

## Supplementary information

### Pseudo-ternary $\text{LiBH}_4\cdot\text{LiCl}\cdot\text{P}_2\text{S}_5$ system as structurally disordered bulk electrolyte for all-solid-state lithium batteries

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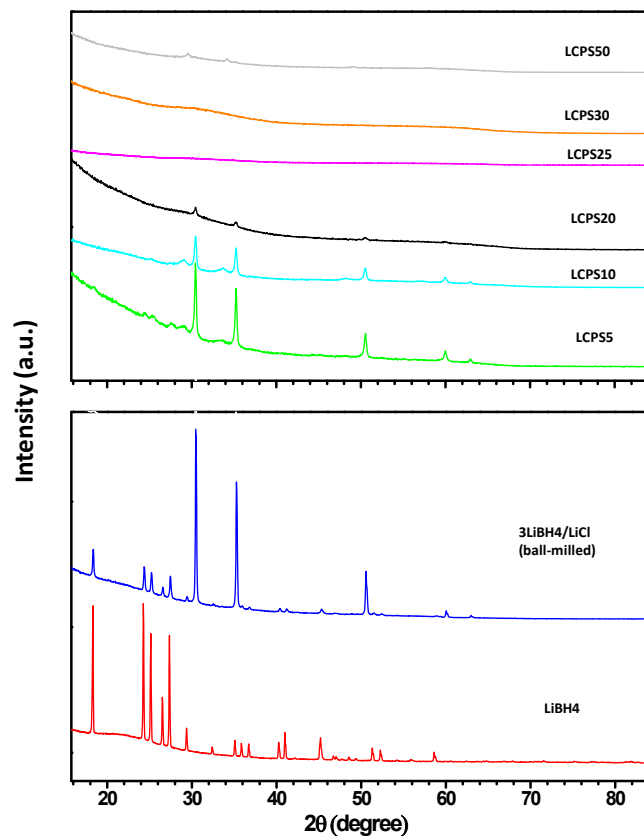
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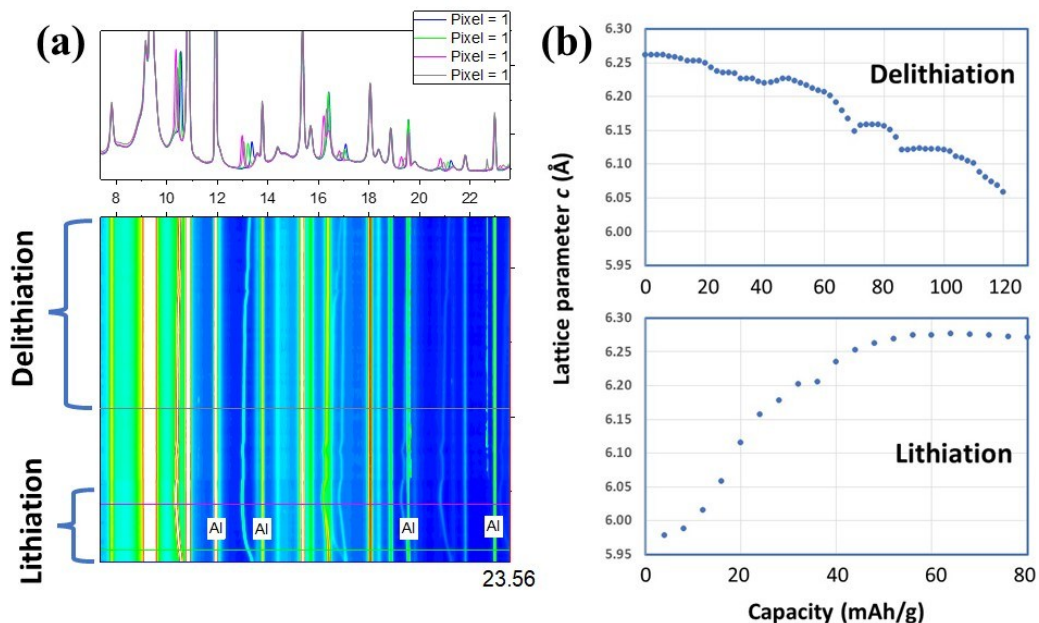
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## Experimental

Lab-PXD data were obtained with a Bruker AXS D8 Advance diffractometer equipped with a Göbel mirror and a LynxEye 1D strip detector. The patterns were obtained in a Debye–Scherrer geometry using Cu K $\alpha$  radiation (1.5418 Å) and rotating glass capillaries, filled and sealed under Ar atmosphere. Phase identification from the PXD data was performed using the DIFFRAC.SUITE EVA software with the PDF-4 database.



**Figure S1.** Lab-PXD patterns ( $\text{Cu } K_{\alpha}$ ,  $1.5418 \text{ \AA}$ ) of  $\text{LiBH}_4$ , ball-milled  $3\text{LiBH}_4\text{-LiCl}$ , and in the top figure  $\text{LiBH}_4\text{-LiCl-P}_2\text{S}_5$  based mixed systems and further ball-milling with Spex milling; e.g. LCPS5 corresponds to  $95(3\text{LiBH}_4/\text{LiCl}) - 5\text{P}_2\text{S}_5$ , and similar for the other compositions.



**Figure S2.** (a) 2D *in-operando* SR-PXD patterns of LCPS10-based battery cell during 1 cycle using  $\text{TiS}_2$  electrode (extracted 1D pattern is shown on the top); (b) evolution of the *c*-axis during lithiation/delithiation of  $\text{TiS}_2$ . The cell was relaxed after lithiation for few hours while the PXD data are continuously collected.