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Hydrothermal synthesis of α -Ni(OH)₂ and its conversion to NiO with electrochemical properties



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ABSTRACT

The paper reports the fabrication of microscale NiO matrixes with enhanced electrochemical properties through annealing the corresponding chrysanthemum-like α -Ni(OH)₂ microspheres. The precursor α -Ni(OH)₂ can be synthesized by a hydrothermal method using triethanolamine as the alkaline source. The formation mechanism of chrysanthemum-like α -Ni(OH)₂ microspheres is properly discussed. Furthermore, the electrochemical experiments demonstrate that the microscale NiO matrixes show superior electrochemical behavior in lithium-ion batteries due to their unique structures.

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1. Introduction

Nickel hydroxide (Ni(OH)₂) has attracted great interest in many fields, such as asymmetric supercapacitors [1–5], Ni–HM batteries, [6,7] lithium-ion batteries [7,8], electrocatalysts [9–11], and biosensors [12–16], and so on. Thus, great effort has been focused on the preparation of Ni(OH)₂ nanomaterials with different nanostructures to achieve superior properties and performance, such as nanoplates [17,18], nanorings [19], nanowires or nanorods [20–22], nanotubes [23,24] as well as assembled structures [17,25–28]. In addition to the shape control, another topic approach is the phase control of Ni(OH)₂, i.e., α - and β -phase, to utilize unique properties associated with them.

Structurally, the α -Ni(OH)₂ phase is isostructural with a hydrotalcite-like structure, with possessing a larger interlayer spacing (>7.5 Å) (Fig. 2b). The layers are randomly arranged with water, anionic species and organic components as intercalation in the α phase [29,30], rather than well-ordered and closely packed layers in the β -phase. Nevertheless, the sheet-like α -Ni(OH)₂ along the *c*-axis is also thermodynamically stable, and thus readily tends to form thin sheets in shape due to their intrinsic lamellar structure. Due to the complicated compositions of α -Ni(OH)₂, the synthesis of α -Ni(OH)₂ phase is usually involved with some inorganic ions or organic reagents, such as Al³⁺ [31], dodecyl sulfate anions [32], Cl⁻ [32], NO³⁻ [32], OAc⁻ [32], SO²⁻₄ [32], and block copolymer [33], organic alkali [34]. Therefore, previous studies have demonstrated that it is possible to obtain the α -Ni(OH)₂ phase if the reaction system is appropriate.

In addition to the above-mentioned applications, Ni(OH)₂ can also be used as a precursor for the synthesis of NiO. Due to its high theoretical capacity (about 718 mAh/g), NiO has become one of the most promising electrodes materials, which is widely investigated in the aspects of electrochemical performance in lithium ion batteries [35-39]. However, some nanostructured NiO electrodes displayed undesired cycling performance [17,39]. The electrochemical performance mainly depends on the morphology and structure of the material which are determined by the reaction schemes. In recent years, some efforts have been made to improve the electrochemical performance of NiO electrodes. Sow and co-workers [40] prepared the vertically aligned NiO nanowalls on a nickel foil with excellent capacity retention and high rate capability upon cycling by a plasma assisted oxidation method. They found that the excellent electrochemical results can be attributed to its large surface area and shorter diffusion length for mass and charge transport. As reported by Yang and co-workers [41], highly ordered NiO coated Si nanowire array films was fabricated via depositing Ni on electroless-etched Si nanowires followed by annealing, exhibiting superior cycling properties. A reversible capacity of 606.13 mAh/g is obtained when the cell is cycled at a rate of 50 mA/g after 30 cycles.

In this work, we have fabricated the chrysanthemum-like α -Ni(OH)₂ microspheres by a hydrothermal method with



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triethanolamine (TEA) as a chelating reagent, alkali resource, and structure-directing reagent. Moreover, the as-obtained microscale NiO after annealing α -Ni(OH)₂ display excellent capacity retention as an anode material in lithium-ion batteries.

2. Experimental

All the chemicals were of analytical grade and used without further purification. In a typical synthesis of chrysanthemum-like α -Ni(OH)_2 microspheres, 1.45 g of Ni(NO_3)_2-6H_2O was first dissolved into 15 mL of a mixed solution of triethanolamine (TEA, 88%) and distilled water with a volume ratio of 3:12 under mild stirring. Then, the homogeneous solution was transferred into a 20 mL Teflon-lined stainless steel autoclave, sealed, and then heated to 180 °C. After the autoclaves were maintained at 180 °C for 48 h, the resulting green product was centrifuged, rinsed with distilled water, and finally dried at 60 °C in a vacuum oven.

