

## Supplementary Materials

# Acid leaching of Al- and Ta-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) solid electrolyte

Kirstin Schneider <sup>1,\*</sup>, Vivien Kiyek <sup>2</sup>, Martin Finsterbusch <sup>2,3</sup>, Bengi Yagmurlu <sup>1</sup>, and Daniel Goldmann <sup>1</sup>

<sup>1</sup> Institute of Mineral and Waster Processing, Recycling and Circular Economy Systems, Clausthal University of Technology, Walther-Nernst-Str. 9, 38678 Clausthal-Zellerfeld, Germany

<sup>2</sup> Institute of Energy and Climate Research – Materials Synthesis and Processing (IEK-1), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

<sup>3</sup> Helmholtz Institute Münster – Ionics in Energy Storage (IEK-12), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

\* Correspondence: kirstin.schneider@tu-clausthal.de

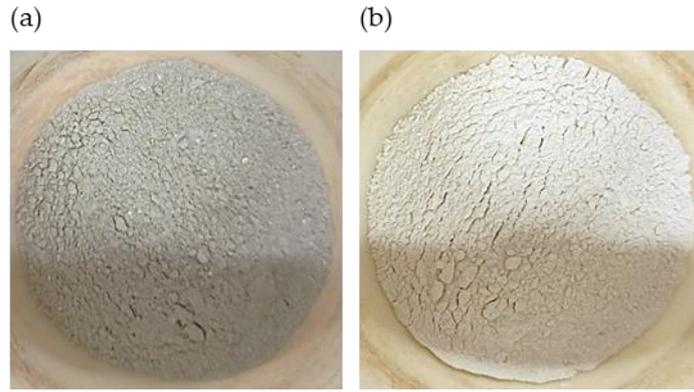
### S1 LLZO Powder Synthesis

For LLZO powder synthesis, a solid-state reaction with stoichiometrically weighed precursors was used:  $\text{LiOH}\cdot\text{H}_2\text{O}$  (98%, Merck, KGaA, Darmstadt, Germany),  $\text{La}_2\text{O}_3$  (99.9%, Merck KGaA, Darmstadt, Germany, 10 hours pre-dried at 900 °C),  $\text{ZrO}_2$  (99.5% Treibacher),  $\text{Al}_2\text{O}_3$  (99.9%, Inframat Advanced Materials LLC, Manchester, CT, USA) and  $\text{Ta}_2\text{O}_5$  (99.95% Inframat Advanced Materials LLC, Manchester, CT, USA). The precursors were ground with an electrical mortar for 1 hour (RM200, Retsch GmbH, Haan, Germany) and twice calcined in  $\text{Al}_2\text{O}_3$  crucibles at 850 °C for 20 hours to yield cubic LLZO. After each calcination step, the pellets were ground to powder and pressed to pellets again. This powder was stored in air for several months and later referred as calcined LLZO #1. The fresh synthesized powder was referred as calcined LLZO #2.

The fresh synthesized powder can be in a second way pressed to pellets (uniaxial with a 13 mm diameter at 120 MPa) and sintered on a MgO plate in an  $\text{Al}_2\text{O}_3$  crucible at 1175 °C for 10 hours. Heating and cooling were performed with 5 K/min. These pellets were later referred as sintered LLZO #2.

### S2 Thermal Treatment of Aged Calcined LLZO

The calcined LLZO #1 sample was aged due to temporary storage outside of the glove box (Figure S1 left). To restore its original properties, this batch was subjected to thermal treatment. The procedure was adapted from with the calcination process during synthesis. In an  $\text{Al}_2\text{O}_3$  crucible, 85 g of calcined LLZO #1 were covered with battery grade Al-doped LLZO powder (Sigma Aldrich). The thermal treatment was performed in a muffle furnace without air ventilation to prevent Li loss. The crucible was heated up with a heating rate of 4 K/min to reach 750 °C. This temperature was kept constant for 4 hours. For cooling, the sample was transferred into a desiccator. After the thermal treatment, the powder retained its typical white color (Figure S1 right). The loss on ignition was 4.4 %.



**Figure S1.** Thermal treatment of calcined LLZO #1 at 750 °C for 4 hours in air atmosphere. The process was performed in an Al<sub>2</sub>O<sub>3</sub> crucible. Image (a) shows the sample before and image (b) after the thermal treatment. Before thermal treatment, the sample was grey due to aging processes. After thermal treatment, the original white appearance was restored.

### S3 Sintered LLZO Pellets

Photo of sintered LLZO #2 before grinding with vibratory disk mill showing the original sample (Figure S2). The pellets had no uniform appearance related to color and dimensions.



**Figure S2.** Sample sintered LLZO #2 before grinding.

#### S4 Elemental concentration of the pregnant leach solutions

The elemental concentration of the pregnant leach solutions after 24 hours leaching is provided in Table S1.

