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Synthesis of Nanosized α-Nickel Hydroxide by a Sonochemical Method

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ABSTRACT

Nanosized α-nickel hydroxide with an interlayer spacing of 7.2 Å has been synthesized with the aid of ultrasound radiation. This method was found to be a simple and convenient method to produce α-nickel hydroxide. The synthesized hydroxide was found to possess good stability in KOH medium and the material might be interesting from the application point of view in secondary alkaline batteries. The α-nickel hydroxide has been characterized by powder X-ray diffraction, transmission electron microscopy, DSC, thermogravimetric analysis, FT-IR spectroscopy, and elemental analysis.

Nickel hydroxide has received increasing attention in recent years on account of its applications in alkaline secondary batteries and also as a precursor of catalysts.[1] It has a hexagonal layered structure with two polymorphs, α and *β*.[2] The α-form is isostructural with hydrotalcite (HT)-like compounds and consists of a stacking of positively charged $Ni(OH)_{2-x}$ layers, with intercalated anions (e.g., carbonate, nitrate, etc.) and water molecules in the interlayer space to restore charge neutrality. The *β*-form possesses a brucite-like ($Mg(OH)_2$) structure and does not contain any intercalated species. The HT and the brucite structures are not very much different: the HT structure can be easily derived from the brucite by a partial Mg/Al substitution with a concomitant introduction of interlayer anions. In most cases, the active material of positive electrodes belongs to the *β*-form. It is generally accepted that α-nickel hydroxide will exhibit superior electrochemical properties compared to the *β*-form.[3] However, the α-nickel hydroxide is a metastable phase and is difficult to synthesize because it changes rapidly to the *β*-form during synthesis or on storage in a strong alkali.[4] The overall performance of nickel cathodes depends on the microstructure, textural characteristics, and the crystallite size of the active material.[5,6] Hence, the synthesis of nanosized α-nickel hydroxide particles is of utmost importance.

The electrochemical efficiency of α-nickel hydroxide is inversely proportional to its aging time in the alkali solution. At room temperature and in 7 M KOH solution, the transformation of α to *β* phase is complete within 3 h.[4] Attempts have been made to block the α to *β* conversion, e.g., by substituting 20% cobalt for nickel[7] and by doping with trivalent ions such as Al^{3+}, Co^{3+}, etc., in the $Ni(OH)_2$ structure.[8] The commonly used precipitation methods to prepare α-nickel hydroxide by employing nickel salt and bases often end up in irreproducibility. LeBihan et al.[9] and Genin et al.[10] reported the synthesis by precipitation with liquid NH_3 and the material produced was poorly ordered in both studies. Cathodic reduction of nickel nitrate is an another method to yield α-nickel hydroxide, but it is a very slow process.[11] There has been a great deal of interest in finding a fast chemical route to bulk α-nickel hydroxide.

The chemical effects of ultrasound radiation arise from acoustic cavitation:[12] the extreme conditions ($T \sim 5000$ K, $P > 20$ MPa) and cooling rates ($>10^{10}$ K/s) attained during the cavitation have been exploited to prepare nanoscale metals, alloys, colloids, metal oxides, and nanocomposites.[13,14] Synthesis of metastable/novel modifications of inorganic compounds using sonochemical methods is also well studied.[13d−f] Homogeneous precipitation by employing urea, a Bronsted base,[15] provides a good opportunity to synthesize pure α-nickel hydroxide since the pH of the medium remains relatively low throughout the process. Avena et al.[16] attempted to synthesize α-nickel hydroxide in a porous nickel electrode by a urea method, but the yield was low. Akinc et al.[17] reported synthesis of submicrometer-sized spherical agglomerates of α-nickel hydroxide. Homogeneous precipitation using urea in a domestic pressure cooker was also used to synthesize α-nickel hydroxide.[18] More recently, Regazzoni et al.[19] reported the synthesis by a urea method, but the average particle size is not in the nanoscale range and the shape of the particles is petal-like. In some cases of the urea method, a mixture of α and *β* phases is obtained. The objective of the present work is to utilize ultrasound radiation in the process of homogeneous precipitation for the synthesis of phase pure nanosized α-nickel hydroxide and examine its stability in KOH. In an earlier study, we have reported the synthesis of α-cobalt hydroxide using ultrasound radiation.[20]

The synthesis of α-nickel hydroxide has been carried out with the aid of ultrasound radiation. To an aqueous solution of about 1.5 g of $Ni(NO_3)_2 \cdot 6H_2O$ was added 5 g of urea

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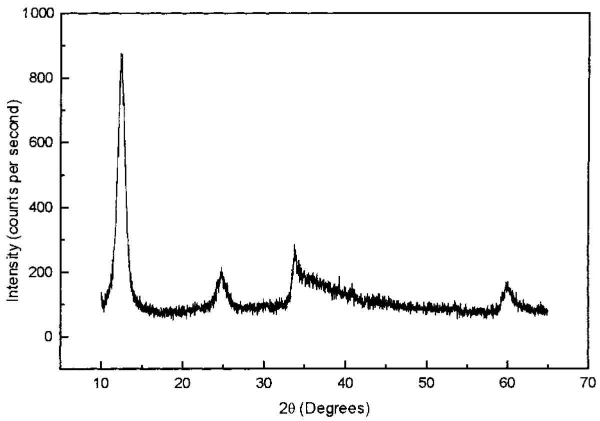

Figure 1. Powder XRD pattern of the sonochemically synthesised α-nickel hydroxide.

