

Supporting Information
Impact of Alkali Metal-Ion Intercalation on Mechanical Deformations in Cobalt Oxide
Cathodes

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EXPERIMENTAL

Electrode Preparation: The composition of the pristine composite electrode is an 8:1:1 ratio in mass for LiCoO₂ powders, carboxymethyl cellulose, and Super P carbon, respectively. A thinky mixer was used to mix the slurries. Then, slurries were blade-casted onto an aluminum foil (MTI, 15 μ m thick) to create LiCoO₂ composite electrodes. For strain measurements, the composite electrode was scraped off the aluminum foil and shaped into a suitable rectangular form for the custom strain cells. For coin cell studies, the dried electrodes were shaped into round forms using quarter-inch punches. In an argon-filled glovebox, we assembled CR2032 coin cells comprising LiCoO₂ electrodes and corresponding alkali metal (Li, Na, or K) as counter electrodes, and a Celgard polyethylene film as a separator. Each layer received 25 μ L of electrolyte solution dispensed carefully using a pipet during the coin cell assembly process. After the assembly process, the coin cells were compressed using a coin cell crimper.

Electrochemical Cycling: There is a 24-hour rest period before electrochemical cycling. The pristine LiCoO₂ electrodes were charged against Li or Na alkali metals at 4.1 and 4.2 V, respectively, using cyclic voltammetry with a 50 μ V/sec scan rate, and followed by voltage hold for 8 hours. Then, galvanostatic cycling was performed at C/25 discharge rate in corresponding electrolyte solutions composed of 1 M LiClO₄ dissolved in a 1:1 (V: V) ratio of ethylene carbonate (EC, anhydrous, 99%, Sigma Aldrich) to dimethyl carbonate (DMC, anhydrous, >99%, Sigma Aldrich) or 1 M NaClO₄ dissolved in propylene carbonate (Anhydrous, 99.7%, Sigma-Aldrich) between 3.0 – 4.2 V against both Li and Na metals. For K-cell studies, the LiCoO₂ electrode was first charged at 4.2 V against Li metal followed by 8 hours of voltage hold. Then, the counter electrode and electrolyte were replaced with potassium metal and 0.5 M KPF₆ in EC:DMC electrolyte, respectively. The electrodes cycled between 3.0 and 4.2 V (vs K/K^{0/+}) at C/25 in K-cells.

Operando Strain Measurements: To facilitate strain measurements on the composite electrodes, a custom cell design was implemented. The detailed utilization of the in-home-made custom cell was discussed in our previous publication (Ozdogru et al., Nano Lett., 21, 18, 7579–7586, 2021). Optical investigations of the cobalt oxide electrodes were carried out using the digital image correlation (DIC) technique. Fluorescent silica particles were used as an artificial speckle pattern. During electrochemical cycling, images were captured at specific intervals: every 10 minutes for open circuit potential measurements and every 4 minutes at a C/25 discharge rate. The image

capture process was efficiently managed by a LabVIEW program. For full-field strain measurements, a designated region of interest, measuring $750\text{ }\mu\text{m}$ (width) \times $500\text{ }\mu\text{m}$ (height), was analyzed using Vic2D software. This software utilized a subset size of 111×111 pixels and a step size of 15. Horizontal normal strains were selected for assessing the strain values, which were then synchronized with the electrochemical response of the electrodes (current and voltage) using a custom MATLAB program.

Structural Characterization: For assessing structural changes in the half-delithiated ($\text{Li}_{0.5}\text{CoO}_2$) electrodes against both lithium and sodium metal, x-ray diffraction (XRD) analyses were conducted over a 2θ range of $15\text{-}40^\circ$, utilizing Cu $K\alpha$ characteristic radiation with the Bruker D8 Advance instrument. X-ray studies were performed on coin-cell-shaped electrodes after simulating the first delithiation that was applied to the strain cells.

