Cycling stability of ultrafine β -Ni(OH)₂ nanosheets for high capacity energy storage device via a multilayer nickel foam electrode

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Abstract

Ultrafine β -Ni(OH)₂ nanosheets with an average diameter of about 14.5 nm have been fabricated by immersing Na(HCO₃)₂ nanoparticles into 6 M KOH solution. The multilayer nickel foam system was introduced to improve the cycling stability of ultrafine β -Ni(OH)₂ nanosheets without using acetylene black. The results demonstrated that the **specific discharge capacity** of the β -Ni(OH)₂ electrode was up to **524.5 C**

g^{-1} at 5 A g^{-1} and retained 83.8% after 1000 cycles, which was better than those of other $\beta\text{-Ni(OH)}_2$ electrodes obtained using acetylene black as conductors (retained 59.1% after 1000 cycles). Even after 5000 cycles, the **specific capacity** also maintained 80.8%. In addition, **a hybrid supercapacitor** was successfully fabricated based on ultrafine $\beta\text{-Ni(OH)}_2$ nanosheets and active carbon, the corresponding energy density and power density at 0.1 A g^{-1} were calculated to be 20.45 Wh kg^{-1} and 75 W kg^{-1} , respectively. What's more, **the hybrid supercapacitor** could light up a set of low-voltage light-emitting diodes.

Key Words: $\beta\text{-Ni(OH)}_2$ nanosheets; **hybrid supercapacitor**; multilayer nickel foam

1. Introduction

Electrochemical energy storage device with higher power density, faster charge-discharge rate and longer cycle life have attached growing research interests for various applications, which can substitute for the fossil fuel energy as a rechargeable and environmentally friendly energy storage device[1-5]. The use of conventional electrochemical double-layer capacitors (EDLCs) for carbon-based nanomaterials is quickly expanding. However, their capacitances (less than 300 F g^{-1}) are too low to meet the growing needs for high-performance energy-storage

equipment[6]. Transition metal oxide or hydroxide-based nanomaterials with remarkable theoretical capacitances, such as RuO_2 [7], MnO_2 [8-10], NiO [11-13], Co(OH)_2 [14, 15] and Ni(OH)_2 [16, 17], are chosen as the alternative electrode materials. Among the investigated transition metal oxide or hydroxide-based nanomaterials, nickel-based compounds such as Ni(OH)_2 have attracted a large amount of attention due to their low toxicity, low cost and excellent electrochemical properties[16-19], in addition, Ni(OH)_2 is also a typical paramagnetic material[20].

Recently, nano-sized Ni(OH)_2 materials with higher specific surface area and appropriate pore size distribution have been demonstrated to be easy for ions to diffuse and transport efficiently, resulting in an enhanced electrochemical performance[21-23]. Zhou et al. demonstrated that nano-sized Ni(OH)_2 exhibited a better electrochemical performance than micro-sized Ni(OH)_2 particles. Zhou et al. also showed that the specific discharge capacity of the nano-sized Ni(OH)_2 electrodes was 381 mA h g^{-1} [24]. However, other related studies mentioned that the rate capability and cycling stability of Ni(OH)_2 were compromised due to the poor conductivity and the faradic redox reactions of Ni(OH)_2 [25-28]. Therefore, in the past

decade, considerable efforts have been made to improve the rate capability and cycling stability of Ni(OH)_2 . For example, Dai and co-workers achieved an excellent electrochemical characteristic and a high cycling stability for Ni(OH)_2 by growing it directly on highly-conductive graphene [29]. Yan et al. also demonstrated that the electron performance of the assembled materials for the ultra-small nickel hydroxide nanoparticles and the reduced graphene oxide (RGO) sheets had an obvious improvement over that of pure Ni(OH)_2 . The capacity retention of Ni(OH)_2 -RGO composite was 89% even after 1000 cycles, much higher than that (59%) of pure Ni(OH)_2 . However measuring or calculating the mass of Ni(OH)_2 on graphene or RGO sheets was complex[30]. Jang and co-workers improved the cycling stability of 3D Ni(OH)_2 nanomaterials from 30% to 80% by depositing gold nanoparticles onto 3D Ni(OH)_2 surfaces[31]. However, as we all know, the introduction of Au nanoparticles can increase the cost.

