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TOWARDS RECYCLING OF THIOPHOSPHATE-BASED ALL-SOLID-STATE LITHIUM-ION BATTERIES

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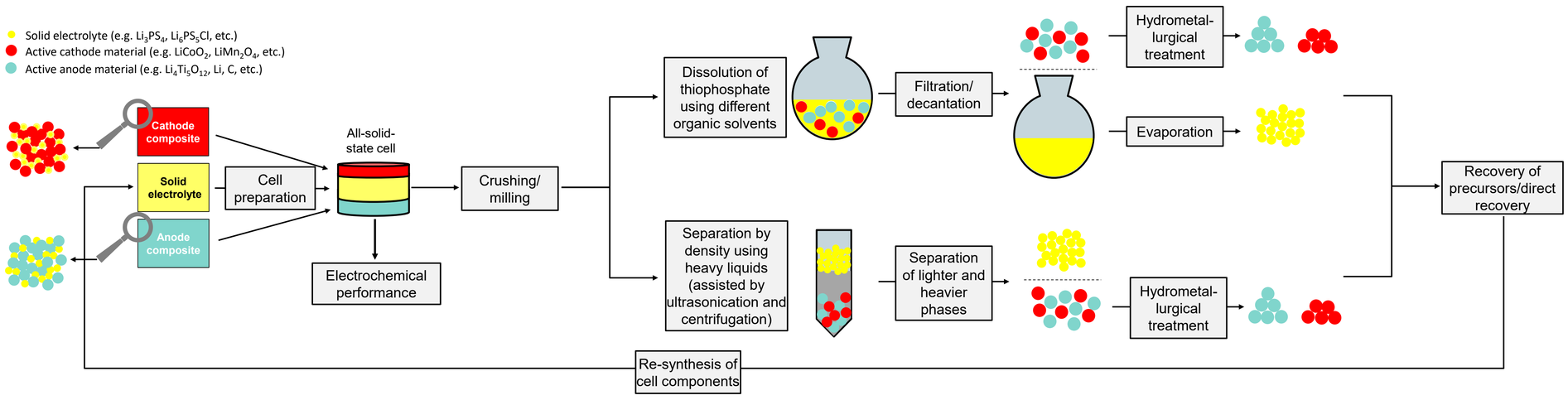
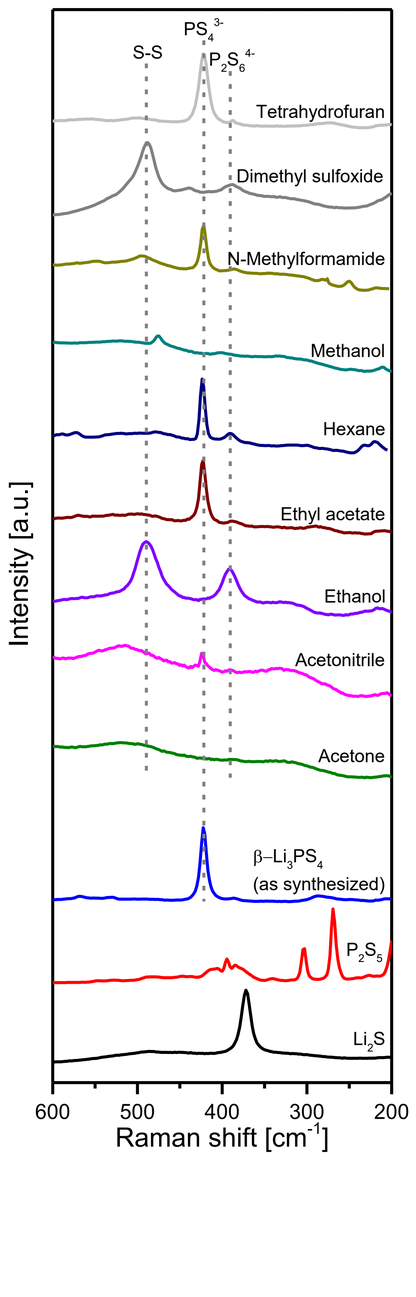
INTRODUCTION

