Supporting Information

Target construction of Co₃O₄ with an improved layer structure for

highly efficient Li-storage property

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EXPERIMENTAL SECTION

Synthesis of Co-MOC and ls-Co₃O₄

The Co-MOC was synthesized by a typical hydrothermal approach. A mixture of $K_3[Co(CN)_6]$, tetraethylammonium chloride ($C_8H_{20}CIN$), sodium oxalate ($Na_2C_2O_4$), and 4,4'-bipyridine ($C_{10}H_8N_2$) was added to a mixed solvent of CH₃OH, C_2H_5OH and H_2O (with a volume ratio of 2:1:1). After hydrothermal reaction at 160°C for 72 h, the Co-MOC was obtained. Then the Co-MOC was calcined at 450°C for 6 h under air atmosphere to obtain the final product of ls-Co₃O₄.

Material characterization

The phase purity and crystallographic data of the as-synthesized samples of Co-MOC and prepared ls-Co₃O₄ were characterized by powder X-ray diffraction (PXRD, Rigaku P/max 2200VPC) using Cu K α radiation. Data were processed using the MDI-Jade version 5.0 software. The X-ray photoelectron spectra (XPS) data were obtained with Al K α radiation and energy step size of 0.1 eV. Transmission electron microscope (TEM, JEM-2010F) and scanning electron microscope (SEM, XL 30 ESEM-FEG, FEI Company) were used to study the morphology of the products. Cyclic voltammetry (CV) measurements were conducted using a VersaSTAT 3 (Princeton Applied Research), with a scanning rate of 0.2 mV s⁻¹ and a voltage range of 0.005–2.9 V.

Electrode prepared and electrochemical measurement

For the preparation of the working electrode, the mixture of active material (ls- Co_3O_4), acetylene black conductor, and PVDF binder (in a weight ratio of 70:15:15) was ground in a mortar with N-methy1-2-pyrrolidone (NMP) as solvent to make slurry. And the loading level of the electrode is ~1.32 mg cm². For assembling Li-ion

batteries, lithium foil was used as the counter electrode and a 1.0 M LiPF₆ in 1:1 v/v ethylene carbonate (EC)/dimethyl carbonate (DMC) as the electrolyte. The two electrodes were separated using Celgard 2400 membranes. The 2032 coin-type half-cells were assembled in an Ar-filled glovebox. Galvanostatic cycling measurements were made using a Land battery test system from 0.005 to 2.9 V. It is known that the capacity values of the prepared electrodes are really difficult to reproduce. In our work, the error of different test results for capacities under the same current density is within +/-10 mAh/g.



Figure S1 The XRD patterns for Co-MOC: the simulated (red line) and the assynthesized (black line).



Figure S2 (a) The schematic structure of Co-MOC along b axis. (b) Asymmetry unit of complex Co-MOC.



Figure S3 Nitrogen adsorption-desorption isotherm loop of ls- Co₃O₄. The inset is the pore size distribution curve calculated from the adsorption branch by the BJH model.



Figure S4 Cycling performance and CE of $ls-Co_3O_4$ at high current densities of 1, and 4 A g⁻¹.



Figure S5 SEM image of ls-Co₃O₄ after 100 deep cycles.

Table S1. EIS results of ls-Co₃O₄ at states of OCV and different cycles.

	$R_{\rm e}(\Omega)$	$R_{\rm sf}(\Omega)$	CPE1 (F)	$R_{\rm ct}(\Omega)$	CPE2 (F)
fresh cell	3.5	7.8	1.4×10 ⁻⁵	85.3	5.2×10 ⁻⁶
after 15 th cycles	2.7	5.4	8.6×10 ⁻⁶	44.6	8.4×10 ⁻⁶
after 30 th cycles	2.6	4.7	8.6×10 ⁻⁶	45.8	7.5×10 ⁻⁶