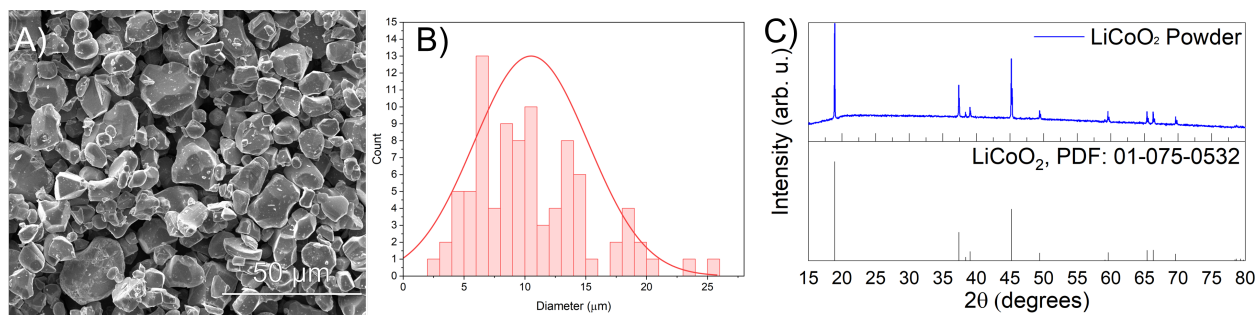


Figure S1: Scanning electron microscopy image, B) particle size distribution, and x-ray diffraction spectra of the LCO pristine powders.

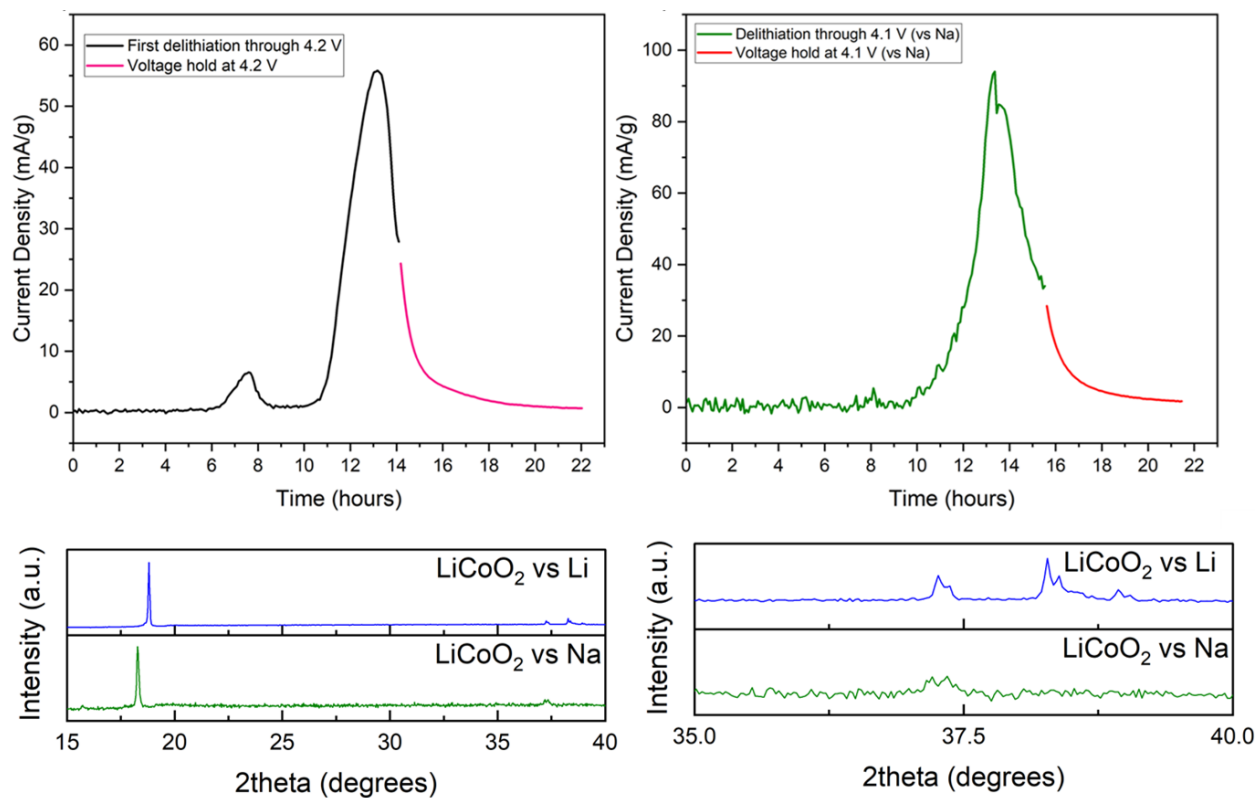


Figure S2: The current evolution of LiCoO_2 electrodes during the first charge against the Li and Na metals. The corresponding x-ray spectra after the first charge.