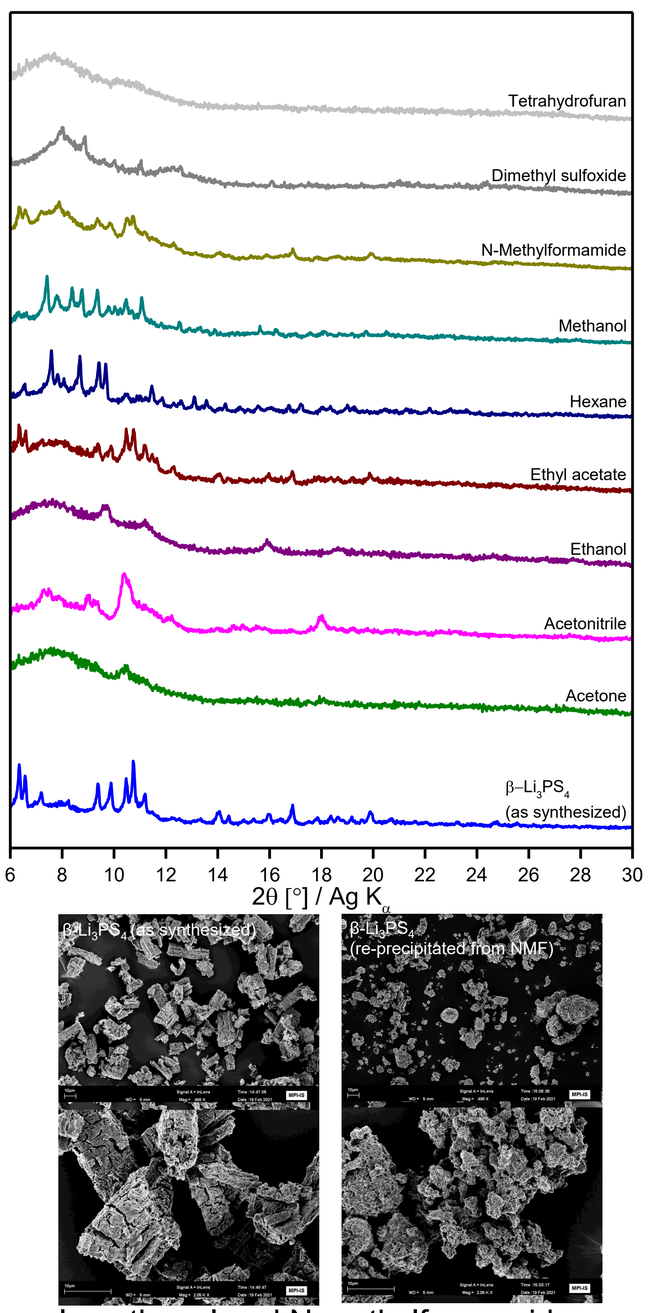
- Thiophosphate electrolyte-based all-solid-state Li-ion batteries are highly promising for future commercial applications
- The development of recycling strategies for such next-generation batteries before market entry offers great potential since battery engineering targeted on better recyclability is possible
- Two recycling strategies are exemplarily studied based on the electrolyte β-Li_3PS_4, synthesized via a solution-based process [1], and the active electrode materials $LiMn_2O_4$ and $Li_4Ti_5O_{12}$



DISSOLUTION OF THIOPHOSPHATE

→ Attempts to dissolve 100 mg of β-Li_3PS_4 in 50 ml of the respective organic solvent





