Preparation of Ni(OH)2/RGO Composite by Chemical Precipitation-Reflux Method and Its Discharge Performance (Postprint)

Authors: Huiying Yu, He Wenxiu, Zhang Yongqiang, An Shengli, Liu Junhong

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Abstract

Using graphite oxide (GO) and NiSO4 · 6H2O as precursors and ammonia water as a precipitant, Ni(OH)2/reduced graphene oxide (RGO) composites were prepared via a chemical precipitation-reflux method. The structure and surface micromorphology of the materials were characterized by XRD and SEM, while the electrochemical performance of the electrode materials was evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS). The effects of GO:Ni(OH)2 mass ratio and ammonia water concentration on the structure, morphology, and electrochemical performance of the composites were investigated. The results demonstrate that the prepared -Ni(OH)2/RGO composite exhibits an intercalated structure consisting of Ni(OH)2 nanosheets and RGO sheets. When the ammonia water concentration is 3 mol/L and GO:Ni(OH)2=1:8 (mass ratio), the composite electrode material delivers a discharge specific capacity as high as 334.9 mAh/g at 0.2C, and the discharge specific capacity at 5C is 260.2 mAh/g, maintaining 90% of the theoretical specific capacity of -Ni(OH)2, thus exhibiting excellent rate capability and cycling performance.

Full Text

Chemical Precipitation-Reflow Synthesis and Discharge Performance of Ni(OH) /RGO Composites

YU Huiying[1], HE Wenxiu[1], ZHANG Yongqiang[1], AN Shengli[1], LIU Junhong[2]

[1] School of Chemistry and Chemical Engineering, Inner Mongolia University of Science & Technology, Baotou 014010, China
[2] Baotou Professional Technology College, Baotou 014010, China

Correspondent: HE Wenxiu, Tel: (0472)5953323, E-mail: nmghwx@sina.com

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Abstract

Ni(OH) /reduced graphene oxide (RGO) composites were synthesized via a facile chemical precipitation-reflux method using graphite oxide (GO) and NiSO ·6H O as precursors with ammonium hydroxide as the precipitating agent. The structure and surface morphology of the materials were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), while the electrochemical performance of the electrode materials was evaluated through cyclic voltammetry (CV), galvanostatic charge/discharge tests, and electrochemical impedance spectroscopy (EIS). The effects of the GO:Ni(OH) mass ratio and ammonium hydroxide concentration on the composite structure, morphology, and electrochemical properties were systematically investigated. The results demonstrate that the synthesized -Ni(OH) /RGO composite exhibits an intercalated structure consisting of Ni(OH) nanosheets inserted between RGO layers. Under optimal conditions (ammonium hydroxide concentration of 3 mol/L and GO:Ni(OH) mass ratio of 1:8), the composite electrode delivered a remarkable discharge specific capacity of 334.9 mAh/g at 0.2C and 260.2 mAh/g at 5C, retaining 90% of the theoretical specific capacity of -Ni(OH) and exhibiting excellent rate capability and cycling performance.

KEY WORDS: composite materials, chemical precipitation-reflux method, -Ni(OH) , reduced graphene oxide, electrochemical performance

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1. Introduction

Lithium-ion batteries for electric vehicles have revealed numerous drawbacks, while other novel battery systems also suffer from various limitations. Nickel-metal hydride (Ni/MH) batteries offer distinct advantages including environmental friendliness, high safety, low cost, and high discharge capacity, making them widely applicable in pure electric vehicles, hybrid electric vehicles, and portable electronic devices. Nickel hydroxide (Ni(OH)) with excellent electrochemical performance can serve as the positive electrode active material in Ni/MH batteries; however, its poor electrical conductivity necessitates the addition of conductive agents or additives [1,2].