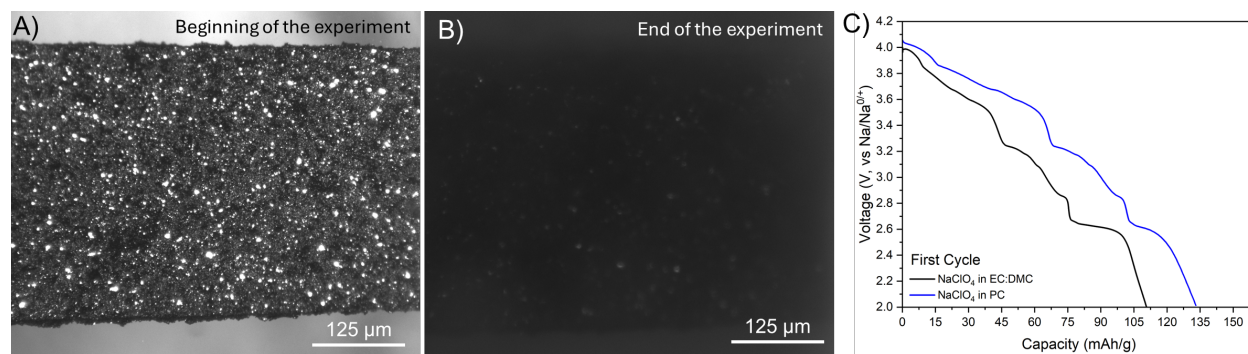


Figure S3: Optical images of the cobalt oxide electrode in 1 M NaClO₄ in EC:DMC at A) beginning of the strain experiment, and B) at the end of the experiment. C) Potential evolution of Na-cells in different electrolyte solutions. Black and blue lines represent 1 M NaClO₄ in EC: DMC and 1 M NaClO₄ in PC, respectively. The experiment was aborted when the captured images became prosperous for calculations.

