Electronic Supplementary Information

A hierarchical $NiCo_2O_4$ spinel nanowire arrays as electrocatalysts for rechargeable Li–air batteries

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Experimental

Preparation of hierarchical $NiCo_2O_4$ nanowire arrays (H-NCO-NWA**)**

Hierarchical $NiCo_2O_4$ spinel nanowire arrays (H-NCO-NWA) were prepared by a modified template-free co-precipitation route. Firstly, urea was dissolved in 300 ml deionized water with constant stirring and heated to 80 ^oC on a hot-plate; Secondly, stoichiometric amounts of $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 200 ml deionized water to obtain a mixed solution, the concentration of total metal ions was 0.06 mol L^{-1}, and the mole ratio of the total metal ions : urea was controlled to be 1 : 20. Thirdly, the mixed solution was added to the urea solution drop by drop through a back titration method. After finishing the drop, precipitates were formed with stirring for 0.5 h, followed by an ageing over 24 h at 80 ^oC to allow the growth of nanowire arrays. The precipitates were filtered and washed several times with deionized water and ethanol, and then dried in an oven at 60 ^oC for 12h to form a NCO spinel precursor powder. At last, the as-obtained precursor powder was calcined at 400 °C for 4 h in air.

Material characterization

The crystal structure of the oxide was determined by X–ray diffraction (XRD, Cu K_α radiation; λ= 0.15418 nm) with a Bede D1 X–ray diffractometer. Brunauer-Emmett-Teller (BET) specific surface areas were determined from nitrogen sorption isotherms that were performed on BEL-SORPmini system (BEL Japan).The morphology and microstructure of the synthesized sample were characterized by a scanning electron microscopy (SEM, Hitachi SU8010) and a transmission electron microscope (TEM; TecnaiG220 operating at 200 kV). The cathodes were also observed on Hitachi SU8010 scanning electron microscope.

Electrochemical measurements

The electrochemical properties were carried out by assembling 2032 coin Li-air batteries in a glove box filled with pure argon gas (< 1 ppm H_2O and O_2), using a clean lithium pellet anode, a glass fibre separator, an electrolyte containing 1 M LiTFSI in TEGDME, an oxygen cathode. The oxygen cathodes were prepared by spraying homogenous ink composed of the mixture of 15 wt.% H-NCO-NWA, 75 wt.%

acetylene black and 10 wt.% polyvinylidene fluoride (PVDF) onto the a nickel foam current collector. 0.5 mg activity materials (C+catalyst) were loaded on nickel foam (Φ 12 mm). The galvanostatic discharge-charge tests were conducted within a voltage window of 2.0-4.5 V (vs. Li/Li^+) with a multichannel battery testing system (LAND CT 2001A) in a testing glove box filled with a dry gas mixture composed of 80 vol.% pure N_2 (99.999 %) and 20 vol.% pure O_2 (99.999 %). The capacity was calculated based on the mass of carbon and electrocatalyst (C+catalyst). Cyclic voltammetry (CV) experiments were carried out with CHI 604B electrochemical workstation from 4.5 to 2.0 V at a scan rate 0.2 mV s^{-1}.

For comparison, a regular $NiCo_2O_4$ powder was synthesized through a sol-gel process.[1] Li-air batteries with pure acetylene black and regular $NiCo_2O_4$ as cathode catalyst were assembled and tested with the same procedure, respectively.

Results and discussion:

