



The Impact of Hydrocalumites Additives on the Electrochemical Performance of Zinc-Nickel Secondary Cells



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ABSTRACT

Hydrocalumites additives are synthesized and proposed as an anodic additive for Zinc/Nickel alkaline secondary batteries. The as-prepared additives are characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). And the results illustrate that hydrocalumites additives are successfully prepared and have the typical structure of layered double hydroxides (LDHs). The effects of hydrocalumites additives on electrochemical performances of ZnO have been investigated by cyclic voltammetry (CV), tafel polarization tests, electrochemical impedance spectroscopy (EIS) and galvanostatic charge and discharge. Compared to the electrode with pure ZnO, the electrodes containing hydrocalumites additives show better reversibility, reveal better anti-corrosion property and exhibit more stable cycle performance. Especially when the electrode added with 12% (wt.) hydrocalumites, it exhibits the best cycle performance than the other electrodes. And its discharge capacity is about 450 mAh g⁻¹ all the time, and hardly declines over all the 400 cycles. Based on these observations, the prepared hydrocalumites may be a promising and efficient additive for the ZnO electrode.

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1. Introduction

Due to the increasing requirement of clean and renewable energy, more and more attention has been paid to developing new materials for solar cells, secondary batteries, fuel cells and electrical double-layer capacitors [1]. Among these power sources, Zinc-Nickel (Zn-Ni) alkaline secondary batteries is one of the most promising candidates because of its advantages in 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 [2–5]. So far ZnO has been the main anodic material of the Zn-Ni alkaline secondary batteries. However, ZnO is easily to develop into zinc dendrite and occur shape change during the charge and discharge process because of its high solubility in the alkaline electrolyte [6–9]. As a result, the cycle performance of pure ZnO electrode is so poor that it presents a significant obstacle to the widespread commercialization of Zn-

Ni alkaline secondary batteries [2,3]. Hence, to improve the electrochemical performance, many attempts have been made. In the past decades, most of the researchers have focused on the improvement of the electrolyte, seeking novel active material and adding additives in the electrodes. Improvement of the electrolyte includes adding citrate, tartrate, gluconate [10], Ca(OH)₂ [11], and so on. And some zinc-containing materials such as calcium zincate and zinc-containing hydrotalcite used as active anode material for Zn/Ni rechargeable battery were investigated [12–15]. Different additives in the electrode, to name only a few, Ca(OH)₂ [16], In(OH)₃ [17], SnO₂ [18], Bi₂O₃ [19] and La₂O₃ [20], were added to study their influences on the electrochemical properties. Many studies show that these additives can prevent zincate from moving away from zinc electrode, suppress H₂ evolution, and improve electronic conductivity as well as current distribution of the zinc electrode [7].

Layered double hydroxides (LDHs) or hydrotalcite-like materials, is a kind of lamellar compounds that contains positively charged brucite-like host layers and hydrated exchangeable anions located in the interlayer gallery for charge balance. And it is a family of synthetic anionic clays as well. The chemical general formula of LDH can be represented as [M(II)_{1-x}M(III)_x(OH)₂]^x

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$^{+}(A^{n-})_{x/n} \cdot H_2O$, where M(II) is a divalent metal cation, M(III) is a trivalent metal cation, and A^{n-} is the interlayer anions, respectively. The applications of LDHs are ranging from catalysis to anti-reflection coatings and drug delivery because of their straightforward synthesis, stability, large surface area and nontoxic nature [21]. Recently, LDHs have been applied as active materials for supercapacitors [22,23], alkaline secondary batteries [24–25] and additives for ZnO batteries [26,27]. And LDHs also display better electrochemical properties, which mainly can be attributed to the typical layered structure [22,24]. But few researchers pay attention to hydrocalumites (Ca–Al LDH). Hydrocalumite is a kind of non-toxicity mineral, which were mainly used as a heat stabilizer for PVC [28,29] and absorbent for metal oxide in solution [30]. Then in this paper, hydrocalumites are successfully synthesized and used as a novel additive for ZnO. The electrochemical performances of ZnO electrode added with this novel additive were also studied in detail.

2. Experimental

2.1. The preparation of hydrocalumites additives

The as-prepared additives were synthesized by a hydrothermal method. The typical process was as follows: The $Ca(OH)_2$ was blended with $Al(OH)_3$ in the excessive deionized water with the molar ratios of $Ca(OH)_2$ and $Al(OH)_3$ being 2:1. And this process was carried out under vigorous stirring for 1 hour. Then, the solution of Na_2CO_3 (0.26 g) was added into the above slurry. After stirring for 2 hour, the resultant slurry was poured into a Teflon-lined autoclave and then kept for 20 hour under $120^\circ C$. 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 $60^\circ C$ and ground to fine powder.