Graphene is a novel two-dimensional carbon nanomaterial featuring a large -bond network that enables free electron delocalization perpendicular to the graphene sheet plane. When these quasi-free electrons flow freely within the carbon network, the graphene surface exhibits metallic-like electrical and thermal conductivity. At room temperature, graphene' s electron mobility exceeds that of carbon nanotubes or silicon crystals, while its resistivity is lower than copper or silver. Additionally, graphene' s unique two-dimensional structure provides a theoretical specific surface area as high as 2630 m^2/g [3].

Batteries employing nano-sized Ni(OH) as electrode materials can achieve approximately 20% capacity enhancement. Nevertheless, Ni(OH) nanoparticles tend to agglomerate and suffer from poor conductivity, while volume expansion during charge/discharge cycles degrades rate performance and cycling stability [4-8]. Compositing Ni(OH) with graphene represents a promising solution to these challenges [9,10]. Using graphene sheets as a substrate or scaffold can enhance the electrochemical activity of Ni(OH) . Xie et al. [11] synthesized -Ni(OH) /RGO composite electrodes via a hydrothermal method; the unique layered structure combined the advantages of both components, maintaining a specific capacitance of 660.8 F/cm after 2000 charge/discharge cycles. Huang et al. [12] employed a coprecipitation method to intercalate hexagonal Ni(OH) nanosheets into RGO layers, suppressing agglomeration of both Ni(OH) and RGO. Fang et al. [13] prepared -Ni(OH) /graphene composites through precipitation, demonstrating large specific capacitance and excellent cycling stability as supercapacitor electrode materials. Fu et al. [14] utilized a modified hydrothermal method to synthesize -Ni(OH) /RGO nanosheet composites, achieving a specific capacitance of 1740.56 F/g at a current density of 2.5 A/g.

Graphene is typically prepared through redox methods involving Hummers' method to produce graphite oxide, followed by ultrasonic exfoliation to form graphene oxide and subsequent chemical reduction. Common reducing agents include hydrazine hydrate, NaBH , and strong alkali-assisted ultrasonic reduction. However, NaBH is relatively expensive and prone to boron residue, while hydrazine hydrate is toxic. This work employs a simple and environmentally friendly chemical precipitation-reflux method to synthesize -Ni(OH) /RGO composites, intercalating Ni(OH) nanosheets between RGO layers to form an intercalated structure, and investigates the influence of GO:Ni(OH) mass ratio and ammonium hydroxide concentration on the composite structure, morphology, and electrochemical performance.

2. Experimental

2.1 Materials Graphite powder (45 m), concentrated sulfuric acid (purity >98%), potassium permanganate (KMnO , analytical reagent), sodium nitrate (NaNO , analytical reagent), hydrogen peroxide (H O , 30 wt%), deionized water (self-prepared), nickel sulfate hexahydrate (NiSO ·6H O, analytical reagent), ammonium hydroxide (NH ·H O, 25.0-28.0 wt%), potassium hydroxide (KOH, analytical reagent), polytetrafluoroethylene (PTFE, 60 wt% emulsion), acetylene black, and nickel foam (specifications: thickness 1 mm, areal density 320 g/cm^2, porosity 95%).

2.2 Preparation of Ni(OH) /RGO Composites Graphite oxide (GO) was prepared using a modified Hummers' method [15,16]. To synthesize the composite, 0.15 g of GO was dissolved in 150 mL deionized water with stirring for 1 h and ultrasonic treatment for 2 h. An appropriate amount of nickel sulfate was dissolved in deionized water, and ammonium hydroxide was added dropwise until the solution turned dark blue. This solution was then added dropwise to the GO suspension, followed by reflux stirring at 40°C for 3 h. Additional ammonium hydroxide was added to adjust the pH to 10.5, after which the temperature was increased to 80°C for reflux stirring for 6 h. The product was filtered, washed repeatedly with deionized water and absolute ethanol, and vacuum-dried at 80°C for 12 h to obtain the Ni(OH) /RGO composite.

