

Electronic Supplementary Material (ESI) for RSC Advances
This journal is © The Royal Society of Chemistry 2013

Supplemental Information for:

Structure and improved electrochemical performance of nanostructured layered double hydroxide/carbon nanotubes composite as a novel anode material for Ni-Zn secondary batteries

Bin Yang^a and Zhanhong Yang^{*a, b}

^a *College of Chemistry and Chemical Engineering, Central South University, Changsha 410083,*

PR China

^b *Key Laboratory of Resource Chemistry of Nonferrous Metals, Ministry of Education, Central*

South University, Changsha 410083, PR China

Preparation of LDH/CNTs nano-composite:

Multi-walled CNTs were purchased from Shenzhen Nanotech Port Co. Ltd. Introduction of carboxyl and hydroxyl groups onto the surface of CNTs to form acidifying CNTs was carried out by oxidation of pristine CNTs with a mixture of nitric acid and sulfuric acid (1:3 by volume) under sonication for 6 h. Then the modified CNTs was filtered and washed with deionized water until pH = 7. Finally, the collected powder was dried under vacuum at 60 °C for 12 h. The other reagents (analytical grade) were used as received without further purification.

LDH/CNTs composite was prepared by a co-precipitation method. In a typical procedure, the modified CNTs (0.25 g) were added to 50 ml of an alkaline solution of NaOH (1 M) and Na₂CO₃ (0.2 M) and placed in an ultrasonication bath for 10 min. Subsequently, the solution was titrated with 100 ml of a salt solution of Zn(NO₃)₂ (0.2 M) and Al(NO₃)₃ (0.05 M) with Zn²⁺/Al³⁺ molar ratio of 4:1 under vigorous stirring for 20 min. The pH value of the solution was adjusted to 10 by further titration with 0.4 M NaOH solution. Thereafter, the suspension was transferred into a 100 ml Teflon-lined autoclave, and the hydrothermal reaction was allowed to continue for 24 h at 120 °C. After cooling to room temperature, the solid products were filtered, washed with deionized

water and ethanol, and followed by vacuum-drying at 60 °C for 12 h. Considering only small losses of LDH and CNTs in the whole experiment, the chemical composition of the as-prepared LDH/CNTs composite can be considered to be the same as the original mass ratio of CNTs to LDH, which is 10:100 in mass. For a comparative study, pure Zn-Al-LDH was prepared under identical experimental conditions but without the introduction of CNTs.

Characterization of as-prepared samples:

Transmission electron microscope (TEM) measurements were conducted on a JEOL 2010 FEG microscope at 200 kV. The phase structure of the as-prepared samples was determined by X-ray diffraction (XRD, Philips X'Pert Pro Super X-ray diffractometer Cu K α radiation).

Preparation of electrodes and test cells:

The composite anode (Zn electrode) was prepared by pasting a mixture consisting of as-prepared LDH/CNTs composite and polytetrafluoro ethylene (PTFE; 10 wt.%, in diluted emulsion) on a copper mesh substrate served as the current collector. For comparison, the Zn electrodes with conventional ZnO and as-prepared Zn-Al-LDH were also fabricated according to the similar process. Because of the poor conductivity of ZnO and Zn-Al-LDH, the anodes with ZnO and Zn-Al-LDH are physically mixed with 10 wt.% conductive acetylene carbon black (CACB) respectively, which is usually used as highly electronic conductive filler to improve the electronic conductivity of Zn electrodes. The weight ratio of active material (ZnO or Zn-Al-LDH), CACB and PTFE was 80:10:10. Herein, the LDH/CNTs composite electrode don't introduce the conductive acetylene carbon black as conductive filler, because the CNTs in the LDH/CNTs composite can forming 3D conductive networks, the electronic conductivity of composite electrode is excellent. In order to investigate the electrochemistry performance improvement is due to LDH/CNTs 3D conductive framework or just addition of more carbon contents, the electrode of active material LDH physically mixed with 10 wt.% CNTs was also fabricated according to the same process. All the anodes (ZnO, Zn-Al-LDH, LDH/CNTs and LDH physically with CNTs) are of the same mass loading. These electrodes were roll-pressed to a thickness of 0.3 mm to enhance the contact between the active materials and the current collector. Finally, the electrodes were dried at 80 °C in a vacuum oven for 12 h.

The cells were made from a anode and a commercial sintered Ni(OH)₂ (Tianjin City Fine

Chemical Research Institute) cathode. The electrolyte was ZnO-saturated 6 M KOH solution. The cells were galvanostatic charged and discharged in a battery test system (NEWARE BTS-610, Neware Technology Co., Ltd., China). In the charge–discharge cycles, the batteries were charged at 1 C for 1 h and discharged at 1 C down to 1.2 V cut-off. Cyclic voltammetry (CV) was carried out using electrochemical workstation (CHI640B) at a scanning rate of 5 mV s⁻¹ shifting from -0.8 to -1.7 V. A three-electrode cell assembly was used with a commercial sintered Ni(OH)₂ electrode as the counter electrode, a Zn electrode as the working electrode and a Hg/HgO electrode as the reference electrode. The electrolyte was ZnO-saturated 6 M KOH solution.