In this paper, a novel electrode was made by dispersing ultrafine β - Ni(OH)_2 nanosheets onto the multilayer nickel foams without acetylene black. The electrochemical results showed that this electrode exhibited a high specific discharge capacity of 524.5 C g^{-1} at a current density of 5 A g^{-1} and the cycling

stability of the ultrafine β -Ni(OH)₂ nanosheets was improved from 59.1% to 83.8% at the same time. The function and mechanism of the multilayer nickel foam system are discussed in detail.

2. Experimental section

2.1 Synthesis of the ultrafine β -Ni(OH)₂ nanosheets

All chemicals were analytical grade and used without any further purification. In a typical procedure, 1.18 g NiCl₂•6H₂O and 0.78 g ammonium carbonate were completely dissolved in 10 and 30 mL deionized water, respectively. Then, the ammonium carbonate solution was added to the nickel chloride solution under continuous stirring. After several seconds, light-green precipitates were observed and a great deal of odorless bubbles appeared. Finally, the color of the mixed solution changed from light-green to blue. Soon afterwards, the above-synthesized suspension was transferred into a 70 mL Teflon-lined stainless steel autoclave, sealed, maintained at 150 °C for 10 h in an electronic furnace. After cooling to the room temperature, the green precipitates were collected by centrifugation, washed with deionized water and absolute ethanol several times, and then dried at 60 °C. The final β -Ni(OH)₂ powder was obtained by immersing the as-dried

green powder into 6 M KOH solution over a night.

2.2 Materials Characterization

The phase of the products was characterized by X-ray powder diffraction (XRD) technique using a Bruker D8 advanced X-ray diffractometer equipped with Cu-K α radiation (K α = 0.15418 nm). The high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) were recorded using a JEOL-2100F transmission electron microscope at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained with a MIRA3 LMH scanning electron microscope. The specific surface area was estimated using the Brunauer-Emmett-Teller (BET) method, and the pore-size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method based on a Quadrasorb SI surface area analyzer (version 5.04).

2.3 Preparation of single electrodes and a hybrid supercapacitor

The working electrode (marked with N1) was prepared by loading 80 wt.% active materials, 10 wt.% acetylene black and 10 wt.% polyvinylidene fluoride (PVDF), along with a few drops of 1-methyl-2-pyrrolidinone onto the monolayer nickel

foams. N2 electrode was made by adjusting the slurry ingredient (a mass ratio of active materials and PVDF was 9:1). N3 electrode was fabricated by dipping two sets of the suppressed bilayer nickel foams into the homogeneous liquid which was formed by diluting the above-mentioned slurry (used for preparing N2 electrode) with 1-methyl-2-pyrrolidinone. The active carbon electrode (AC) electrode was prepared in the above-described method of N2 electrode (The active materials were just changed to active carbon). The loading mass was about 2 mg. All these above-fabricated electrodes (13 mm in diameter) were dried at 60 °C for 24 h and then were pressed at 10 Mpa.

The hybrid supercapacitor was built with N3 and AC electrodes as positive and negative electrode at the loading mass ratio of 1:7.2. A polypropylene separator was placed between positive and negative electrodes and 6 M KOH aqueous solution was used as the electrolyte. Finally it was encapsulated.

2.4 Electrochemical test of single electrodes and a hybrid supercapacitor

The electrochemical measurements of β -Ni(OH)₂ electrode and AC electrode including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical

impedance spectroscopy (EIS) were carried out using a CHI660E electrochemical workstation in a three-electrode cell system with Hg/HgO electrode as a reference electrode, a Pt foil electrode ($3\times 3\text{ cm}^2$) as a counter electrode, samples as working electrode and the 6 M KOH aqueous solution as electrolyte. The electrochemical measurements of **the hybrid supercapacitor** were measured using the same electrochemical working station in a two-electrode cell system at room temperature. The specific capacity together with the energy and power densities of the **hybrid supercapacitor** were all calculated based on the total mass of both the positive and negative electrode materials.

