

Supporting Information

Influence of the Initial Li/Co Ratio in LiCoO₂ on the High Voltage Phase Transitions Mechanisms

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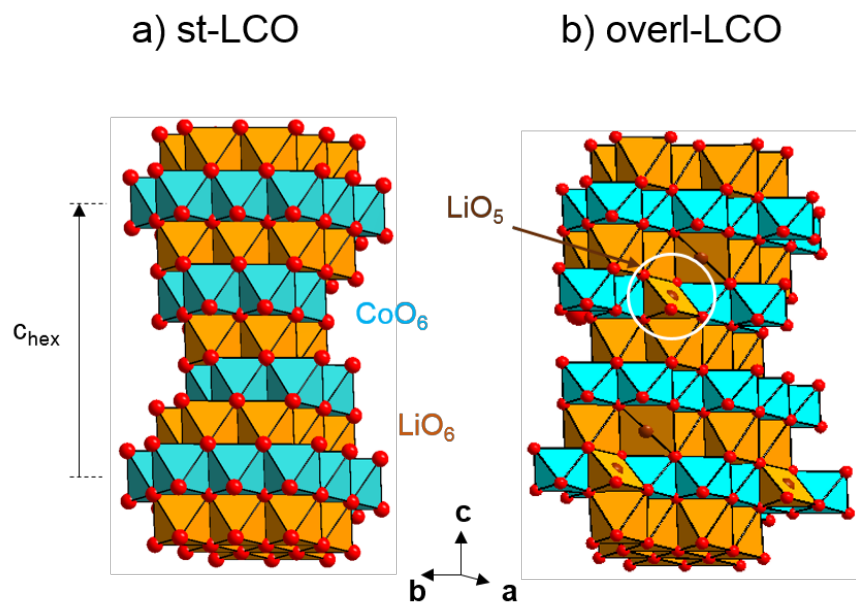


Figure S1. Schematic representation of a) st-LCO and b) overl-LCO structures. In overl-LCO, the excess of Li is believed to be accommodated by Li in the Co layer associated with a O vacancy corresponding to the $\text{Li}_{1+t}\text{Co}_{1-t}\text{O}_{2-t}$ formula.

