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# Supporting Information

## Structural study on the development of high-voltage $Na_4Co_3(PO_4)_2P_2O_7$ cathode materials for sodium-ion batteries by in situ and time-resolved X-ray diffraction

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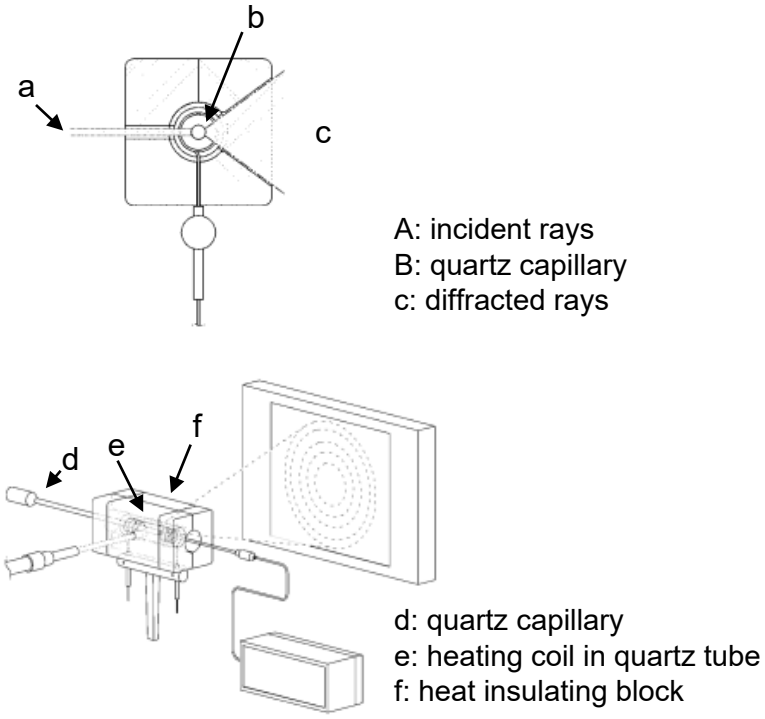



**Figure S1. Schematic and digital images of the TR-XRD test device for studying structural changes during heating.[1]**

1. Kim, D.H., et al., RT-XAMF and TR-XRD studies of solid-state synthesis and thermal stability of NaNiO2 as cathode material for sodium-ion batteries. Ceramics International, 2022.

