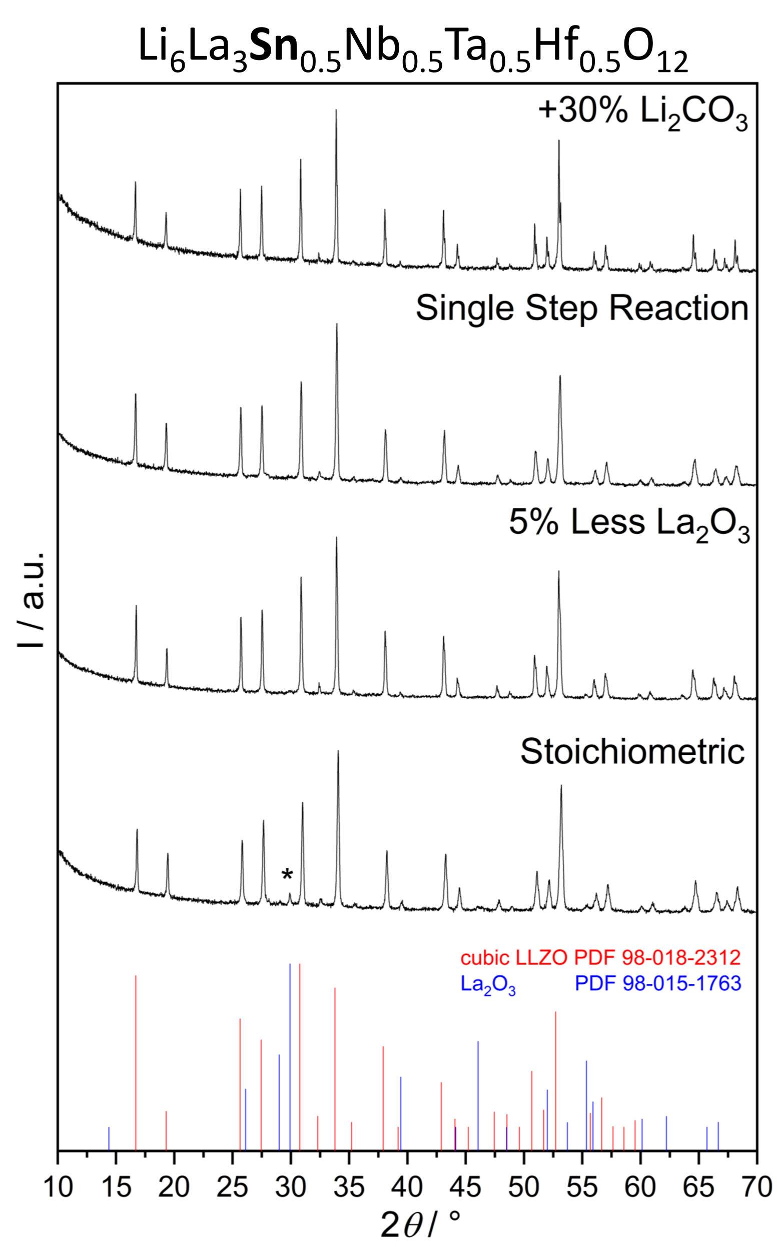
3

- Series of experiments to obtain phase pure material
- Sample purity was improved with different approaches
  - Increasing the lithium excess to offset sublimation
  - Combining calcination and sintering step
  - Less La_2O_3 to reduce side phases

$Li_6La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}\mathbf{Ti}_{0.5}O_{12}$



SEM micrograph showing the morphology of the samples.



XRD patterns of synthesis series.

- Comparable electrochemical properties between samples
- Measured conductivity comparable to literature values without further optimization

Ionic conductivity of different compositions measured using EIS.

Samples	Ionic conductivity σ at RT (S · cm^{-1})	Activation energy E_a (eV)
$Li_6La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$ [7]	$4.67 \cdot 10^{-4}$ * ~$0.9 \cdot 10^{-4}$ **	~0.25 * -
$Li_6La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$	$2.94 \cdot 10^{-4}$	0.49
$Li_6La_3\mathbf{Sn}_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$	$2.22 \cdot 10^{-4}$	0.46
$Li_{6,5}La_3Zr_{0.5}Nb_{0.5}\mathbf{Sn}_{0.5}Hf_{0.5}O_{12}$	$1.94 \cdot 10^{-4}$	0.46
$Li_6La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}\mathbf{Sn}_{0.5}O_{12}$	$2.15 \cdot 10^{-4}$	0.47

* Sintering time of 16 h. ** Sintering time of 12 h

Outlook

→ Further characterization of samples, e.g. chemical composition and homogeneity using SEM-EDX, TEM

→ Further optimization of synthesis to improve microstructure / conductivity

→ Optimization of properties using different / additional elements (Mo, Sc, Cr,…)

→ Correlation of composition-structure-properties relationship

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