Three different NiO micromatrixes were obtained through annealing the corresponding α -Ni(OH)₂ precursor in air at high temperature (450, 600 and 700 °C) for 4 h, which are accordingly denoted as NiO-450, NiO-600 and NiO-750.

The X-ray diffraction (XRD) patterns of the products were recorded with Rigaku D/max Diffraction System using a Cu K α source (λ = 0.15406 nm). The scanning electron microscopy (SEM) images were taken with a JEOL JSM-6700F field emission scanning electron microscope (15 kV). The transmission electron microscopy (TEM) images were taken on a JEOL 2010 high-resolution transmission electron microscope performed at 200 kV. Thermogravimetric analysis (Diamond TG/DTA, Perkin Elmer) was performed with a ramping rate of 5 °C min⁻¹ to 800 °C in flowing air. FT-IR spectra were obtained on a Bruker Vector 22 spectrometer with pressed KBr pellets in the range of 400–4000 cm⁻¹ with 4 cm⁻¹ resolution. Nitrogen adsorption apparatus. The Brunauer–Emmett–Teller (BET) specific surface areas (S_{BET}) were calculated using the BET equation. Desorption isotherm was used to determine the pore size distribution using the Barret–Joyner–Halender (BJH) method.

The electrochemical performance of the NiO samples was investigated in Li test cells. The NiO was mixed with acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 75:15:10 in ethanol to ensure homogeneity. After ethanol was evaporated, the mixture was rolled into a sheet and cut into circular strips of 8 mm diameter. The strips were then dried at 120 °C for 10 h in air. Lithium metal was used as the counter and reference electrodes. The electrolyte was composed of a 1 M LiPF₆ solution in ethylene carbonate (EC)/dimethyl carbonate (DMC) with a weight ratio of 1:1. The assembly of the test cells (CR 2025-type) was performed in an argon-filled glove box with water and oxygen contents less than 1 pm before measurement. The electrochemical measurements were carried out with a Land CT2001 battery tester after the cells were aged for 8 h. The electrochemical performances of the cells were evaluated within the potential range of 1.0–3.0 V versus Li/Li^{*}.

3. Results and discussion

3.1. Structural and morphological characterization

The α -Ni(OH)₂ precursor with the morphology of chrysanthemum-like microsphere could be obtained when the reaction was conducted with 5 mmol of Ni(NO₃)₂·6H₂O and 3 mL of TEA (w, 88%) at 180 °C for 48 h. Fig. 1a shows the SEM of the as-prepared precursor, showing the as-obtained samples are composed of many sphere-like architectures with a diameter ranging from 1 to 1.2 μ m. The TEM images (Fig. 1b–d) reveal that the precursor's microspheres are built from small 2D nanosheets with a thickness of 20 nm. Analogous to chrysanthemum petals, these thin nanosheets are aligned to the spherical surface, pointing toward a common center. Interestingly, when the precursor was irradiated by electron beam, the plates of the precursor would break down into nanoparticles, as shown in the inset of Fig. 1d. This may be due to the fast decomposition of the precursor and release of volatile components.

According to the XRD result of the precursor (Fig. 2a), the reaction system did not yield β -Ni(OH)₂ directly. However, all the peaks for the precursor except the peak (*, unknown) can be indexed to α -Ni(OH)₂, which could be matched with the literature (JCPDS 22-0444). The unknown peak is not attributed to nickel, NiO or β-Ni(OH)₂. As stated in the introduction, there are some composites within the interlayers, just as Fig. 2b. The as-synthesized α -Ni(OH)₂ was further analyzed by thermogravimetric (TG) and Fourier transform infrared spectra (FT-IR) techniques. The TG curve of the as-synthesized α -Ni(OH)₂ is shown in Fig. 2c. Obviously, the α -Ni(OH)₂ underwent two-step weight losses due to dehydration and decomposition. The characteristics of α -Ni(OH)₂ obtained from this analysis are as follows: (i) The initial weight loss of about 6% at 45-246 °C represents the removal of the adsorbed water molecules; (ii) The following weight loss of about 32.4% between 246 and 627 °C can be attributed to the phase transformation from obtained α -Ni(OH)₂ chrysanthemum-like microsphere to NiO. Fig. 2d shows the FT-IR spectrum of the as-synthesized α -Ni(OH)₂ precursor. The broad band at 3600–3300 cm⁻¹ corresponds to the hydroxyl groups and



Fig. 1. The as-synthesized α -Ni(OH)₂ precursor: (a) SEM image and (b-d) TEM images.