For comparison, pure Ni(OH) was prepared using the same method without GO. For convenience, samples with GO:Ni(OH) = 1:8 (mass ratio) and ammonium hydroxide concentrations of 3 mol/L and 5 mol/L are denoted as GN8(3M) and GN8(5M), respectively. Similarly, the sample with GO:Ni(OH) = 1:10 and ammonium hydroxide concentration of 3 mol/L is denoted as GN10(3M).

2.3 Material Characterization and Electrochemical Testing The crystal structure was analyzed using a D8 ADVANCE powder X-ray diffractometer with Cu K radiation (= 0.15418 nm) operating at 300 mA and 40 kV. The scanning range was 10-80° with a scan rate of 4°/min. Surface morphology was observed using an S-3400N scanning electron microscope at an accelerating voltage of 20 kV.

For electrode preparation, the Ni(OH) /RGO composite, acetylene black, and PTFE emulsion were mixed in a mass ratio of 85:10:5 in an agate mortar. The mixture was blended with absolute ethanol as a dispersant to form a uniform paste, which was coated onto 10 mm × 10 mm nickel foam sheets. After vacuum drying at 60°C for 3 h, the electrodes were pressed into thin sheets at 10 MPa.

Electrochemical measurements were performed using a CHI760E electrochemical workstation for CV and EIS tests, and a CT2001A battery testing system for galvanostatic charge/discharge tests. All electrochemical tests were conducted in a three-electrode system with a platinum sheet as the auxiliary electrode, saturated calomel electrode (SCE) as the reference electrode, and 6 mol/L KOH solution as the electrolyte.

3. Results and Discussion

3.1 XRD Analysis [Figure 1: see original paper] presents the XRD patterns of the Ni(OH) /RGO composites. The three composites GN8(5M), GN10(3M), and GN8(3M) exhibit strong diffraction peaks at 2 = 19.5° (001), 33.1° (100), 38.5° (101), 52.0° (102), 59.1° (110), and 62.8° (111), which match well with the standard pattern of -Ni(OH) (JCPDS 14-0117). This confirms the formation of -Ni(OH) on the graphene sheets. No characteristic diffraction peak of RGO near 26° is observed, likely due to its weak intensity being masked by the strong Ni(OH) peaks. The diffraction patterns of GN8(3M) and GN10(3M) are essentially identical, indicating that the Ni(OH) content does not significantly affect the structural regularity of -Ni(OH) . Compared with GN8(3M), GN8(5M) shows higher diffraction peak intensities, suggesting better crystallinity. The slightly larger half-peak width of GN8(3M) indicates increased lattice defects due to stacking faults in the crystal structure, which may contribute significantly to the electrochemical performance of the electrode material [17-20].

3.2 SEM Analysis [Figure 2: see original paper] shows the FE-SEM images of pure Ni(OH) and the Ni(OH) /RGO composites GN8(5M), GN10(3M), and GN8(3M). Pure Ni(OH) [Figure 2a: see original paper] exhibits a sheet-like structure with thickness of several nanometers, with the nanosheets interwoven together. Curled and wrinkled graphene nanosheets are visible in [FIGURE:2b-d], where Ni(OH) nanosheets grow on the graphene layers to form Ni(OH) /RGO sheet structures. In the GN8(3M) composite [Figure 2d: see original paper], controlled electrostatic repulsion between sheets through appropriate pH adjustment with ammonium hydroxide results in uniform dispersion of numerous Ni(OH) nanosheets attached to the graphene surface, forming an intercalated structure. As the ammonium hydroxide concentration increases from 3 mol/L to 5 mol/L, Ni(OH) /RGO stacking and agglomeration become evident, forming a denser intermediate structure [Figure 2b: see original paper]. This occurs because excessive precipitant concentration leads to gelatinous Ni(OH) that is difficult to precipitate and prone to agglomeration. When the Ni(OH) content in the composite increases, numerous Ni(OH) nanosheets cover the graphene surface without forming a uniform intercalated structure.

