ON THE DEVELOPMENT OF RECYCLING STRATEGIES FOR ALL-SOLID-STATE LITHIUM-ION BATTERIES WITH OXIDE ELECTROLYTES

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Introduction

Recycling of (all-solid-state) LIBs: Current state

- Less than 5% of the spent LIBs are recycled in the US and the EU [1]
- Current studies mainly concern about recycling of liquid-based electrolyte LIBs [2]
- Recycling of all-solid-state LIBs, which are expected to enter the battery market, is more challenging due to complexity of the systems
- Only some limited investigations have been performed on all-solid-state LIBs [3]
- Common recycling techniques for LIBs [4]: hydrometallurgical, mechanical and physical methods
- Are these common recycling techniques adoptable for recycling of all-solid-state LIBs?

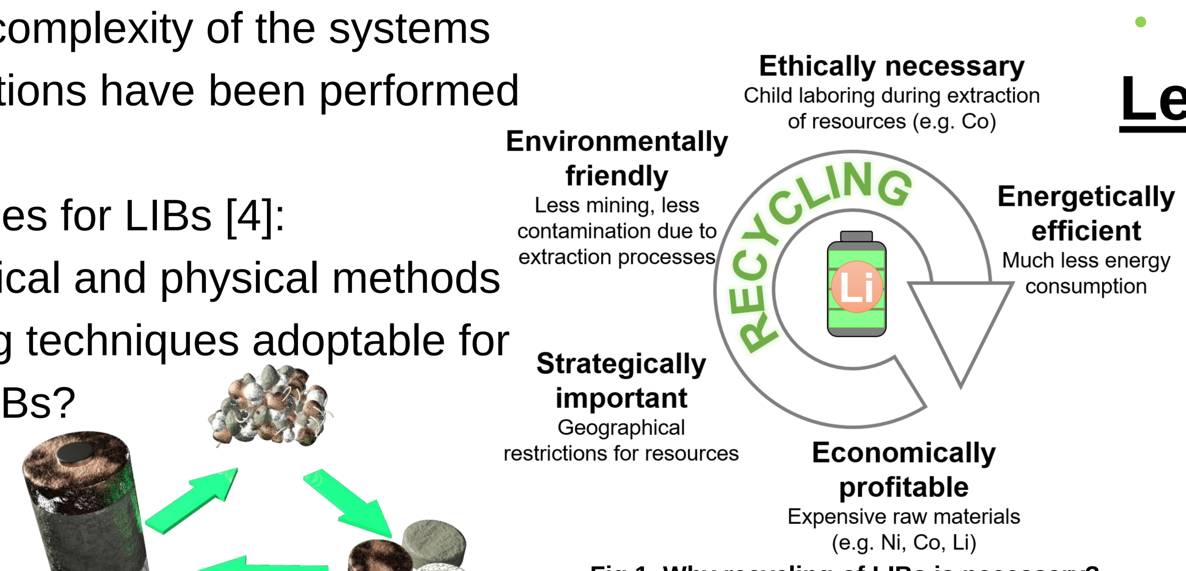

Fig.1. Why recycling of LIBs is necessary?

Materials and Methods

Test cell composition

- Solid electrolyte: Cubic Garnet Al-doped LLZO ($Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$)
- Cathode composite: LFP (carbon coated $LiFePO_4$) 40 wt% + LLZO 40 wt% + C 10 wt% + PVDF 10 wt%
- Anode composite: LTO ($Li_4Ti_5O_{12}$) 40 wt% + LLZO 40 wt% + C 10 wt% + PVDF 10 wt%

