Preparation of Flower-Like Zn-Al Layered Double Hydroxides as Anode Materials with Improved Electrochemical Performance

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Abstract. In this account, a facile approach for preparation of 3D self-assembled flower-like Zn-Al layered double hydroxides (Zn-Al LDHs) through a one-step hydrothermal method is demonstrated, and the resulting material is successfully utilized as negative electrodes of next-generation Zn secondary batteries. The flower-like Zn-Al LDHs possess larger specific surface area and better ion diffusion channel. Due to the unique flower-like nanostructure, the resulting flower-like Zn-Al LDHs exhibit higher charging efficiency and better cycle performance. This is concluded from the combined data of serial electrochemical tests based on galvanostatic charge-discharge tests and cyclic voltammetry (CV) tests. The galvanostatic charge-discharge tests reveals that flower-like Zn-Al LDHs maintained 95.7% of the initial specific capacity after 600 cycles.

1. Introduction

With an increasingly deteriorating of the environment and growing demand for energy, a new kind of energy storage device (e.g. supercapacitors, rechargeable batteries) has become the urgent need to take full advantage of precious un-renewable fossil energy and intermittent clean energy [1, 2]. Among them, Li ion batteries, as the most widely used batteries in smart phones or electric (or hybrid) vehicles, have an advantage of elevated specific energy density and relatively long working life. But limited by the safety problems and low power density owing to the poor conductivity of lithium salts, people are forced to turn their eyes to a safer energy storage device [3].

Zn anode materials, with the highest energy density among all the aqueous battery anode materials, have been attracting the researchers’ attentions during the few decades [4, 5]. So Zn secondary batteries, with the property of elevated power density, high rate performance, lower electrochemical resistance, increased charging efficiency and excellent safety performance, are the most promising secondary batteries for real-life large scale commercial application [6]. However, shape change and unwanted dendrite growth are the main problems urgent to settle, which may cause the sharp capacity loss and sudden short circuit of Zn secondary batteries. So many attempts have been made to enlarge the cycle life of Zn anode, such as electrolyte or electrode additives, structure-modified Zn anode materials.

In this study, we propose a one-step hydrothermal method to fabricate a 3D self-assembled flower-like Zn-Al layered double hydroxides (Zn-Al LDHs) with high energy density and excellent cycle stability. Layered double hydroxides (LDHs), with the property of high ion-exchange ability and
enhanced structure stability, have been a hot spot in catalysts, anion exchanger and energy storage. [7-9] Many methods have been used to improve cyclic stability, including nanostructured active materials, modification of electrolyte. [10-13] In addition, the use of electrode additives is an effective way to improve electrochemical performance. For example, Yang [14] has put forward a silver additive which can effectively improve the electrochemical performance of Zn-Al LDHs as anode materials. The as-prepared Ag/ Zn-Al LDHs exhibits improved electric conductivity and limited polarization as Zn anode materials. But the cycling performance of this materials is still a huge difficulty to be overcome. And Parker [15] has proposed a method to fabricate 3-D porous Zn sponge anode to achieve long cycle life without anode passivation and dendrite formation. However, the complex preparation process seriously hinders the real-life application of Zn sponge anode. Yuan et al. [16] prepared ZnO nanoparticles by PCVD in presence of Bi2O3 and SnO2 as additives. They found that electrodes made by as-synthesized ZnO could continue working more than 250 times. On the other hand, the original morphology of Zn anode materials should be maintained in order to efficiently extend the working life of the anode. For example, Ma et al [17] prepared a 2D plate-like ZnO with extended cycle life. Therefore, we urgently need a facile and practical method to prepare zinc anode material to achieve long cycle performance and high electrochemical performance.

Here we propose a simple method to synthesize self-assembled flower-like Zn-Al LDHs as anode materials through a highly controllable one-step hydrothermal route. A rosette-type Ni-Al LDHs were applied to the positive electrodes in our previous work, and the results showed that Ni-Al LDHs have an improved cycle performance as cathode materials [18]. The formation of flower-like structure is assisted by poly(sodium p-styrenesulfonate) (PSS) working as the soft-template and promoting a better crystallinity of flower-like Zn-Al LDHs (as shown in figure 1), which might give a promising way to develop the next-generation Zn-based energy storage devices.

2. Experiments

2.1. Synthesis of flower-like Zn-Al LDHs
In this study, 3-D flower-like Zn-Al LDHs were prepared by a facile one-step method. All of the chemicals were analytical grade and used as received. Typically, 30 mg Zn(NO3)2, 40 mg Al(NO3)3, and 70 mg urea were mixed with 35 ml poly (sodium-p-styrenesulfonate) (PSS) aqueous solution (from 0 g L⁻¹ to 0.5 g L⁻¹ to 0.75 g L⁻¹ to 1 g L⁻¹) and continuously stirred for 30 min to get an uniform solution without deposition. Then the solution was transferred into a 60 ml autoclave vessel and kept at 190 ºC for 12 h. Finally, the resulting precipitates were filtered and dried at 70 ºC in air for 20 h.

2.2. Characterizations of flower-like Zn-Al LDHs
The structure and morphology of 3-D flower-like Zn-Al LDHs were investigated by the SEM (Inspect F, FEI). The XRD characterization of the sample was measured by a PANalytical X'pert Pro system using Cu-Kα.