3. Result

3.1 Morphology and structural characterization

Fig. 1

Fig. 2

The phase and morphology of as-synthesized samples were investigated by XRD and TEM. The XRD patterns of Ni(OH)_2 powder and $\text{Ni(HCO}_3)_2$ precursor were showed in Fig. 1 and Fig. S1. In Fig.1 the diffraction peaks at about 19.3° , 33.1° , 38.5° , 52.1° , 59.1° and 62.7° were indexed as (001), (100), (101), (102), (110), and (111) reflections of $\beta\text{-Ni(OH)}_2$ (JCPDS, No.

14-0117). The broad middle-intensity diffraction peaks indicated that the size of β -Ni(OH)₂ was nano scale. The average crystallite size of β -Ni(OH)₂ sample was calculated by the Scherrer equation to be 9.8 nm, which is further supported by TEM images (Fig. 2). The average particle size estimated from Fig. 2a was about 14.5 nm. The difference of the particle size values from XRD and TEM could be ascribed to the hexagonal plate structure of β -Ni(OH)₂ sample[32]. Fig. 2a shows two morphologies of β -Ni(OH)₂ sample with a different view. Some are laid flat (marked by rectangular c) and some are the side stack (marked by round circle d). Fig. 2b is a set of weak and large concentric SAED patterns, which is an evidence for a poor-polycrystalline structure and a small-size β -Ni(OH)₂. Fig. 2c and Fig. 2d are the corresponding HRTEM images from c and d in Fig. 2a. The observed lattice plane distances of 0.27 nm in Fig. 2c corresponded to the (100) planes of hexagonal β -Ni(OH)₂, and the corresponding fast Fourier transform (FFT, top right) indicates that the particle was imaged along [001] zone axis. Fig. 2d shows the interplanar spacing of the round circle (d) in Fig. 2a is about 0.23 nm, which corresponds to the distance between two (101) planes, (FFT, top right in Fig. 2d).

3.2 Surface area and porosity distribution

Fig. 3

As showed in Fig. 3, the pore size was also narrow and centered at around 3.4 nm. The inset of Fig. 3 is the nitrogen adsorption-desorption isotherm. The curve exhibits type IV isotherm in the Brunauer classification with an H2-type loop according to the IUPAC classification, which is the typical feature of mesoporous material with relatively uniform channel-like pores[33]. The specific surface area of ultrafine β -Ni(OH)₂ powder calculated by BET method is about 192.2 m² g⁻¹, much higher than those previously-reported values (121.4, 45.7 and 17.3 m² g⁻¹)[34, 35]. The nitrogen adsorption-desorption isotherm and the BJH pore-size distribution plots of Ni(HCO₃)₂ precursor are showed in Fig. S2, resulting in the formation of ultrafine β -Ni(OH)₂ with high specific surface area and the relatively uniform channel-like pores. The ultrafine structure of β -Ni(OH)₂ nanasheets would be easy for the electrons and ions to transport efficiently in the electrode.

3.3 Electrochemical properties for single electrodes

Fig. 4

Fig. 4a shows the CV curves of N1, N2 and N3 electrodes at the scan rate of 10 mV s^{-1} within the potential range of 0.05 - 0.65 V (vs. Hg/HgO). All CV curves exhibited a set of reversible redox peaks ($\text{Ni}^{2+}/\text{Ni}^{3+}$), indicating their typical Faradaic-capacity feature. The Faradaic reaction is based on the following electrochemical reaction:

The anodic peak was ascribed to the oxidation from $\beta\text{-Ni}(\text{OH})_2$ to NiOOH, and the corresponding cathodic peak was its reverse change. The specific capacity values of N1, N2 and N3 electrodes were calculated to be 692.6 369.8 and 732.2 C g^{-1} , respectively. It could be found that the specific capacities of N1 and N3 electrodes were two times as high as that of N2 electrode.

GCD curves for N1, N2 and N3 electrodes are displayed in Fig. 4b. Their current densities are 5 A g^{-1} with the voltage range of 0.05 - 0.5 V (vs. Hg/HgO). Their curves were asymmetric with a flat stage in the discharge part, further confirming their typical Faradaic-capacity feature. Their specific capacity values were calculated to be 482.9, 243.5 and 524.5 C g^{-1} , in accordance with the CV calculation results. Hence, the ultrafine

structure of β -Ni(OH)₂ with high surface area was not the only factor to lead to a high specific capacity.