Leaching / Precipitation process

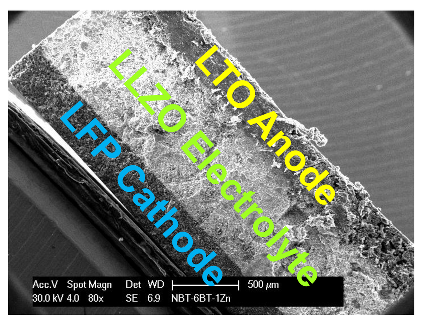

Fig. 2. Cross sectional SEM image of a LFP/LLZO/LTO pellet used in this study

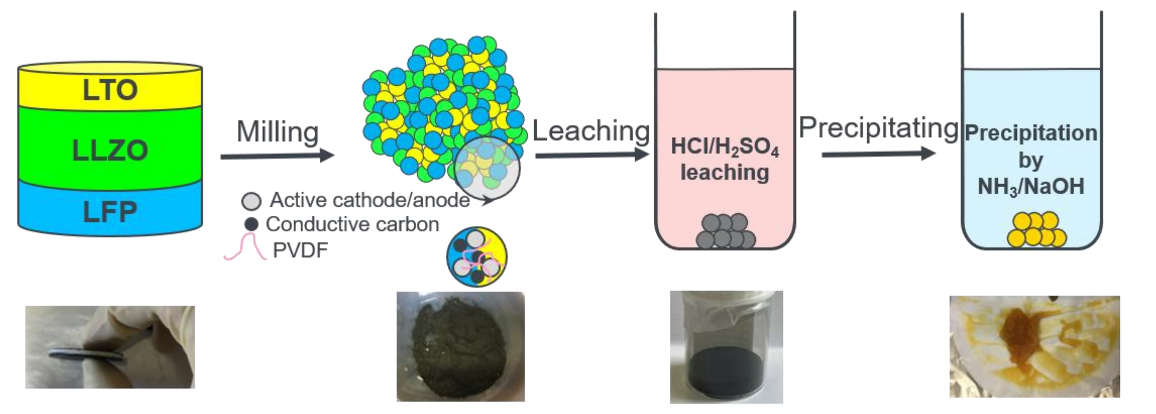

Fig. 3. A general overview of the experimental procedure followed in this study based on ref. [5]

Results and Discussion

HCl Leaching

- Pure LLZO was found to be stable in the HCl leaching solution
- In contrast LLZO is decomposed by HCl leaching within the LFP/LLZO/LTO mixture
- Leaching time influences the amount of dissolved LLZO