2.2. The characterization of hydrocalumites additive

Fourier transform infrared (FT-IR) spectroscopy was conducted on a Nicolet Nexus-670 FT-IR spectrometer (as KBr discs, with wavenumber $400\text{--}4000\text{ cm}^{-1}$, resolution 0.09 cm^{-1} , and the weight of measured sample 2 mg). 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 hydrocalumites additives was observed by using a scanning electron microscope (SEM, JSM-6360LV).

2.3. The preparation of the Zn electrodes

The Zn electrodes were prepared by incorporation slurries containing ZnO, hydrocalumites additives, acetylene black and 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. The mass ratio of ZnO, hydrocalumites additives, acetylene black and PTFE was 80:5:10:5, 73:12:10:5, and 65:20:10:5, respectively. Then, the obtained zinc electrodes were pressed to a thickness of 0.20 mm, the pressed pressure is 10 MPa, and then dried at $60^\circ C$ in vacuum environment. And the electrode composed of pure ZnO also was fabricated in the same way in comparison. And the total weight of the active material on the electrode is about 35 mg. To distinguish the zinc electrodes better, these zinc electrodes added with content of hydrocalumites additives being 0, 5% (wt), 12% (wt) and 20% (wt) are coded as pure ZnO, HZO-1, HZO-2 and HZO-3, respectively. The sintered Nickel electrodes were used as positive electrodes and its capacity was high enough to make full use of the capacity of Zn electrodes,

and it would make sure that the capacities of cells was controlled by zinc anode. 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 0.2C to a cut-off voltage of 1.2 V.

2.4. The measurements of electrochemical properties

The galvanostatic charge and discharge tests were performed by using a BTS-5 V/50 mA battery-testing instrument (Neware, China) at room temperature ($25 \pm 2^\circ C$). A two-electrode cell system was assembled for cyclic testing with a counter electrode of sintered Nickel electrode. During cycling process, the cells were charged at 1C for 60 min and discharge at 1C down to a 1.2 V cut-off voltage. A three-electrode cell was assembled for cyclic voltammograms (CV) and Tafel polarization test, with an Hg/HgO electrode (0.098 V vs. SHE) served as the reference electrode, the sintered Nickel electrode as counter electrode and the pre-activated pasted zinc electrode as the working electrode. A solution of 6 M KOH saturated with ZnO was used as the electrolyte. The cyclic voltammetry and the Tafel polarization measurements were carried out on an electrochemical workstation RST-5000 type electrochemical system at room temperature. The Tafel polarization measurements were performed with a scanning rate of 0.5 mV s^{-1} . EIS measurements were performed on a PARSTAT 2273-type electrochemical system (Princeton Applied Research) at room temperature. The frequency range was between 0.01 Hz and 100 kHz, and the amplitude of AC signal was set at 10 mV.

All the electrolytes were prepared with deionized water. And all chemicals were analytical grade and were used as received without any further treatment.

3. Results and discussion

3.1. The structural and morphology characteristics of hydrocalumites additive

The typical FT-IR spectrum of the as-prepared additives is depicted in Fig. 1. As depicted in Fig. 1, the broad peak around 3345 cm^{-1} can be ascribed to the stretching of OH groups attached to Al^{3+} and Ca^{2+} . The bending vibration of interlayer water appears at 1643 cm^{-1} . The prominent absorption bands (1418 cm^{-1} and 1365 cm^{-1}) are due to O–C–O asymmetric stretching [29]. And a considerably lower shifted absorption peak at 1365 cm^{-1} , as compared with CO_3^{2-} of $CaCO_3$ (1430 cm^{-1}), shows that there is an intercalation between CO_3^{2-} and interlayer H_2O through the strong hydrogen bonding. And the lower wavenumber bands at $400\text{--}900\text{ cm}^{-1}$ are due to Ca–O and Al–O.

Fig. 2 presents the typical XRD patterns of the as-prepared additives. It can be seen from Fig. 2 that the diffraction peaks of the

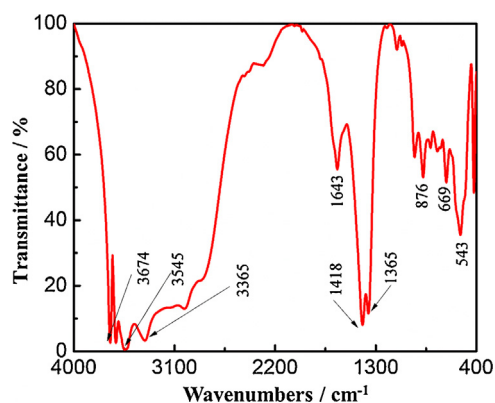


Fig. 1. FT-IR curve for the as-prepared hydrocalumites additives.

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