Fig. 4c shows the specific capacity variation of N1, N2 and N3 electrodes with the current densities changed from 1 to 20 A g⁻¹. The specific capacity value of N2 electrode showed a dramatic decrease from 300.7 C g⁻¹ at 1 A g⁻¹ to 134.1 C g⁻¹ at 20 A g⁻¹ (only 44.5%), while those of N3 and N1 electrodes decreased from 609.2 to 379.9 C g⁻¹ (62.4%) and from 584.9 to 293.9 C g⁻¹ (50.3%), respectively. From Fig. 4c, the specific capacity of N3 electrode measured at different current densities were higher than those of N1 and N2 electrodes, suggesting that N3 electrode had a better rate capability.

The cycle life is another important characteristic for electrochemical energy storage device. Fig. 4d displays the capacity retention curves of N1, N2 and N3 electrodes as a function of cycle number measured at a current density of 5 A g⁻¹. The capacity of N3 electrode could remain 83.8% (439.6 C g⁻¹) of the maximum value after 1000 cycles, while the capacity retention of N2 and N1 electrodes were 71.3% and 59.1%, respectively. Compared with N1 and N2 electrodes, the cycle stability of N3 electrode was improved remarkably.

Fig. 4e and 4f are the EIS spectrograms of N1 and N3 electrodes investigated before and after 1000 cycles. The Nyquist plots ranging from 100 kHz to 0.01 Hz showed that the spectra had a compressed semicircle in the high-to-medium frequency zone and a straight line in the low-frequency zone. In general, a semicircle diameter is associated with the charge transfer resistance (R_{ct}) of the electrode based on the property of electrode surface and the electrolyte accessible area, and a straight line accounted for the diffusion of the electroactive species[36]. The semicircle diameter for N1 electrode reduced remarkably after 1000 cycles in Fig. 4e, while that for N3 electrode changed a little in Fig. 4f. The insets of Fig. 4e and 4f were the corresponding equivalent circuits for the impedance analysis, where, R_s , C_d , R_{ct} , R_w and C_F were the total ohmic resistance for the solution and electrodes, the capacitance of the double layer, the electrochemical reaction impedance, the Warburg impedance and the Faradaic pseudocapacitance, respectively[37]. These parameters calculated with Zview software were presented in Table 1 in the supporting information. R_{ct} values of N1 electrode were 1.92 Ω (before cycle) and 0.82 Ω (after cycle), respectively, while R_{ct} values of N3 electrode were both 0.11 Ω .

3.4 Electrochemical properties for a **hybrid supercapacitor**

Fig. 5

A **hybrid supercapacitor** was assembled by N3 as a cathode electrode and AC as an anode electrode. Fig. 5a shows the CV curves of the cathode electrode at different scan rates ranging from 2 to 30 mV s^{-1} in the potential range 0.05 - 0.65 V (vs. Hg/HgO). A slight negative/positive shifts were observed with the increase of the scan rate possibly due to the increasing internal diffusion resistance of N3 electrode[38]. Their specific capacity values were **1173.4, 885.7, 732.2, 632.9 and 548.3 C g^{-1}** at 2.0, 5.0, 10, 20 and 30 mV s^{-1} , respectively. **The specific capacity** of N3 electrode decreased gradually with the scan rate increases. Fig. 5b is GCD curves for N3 electrode at the current density range of 1.0 to 20 A g^{-1} within the voltage range of 0.05 - 0.5 V (vs. Hg/HgO). All the curves with a flat stage in the discharge part were asymmetric, further confirming their typical Faradaic-capacity feature. Their specific capacity values were calculated to be **609.2, 549.9, 524.5, 449.0 and 379.9 C g^{-1}** at the current densities of 1.0, 2.0, 5.0, 10 and 20 A g^{-1} , respectively. The specific capacity decreased with the increase of the current densities, in accordance with the CV calculation results.