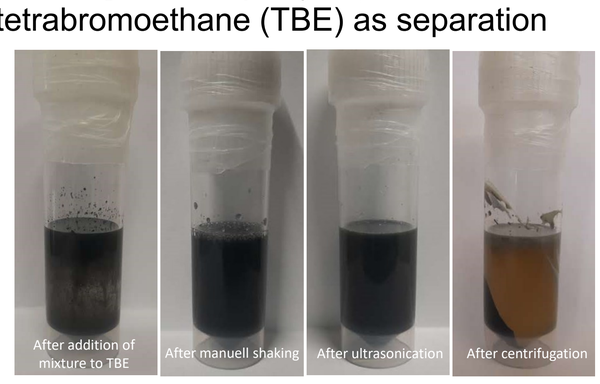
- Complete dissolution of β-Li_3PS_4 in ethanol, methanol and N-methylformamide (NMF)
- Retention of PS_4^{3-} thiophosphate units after removal of acetone, ethyl acetate, hexane and NMF
- Partial recovery of β-Li_3PS_4 after removal of ethyl acetate, methanol and NMF
- Morphology of the particles changes significantly after the re-precipitation from NMF

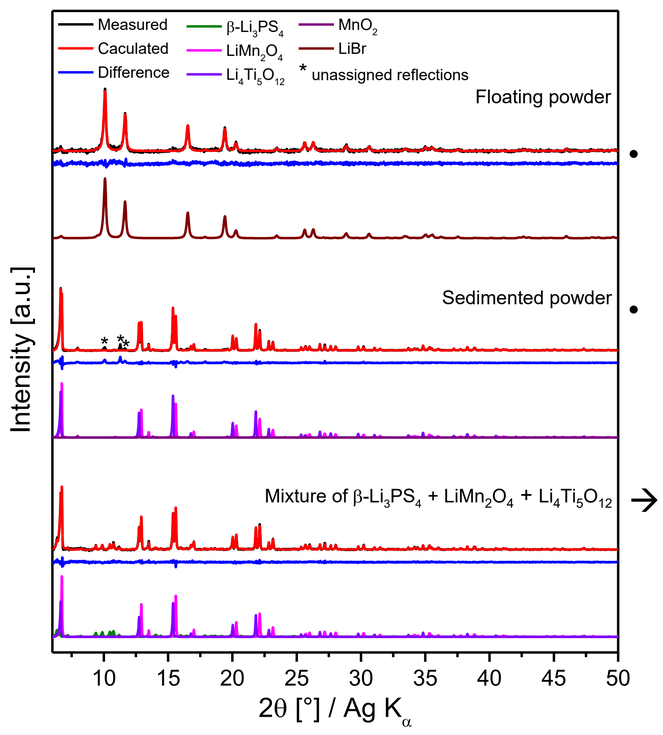
→ Most promising results so far using NMF as solvent

SEPARATION BY DENSITY

→ Attempt to separate 300 mg of a mixture containing 33 wt% β-Li_3PS_4, 33 wt% $LiMn_2O_4$ and 33 wt% $Li_4Ti_5O_{12}$ using 10 ml tetrabromoethane (TBE) as separation medium

Densities: β-Li_3PS_4: 1.9 g/cm^3
$LiMn_2O_4$: 4.1 g/cm^3
$Li_4Ti_5O_{12}$: 3.5 g/cm^3
TBE: 3.0 g/cm^3





- Floating phase contains only LiBr as crystalline phase pointing to an undesired reaction between β-Li_3PS_4 and TBE
- Sediment contains primarily $LiMn_2O_4$ and $Li_4Ti_5O_{12}$, a minor degree of decomposition is found to take place (formation of MnO_2 and presence of additional unassigned reflections)

→ While the separation of the active electrode materials from the electrolyte is possible (allowing for a hydrometallurgical treatment), the recovery of β-Li_3PS_4 (or of suitable precursors) remains challenging

Outlook

- Optimization of dissolution process and thermal post-treatments for a preferably full direct recovery of β-Li_3PS_4
- Extension of separation by density study to other heavy liquids (e.g., diiodemethane or dibromomethane)
- Hydrometallurgical treatment [2, 3] of active electrode materials to recover precious metals
- Re-synthesis of electrolyte and active electrode materials
- In-depth characterization of obtained products by means of X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy, etc.
- Electrochemical characterization of pristine and recycled electrolyte and cells with pristine and recycled electrolyte and active electrode materials

ACKNOWLEDGEMENTS

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