Supplementary Information

Unveiling mechanism of sodium ion storage for needle-shaped $Zn_xCo_{3-x}O_4$ nanosticks as anode materials

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Synthesis

For comparison, $Zn_xCo_{3-x}O_4$ nano-particles were also synthesized by sol-gel method. In a typical synthesis, 67.5 mL of 0.1 M $Co(NO_3)_2 \cdot 6H_2O$ (sigma) aqueous solution, 22.5 mL of 0.1 M $Zn(NO_3)_2 \cdot 6H_2O$ (Junsei Chemical Co.) aqueous solution, and 90 mL of ethanol were mixed at room temperature. An ethanol solution (92 mL) of oxalic acid (0.1 M) was slowly added under constant magnetic stirring. The mixture was then evaporated at 80° C under constant stirring, which led to the formation of a sol. The sol was vacuum oven heated at 120° C for 12 h; a gel was formed. After ground the gel, the oxalate precursor powder was achieved. The resulting material was calcined at 350° C for 5 h and well-crystallized spinel was obtained [1].

Reference

[1] X. Wei, D. Chen, and W. Tang, *Mater. Chem. Phys.*, 2007, **103**, 54.

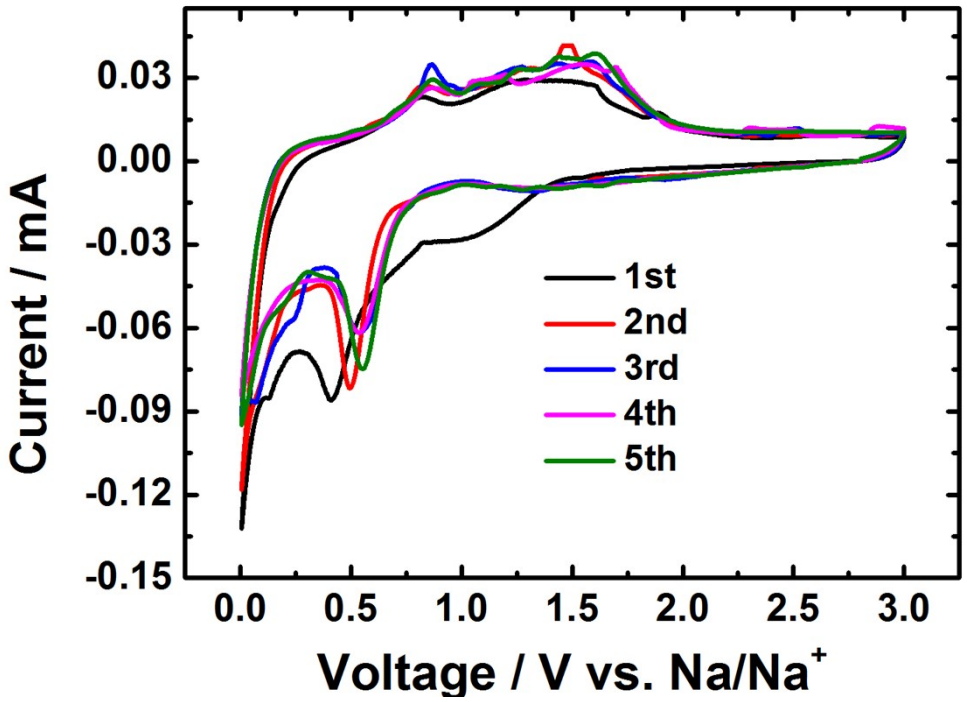

Figure S1. Cyclic voltammetry (CV) curves for the $Zn_xCo_{3-x}O_4$ microspheres electrode representing first five cycles at a scan rate of 0.05 mV s^{-1} in the voltage window of 0.005–3.0 V.

