

ELECTROCHEMICAL ALKALI-ION EXCHANGE IN ELECTRODE MATERIALS FOR SECONDARY BATTERIES

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MOTIVATION

- Room-temperature Na/K-ion batteries currently attract increasing interest in research and industry → Extensive research on novel anode and cathode materials
- Electrochemical alkali-ion exchange technique (Fig. 1) is considered a powerful tool to
 - Synthesize novel active materials
 - Study Li/Na/K analogous intercalation compounds, hybrid materials and Na/K doped Li-materials
 - Generate fundamental insights regarding the differences of Li-, Na- and K-ion analogues intercalation materials
- Alkali-ions stored in an intercalation material are electrochemically extracted and replaced by another ionic species
- Preservation of a desired (metastable) host structure or to prepare mixed ionic species (charge controlled)

- The substitution of Li-ions by Na-ions in the framework of the cathode material LiCoO_2 is investigated for the first time
- Comprehensive electrochemical studies are complemented by operando and ex-situ materials characterization to understand the Li-Na substitution mechanism and corresponding phase evolution behavior

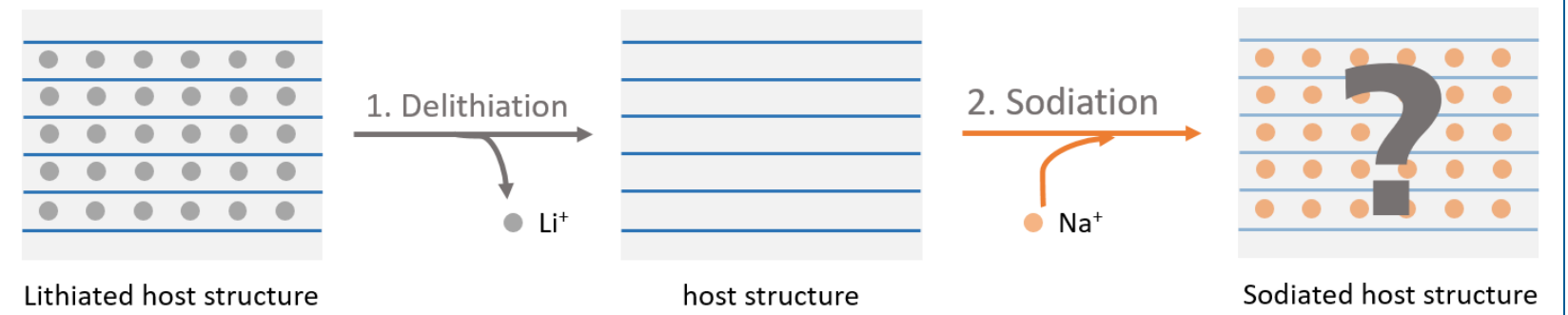


Fig. 1: Electrochemical alkali-ion exchange technique (e. g.: Li-Na-exchange).

RESULTS

1. Delithiation of LiCoO_2

- Delithiation to 4.2 V generates substoichiometric $\text{Li}_{0.5}\text{CoO}_2$

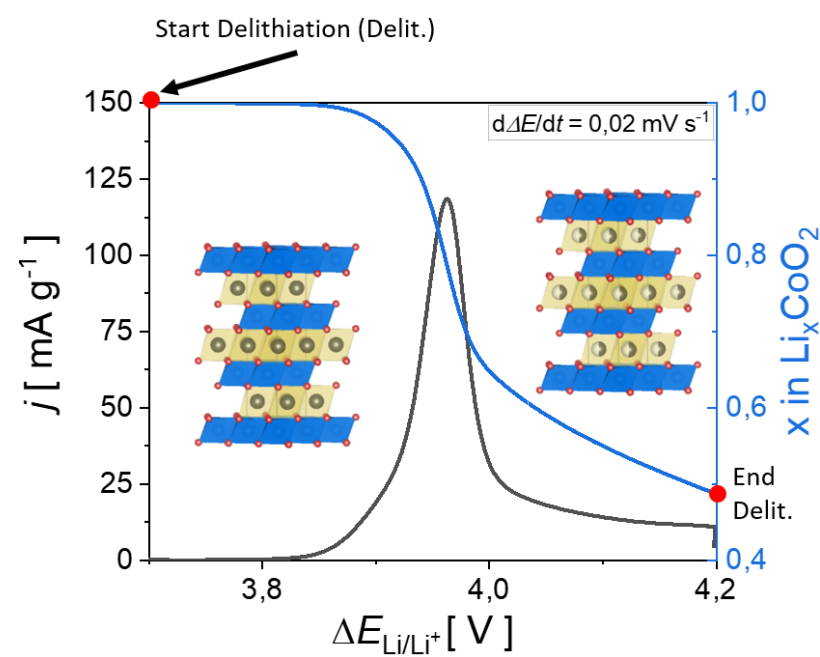


Fig. 2: Specific current measured during a linear sweep scan in the Li-setup and corresponding change in stoichiometry computed from the consumed charge during delithiation of LiCoO_2 .