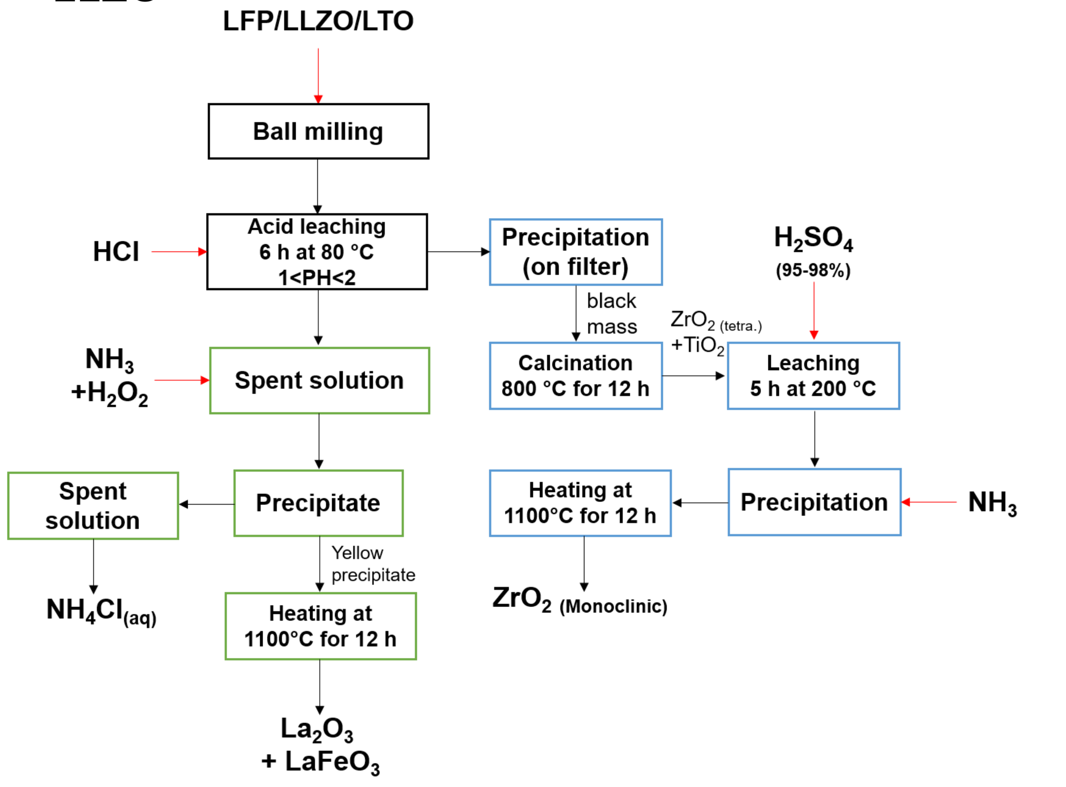

Fig. 4. HCl Leaching process of LFP/LLZO/LTO mixture and the obtained products

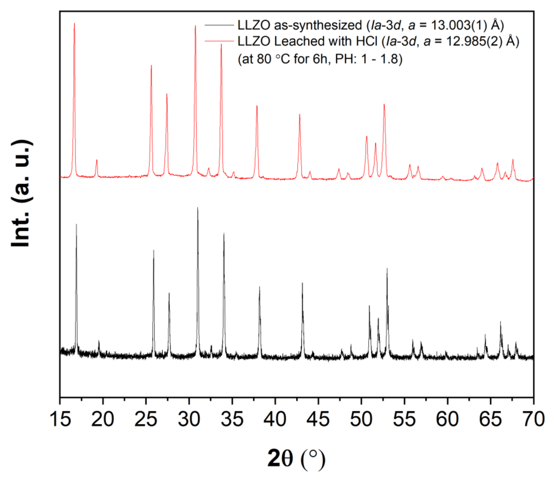

Fig. 5. XRD pattern of as-synthesized and leached (in the HCl solution) pure LLZO

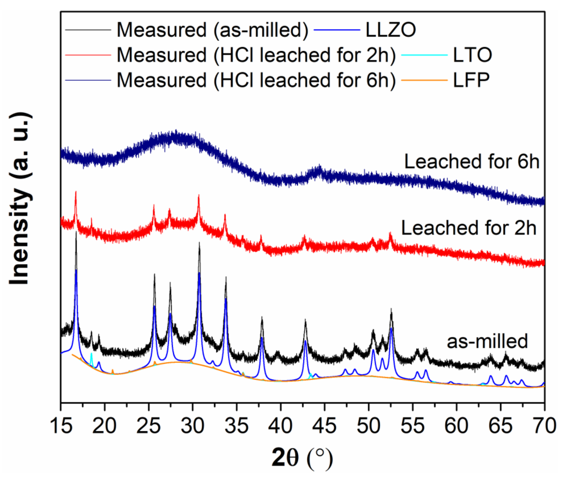

Fig. 6 XRD pattern of the as-milled and leached (at different leaching time) of the LFP/LLZO/LTO mixture

- A mixture of ZrO_2 / TiO_2 is obtained from the precipitate after HCl leaching
- Obtained ZrO_2 can be further purified by H_2SO_4 (high concentration) washing
- More than 99% of ZrO_2 can be recycled
- La_2O_3 can be extracted from the spent solution