(a) Calcination

(b) Sintering

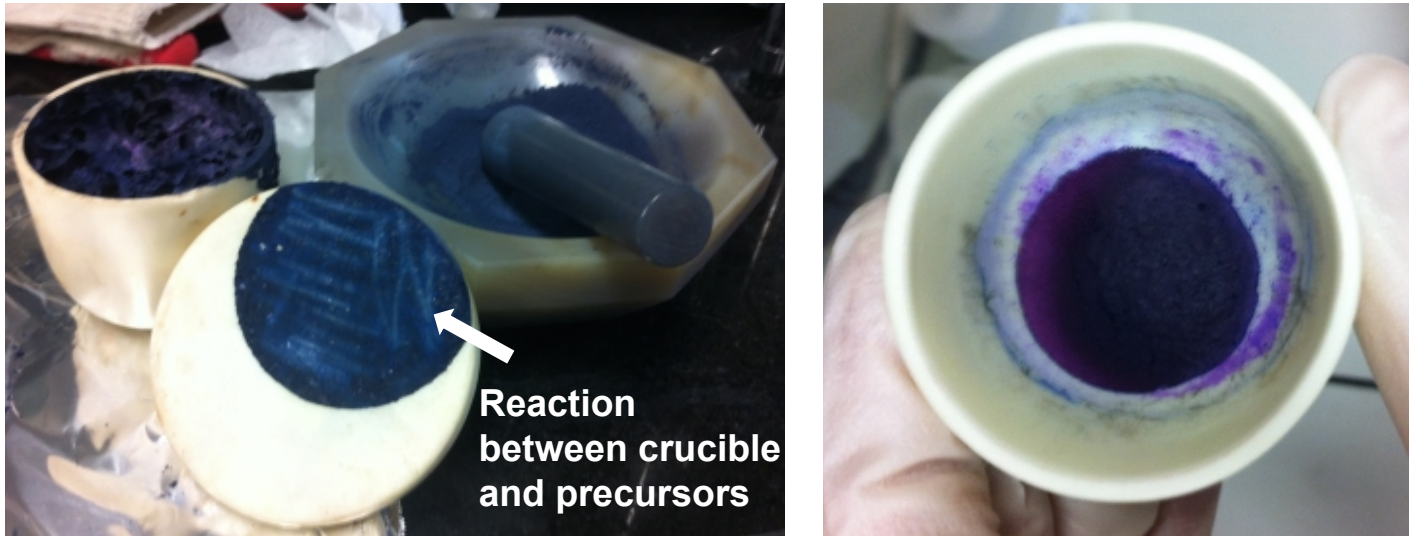



**Figure S2. Raw material loss caused by reaction with the container during the heat