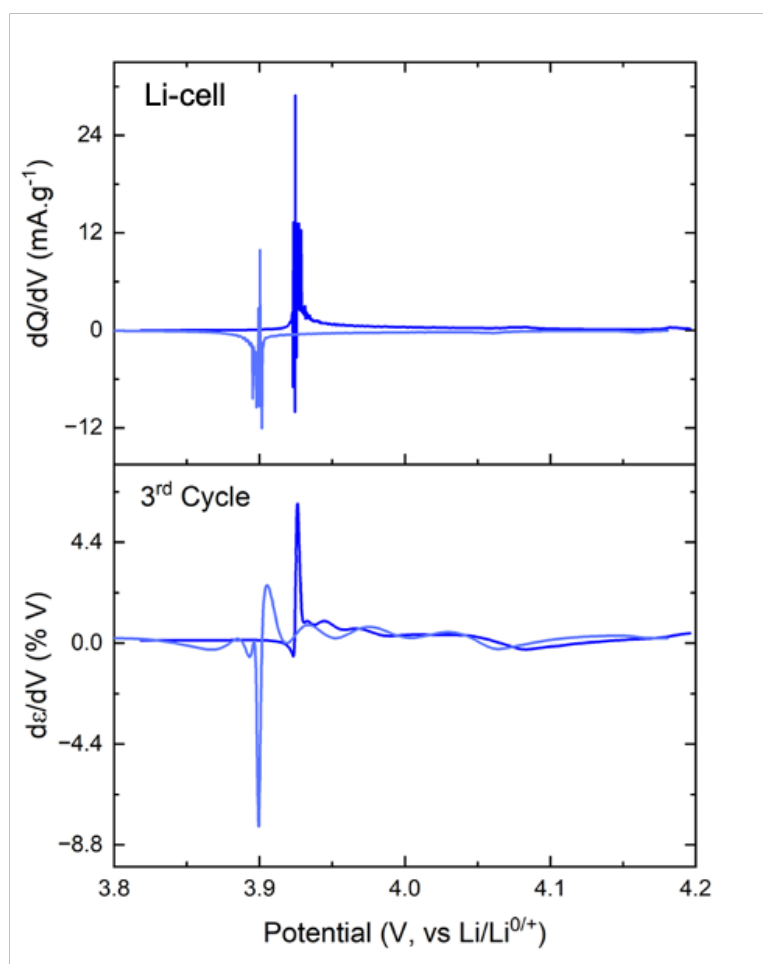


Figure S4: Current and strain derivatives of the electrodes in Li-cell during the third cycle. Dark blue line represents charge, and light blue line shows the discharge.

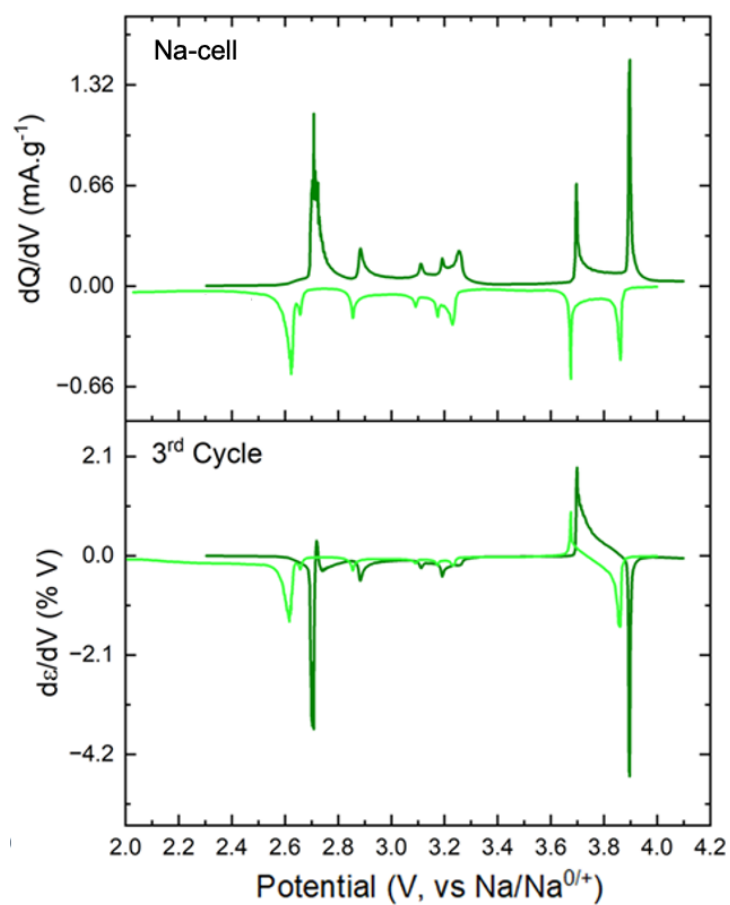


Figure S5: Current and strain derivatives of the electrodes in Na-cell during the third cycle. Dark green line represents charge, and light green line shows the discharge.