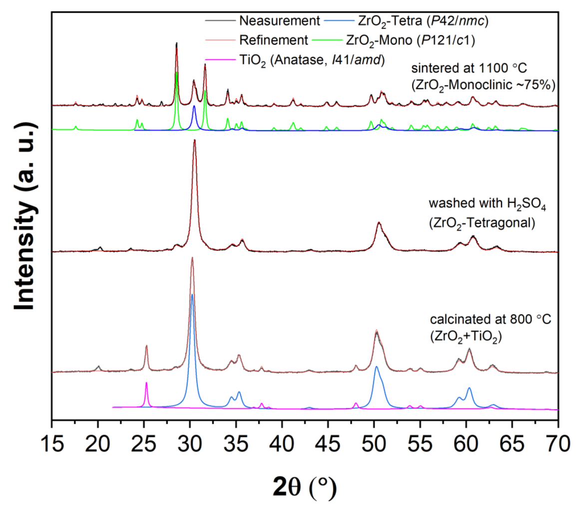

Fig. 7. XRD pattern of the recovered ZrO_2

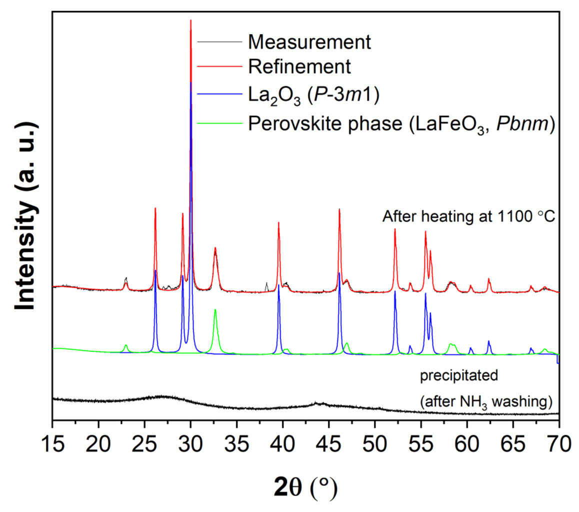

Fig. 8. XRD pattern of the precipitate by NH_3 washing and recycled La_2O_3

Recycled compounds	ZrO_2 / TiO_2	La_2O_3 / $LaFeO_3$
Expected weight ratio	80.8% / 19.1%	77.9% / 22.1%
Obtained weight ratio	80.1(3)% / 19.9(3)%	77.7(3)% / 22.3(3)%

Reformation of LLZO from recycled products

- Cubic garnet-type phase of LLZO can be recycled from the recovered ZrO_2/La_2O_3
- The impurity phases are due to impurity in recovered ZrO_2 and La_2O_3
- Recovery of lithium is still in progress

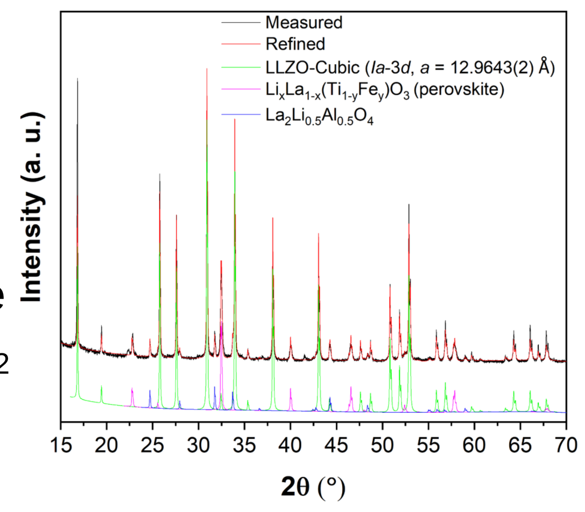

Fig. 9. XRD pattern of the recycled LLZO

H_2SO_4 Leaching

- TiO_2 and a part of ZrO_2 can be obtained from precipitate after H_2SO_4 leaching
- $La_2Zr_2O_7$ can be extracted and purified