3.3 Cyclic Voltammetry Characteristics [Figure 3a: see original paper] displays the CV curves of Ni(OH) , GN8(5M), GN10(3M), and GN8(3M) electrode materials at a scan rate of 5 mV/s. Each curve exhibits a distinct pair of oxidation and reduction peaks. The anodic peak (positive current) occurs near 0.47 V, corresponding to the oxidation of Ni(OH) to NiOOH, while the cathodic peak (negative current) appears near 0.22 V, representing the reduction of NiOOH back to Ni(OH) [21]. The electrochemical reaction can be expressed as [22]:

$$\mathrm{Ni(OH)}_2 + \mathrm{OH}^- \leftrightarrow \mathrm{NiOOH} + \mathrm{H_2O} + e^-$$

The GN8(3M) composite electrode shows the smallest oxidation peak potential, indicating a higher oxygen evolution potential and thus higher charging efficiency. It also exhibits the highest oxidation peak current, demonstrating improved electrochemical performance, particularly superior rate capability. The potential difference between oxidation and reduction peaks (ΔE) can evaluate electrode reaction reversibility; GN8(3M) shows the smallest ΔE of 0.28 V, indicating the best electrochemical reversibility. The synergistic contribution from

Ni(OH) and RGO facilitates electron transfer and electrolyte ion migration, enhancing electrochemical activity.

[Figure 3b: see original paper] presents CV curves of the GN8(3M) electrode at various scan rates from 2 mV/s to 50 mV/s within a voltage range of 0-0.7 V. As the scan rate increases, electrode polarization becomes more severe, with the oxidation peak shifting positively and the reduction peak shifting negatively. The increased ΔE and peak current values reduce reaction reversibility. The specific capacity of GN8(3M) decreases with increasing scan rate from 2 mV/s to 50 mV/s, primarily due to increased internal resistance. At low scan rates, both internal and external active materials participate in redox reactions, whereas at high scan rates, only surface-active materials contribute to ion transport. Consequently, the effective interaction between electrolyte ions and the electrode diminishes at higher scan rates, affecting reversibility. At 50 mV/s, the oxidation peak becomes indistinct, suggesting overlap with the oxygen evolution peak and decreased charging efficiency during early charging stages.

3.4 Galvanostatic Charge/Discharge Performance [Figure 4: see original paper] shows the charge/discharge curves of Ni(OH) and Ni(OH) /RGO electrode materials at 0.2C. The composite electrodes exhibit two distinct plateaus in the charging curves, with the charging potential profiles being essentially consistent. Pure Ni(OH) shows a higher charging potential plateau and more significant oxygen evolution potential. The discharge curves reveal that pure Ni(OH) has a shorter discharge potential plateau, while the composite electrodes display longer and flatter discharge platforms. The GN8(3M) electrode shows the longest discharge plateau, achieving a specific discharge capacity of 334.9 mAh/g. This enhancement arises from -Ni(OH) loading on graphene sheets, which suppresses agglomeration of both Ni(OH) and RGO layers. Their synergistic effect significantly improves the discharge specific capacity compared to pure Ni(OH) . Compared with Lei et al.' s [23] mixed-phase Ni(OH) synthesized by coprecipitation (330 mAh/g at 0.2C) and Yang et al.' s [24] graphene-doped Ni(OH) (326.8 mAh/g at 0.2C), the GN8(3M) composite shows markedly improved capacity. This demonstrates that the synthesis method enhances overall discharge capacity, while the unique intercalated structure of RGO nanosheets and -Ni(OH) nanosheets facilitates electrolyte ion diffusion and increases the contact area between active material and electrolyte, thereby improving electrochemical performance.

[Figure 5: see original paper] illustrates the discharge specific capacity curves of Ni(OH) and Ni(OH) /RGO electrodes at various rates (0.2C, 0.5C, 1C, 2C, and 5C). All four materials show significant capacity degradation with increasing charge rate. This occurs because at higher rates, redox reactions are confined to the electrode surface, drastically reducing active material utilization and leading to incomplete reactions and lower capacity. Among the four electrodes, GN8(3M) delivers 334.9 mAh/g at 0.2C and 260.2 mAh/g at 5C, representing only a 22% capacity loss and demonstrating excellent capacity retention.