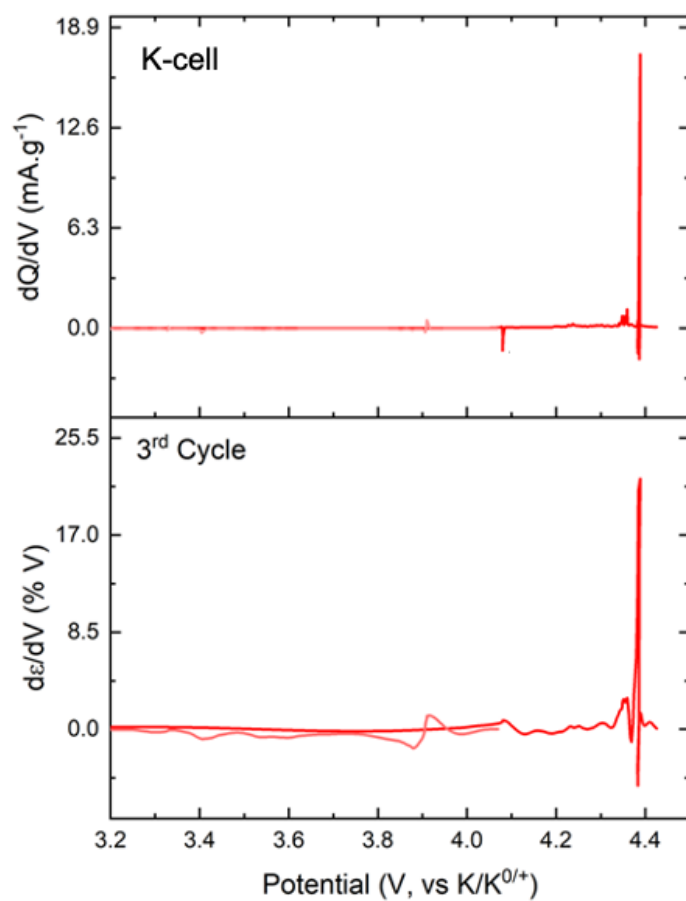


Figure S6: Current and strain derivatives of the electrodes in K-cell during the third cycle. Red line represents charge, and light red line shows the discharge.

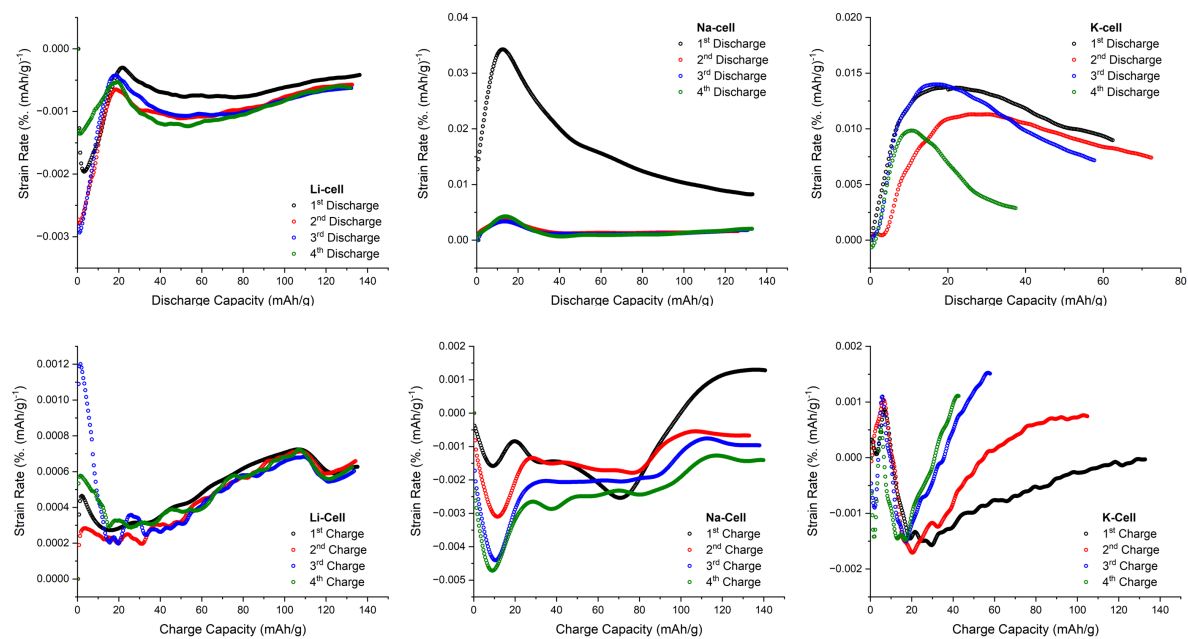


Figure S7: Strain rate evolution with respect to state of charge/discharge for all cells during the first four cycles.