(both from Aldrich) in a sonication flask (total capacity 80 mL, 26 mm o.d). The solution was purged with argon for 20 min and irradiated with high-intensity ultrasound radiation for about 3 h by employing a direct immersion titanium horn (20 kHz, 100 W cm^{-2}). The temperature during the sonication experiment increased to 80 °C, as measured by an iron−constantan thermocouple. The pH of the solution changed from 6.1 prior to the sonication to 6.8 at the end of the reaction. After the precipitation process was complete, the precipitate was separated from the solution by centrifugation, washed repeatedly with distilled water, and then dried under vacuum. A controlled experiment was also carried out by heating the reagent solutions at 80 °C for about 3 h. The yield of the product was found to be very low, which did not warrant its further characterization. However, if the heating was prolonged approximately overnight, more product was found to be formed. A further characterization of this product was not carried out since it is already reported in the literature.[19] The sonochemically synthesized α-nickel hydroxide was characterized using an array of analytical techniques.[21] The stability of the sonochemically synthesized α-nickel hydroxide toward alkaline media was examined by powder XRD measurements using 6 and 10 M solutions of KOH.

From the elemental analysis in combination with the results obtained from thermal gravimetric measurements, the stoichiometry of the synthesized nickel hydroxide was found to be $[Ni(OH)_{1.33}](CO_3)_{0.07}(OCN)_{0.54}(H_2O)_{0.31}$. This means that there are about 33% defects present in an otherwise ideal $[Ni(OH)_2]$ layer. α-nickel hydroxide with a stoichiometry close to that in the present study has been reported by other workers too: Akinc et. al. has reported a stoichiometry of $[Ni(OH)_{1.33}](HCO_3)_{0.616}(NO_3)_{0.054}$ and Regazzoni et. al. has reported a stoichiometry of $[Ni(OH)_{1.27}](CO_3)_{0.17}(OCN)_{0.39}(H_2O)_{0.46}$. Figure 1 displays the powder XRD pattern of the nickel hydroxide prepared. It shows peaks at $d = 7.2$, 3.60, 2.66, and 1.54 Å that could be assigned to (003), (006), (101) and (110) planes, indicating the formation of an α-phase.[22] No peaks due to β-$Ni(OH)_2$ were observed in the XRD pattern. From the fwhm of the (003) reflection, the crystallite size along the *c*-axis was calculated to be ca. 80 Å using the Debye−Scherrer equation. This means that the number of sheets per crystallite of the hydroxide is around 11 since the interplanar spacing is 7.2 Å. The asymmetric nature of the reflection at about $d = 2.66$ Å indicates the formation of a turbostratic phase observed in most of the α-type hydroxides. In Figure 2, the results of transmission electron microscopic investigations of the prepared α-nickel hydroxide are shown. The TEM picture consists of scaly particles with a length of ca. 200 nm and a width of ca. 15 nm. Although hydrotalcite-like compounds with a fibrous character have been some times reported, the usual shape observed for these crystals corresponds to platelet-like particles and their shape could be obtained from XRD peak widths. The sonication of the solution during the homogeneous precipitation process not only helps in the formation of shaped particles, but it also helps in the formation of nanosize particles after the precipitation step. The formation of nanoparticles is enhanced with the utilization of ultrasound irradiation. The IR spectrum of the sample showed vibrational bands at ca. 3635, 3495, 3405, 2230, 1623, 1358, 1280, 645, and 484 cm^{-1} in addition to a weak band at ca. 990 cm^{-1}, which are typically observed for α-type hydroxides.[4] A narrow band observed at ca. 3635

Figure 2. TEM picture of the sonochemically synthesized α-nickel hydroxide at two different magnifications.