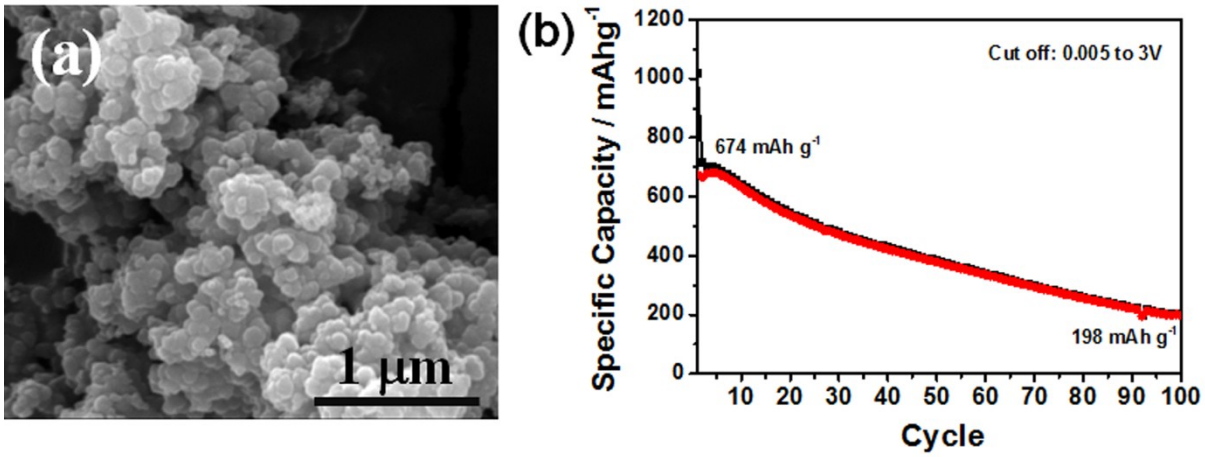

Figure S2. $Zn_xCo_{3-x}O_4$ nano-particles (a) SEM image and (b) electrochemical cycling in SIBs half-cell.

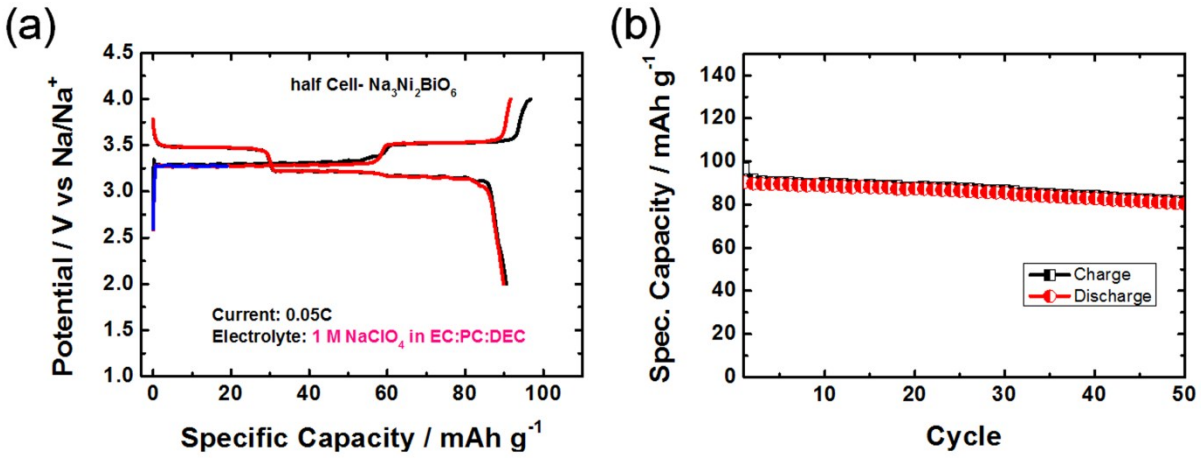

Figure S3. (a) Galvanostatic charge-discharge profiles during initial two cycles and (b) cycle performance of $NaNi_{2/3}Bi_{1/3}O_2$ cathode material in a half-cell at a rate of 0.05 C (1 C = 109 mAh g^{-1}).

