



Layered Double Oxides Nano-flakes Derived From Layered Double Hydroxides: Preparation, Properties and Application in Zinc/Nickel Secondary Batteries



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ABSTRACT

Layered double oxides (LDOs) samples derive from layered double hydroxides (LDHs) by thermal treatment at different temperatures are prepared in this paper. The as-prepared LDOs samples are characterized by X-ray diffraction (XRD), thermogravimetry-differential thermal analysis (TG-DTA) and scanning electron microscope (SEM) technique. The results show that the LDHs are decomposed to ZnO with amorphous aluminium species dispersed in the lattice. After calcinations, LDOs inherit the lamellar structure of LDHs. LDOs with thermal treatment at different temperature are tested as the anode active materials for Zn/Ni secondary battery. Cyclic voltammetries (CV) and Tafel curves measurements reveal that the calcined products have better electrochemical performances, lower polarization and better reversibility. Galvanostatic charge/discharge shows that the calcined products have excellent cycle stability and higher specific discharge capacity. More interesting, the sample calcined at 500 °C exhibits the best electrochemical performances among all samples. These findings promote new opportunities for anode materials as Zn/Ni batteries and other energy-storage devices.

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1. Introduction

Among various secondary alkaline storage batteries, such as Ni/Fe, Ni/Cd, Ni/MH and Ni/Zn batteries, Zn/Ni battery will become the dominant role in green power sources for hybrid electric vehicle (HEV) or electric vehicle (EV) because they possess a number of attractive properties (e.g. high specific power density, abundant inexpensive raw materials and non-pollution for environmentally) [1–3]. However, a fundamental problem of Zn electrode that short and unpredictable lifetime during charge-discharge cycling, hamper the further development of the technology of Zn–Ni battery. These problems are traced back to the formation of the harmful anode morphologies (Zn dendrites, filamentary growths, nodules) and the redistribution of anode active material (Zn shape change) during charge-discharge processes [4–7]. Extensive work has been made to conquer the problems, most of researchers focused on the modification of ZnO, additives in the electrodes and alternative active materials.

Layered double hydroxides (LDHs), or hydrotalcite-like compounds, is a lamellar hydroxides compounds. The layers are consisted of edge-sharing $[M(OH)_6]$ octahedral [8]. Generally, it

can be expressed by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^x(A^{n-})_{x/n} \cdot mH_2O$. M^{II} and M^{III} in the formula stand for di- and trivalent metal cations, respectively. The formula A^{n-} in interlayer is expressed the intercalation anion, which is to balance the redundant positive charges [9,10]. LDHs have become a research focus because of their unique structural anisotropy and flexibility in composition. In electrochemical field, LDHs or modified LDHs [6,11–13] were tried as electrode active materials for supercapacitors or alkaline secondary battery owe to their high redox activity and effective utilization ratio of metal atoms [14]. For instance, Fan et al. [15] used ZnAl-LDHs as anode active materials in Zn/Ni secondary cells, the results show that ZnAl-LDHs electrode exhibits better reversibility, more stable electrochemical cycling performance and superior utilization ratio in KOH solution compared with the ZnO anode. Wang et al. [2] found that the modified ZnAl-LDHs (Zn–Sn–Al LDHs) exhibited better electrochemistry behavior than the precursor ZnAl-LDHs. Feng et al. [16,17] used LDHs as additive of ZnO electrode, the results indicate that the LDHs additive is conductive to slowing down the dissolution of ZnO due to its special layer structure and better stability in alkaline electrolyte. Unfortunately, the low conductivity of this kind of materials largely suppresses the electron transfer in electrode reaction. Moreover, the poor capacity also affects the electrochemical performances.

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During thermal treatment, layered double hydroxides will gradually lose the interlayer water molecule, furthermore, LDHs suffers dehydroxylate and decarbonate to a large extent with the increase of temperature, result in the formation of a layered double oxides [18,19]. In fact, LDHs compounds decompose into a mixture of oxides named layered double oxides (LDOs). LDOs have higher theoretical capacity than LDHs on account of the absence of interlayer anion and water. Above all, LDOs still keeps the sheet structure of LDHs, which benefit to the electrode. LDOs has been applied in Zn/Ni secondary battery in our previous work [20]. During the preparation process, the heating temperature is crucial in the control of particle sizes, size distributions, and shapes. Therefore, the main work for this paper is research the influence of heating temperatures on the electrochemical performances of LDHs when it is used as anode active material for Zn/Ni batteries.