2.3. Fabrication of the electrodes
The negative electrodes of 3-D flower-like Zn-Al LDHs were fabricated by pasting the slurry of active materials, acetylene black, and polytetrafluoroethylene (PTFE) in a weight ratio of 70:20:10 on the copper mesh. Then the electrodes were kept at 80 ºC in air for 24 h. The negative electrodes of Ni(OH)₂ were made by same method.

2.4. Characterizations of the electrodes
All the tests of the electrodes were carried out at room temperature. The cycle performance of the electrodes was evaluated by electrochemical workstation (RST).
3. Results and discussion

3.1. Materials characterizations

The SEM images of 3-D flower-like Zn-Al LDHs with a varying content of PSS are shown in Figure 1. We can clearly observe that the content of PSS has great influence on the morphology and structure of the final product of flower-like Zn-Al LDHs. Figure 1a exhibits the morphology of conventional Zn-Al hydrotalcite plate without PSS, which show a great quantity of stacked laminated nanostructures. As the concentration of PSS increased to 0.5 g/L, the flower-like Zn-Al LDHs dominate the entire Figure 1b. The size of hollow-structure flower-like Zn-Al LDHs are uniform, and the diameter of them are around 3 μm. With the enhancement of PSS concentration to 0.75 g/L (as shown in Figure 1c), the hollow-structure flower-like Zn-Al LDHs begin to disappear gradually, and the spherical-structure Zn-Al LDHs begin to form gradually. Finally, when the PSS concentration is elevated to 1 g/L, the flower-like Zn-Al LDHs disappear in Figure 1d completely, and spherical-structure Zn-Al LDHs dominate in the picture. Due to the larger specific surface area and better ion diffusion channel, 3-D hollow-structure flower-like Zn-Al LDHs gain substantial electrochemical improvements in the unique nanostructure, which will be further verified by the following electrochemical tests.

![Figure 1. SEM images of Zn-Al LDHs with different concentration of PSS: 0 g/L (a), 0.5 g/L (b), 0.75 g/L (c), 1 g/L (d).](image_url)

3.2. Electrochemical characterizations

Compared to conventional Zn-Al hydrotalcite plate, 3D flower-like Zn-Al LDHs has a higher average specific capacity of 530 mA h g\(^{-1}\), and could maintain 95.7% of initial specific capacity after 600 cycles. As for conventional Zn-Al hydrotalcite plate, a lower average specific capacity of 520 mA h g\(^{-1}\) could be maintained in the first 80 cycles and then it suffers a sharp capacity fading during subsequent cycles (as shown in figure 2a). Besides, as-prepared flower-like Zn-Al LDH exhibits a good rate performance in galvanostatic charge/discharge test. The CV (cyclic voltammetry) curves of the conventional Zn-Al hydrotalcite plate and 3D flower-like Zn-Al LDHs at the scan rate of 10 mV/s are illustrated in figure 2b. Obviously, the cathodic peak voltage of conventional Zn-Al hydrotalcite plate is more negative than that of 3D flower-like Zn-Al LDHs. A lower cathodic peak voltage means an easy charging process and more active electrochemical reaction kinetics. In another word, 3D flower-like Zn-Al LDHs exhibit better conductive properties, which facilitates the electron transfer and leads to smaller voltage division in the internal resistance. The unique nanostructure has greatly enlarged the specific surface area and further increased the contact area between flower-like Zn-Al LDHs and electrolyte, leading facilitated
redox reactions. Although the area of the anodic peak of conventional Zn-Al hydrotalcite plate approaches to that of 3D flower-like Zn-Al LDHs, the area of the cathodic peak (S1) is much larger than that of 3D flower-like Zn-Al LDHs (S2). Thus, 3D flower-like Zn-Al LDHs has about 50% higher charging efficiency than conventional Zn-Al hydrotalcite plate. According to Huang et al [19], the electrochemical stability of active materials can be evaluated by voltage balance ($E_v$) between the anodic and the cathodic peaks. Smaller $E_v$ means stronger electrochemical stability of materials. As depicted in figure 2b, the voltage balance of 3D flower-like Zn-Al LDHs ($E_{v1}$) is smaller than that of conventional Zn-Al hydrotalcite plate ($E_{v2}$). Hence, the CV tests reveal the improved charging efficiency and long-life cycle stability of 3D flower-like Zn-Al LDHs owing to the unique nanostructure. Owing to the larger contact area with electrolyte and relatively stable flower-like structure, as prepared 3D flower-like Zn-Al LDH has a better electrochemical performance and enhanced cycle stability, making it a promising anode material for the next-generation energy storage devices.

![Figure 2](image_url)

**Figure 2.** Results of the tests of cycle performance (a) and CV curves (b) of conventional Zn-Al hydrotalcite plate and 3D flower-like Zn-Al LDHs.

4. Conclusion
The preparation of 3D flower-like Zn-Al LDHs as anode materials for Zn secondary batteries was successfully completed through a one-step hydrothermal method. As we expected, flower-like Zn-Al LDHs exhibit enhanced electrochemical performance in terms of better cycle performance and more ion diffusion channel. The synthesis process of 3D flower-like Zn-Al LDHs was validated by a series of control variable experiments. The as-prepared flower-like Zn-Al LDHs exhibited only a little capacity loss after 600 cycles, which might be a promising alternative anode material for the next-generation Zn secondary batteries.

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