Fig. 2. The as-synthesized α -Ni(OH)₂ precursor: (a) XRD pattern; (b) crystal structure; (c) TG curve and (d) FT-IR spectrum.

water molecules, which were extensively hydrogen bonded [42–45]. The narrow band located at 1630 cm⁻¹ is assigned to the bending mode of the water molecule within the interlayers [46]. The band at 1385 cm⁻¹ is due to the interaction of the sample with KBr in the pellet [46]. The narrow bands at 1212 and 915 cm⁻¹ are attributed to nitrate groups. The narrow bands around 1120, 1070, and 1032 cm⁻¹ originate from δ_{C-N} , δ_{C-OH} , and δ_{C-C} vibration individually [47]. The bands around 616 and 468 cm⁻¹ are attributed to the δ_{OH} and v_{Ni-OH} vibrations individually [44]. The result of FT-IR further verifies the chemical species of the α -Ni(OH)₂ precursor.

3.2. Formation mechanism and conversion of $\alpha\text{-Ni}(OH)_2$ precursor to NiO

To disclose the formation mechanism of the chrysanthemumlike α -Ni(OH)₂ microspheres, we performed the experiments that involve the intermediates at different reaction times to investigate the morphological evolution process of the chrysanthemum-like microspheres. In the synthetic process, TEA can not only chelate with Ni^{2+} to produce a $[Ni(TEA)_2]^{2+}$ complex [48], but also act as a weak base due to the lone pair of electrons on the nitrogen atom. Afterwards, the α -Ni(OH)₂ microparticles (Fig. 3a) would appear in this unique weak base media, with Ni²⁺ released from the complex at the increased temperature. The formation of α -Ni(OH)₂ might be attributed to the presence of polyol TEA, the similar results have been reported in the other literature [49–51]. Subsequently, as the reaction proceeds, due to the anisotropic crystal structure, these initial α -Ni(OH)₂ nuclei grow into the quasi-spherical petal-built aggregates with rugged surfaces (Fig. 3b) based on the precipitation solubility equilibrium in the solution [52–54]. With the increase of reaction time, the reaction develops into Ostwald ripening process. Finally, well-defined 3D α -Ni(OH)₂ chrysanthemum-like microspheres (Fig. 3c) were formed due to the Ostwald ripening.

When the precursor was annealed at different temperatures (450, 600 and 750 °C), the corresponding NiO samples (NiO-450, NiO-600 and NiO-750) could be obtained, as shown in Fig. 4a–i, respectively. The SEM images of the NiO samples (NiO-450 in Fig. 4a, NiO-600 in Fig. 4d, NiO-700 in Fig. 4g) show that the size and shape of the NiO nanostructures are consistent with the nano-structures of the precursor. However, the further investigation by TEM found that the morphologies for all the annealed samples (NiO-450, NiO-600 and NiO-750), showing microstructures assembled by rough surfaces with soft recrystallized grains (linked nano-particles), were largely different from the structural characteristics of the precursor, as shown in Fig. 4b and c, e and f, h and i, respectively. This could be attributed to the recrystallization of NiO at higher temperatures.

Fig. 5 shows the XRD patterns of the calcined samples. The pronounced peaks at (111), (200) and (220) in Fig. 5a–c illustrate that the phase of the calcined samples at different temperatures from 450 to 750 °C is well crystallized cubic NiO (JCPDS 47-1049), and the line widths of the Bragg lines of the as-obtained NiO nanomaterials gradually become keen-edged. Moreover, the evolution in the line widths of the Bragg lines probably demonstrates the crystallite growth of NiO at elevated calcination temperatures.

3.3. BET measurements

The textural properties of the NiO samples were further investigated by measuring N_2 adsorption/desorption isotherms at



Fig. 3. Morphological evolution process of the chrysanthemum-like α -Ni(OH)₂ microspheres at different time: (a) 0.5 h; (b) 5 h and (c) 12 h.



Fig. 4. (a) SEM image and (b and c) TEM images of NiO-450; (d) SEM image and (e and f) TEM images of NiO-600; (g) SEM image and (h and i) TEM images of NiO-750.



Fig. 5. XRD patterns for the samples: (a) NiO-450; (b) NiO-600 and (c) NiO-750.



Fig. 6. Nitrogen adsorption-desorption isotherms for the annealed samples: (a) NiO-450; (b) NiO-600 and (c) NiO-750. Corresponding pore size distribution curves for the annealed samples (the inset of figure).