2. Experiment Sections

2.1. Preparation of Materials

The synthesis of ZnAl-LDHs was carried out by a hydrothermal method. A mixture salt solution containing zinc nitrate hexahydrate (0.3 M) and aluminum nitrate nonahydrate (0.1 M), and an alkali solution dissolved with 1 M sodium hydroxide and 0.2 M sodium carbonate, were simultaneously dropped into the beaker with 50 mL deionized water. The pH of the mixed solution was kept at about 10. The suspension was centrifuged at 4000 rpm for 5 min after stirred 30 min at 65 °C and washed to neutral with deionized water and ethanol. Then the product transferred into a reaction kettle and kept it in 120 °C oven for 24 h. The slurries were filtered, washed and dried at 65 °C for 24 h. The as-prepared ZnAl-LDHs was heating for 3 h with the temperature increasing rate of 5 °C min⁻¹ in a muffle furnace at 400, 500, 600 and 700 °C. The products denoted as CL-4, CL-5, CL-6 and CL-7, respectively.

2.2. Characterizations

Structural properties of samples were studied with X-ray diffraction (XRD) on a D500 (Siemens), using Cu K α radiation ($\lambda = 0.15418$ nm) with a scanning rate of $2\theta = 8^\circ \text{ min}^{-1}$. The

morphologies of samples were analyzed by a FEI Quanta 250 FEG emission scanning electron microscope (SEM) operated at 10 kV. Simultaneous thermogravimetry-differential thermal analysis (TG-DTA) curves were obtained in air on a NET ZSCH STA 449C (Germany) thermal analysis system for analyzing the thermal stability/degradation temperature of the precursor material from ambient temperature to 700 °C, the heating rate is 10 °C min⁻¹. The specific surface area and pore size of LDHs, ZnO and CL-5 were detected by the Brunauer–Emmett–Teller (BET) method using a Quantachrome Autosorb-1C-VP Analyzer. Before the measurements, LDHs, ZnO and CL-5 were degassed at 100 °C and 300 °C for 2 h, respectively.

2.3. Preparation of Electrodes

The electrodes were made by pasting a compound including 80 wt.% as-prepared active materials, 10 wt.% polytetrafluoroethylene (PTFE, 10 wt.% in diluted emulsion) and 10 wt.% acetylene black on a piece of copper mesh substrate about 1 cm \times 1 cm. The total mass of the active materials is about 10 mg cm⁻². All obtained electrodes were roll-forming to a thickness of about 0.3 mm, dried under vacuum at 60 °C for 12 h. As a comparison, a pure Zn-Al-LDHs electrode and commercial ZnO electrode were made as the same procedures. The cathode used the commercial sintered nickel hydroxide electrode. The capacity of the cathode is far more than those of the work electrodes in order to make sure that the active materials in anodes are fully utilized. The electrolyte is a solution 6M potassium hydroxide saturated with zinc oxide. All the electrodes were activated 8–10 times before electrochemical test, the active steps as follows: charged at 0.1C for 600 min, and discharged at 0.2C to a cut-off voltage of 1.2V at ambient temperature.

2.4. Electrochemical Measurements

The electrochemical performances of electrodes were tested in a conventional three-electrode system, which used an Hg/HgO electrode as reference electrode. The cyclic voltammetry (CV) of zinc anodes were examined on an electrochemical workstation CHI660D with a scanning rate of 10 mV s⁻¹, scanning from -0.95 to

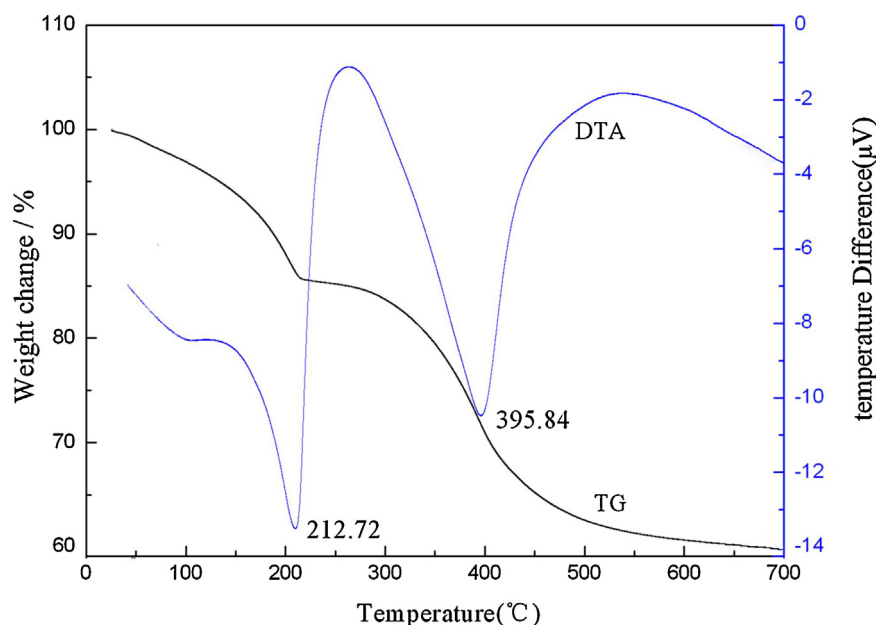


Fig. 1. TG-DTA curves of the ZnAl-LDHs precursor.

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