2. Sodiation of $\text{Li}_{0.5}\text{CoO}_2$

- Li-ions, Na-ions or both species take part in the reactions? → operando XRD measurements

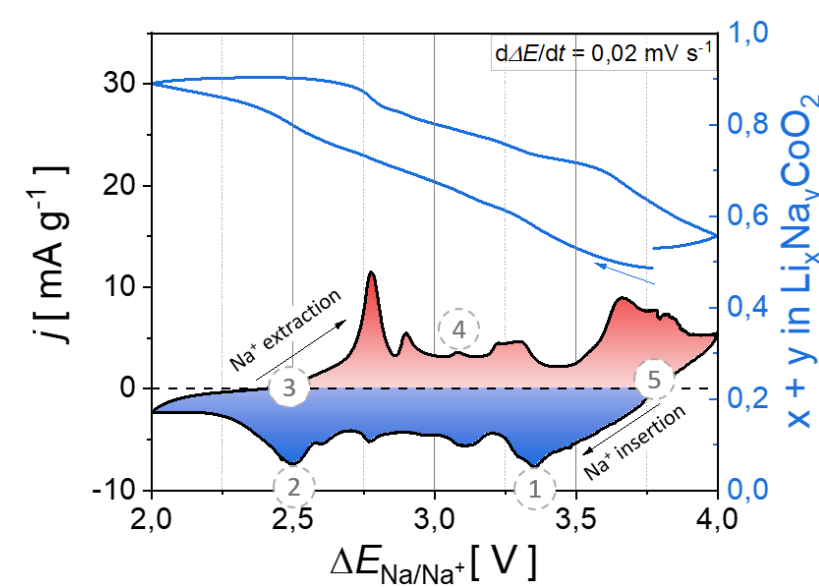


Fig. 3: CV obtained from the partially delithiated $\text{Li}_{0.5}\text{CoO}_2$ electrode in Na-ion containing electrolyte and corresponding change in stoichiometry in a potential range of 2.0–4.0 V vs. Na/Na+.

