



The effects of element Cu on the electrochemical performances of Zinc-Aluminum-hydrotalcites in Zinc/Nickel secondary battery



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ABSTRACT

Zn-Cu-Al-CO₃ layered double hydroxides (LDHs) have been successfully synthesized by using the method of constant pH co-precipitation. And it also has been proposed as a novel anodic material in Zinc-Nickel secondary batteries. The X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images of the as-prepared sample exhibit that the samples are well crystallized and have hexagon structure. The electrochemical performances of Zn-Al-LDHs and Zn-Cu-Al-LDHs with different Zn/Cu/Al molar ratios are investigated by the measurements such as galvanostatic charge-discharge, cyclic voltammogram and electrochemical impedance spectroscopy (EIS). Comparing with the pure Zn-Al-LDHs, Zn-Cu-Al-LDHs show more stable cycling performance, exhibit better reversibility and display lower charge-transfer resistance. Especially, the Zn-Cu-Al-LDHs with the Zn/Cu/Al molar ratio being 2.8:0.2:1 exhibits the best electrochemical properties than other samples. After 800 cell cycles, the specific discharge capacity of Zn-Cu-Al-LDHs with the Zn/Cu/Al molar ratio of 2.8:0.2:1 is 345 mA h g⁻¹, while that of pure Zn-Al-LDHs is only 177 mA h g⁻¹. Based on these observations, the prepared Zn-Cu-Al-LDHs may be a promising anode active material for Zinc/Nickel secondary batteries.

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1. Introduction

Of all new generations of green power sources used in electric vehicle (EV) or hybrid electric vehicle (HEV), Zinc/Nickel (Zn-Ni) alkaline secondary batteries is one of the most promising candidates because of its advantages of high energy (with the specific energy density being 80 Wh·kg⁻¹) and power densities (with the specific power density being 500 W·kg⁻¹), high open circuit voltage, excellent low-temperature performance, low cost and environment friendly [1–6]. However, Zn-Ni alkaline secondary batteries are faced with problems of the zinc electrode including shape change, zinc dendrite formation, surface passivation, zinc self-corrosion and self-discharge, leading to the restriction of commercial applications [7–9]. And these problems are mainly due to a high solubility of the zinc discharge product in the alkaline electrolyte and the non-uniform deposition of zinc active material during charging [10,11]. Hence, to improve the electrochemical performance, many attempts have been made, and most of the researchers have focused on the improvement of the electrolyte [8,12,13], modification of the zinc electrode

[10,11,14–16] and adding additives in the electrodes [17–19]. Though these attempts could effectively address many problems mentioned above, there is still a long way to go for the commercial applications of ZnO. Hence, it's necessary to find a better and novel anode material to address these problems.

Layered double hydroxides (LDHs) or hydrotalcite-like compounds, with a brucite-like layered structure are a family of synthetic anionic clays. And the general formula of layered double hydroxides is [M(II)_{1-x}M(III)_x(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·nH₂O, where M(II) is a divalent metal cation, M(III) is a trivalent metal cation, and Aⁿ⁻ is the interlayer anions. In recent years, LDHs has been serving as catalysts [20], nanofillers [21], drug delivery material [22], and chemically tailored functional material [23], which has attracted great attention. The electrochemistry properties of LDHs as new modified electrodes have attracted much attention [24–26], which shows that LDHs may be a promising electrode material for alkaline batteries due to their alkaline, layered structure and stability in alkaline solution. And Zn-Al-LDHs working as novel anode material in Zn-Ni secondary battery had been studied by our group [27]. Compared with ZnO, Zn-Al-LDHs working as novel anode material in Zn-Ni secondary battery have many advantages, including better reversibility, superior electrochemical cycling stability and more excellent utilization ratio in the alkaline

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solution. However, pure Zn-Al-LDHs as anode material has the disadvantage of poor conductivity, which largely suppresses the electron transfer in the electrode reaction. Therefore, it should be further improved on pure Zn-Al-LDHs. The effect of partial replacement of bivalent transition metal cation (Sn^{2+}) on the electrochemical performance has been studied by Wang [28], and it has been revealed that the presence of Sn additive can help to improve the conductivity. Yang [29–31] has studied the effect of Ag-coated Zn-Al-LDH and found that Ag addition can help to improve the electron conductivity of Zn-Al-LDHs. Wang [32,33] found that a partial replacement of Al by In can help to improve the corrosion potential. As we all know, of all the metals, except for Ag, metal Cu has the best conductivity. Then in this work, to further improve the conductivity of Zn-Al-LDHs, we focus on the partial replacement of divalent metal by Cu and proposed the Zn-Cu-Al-LDHs as a novel anode material. Meanwhile the electrochemical properties of Zn-Cu-Al-LDHs were studied in details.