3.5 Cycling Stability [Figure 6: see original paper] presents the cycling stability curves of Ni(OH) and Ni(OH) /RGO electrodes at different rates. All four electrodes undergo an activation process in the initial stage, where discharge specific capacity gradually increases due to increasing active sites and facilitated particle diffusion. After approximately 9 cycles, the materials reach stable performance. As the discharge rate increases, the hydrogen nickel oxide electrode shows significant capacity decline. In the composite electrodes, graphene serves not only as a highly conductive additive but also as an elastic support material, with its high surface area accommodating volume changes during charge/discharge cycles. The GN8(3M) electrode exhibits the best cycling stability under high-rate conditions because the intimate contact between Ni(OH) nanosheets and RGO layers effectively prevents Ni(OH) agglomeration and RGO restacking, increasing the effective solid-liquid contact area and improving active material utilization.

3.6 Electrochemical Impedance Spectroscopy [Figure 7: see original paper] displays the electrochemical impedance spectra of Ni(OH) and Ni(OH) /RGO electrodes over the frequency range of 0.01-100,000 Hz. Each curve consists of a semicircle in the high-frequency region and a straight line in the low-frequency region. The intersection with the real axis in the high-frequency region represents solution resistance (Rs), while the semicircle diameter corresponds to the electron transfer process and reflects charge transfer resistance (Rct). The slope of the straight line in the low-frequency region relates to solid-phase proton diffusion, with a larger slope indicating better proton diffusion performance. An equivalent circuit model [25] was used to analyze the impedance data.

In the equivalent circuit, Rs (Ω) represents solution resistance, Cdl (F) represents interfacial capacitance, and Zw represents Warburg impedance (the linear portion). The enlarged high-frequency region reveals Rs values of 0.430, 0.515, 0.423, and 0.409 Ω for Ni(OH) , GN8(5M), GN10(3M), and GN8(3M), respectively, with GN8(5M) showing the highest Rs. This occurs because at high ammonium hydroxide concentrations, OH ions become saturated, leaving portions of the Ni(OH) electrode surface unutilized during high-rate charge/discharge and hindering charge transfer. GN8(3M) exhibits the smallest Rs and, as shown in the magnified view, the smallest semicircle diameter with an Rct of 0.390 Ω, lower than the other three electrodes. Additionally, GN8(3M) shows the largest slope in the low-frequency region, indicating the smallest Warburg impedance and relatively high electrochemical activity. This results from RGO enhancing electrode conductivity and the uniform growth of Ni(OH) nanosheets on RGO layers, which improves both conductivity and active surface area. The effective RGO-Ni(OH) composite facilitates charge transfer and ion diffusion during electrochemical reactions, enabling excellent high-rate performance. Furthermore, GN8(3M) possesses more crystal defects that enhance the proton diffusion coefficient, consistent with the XRD and SEM results.

4. Conclusions

1. Ni(OH) /RGO composites with different loading ratios can be prepared by the chemical precipitation-reflux method. The -Ni(OH) /RGO composite exhibits an intercalated structure composed of RGO nanosheets and -Ni(OH) nanosheets. The composite sheets are thicker compared to pure -Ni(OH) . While the Ni(OH) content does not affect the crystal structure, composites prepared with 3 mol/L ammonium hydroxide contain more crystal defects.
2. The Ni(OH) /RGO composite prepared with 3 mol/L ammonium hydroxide and a GO:Ni(OH) mass ratio of 1:8 demonstrates superior electrochemical performance, achieving a discharge specific capacity of 334.9 mAh/g at 0.2C—significantly exceeding the theoretical capacity of -Ni(OH) (289 mAh/g). The composite also shows excellent rate capability and cycling stability, making it a promising candidate for high-performance Ni/MH battery cathodes.

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Note: Figure translations are in progress. See original paper for figures.