treatment process. (a) Calcination at 500 ℃, and (b) sintering at 700~770 ℃.**

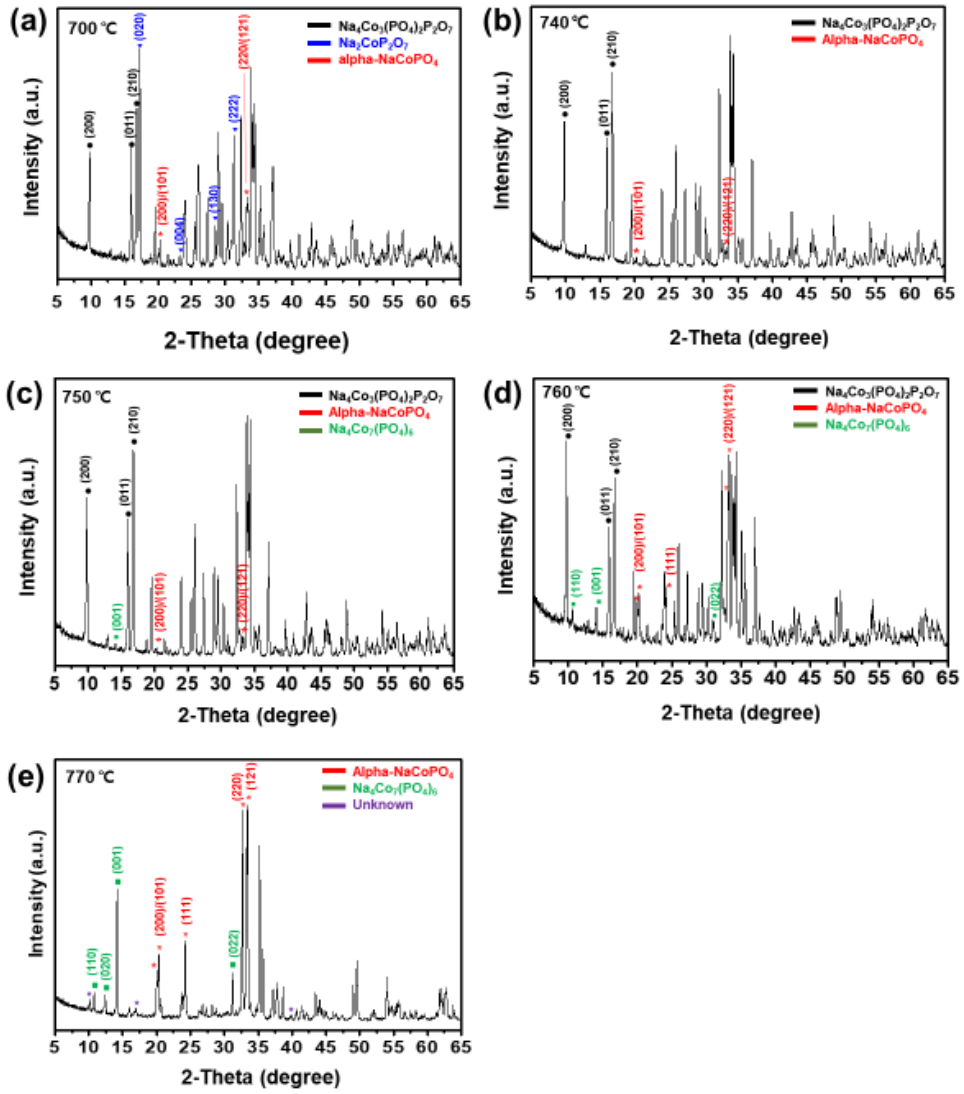
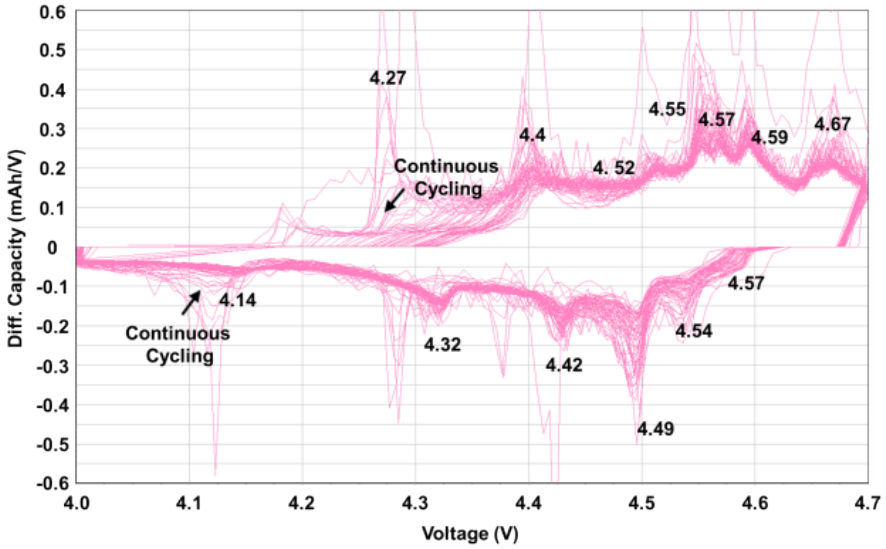



