Precipitation Process Optimization Research on Zinc-Based Electrode Materials Synthesis

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Abstract. Optimization of electrode material is one of the most important measures to improve the performance of supercapacitors. Layered double hydroxide electrode materials supported by foam Ni were synthesized by in situ hydrothermal synthesis with CO(NH$_2$)$_2$/NaOH/Na$_2$CO$_3$ as precipitants and inorganic Zn(II) and Al(III) as precursors. The catalytic layer is composed of Zn$_6$Al$_2$(OH)$_{16}$CO$_3$·4H$_2$O and Zn$_4$(OH)$_6$CO$_3$·H$_2$O. Specific capacitance of the electrode materials can reach as high as 1259 F g$^{-1}$ at 1.0 A g$^{-1}$. Urea in precipitants optimized the composition, structure, and properties of the electrode materials. These encouraging results make these low-cost and eco-friendly materials promising for supercapacitor applications.

1. Introduction
Fossil energy depletion and climate warming have accelerated new sustainable energy conversion and storage technology [1, 2]. Among these energy storage devices, supercapacitors (SC) have attracted the attention due to their high power density, good cycling stability, rapid charging and discharging, economic and safe operation performance. However, the low energy density of SC limits its further application [3]. An effective approach to increase energy density is to improve the specific capacitance of electrode materials. According to the different electrode materials, it can be divided into double layer capacitor and pseudocapacitor. RuO$_2$, MnO$_2$, NiCo$_2$O$_4$ and V$_2$O$_5$ are the most widely used electrode materials for pseudocapacitor [4].

In recent years, two-dimensional materials (2D) have attracted more and more attention in the research of chemical energy storage and conversion [5-7]. This kind of material is characterized by high specific surface area, unique layered structure and rich physical and chemical properties. It has shown great potential in charge and ion storage areas, such as graphene, transition metal oxides, carbides, sulfides, and layered bimetallic hydroxide [8].

Layered double hydroxides (LDHs), as typical 2D materials, can be expressed as the general formula [M$^{II}$]$_{1-x}$M$^{III}$$_{x}$(OH)$_2$]^{x-}(A$^{n-}$)$_{z/y}$H$_2$O[9, 10]. Metal ions and interlamellar anions in LDHs structural materials can be adjusted in a large range without changing the main structure, so that the allocation and combination of ions can be conducted according to the actual needs of electrochemical activity [9].

The main challenge of LDHs materials application in supercapacitors comes from poor electrical conductivity and severe agglomeration, which will bring a rapid decline in its performance and reduce its energy output [11]. At present, lots of efforts focus on combination it with other materials with good electrical conductivity, such as carbon nanotubes, graphene, nano-carbon powder and other carbon-based materials. These LDHs/C composite nanomaterials gives better performance [12].

In this work, ZnAl-LDHs composite electrode material supported by foam Ni was prepared by in-situ hydrothermal synthesis with urea, sodium hydroxide and sodium carbonate as precipitants. The function
of urea in the precipitants was analyzed and the electrochemical performance of the electrode was evaluated.

2. Experimental Section

2.1. Preparation of Zn-Al-LDHs Materials
ZnAl-LDHs electrode materials were prepared by in situ hydrothermal synthesis. The precursors were zinc nitrate and aluminum nitrate with Zn/Al molar ratio of 3:1, and the total amount of urea, sodium hydroxide, and sodium carbonate with precipitator/metal molar ratio of 5:1. The precursors and precipitators were dissolved in 36 ml deionized water and transferred to 50 ml hydrothermal reactor. The pre-treated nickel foam was added in solution. Hydrothermal process was maintained at 120 °C for 12 h. At the end of the reaction, the products were washed and dried at 60 °C overnight. The samples were labeled as in-situ-LDHs.

2.2. Characterization
The microstructure was characterized by X-ray diffraction (XRD) on X’pert proSuper ray diffractometer of PAN Analytical with copper target as the light source (λ=1.5432 nm), the graphite monochromator, the tube voltage is 40 kV, and the tube current is 100 mA.

The surface morphology was characterized by scanning electron microscopy (SEM, JEOL-6360LV) with an accelerating voltage of 20-30 kV.

Electrochemical performance of the electrodes was measured at an electrochemical workstation (CHI660E) in 6 mol L\(^{-1}\) KOH solution. The classical three-electrode system was adopted with LDHs, Pt mesh, and saturated calomel electrode (SCE) as work electrode, counter electrode and reference electrode respectively. The scanning voltage range of cyclic voltammetry (CV) test is 0-0.6 V.

3. Results and Discussions

3.1. Structural and Morphological Analysis

3.1.1. Foam Ni Etching during Situ Hydrothermal Synthesis. Figure 1 shows SEM analysis of foam Ni surface after different hydrothermal treatments. The surface of foam Ni from NaOH/Na\(_2\)CO\(_3\) precipitation system (figure 1a) appears relatively uniform nanosheets with small angle due to the reaction in alkaline system. After hydrothermal treatment in CO(NH\(_2\))\(_2\) system, the surface of foam Ni changed significantly (figure 1b). The surface of foam Ni was transferred to a three-dimensional network structure interwoven with nanowires of about 60 nm in diameter. This special structure provides three-dimensional nucleation site for in-situ growth of electrode active substances.