**Table S1.** Elemental concentration of the pregnant leach solutions after 24 hours leaching.

Lixiviant	Sample	Concentration (mg/L)				
		Li	Al	La	Zr	Ta
Water	Calc. LLZO #1	1,065	<1	<1	<1	<1
	Calc. LLZO #2	1,495	112	<1	<1	<1
	Sint. LLZO #2	841	126	<1	<1	<1
Sulfuric acid	Calc. LLZO #1	2,955	244	17,976	7,152	3,088
	Calc. LLZO #2	2,464	221	19,566	6,283	2,723
	Sint. LLZO #2	2,795	328	22,055	7,284	3,443
Hydrochloric acid	Calc. LLZO #1	2,868	244	18,062	6,849	2,965
	Calc. LLZO #2	2,389	226	19,353	6,548	2,876
	Sint. LLZO #2	2,776	344	22,288	7,056	3,199
Acetic acid	Calc. LLZO #1	1,214	20	1,222	378	16
	Calc. LLZO #2	1,498	135	4,745	1,185	364
	Sint. LLZO #2	1,019	188	3,208	951	370
Formic acid	Calc. LLZO #1	1,400	90	202	612	11
	Calc. LLZO #2	1,622	154	145	452	37
	Sint. LLZO #2	1,318	253	195	622	63
Oxalic acid	Calc. LLZO #1	2,916	248	11	6,972	3,131
	Calc. LLZO #2	2,629	251	10	6,492	2,905
	Sint. LLZO #2	2,788	352	13	7,339	3,408
Citric acid	Calc. LLZO #1	1,942	124	9,791	3,946	1,391
	Calc. LLZO #2	1,757	147	9,323	2,344	903
	Sint. LLZO #2	1,419	196	8,803	2,776	1,203

#### S5 Calculations for the Assessment of Lixiviants

Five parameters were selected to evaluate the technical performance of the lixiviants studied: critical raw material (CRM) leaching efficiency, Li selectivity, La selectivity, increase of leaching efficiency, and share of residue after leaching. The equations for calculating these parameters are outlined below.

The average leaching efficiency  $\bar{Y}_{i,t}$  was calculated as described in Equation 1.

$$\bar{Y}_{i,t} = \frac{1}{n} \sum_{j=1}^n Y_{i,j,t} \quad (1)$$

where  $i$  denotes the element,  $j$  denotes the number of samples, and  $t$  denotes the leaching duration. In all experiments, the Al leaching efficiency of calcined LLZO #1 differed from that of the other two LLZO samples. As a result, this single value has been excluded from the calculation of the average Al leaching efficiency.

The CRM leaching efficiency  $Y_{CRM}$  was calculated for the CRMs Li, La, and Ta according to:

$$Y_{CRM} = \frac{\sum_{i=1}^{b_{CRM}} \bar{Y}_{i,24h}}{b_{CRM} \cdot 100\%} \cdot 100\% \quad (2)$$

where the average leaching efficiencies of the CRMs after 24 hours of leaching were normalized to 100 %. This was done by dividing the sum of the average CRM leaching efficiencies by the number of CRMs  $b_{CRM}$  multiplied by 100 %.

The Li selectivity  $S_{Li}$  was calculated according to:

$$S_{Li} = \frac{1}{b} \cdot \frac{\bar{Y}_{Li,24h}}{\sum_{i=1}^b \bar{Y}_{i,24h}} \quad (3)$$

where  $b$  denotes the number of elements analyzed. The calculation of the La selectivity  $S_{La}$  is the same as the calculation of the Li selectivity:

$$S_{La} = \frac{1}{b} \cdot \frac{\bar{Y}_{La,24h}}{\sum_{i=1}^b \bar{Y}_{i,24h}} \quad (4)$$

If La was not leached with the tested lixiviant, the La selectivity  $S_{La}$  was calculated for the residue. This was calculated as described in Equation 5.

$$S_{La} = \frac{1}{b} \cdot \frac{100 - \bar{Y}_{La,24h}}{\sum_{i=1}^b (100 - \bar{Y}_{i,24h})} \quad (5)$$

The increase of leaching efficiency  $\Delta Y$  was calculated according to:

$$\Delta Y = \frac{1}{n} \sum_{j=1}^n \sum_{i=1}^b \frac{Y_{i,j,24h}}{Y_{i,j,3h}} \cdot x_{0,i,j} \quad (6)$$

where  $x_{0,i,j}$  is the normalized content of the element  $i$  in the feed material of sample  $j$ .

The share of solid residue after leaching  $w_{residue}$  was calculated as mass percent according to:

$$w_{residue} = \frac{1}{n} \sum_{j=1}^n \frac{m_{residue,j}}{m_{feed,j}} \cdot 100\% \quad (7)$$

where  $m_{residue,j}$  is the mass of dried residue of sample  $j$  and  $m_{feed,j}$  is the mass of feed material of sample  $j$ .