**Figure S3. XRD patterns of sodium cobalt phosphates synthesized at (a) 700 ℃, (b) 740 ℃, (c) 750 ℃, (d) 760 ℃, and (e) 770 ℃.**

(a) Bare $Na_4Co_3(PO_4)_2P_2O_7$ (in this study)




(b) Carbon-coated $Na_4Co_3(PO_4)_2P_2O_7$

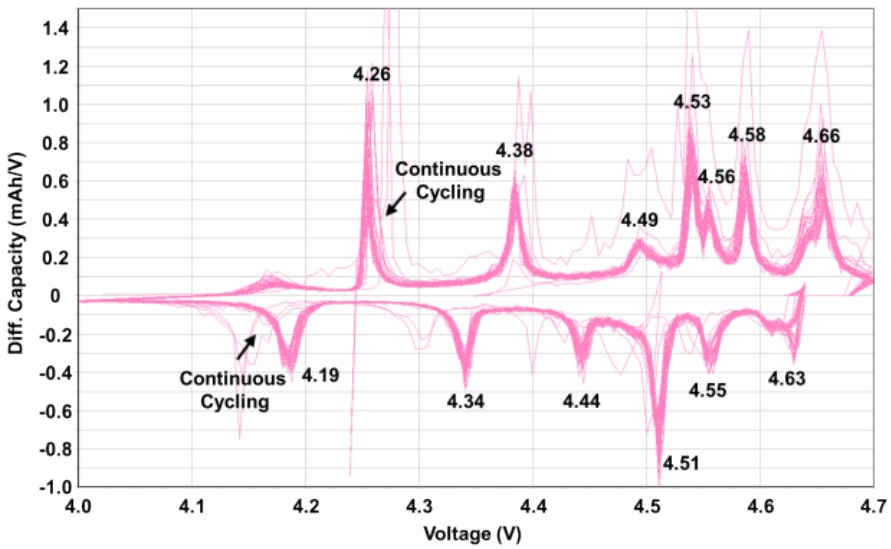



**Figure S4. Differential capacity (dQ/dV) vs. voltage of (a) the $Na_4Co_3(PO_4)_2P_2O_7$ synthesized at 740 ºC. For comparison of structural changes, dQ/dV data of (b) carbon-coated $Na_4Co_3(PO_4)_2P_2O_7$ were included. Note that the $Na_4Co_3(PO_4)_2P_2O_7$ used in this study is not carbon coated.**

| | Na | Co | P | Na/Co | P/Co |
|---|---|---|---|---|---|
| Theoretical molar ratio | 4 | 3 | 4 | 1.33 | 1.33 |
| Experimental value (mmol/L) | 17.46 | 13.53 | 16.34 | 1.29 | 1.22 |
| Calculated molar ratio | 3.87 | 3.00 | 3.65 | | |

**Table S1. ICP data of $Na_4Co_3(PO_4)_2P_2O_7$ synthesized at 740 ℃.**

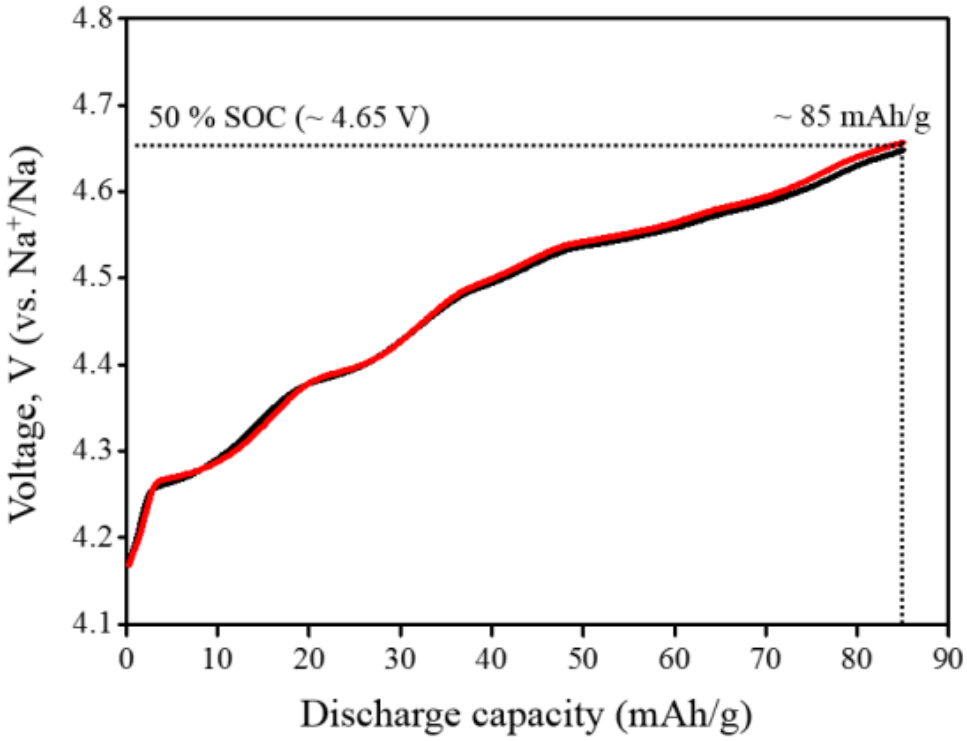



**Figure S4. Charge curves of $Na_4Co_3(PO_4)_2P_2O_7$ cathodes for the preparation of charged $Na_{4-x}Co_3(PO_4)_2P_2O_7$ (x = 2) cathodes for TR-XRD.**