Supporting Information

Voltage hysteresis loop as a fingerprint of slow kinetics Co²⁺-to-Co³⁺ transition in layered Na_xCo_{x/2}Ti_{1-x/2}O₂ cathodes for sodium batteries

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Figure S1

Discharge-charge cycle of a battery containing carbon black electrode (carbon black to binder ratio of 90:10), Na metal counter electrode and $1M \text{ NaClO}_4$ dissolved in a mixture of PC and EC (1:1 ratio) with adding 5% FEC as electrolyte solution.



Figure S2

Experimental and simulated Fourier transformations of the k^3 -weighted Co-K EXAFS data for the O3 material in selected states of sodiation.



Figure S3

A chemical Na⁺ diffusion coefficient in O3 and P2 materials was qualitatively estimated from GITT measurements (see main text) using the procedure described in W. Weppner, R. A. Huggins, Determination of the kinetic parameters of mixed-conducting electrodes and application to the system Li₃Sb, *J. Electrochem. Soc.* 124 (1977) 1569.



Figure S4

Entropic potential of the P2-Na_xCo_{0.33}Ti_{0.67}O₂ I Na half-cells plotted against OCV (left), and the composition dependence of the partial molar entropy change of P2-Na_xCo_{0.33}Ti_{0.67}O₂ with respect to x for two identical cells (right). Shaded areas indicate anomalous temperature dependence of OCV either after charging or discharging, in which reliable entropy determination was not always possible.