3. Operando XRD investigations

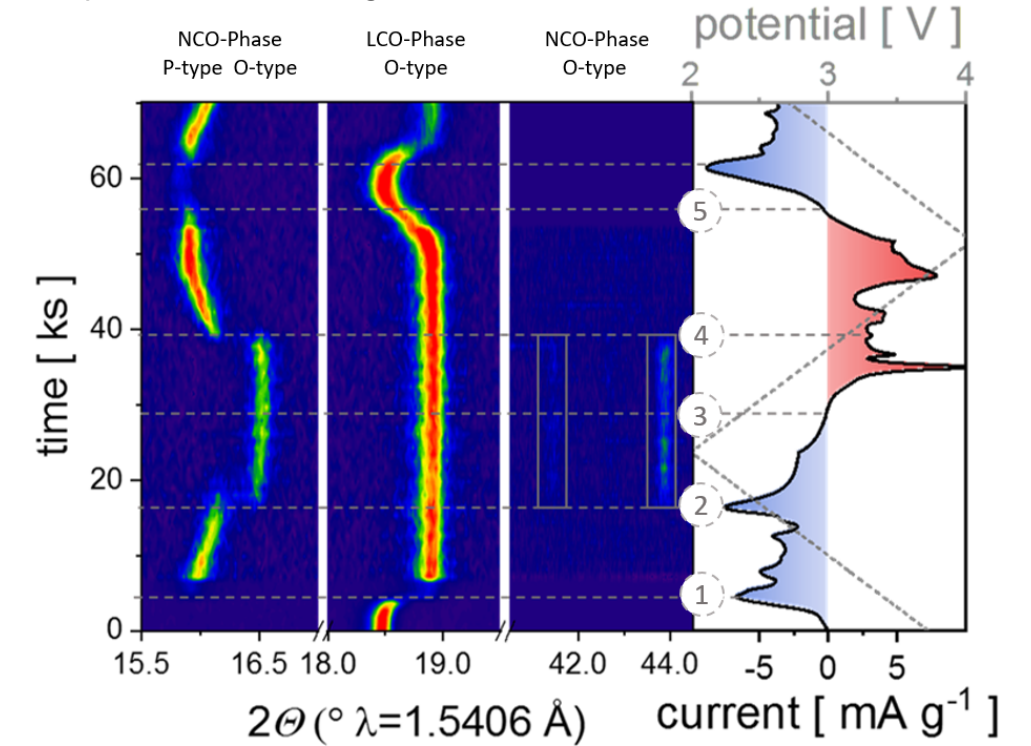


Fig. 4: Operando XRD pattern for three selected angle regions (O-type LCO ($2\theta = 18.0 - 19.5^\circ$), P-type NCO ($2\theta = 15.5 - 17.0^\circ$), O-type NCO ($2\theta = 41.0 - 44.5^\circ$)) and current response during sodium insertion and extraction as a function of time (potential). The dashed lines indicate particularly noticeable states during electrochemical cycling.

DISCUSSION

Formation of Li- and Na-rich domains during Na-insertion into $\text{Li}_{0.5}\text{CoO}_2$ due to the different ionic radii of Li- and Na-ions and the corresponding lattice mismatch

- Reversible cycling of the Li-Na-mixed intercalation compound is dominated by Na-insertion and -extraction