2. Experimental

2.1. The preparation of Zn-Cu-Al-LDHs

The Zn-Cu-Al-LDHs were synthesized by the constant pH co-precipitation method. The typical experimental operation was as follows [27]: An aqueous solution (100 ml) of Zn, Cu and Al nitrates (with Zn/Cu/Al molar ratio equal to 3:1:0, 2.9:0.1:1, 2.8:0.2:1, 2.6:0.4:1) and the total metal ion concentration of 0.25 M was added with flow rate of 5 ml min^{-1} into a batch reactor containing 50 ml of distilled water. And the pH of the solution was controlled at 10 by the addition of alkaline solution (100 ml) of Na_2CO_3 (0.0125 mol) and NaOH (0.05 mol). This process was carried out at 65°C with vigorous stirring. After stirring for 30 min, the product was filtered off and transferred into a 100 ml teflon-lined autoclave at 120°C for ten hours. The product was cooled to room temperature then filtered and washed for several times with deionized water until the pH reached 7. Finally, the product was dried for 24 h under 60°C and ground to fine powder.

2.2. The characterization of the Zn-Cu-Al-LDHs

X-ray diffraction (XRD) of samples were recorded by a D-500 (Siemens) power diffractometer (36 Kv, 30 mA) using Cu $K\alpha$ radiation at a scanning rate of $2\theta = 8^\circ \text{ min}^{-1}$. The morphology of as-prepared Zn-Cu-Al-LDHs was observed using a scanning electron microscope (SEM, JSM-6360LV). ICP-AES was studied by using a PE 5300DV. And the XPS spectra was recorded by a X-ray photoelectron spectroscopy (XPS, Phi Quantum 2000 spectrophotometer with Al $K\alpha$ radiation = 1486.6 eV and penetration depth of the X-ray $< 10 \text{ nm}$). And the particle size distribution of the as-prepared samples were measured in a Malvern 2000 laser particle size analyzer.

2.3. The preparation and electrochemical measurements of the Zn-Cu-Al-LDHs electrodes

The Zn-Cu-Al-LDHs electrodes were prepared by incorporation slurries containing 90 wt.% Zn-Cu-Al-LDHs, 5 wt.% acetylene black and 5 wt.% additives of polytetrafluoroethylene (PTFE, 60 wt.%, in diluted emulsion) to a copper mesh substrate ($1.0 \text{ cm} \times 1.0 \text{ cm}$ in size) which was served as the current collector. Afterwards, the obtained Zn-Cu-Al-LDHs electrodes were dried at 60°C under vacuum. And the total weight of the active material on the electrode is about 15 mg. The electrode composed of Zn-Al-LDHs also was fabricated in the same way in comparison. The sintered Nickel electrodes were used as positive electrodes and its capacity was high enough to make full use of the capacity of Zn-Cu-Al-LDHs electrodes during cycling processes. All the cells were pre-activated for 10 times by the following operations: The cells were charged at 0.1C for 600 min, and discharged at 0.2 C to a cut-off voltage of 1.2 V.

2.4. The measurements of electrochemical properties

The galvanostatic charge-discharge tests were performed using a BTS-5 V/20 mA battery-testing instrument (Neware, China) at

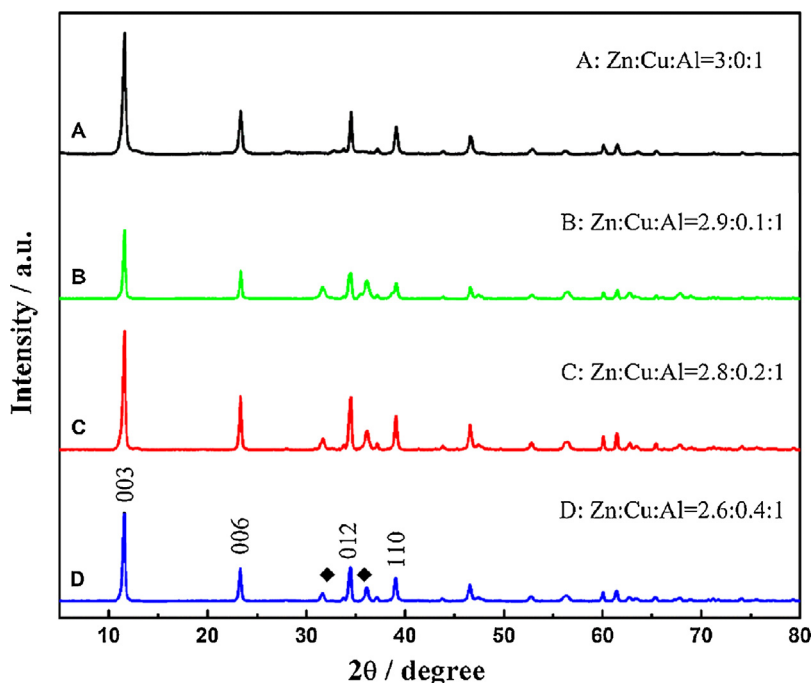


Fig. 1. XRD patterns of the Zn-Al-LDHs and different Zn/Cu/Al molar ratios of Zn-Cu-Al-LDHs. A: Zn/Cu/Al = 3:1:0; B: Zn/Cu/Al = 2.9:0.1:1; C: Zn/Cu/Al = 2.8:0.2:1; D: Zn/Cu/Al = 2.6:0.4:1.

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