77 K, as shown in Fig. 6. In Fig. 6, all the calcined samples have typical IV type curves with a hysteresis loop, which implies that the obtained NiO samples are mesoporous materials. The hysteresis features of annealed samples (NiO-450 at the relative pressures of 0.85-1; NiO-600 at the relative pressures of 0.9-1 and NiO-750 at the relative pressures of 0.9-1) should be classified as type H3 loop, which does not show any limiting adsorption at the higher side of this relative pressure range (Fig. 6), suggesting the presence of aggregates of plate-like particles which give rise to slit-shaped pores [55]. The pore size distribution (PSD) plots calculated from the desorption branches of the nitrogen sorption isotherms are shown in the inset of Fig. 6. As shown in the PSD curves (the inset of Fig. 6), all the three samples have a bimodal pore distribution using the Barrett-Joyner-Halenda (BJH) method. Furthermore, from Fig. 6, it can also be found that the hysteresis loops of the annealed samples (NiO-450, NiO-600 and NiO-750) begin from P/ $P_0 = 0.85$ to $P/P_0 = 0.95$, indicating that the pore size of the annealed samples increase and PSDs are broadened at the same time while the NiO particles grow larger at elevated calcination temperatures due to the Oswald ripening. The specific surface areas using the Brunauer-Emmett-Teller (BET) method for NiO-450, NiO-600 and NiO-750 samples are 26.4, 7.6 and 5.4 $m^2 g^{-1}$, respectively.

3.4. Electrochemical performance toward lithium storage

It is well known that the changes occur in the cell voltage during the charge/discharge of a lithium battery providing information on the changes in structure and physical properties induced by intercalation/deintercalation processes. Fig. 7 shows the first cycle discharging voltage profiles for the different NiO samples with different microstructures with a cutoff voltage of 0.01 V at a current density of 50 mA/g. As shown in Fig. 7, there is an abrupt drop in potential down to about 0.8 V in the first discharge curve for each sample, followed by a long plateau of 0.68 V. Moreover, the three samples display higher capacities (1294 mAh/ g for NiO-450, 1118 mAh/g for NiO-600 and 1374 mAh/g for NiO-750) than the theoretical value (about 718 mAh/g). The irreversible capacity loss during the first cycle can be attributed to several factors: (i) reduction of metal ions to the metal nanoparticles; (ii) the formation of solid electrolyte interface (SEI) [56,57]; (iii) the intrinsic nature of the materials due to kinetic limitations and current density [56].

Fig. 8 shows the plots of specific discharge/charge capacity vs. cycle number for the electrodes made from NiO samples



Fig. 7. First charge–discharge curves of different NiO samples tested at a current density of 50 mA g^{-1} in the potential range of 0.01–3.0 V.



Fig. 8. Cycling performances of different NiO samples tested at a current density of 50 mA g^{-1} in the potential range of 0.01–3.0 V.

(NiO-450, NiO-600 and NiO-750). One could find that the discharge capacities for the three NiO samples (NiO-450, NiO-600 and NiO-750) after 20 cycles is still as high as 380, 517, 501 mAh/g, respectively. The cycling performance of these materials is better than that of our synthesized NiO nanoplates (78 mAh g⁻¹ after 20 cycles) [17]. Generally, the severe capacity degradation and poor cycling performance of electrode materials can be attributed to the large volume expansion-constriction, which not only results in the pulverization and degradation of the electrode, but also leads to the repeated destruction and formation of the solid electrolyte interface (SEI) film [58-60]. Herein, the NiO-600 and NiO-750 electrodes display excellent cycling performances due to their linked nanoparticle networks, which not only make the diffusion length shorter for mass and charge transport as well as the interface between electrode and electrolyte larger, but also buffer the large volume expansion-constriction. It should be noted that the surface area of such microstructured NiO is not the key factor determining the electrochemical performance, the structural characteristics of electrode materials played more important roles in determining the cycling performance in this work.

4. Conclusions

In summary, we have successfully developed a solvothermal route for the fabrication of the chrysanthemum-like α -Ni(OH)₂ microsphere with triethanolamine. The microscale NiO matrixes are demonstrated as promising anode materials for lithium-ion batteries. On the basis of the observation of intermediate products in the growth process, the formation mechanism of the chrysanthemum-like α -Ni(OH)₂ microspheres was rationally proposed. In addition, this method will provide a novel route for the fabrication of electrode materials with matrixes in the lithium-ion battery applications.

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