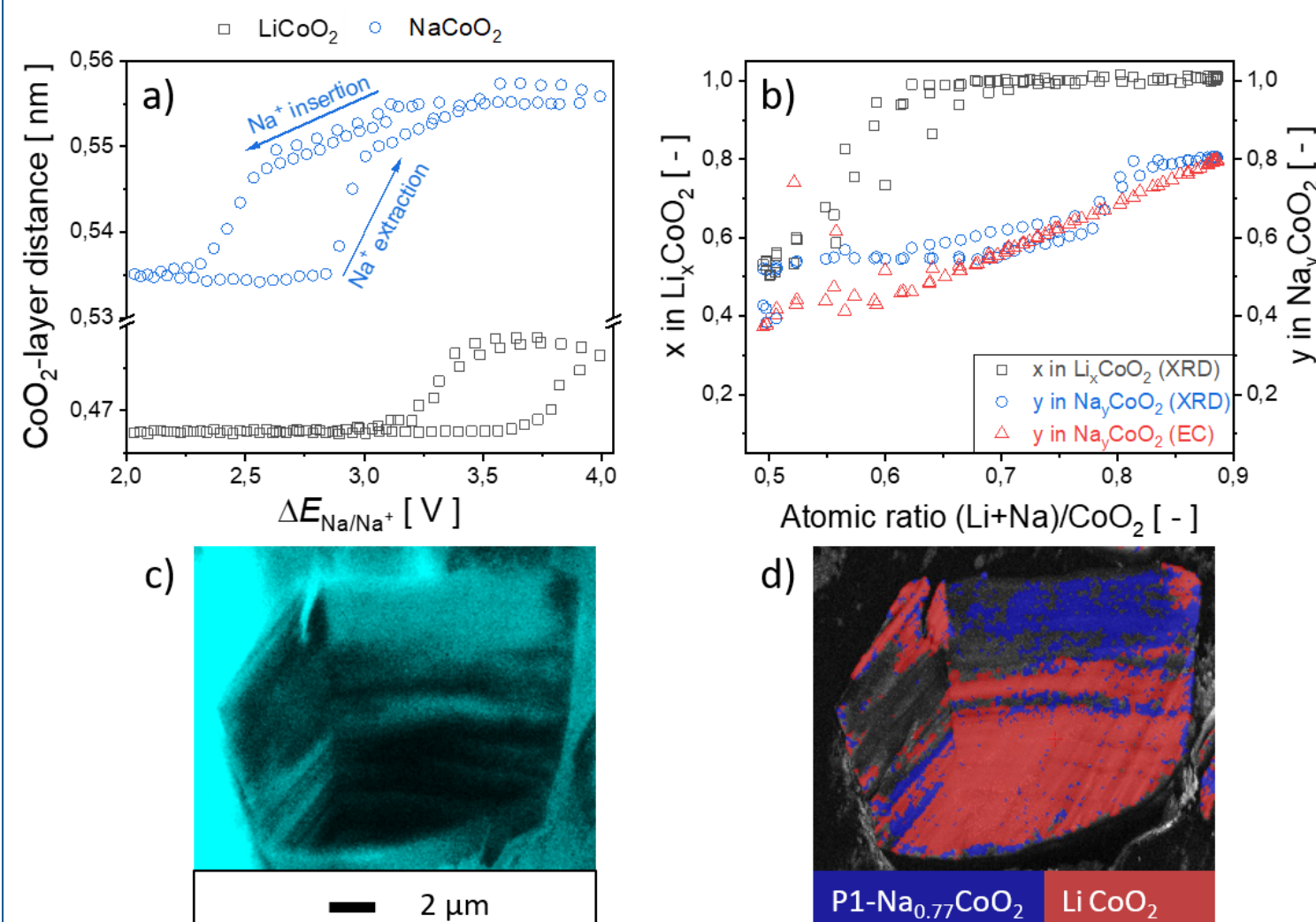


Fig. 5: a) Potential dependence CoO_2 -layer distance in Li_xCoO_2 and Na_yCoO_2 phases. b) Stoichiometric changes of Li_xCoO_2 and Na_yCoO_2 phases estimated from the XRD results and the consumed charge (EC) during sodium insertion and extraction. c) Na-distribution (EDS). d) Phase-distribution of LiCoO_2 and P1-type $\text{Na}_{0.77}\text{CoO}_2$ (EBSD).

MECHANISTIC MODEL OF THE PARTIAL LI-NA SUBSTITUTION IN LCO

- a) The delithiation step generates a sub-stoichiometric $\text{Li}_{0.5}\text{CoO}_2$.
- b) Phase separation and formation of Na-rich and Li-rich domains.
- b - c) Growth of Na-rich and shrinkage of Li-rich domains
- c - d) Na-insertion in Na-rich domains
- d) Final state of the Li-Na-mixed intercalation compound

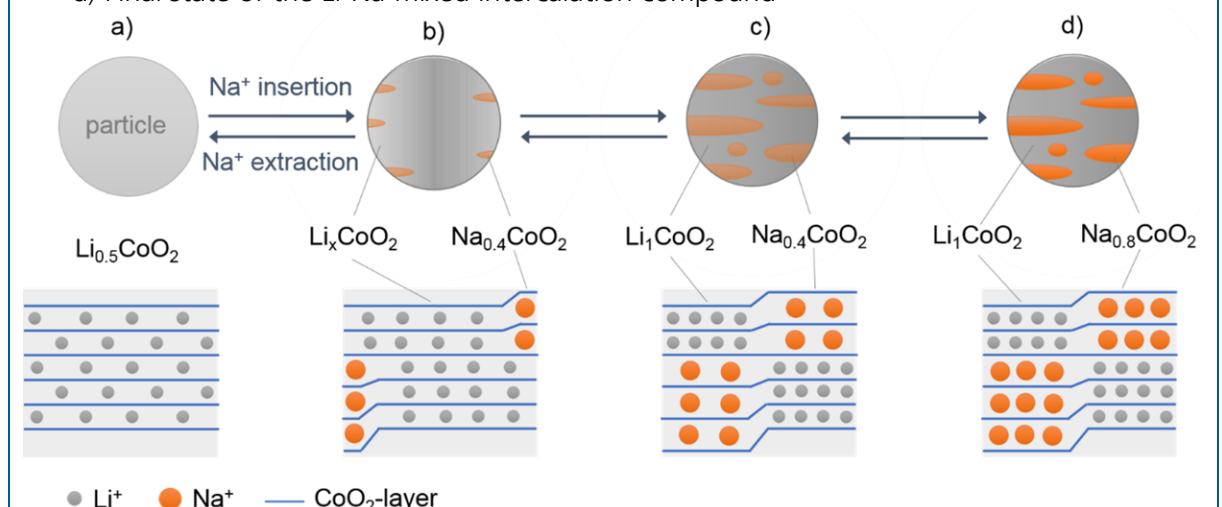


Fig. 6: Mechanistic model of the partial Li-Na substitution in LiCoO_2

CONCLUSION

- Li-Na-substitution in LiCoO_2 leads to Li-Na-mixed intercalation compound $\text{Li}_{0.5}\text{Na}_{0.4}\text{CoO}_2$.
- Evolution of Li- and Na-rich domains. Cycling is dominated by Na-ions.
- Mixed alkali-metal intercalation compounds appear for other applications, such as superconductors, thermoelectrics, and catalysis.
- Electrochemical cation exchange technique is highly suitable for the expedient preparation and investigation of metastable phases with desired compositions.