Moreover, the specific capacity was higher than other reported values (700 F g⁻¹ at 1 A g⁻¹[39], 1055 F g⁻¹ at 1 A g⁻¹[40], 720 F g⁻¹ at 20 A g⁻¹[41]). Fig. 5c displays the capacity retention curve of N3 electrode at a current density of 10 A g⁻¹ for 5000 cycles. The capacity retention could maintain 80.8% after 5000 cycles.

The CV and GCD curves of the anode electrode were also measured and displayed in Fig. S3. The specific capacitance of AC electrode was calculated to be 112.1 F g⁻¹ at 1 A g⁻¹. It is well known that the optimal mass ratio between the positive and negative electrodes is obtained when the charge (Q) is balance between the two electrodes (Q₊=Q₋). The charge could be calculated by the equation (5) showed in the supporting information. On the basis of the specific capacitances (1 A g⁻¹) of N3 and AC electrodes, a hybrid supercapacitor had been designed and fabricated with N3 and AC electrodes at the mass ratio of 1:7.2.

Fig. 5d shows CV curves of β -Ni(OH)₂//AC hybrid supercapacitor at different scan rates from 5 to 50 mV s⁻¹ with a potential window of 0.0 to 1.6 V. Fig. 5e is GCD curves at the current densities range from 0.1 to 2.0 A g⁻¹. The specific capacitance of β -Ni(OH)₂//AC device was 74.4 F g⁻¹ at 0.2 A g⁻¹ based on the total active material mass of two electrodes

(β -Ni(OH)₂: 1.6 mg and AC: 11.5 mg). However, the specific capacitance of β -Ni(OH)₂//AC device was not so high as expected. The possible reason was the low specific capacitance of AC cathode ($\sim 112 \text{ F g}^{-1}$)[42]. The Ragone plots of the β -Ni(OH)₂//AC hybrid supercapacitor based on the GCD tests are shown in Fig. 5f. The corresponding energy density and power density at 0.1 A g^{-1} were calculated to be 20.45 Wh kg^{-1} and 75 W kg^{-1} , respectively. As the power density of β -Ni(OH)₂//AC device increased from 75 to 1500 W kg^{-1} , the energy density decreased from 20.45 to 10.75 Wh kg^{-1} . Moreover, the β -Ni(OH)₂//AC device could successfully light up a set of low-voltage LEDs (the inset of Fig. 5f).

4. Discussion

Fig. 6

N1, N2 and N3 electrodes were prepared using the same ultrafine β -Ni(OH)₂ nanosheets, while different electrode fabrication methods would lead to their different electrochemical properties. It can be known that the capacity decrease was quite normal with the proceeding of charge/discharge due to the Faraday reaction of the β -Ni(OH)₂. However, the cycle stability of N3 electrode (83.8% after 1000

cycles) was better than those of N1 (59.1%) and N2 (71.3%) electrodes.

SEM images of Ni foams, N1, N2 and N3 electrodes before the electrochemical tests were observed in Fig.S4. On the basis of the SEM figures and the above results, a schematic diagram of N1, N2 and N3 electrodes during the discharge/charge process was illustrated (Fig. 6). The red arrows represent the possible electron transport paths. The electrons of N1 electrode (Fig. 6a) undertook a new exploration and got through acetylene black and β -Ni(OH)₂ randomly in the initial stage of discharge/charge, in this case, most β -Ni(OH)₂ could be involved in the redox reactions. After a couple of cycles, the electrons gradually discovered their best path through acetylene black and Ni foam to reach the current collector (Fig. 6b). These factors were the reason for the R_{ct} (N1) decreased from 1.92 Ω (before cycle) to 0.82 Ω (after cycle). In addition, some β -Ni(OH)₂ nanosheets away from the conductive agent became “dead” materials, which would give rise to the dramatic decrease of the capacity with the proceeding of the charge/discharge. N2 electrode (Fig. 6c) was fabricated using the bad-conductivity β -Ni(OH)₂ nanosheets so that the β -Ni(OH)₂ nanosheets could not be fully utilized. However, the

cycling stability of N2 was better than that of N1 because the utilization rate of β -Ni(OH)₂ in N1 decreased more seriously than that of N2 during the cycling process. In the multilayer nickel foam system (Fig. 6d), β -Ni(OH)₂ nanosheets were uniformly dispersed on the multilayer nickel foam (N3 electrode) and almost every β -Ni(OH)₂ nanosheet could be involved in the redox reactions. That is to say the electrons had nearly equal opportunities to engage in the β -Ni(OH)₂ nanosheets during the long-term cycling. Hence the R_{ct} of N3 electrode was unchanged (about 0.11 Ω) before and after the charge/discharge cycling, indicating its good cycle performance.

