Electronic Supplementary Information (ESI) for

Electrochemical investigation of sodium reactivity with nanostructured Co$_3$O$_4$ for sodium-ion batteries

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Experimental details

Synthesis of Co$_3$O$_4$ nanoparticles

The Co$_3$O$_4$ powder was synthesized by mixing together CoCl$_2$·6H$_2$O (Sigma-Aldrich, 98%), LiNO$_3$ (Sigma-Aldrich, 99.9%), LiOH·H$_2$O (Sigma-Aldrich, 98%), and H$_2$O$_2$ (Sigma-Aldrich, 35%) with a molar ratio of 0.01: 0.1: 0.02: 0.05, respectively. The mixture was grinding in an agate mortar until it became homogenous. The mixture was immediately transferred to a muffle furnace and heat treated in air at 300°C for 3 h. After cooling naturally in air, the solid mass was washed with a large amount of de-ionized (DI) water to dissolve unreacted salts and Co$_3$O$_4$ solid particles were separated by centrifugation. The product was then dried under vacuum at 100°C overnight to remove the residual water.

Material characterization

X-ray diffraction (XRD) data were collected from powder sample on a PANalytical X’Pert Pro instrument using a CuKa radiation source ($\lambda = 1.54181$ Å) and operated at 40 kV with 50 mA current. The X’Pert data collector software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files was used to identify the phases present. The morphology of sample was examined using scanning electron microscopy (SEM, Carl Zeiss Supra 55 VP Instrument). Transmission electron microscopy (TEM) analysis was performed on a JEOL JEM 2100F instrument operated at 200 kV.

To test the electrochemical performance, Co$_3$O$_4$ powder sample was mixed with acetylene carbon black (AB) and a binder, carboxymethyl cellulose (CMC), in a weight ratio of 80: 10: 10 in a solvent (distilled water). The slurry was spread onto Cu foil substrates and these coated electrodes were dried in a vacuum oven at 100°C for 24 h. The electrode was then pressed using a disc with a diameter of 25 mm to enhance the contact between the Cu foil and
active materials. Subsequently, the electrodes were cut to $1 \times 1 \text{cm}^2$. The electrochemical half cells were assembled in an Ar-filled glove box (Innovative Technology, USA) using CR 2032 coin cells with Na metal as the counter electrode, 1M NaClO$_4$ dissolved in propylene carbonate (PC) with 2 % FEC (fluoroethylene carbonate) additive as the electrolyte, and Whatman Glass Microfibre Filter (Grade GF/F) as a separator. The cells were galvanostatically discharged-charged in the range of 0.01-3.0V with a Land battery testing system. Cyclic voltammogram (CV) tests were performed on a Solartron Analytical electrochemical work station. For the ex situ XRD measurements, the tested electrochemical cells were disassembled in an Ar-filled glove box. The cycled electrodes were taken out and washed with propylene carbonate (PC) to remove the residual electrolyte.
Fig. S1 SEM images of Co$_3$O$_4$ sample: (a) low magnification; and (b) high magnification agglomerated clusters.
Fig. S2 Bright-field TEM imaging of the sample reveals agglomerates of fine and much coarser crystalline with (a) low and (b) high magnification.