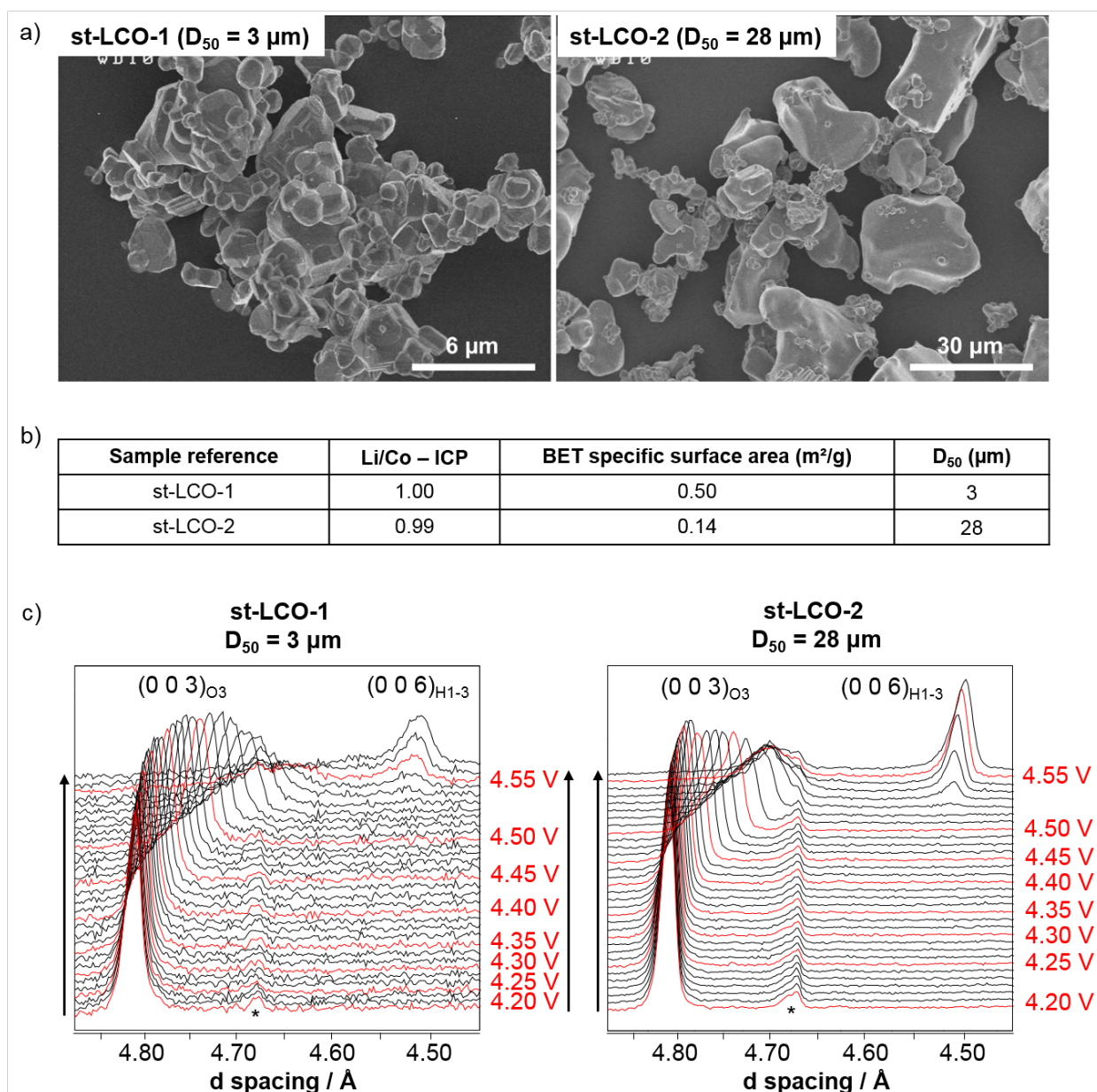


Figure S2. a) Scanning electron micrographs obtained for two different st-LCO materials with different particles size in the micrometer scale. ICP measured Li/Co ratios, BET specific surface areas and D_{50} for both samples are given in table b). c) Cumulated XRD patterns recorded *in situ operando* during the charge of the two stoichiometric LCO samples between $\sim 4.20 \text{ V} - 4.60 \text{ V}$ plotted as a function of d spacing. It represents here the average distance between two layers of CoO_6 units. XRD patterns are plotted from the bottom to the top as we charge the compounds. The peak identified with (*) is a line from the cell.

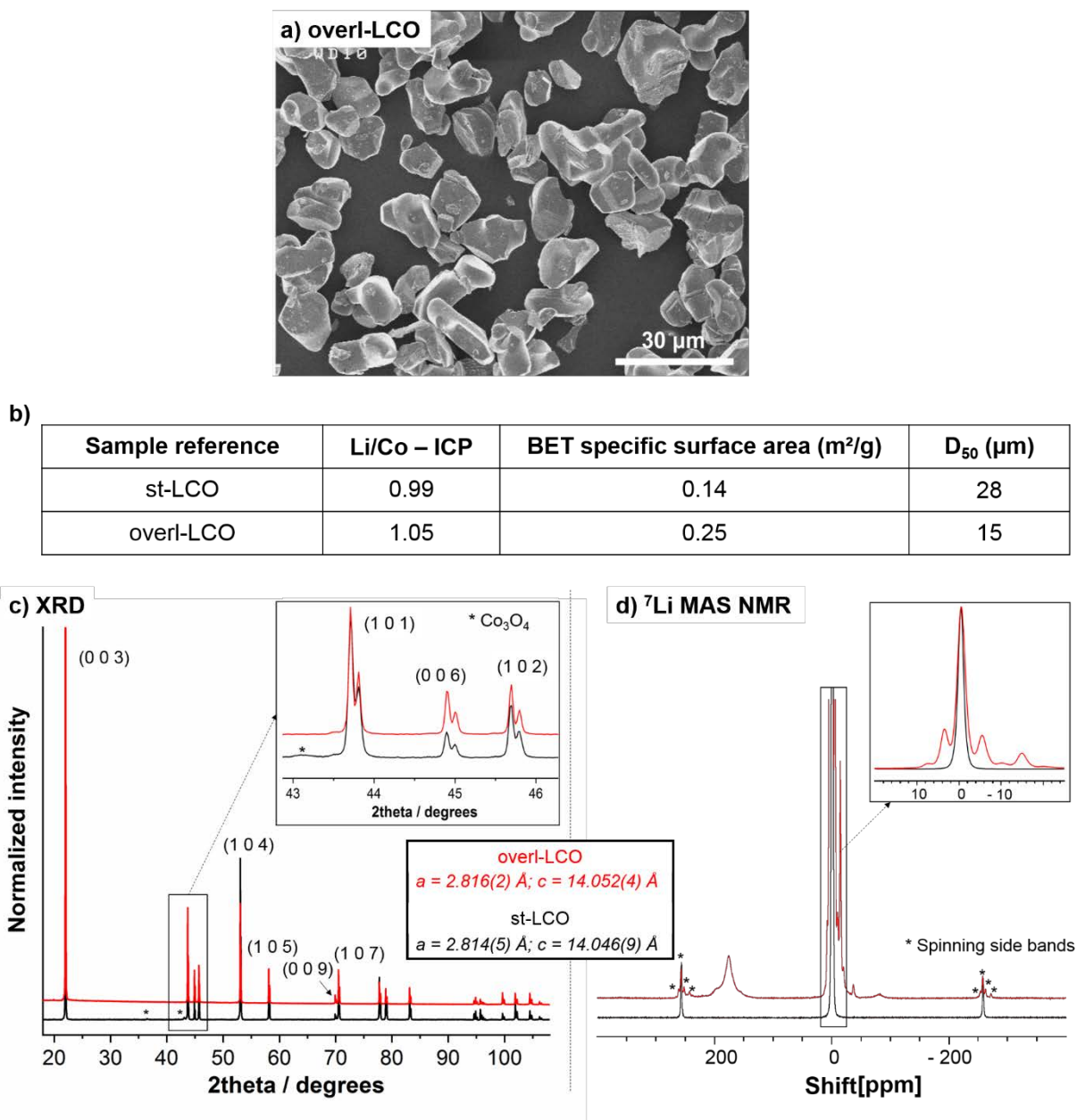


Figure S3. a) Scanning electron micrographs obtained for overl-LCO. ICP measured Li/Co ratios, BET specific surface areas and D₅₀ for the former overl-LCO as compared to st-LCO-2 are given in table b). Associated XRD patterns recorded using a cobalt source ($\lambda(K\alpha_1) = 1.789$ Å; $\lambda(K\alpha_2) = 1.793$ Å) and ⁷Li MAS NMR spectra for each LCO sample are respectively plotted in c) and d). Zooms are provided for both techniques, and Miller indexes (*h k l*) for some of the most intense peaks as well as cell parameters can be found on the diffraction patterns.