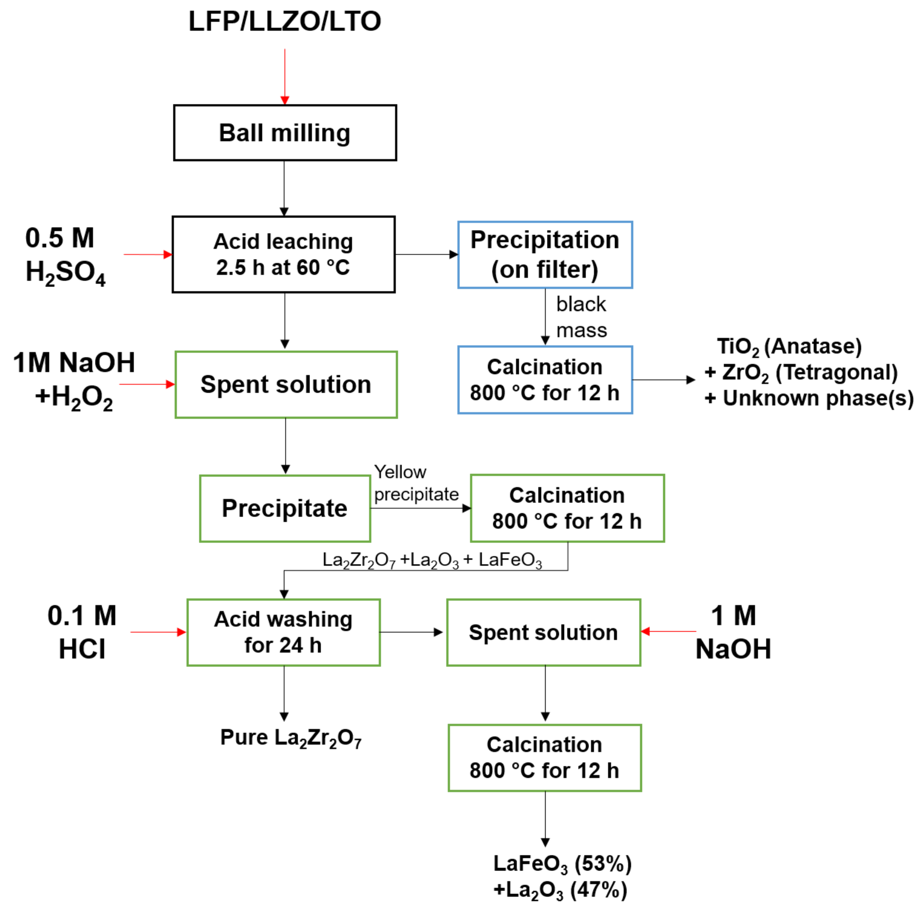

Fig. 10. H_2SO_4 Leaching process of LFP/LLZO/LTO mixture and the obtained products

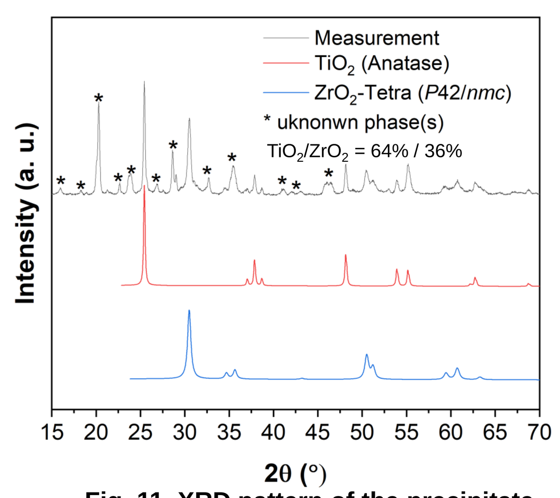

Fig. 11. XRD pattern of the precipitate products after leaching by H_2SO_4 (calcinated)

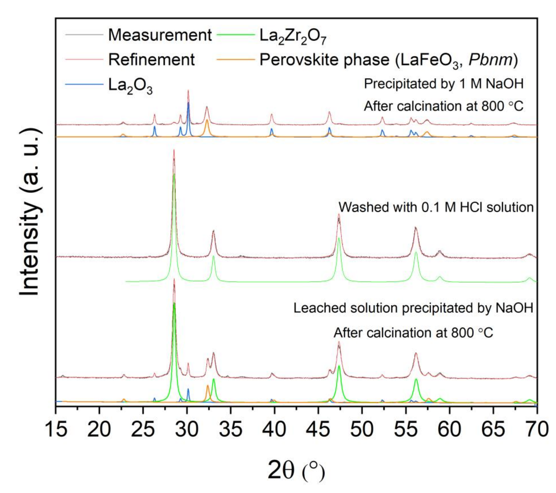

Fig. 12. XRD pattern of the products after precipitation by NaOH

Conclusions

- LFP/LLZO/LTO complex system can be recycled in form of oxides (e.g. ZrO_2, TiO_2, La_2O_3 and $LaFeO_3$)
- Lithium is still missing: perhaps recovered Li_2O reacted to the Al_2O_3 crucible
- Cubic garnet-type LLZO compound can in principle be recycled from the recovered oxides
- The purity of the recovered LLZO still remains a challenge: further purification of the recovered precursors is required
- How would be the electrochemical properties of a cell made by recycled components?

Acknowledgments

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