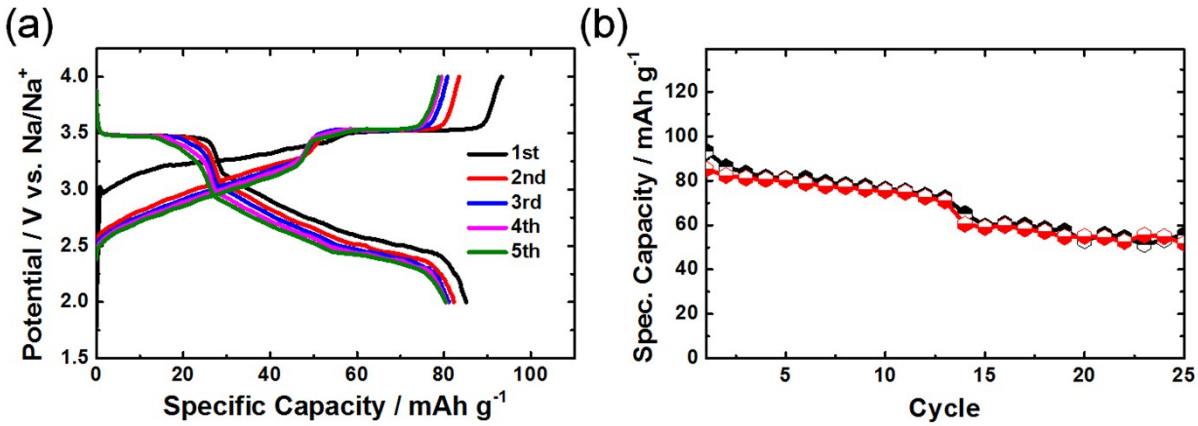

Figure S4. (a) Galvanostatic charge-discharge profiles during initial five cycles and (b) cycle performance of $Zn_xCo_{3-x}O_4/NaNi_{2/3}Bi_{1/3}O_2$ full sodium cell at a rate of 0.05 C (1 C = 109 mAh g^{-1}).

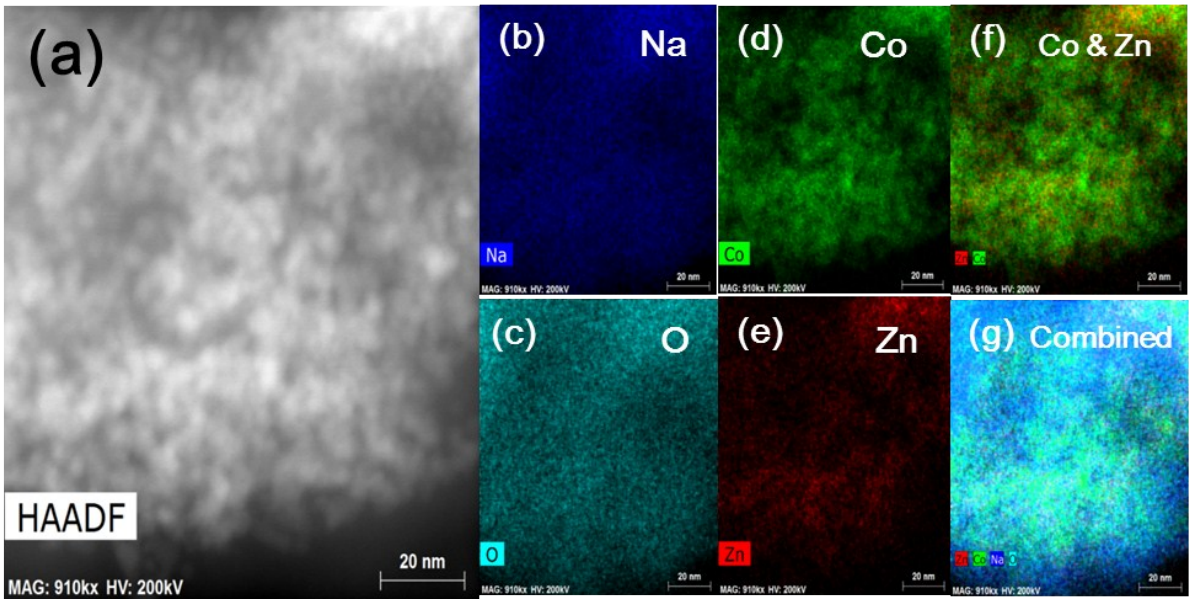

Figure S5. (a) Dark field TEM image, and (b–g) the corresponding EDS mappings of the $Zn_xCo_{3-x}O_4$ microsphere electrode in the fully discharged state.