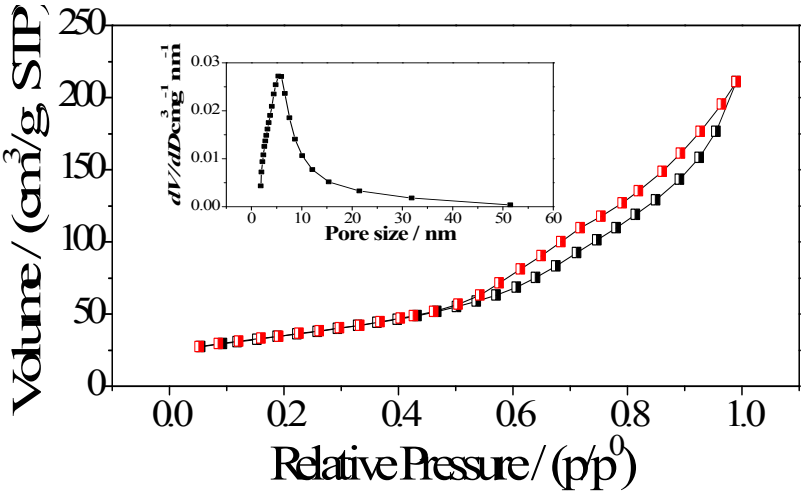

Fig. S1, N_2 adsorption-desorption isotherm loop and pore distribution plot (inset) of H-NCO-NWA.

The N_2-adsorption isotherm and the pore-size distribution are shown in Fig. S1. The N_2-adsorption isotherm of the H-NCO-NWA exhibited the combined characteristics of type IV, with a surface area of 124 m^2 g^{-1} and a total pore volume of 10.32 cm^3 g^{-1}. The hysteresis loop in the P/P_0 range of 0.5–1.0 is indicative of mesoporosity. From the pore-size distribution, it was clearly observed that there were main mesopores with a wide size range of about 8 nm, in agreement with the TEM

results.

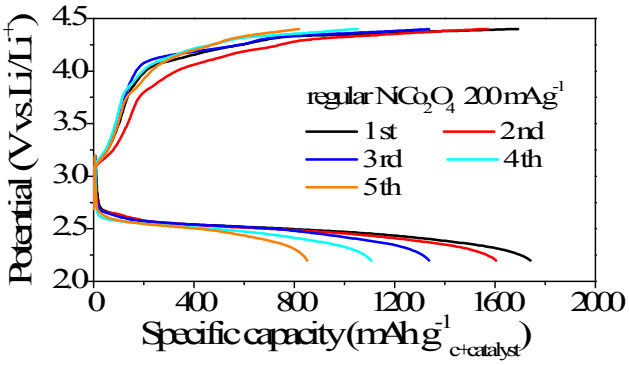

Fig. S2, Typical fully discharged and charged profiles of a Li-air battery based on regular $NiCo_2O_4$ electrode at a discharge-charge current density of 200 mA g^{-1}.

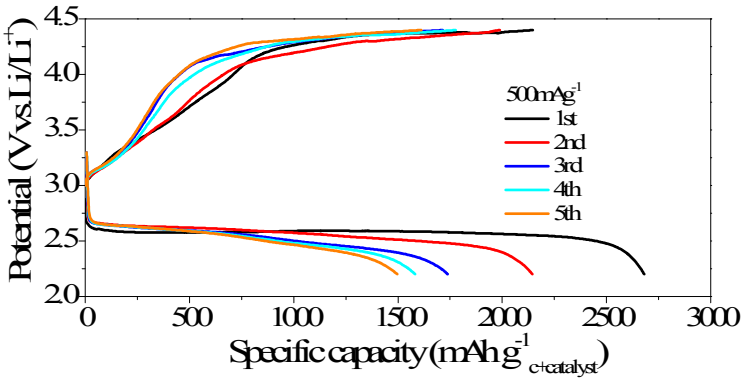

Fig. S3, Profiles of a Li-air battery using the H-NCO-NWA-based electrode under different discharge–charge cycles at a deep discharge-charge current density of 500 mA g^{-1}.

Table S1, Comparison of BET results between the H-NCO-NWA and other reported $NiCo_2O_4$ materials

	Specific surface area (cm^3/g, STP)	Pore size (nm)	References
NCO nanoplatelet @ GO	77	11.8	2
NCO nanosheets	89		3
NCO @ stainless steel	119	6	4
NCO chain-like nanowire	42	10.4	5
NCO hollow nanocube	82	3	6
Flower-like NCO	80	8	7
NCO nanowire arrays	124	8	this work

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