From the foregoing, it is crucial to choose a suitable conductor for the ultrafine materials. The diameter of acetylene black is about 35 nm (Fig. S5) and it is too large relative to the ultra-fine materials. In other words, acetylene black is a “rock” while the ultrafine β -Ni(OH)₂ nanosheets are “sands”. Consequently, in N1 electrode, only a small portion of β -Ni(OH)₂ nanosheets could be utilized after cycling. In our multilayer Ni foam system, the multilayer Ni foam was both as a conductor and as a current collector to contact β -Ni(OH)₂ nanosheets fully, which could improve the capacity and the cycle stability of β -Ni(OH)₂.

In terms of the ultra-fine particle system, multilayer nickel foam could be used as a proper conductor to substitute acetylene black and to enhance the electrochemical performances of the bad-conductivity metal oxide or hydroxide materials. Based on the multilayer nickel foam system, we also conducted other experiments using micro-scale Ni(OH)_2 and NiO as active materials to confirm their conductor role, whose results were in accordance with our inferences (for more details, see the supporting information). Hence, the multilayer nickel foam system was not only suitable for the ultra-fine materials but also the micro-scale materials.

5. Conclusion

We presented a new method (the multilayer nickel foam system) to improve the rate capability and the cycle stability of ultrafine $\beta\text{-Ni(OH)}_2$. The multilayer nickel foam could be used as a current collector and a conductor simultaneously to substitute for acetylene black conductor. This system gave a great improvement in the capacity (609.2 C g^{-1} at 1 A g^{-1}), the rate capability (remained 62.4% from 1 to 20 A g^{-1}), and the cycle life (retained 83.8% after 1000 cycles) of ultrafine $\beta\text{-Ni(OH)}_2$ nanosheets. In addition, the energy density of the hybrid supercapacitor was 20.45 Wh kg^{-1} at a power density of

75 W kg⁻¹. The **hybrid supercapacitor** based on ultra-fine β -Ni(OH)₂ nanosheets and AC fabricated by the multilayer nickel foam system could light up a set of low-voltage LEDs.

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Fig. 1 XRD pattern of β -Ni(OH)₂ nanosheets.

Fig. 2 (a) TEM of β -Ni(OH)₂ nanosheets; (b) The SEAD of β -Ni(OH)₂ nanosheets; (c) & (d) HRTEM images of β -Ni(OH)₂ nanosheets with the corresponding fast Fourier transform images in the top right and the simulated geometrical model images in the bottom right.

Fig. 3 The BJH pore-size distribution plots and the inset part is nitrogen adsorption-desorption isotherm of β -Ni(OH)₂.

Fig. 4 (a) CV curves; (b) GCD curves; (c) Variations in the specific capacity as a function of current density; (d) Cycling performance at a current density of 5 A g^{-1} of the N1, N2 and N3 electrodes; (e) & (f) Nyquist plots of N1 and N3 electrodes before and after 1000 cycles, respectively. (The insets are their enlarged views of Nyquist plots and the equivalent circuits.)

Fig. 5 (a) CV curves of N3 obtained at various scan rates of 2, 5, 10, 20, and 50 mV s⁻¹; (b) GCD curves of N3 measured at different current densities; (c) Cycling performance of N3 electrode at a current density of 10 A g⁻¹; (d) CV curves of the β -Ni(OH)₂//AC asymmetric device at different scan rates; (e) GCD curves of the β -Ni(OH)₂//AC device at different current densities; (f) Ragone plot of the β -Ni(OH)₂//AC device (The inset is a digital photograph of the lighted LEDs.).

Fig. 6 Scheme illustration of N1 (a) and (b), N2 (c) and N3 (d) electrodes in the discharge/charge process. The red arrows represent the possible electron paths.