![Figure 1. SEM images of foam Ni after hydrothermal process in (a) NaOH/Na\(_2\)CO\(_3\) and (b) CO(NH\(_2\))\(_2\).](image-url)
3.1.2. Three Dimensions Growing of Electrode Materials. As shown in figure 2, in the NaOH/Na₂CO₃ precipitators system, LDHs on foam Ni is mainly grows along the surface of foam Ni or present a certain angle (figure 2a), which is related to the layered structure of LDHs and relatively flat surface morphology of foam Ni in this alkaline system. In CO(NH₂)₂/NaOH/Na₂CO₃ precipitant system, LDHs products show totally different morphology with zigzag structures and extending into three-dimensional space (figure 2b). This result indicates that CO(NH₂)₂ can promote the 3D growth of LDHs. Such a 3D active electrode arrangement with a relatively orderly lamellar structure not only effectively reduces the agglomeration and growth of particles, but also improves the specific surface area, and further forms abundant channels for electron transport [13-14].

![Figure 2. SEM images of in-situ-LDHs in (a)NaOH/Na₂CO₃ and (b) CO(NH₂)₂/NaOH/Na₂CO₃ system with CO(NH₂)₂/NaOH ratio of 3:1.](image)

3.1.3. Urea Promoted the Formation of New Phase. XRD test was used to analyze the influence of CO(NH₂)₂/NaOH ratio in the precipitant on crystal phase composition of the product. As shown in figure 3, in NaOH/Na₂CO₃ system, XRD diffraction peaks appeared at 2θ=11.64, 23.39, 34.56, 39.15 and 46.64 °, which were respectively corresponding to the diffraction peaks of (003), (006), (012), (015), and (018) crystal planes of hydrotalcite structure Zn₆Al₂(OH)₁₆CO₃·4H₂O (JCPDS No.038-0486), indicating that the product was the hydrotalcite structure Zn₆Al₂(OH)₁₆CO₃·4H₂O. When CO(NH₂)₂ is added to the hydrothermal system, several new diffraction peak appear in the XRD pattern at 2θ=12.83, 19.25, and 23.91 °, indicating that new crystal phases are generated in the product. These new diffraction peaks correspond to the characteristic diffraction peaks of Zn₄(OH)₆CO₃·H₂O and are consistent with the standard card (JCPDS No.011-0287). With the increase of precipitant CO(NH₂)₂/NaOH ratio, the characteristic diffraction peak strength of Zn₄(OH)₆CO₃·H₂O increased significantly. When CO(NH₂)₂/NaOH ratio was 4:0, the characteristic diffraction peak of Zn₆Al₂(OH)₁₆CO₃·4H₂O disappeared completely, indicating that the presence of CO(NH₂)₂ in the synthesis system promoted the transformation of crystal phase structure.

3.2. Electrochemical Properties
CV results at scanning speed of 10 mV s⁻¹ in three-electrode system is shown in figure 4. It can be seen that each electrode presents a pair of REDOX peaks, indicating that the electrode has obvious Faraday pseudocapacitance characteristics [15-16]. the electrodes synthesized with CO(NH₂)₂ as the precipitant component show higher activity than that one without CO(NH₂)₂ during hydrothermal process, which indicates that the Zn₄(OH)₆CO₃·H₂O has higher electrochemical activity than Zn₆Al₂(OH)₁₆CO₃·4H₂O. Additionally, the peak current response value of the main peak of REDOX increased first and then decreased with the increase of the proportion of CO(NH₂)₂/NaOH substances.
Figure 3. XRD patterns of in-situ-LDHs materials for CO(NH$_2$)$_2$/NaOH/Na$_2$CO$_3$ hydrothermal synthesis conditions.

Figure 4. (a) CV curves of the electrodes at a scan rate of 10 mV s$^{-1}$ and (b) galvanostatic charge/discharge curves at 1 A g$^{-1}$ for different CO(NH$_2$)$_2$/NaOH ratio hydrothermal synthesis conditions.

Galvanostatic charge/discharge curves with current density of 1 A g$^{-1}$ shows obvious charge-discharge platform in figure 4b, indicating that the electrode material exhibits good Faraday pseudocapacitance characteristics in the potential range investigated [17-18]. The specific capacitance of the electrode increases first and then decreases with the increase of CO(NH$_2$)$_2$/NaOH ratio. The specific capacitance of the electrode can be as high as 1259 F g$^{-1}$ when the ratio of CO(NH$_2$)$_2$/NaOH ratio is 3:1, which is much higher than that of electrode with NaOH/Na$_2$CO$_3$ as the precipitant showing superior electrochemical activities.

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