cm^{-1} was attributed to the free hydroxyl groups of the brucite-like structure. A broad band at ca. 3400 cm^{-1} was attributed to the hydroxyl groups, which are extensively hydrogen bonded. The band at ca. 1620 cm^{-1} was assigned to the bending vibrational mode of the interlayer water molecules. The absorption band at ca. 2230 cm^{-1} was attributed to the existence of intercalated OCN^- species, as suggested in ref 19. The IR spectrum provides the evidence for the presence of intercalated carbonate ions. The ν_3 mode is observed at 1410 cm^{-1} for free carbonate ion shifts and splits into two bands at ca. 1280 and 1357 cm^{-1} owing to the reduction in symmetry from D_{3h} in free carbonate to C_{2v} in the α-nickel hydroxide. It is reported that the greater the degree of splitting of the ν_3 mode, the stronger the covalent interaction between Ni(II) ions and carbonate ions.[23] It may be recalled that this interaction in turn is related to the stability of α-nickel hydroxide in an alkaline medium. The α-nickel hydroxide sample synthesized in the present study showed a rather large ν_3 splitting of 130 cm^{-1}, indicating a stronger $Ni(II)-CO_3^{2-}$ interaction. The weak band at ca. 990 cm^{-1} was assigned to the ν_1 mode of the carbonate anion that remains inactive in the free ion, and the mode becomes active in the hydroxide due to the reduction of its symmetry. The band at ca. 645 cm^{-1} was assigned to δ_{OH} and the band at ca. 484 cm^{-1} was ascribed to $\nu_{Ni-OH.}$ vibration. The thermogravimetric pattern of the α-nickel hydroxide sample in the temperature range 30−900 °C showed two steps at ca. 320 and ca. 350 °C with a net weight loss of ca. 34%. The α-nickel hydroxide is known to undergo multistep and larger mass losses compared with the β-hydroxide phase, which shows a weight loss of ca. 18%. During the decomposition of the α-hydroxide phase, a peak at m/e 44 was detected in the mass spectrum, which can be ascribed to the evolution of carbon dioxide. This further proves the presence of intercalated carbonate anions. The observed mass loss agrees well with what is expected from the formulas obtained from chemical analysis (expected weight loss = 35%; observed weight loss = 34%). The end product of TGA was found to be pure NiO, as observed by powder XRD measurements. The DSC pattern of the hydroxide showed a broad endotherm at about 80 °C attributed to the loss of water and a very strong irreversible endotherm at about 340 °C ascribed to the decomposition of the hydroxide. On heating at 350 °C, the thermal decomposition products of the α-nickel hydroxide were found to be NiO if heated in nitrogen as well as in air, as inferred from the XRD results. The nickel oxide so obtained has a particle size in the nanometer range, ca. 12 nm, as calculated from the powder X-ray pattern using the Debye−Scherrer equation.

Sonication experiments were also performed by changing the time the materials are exposed to ultrasound irradiation. The sonication experiments were carried out for 2 and 5 h of ultrasound irradiation. The TEM results showed that both the materials produced (2 and 5 h of sonication time) possess fibrous character. However, the dimensions of the particles were found to be different. The α-nickel hydroxide sample prepared by 2 h of sonication has an average length of ca. 200 nm and width 18 nm. However, the sample prepared by 5 h of sonication time showed a reduction in dimension (length ca. 120 nm and width 10 nm). The other experimental parameters such as concentration of the reactants (nickel nitrate and urea) were found not to affect the morphology and the dimension of the particles.

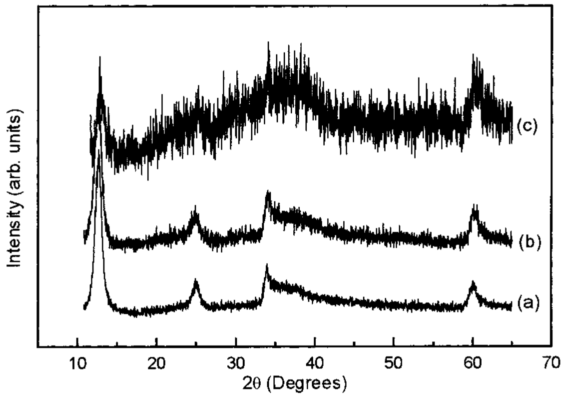

Figure 3. Powder XRD pattern of the sonochemically synthesised α-nickel hydroxide in (a) 6 M KOH for 44 h and (b) 10 M KOH for 15 h.

The stability of the synthesized nanosized α-nickel hydroxide toward KOH solutions (6 and 10 M) was investigated using powder XRD measurements. During the conversion of the α → β phase, the XRD peak of the α-phase at d = 7.2 Å disappears and a new peak due to the β-phase at d = 4.6 Å is observed. It was observed that in 6 M KOH solution and at room temperature, the α-phase is stable at least for 44 h and, in 10 M KOH solution, it is stable for about 15 h (Figure 3). The role of KOH leading to a decrease in the basal spacing is due to the extraction of the interlayer carbonate anions from the α-phase. The hydroxide synthesized in the present study shows better stability toward alkline media than the α-nickel hydroxide synthesized by other reported methods. This property might be exploited in using this material as a positive electrode in alkaline batteries. A detailed electrochemical characterization of the synthesized α-hydroxide is under progress and it will be reported elsewhere.

In summary, an easy and convenient approach to the preparation of α-nickel hydroxide using ultrasound radiation and its characterization have been described. The sample showed good stability in alkaline medium. Thermal decomposition of the synthesized α-nickel hydroxide gives rise to nanosized NiO. Synthesis of materials with the aid of ultrasound radiation proves to be a convenient method to produce novel materials with new modifications.

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(21) The powder X-ray diffraction patterns were recorded by employing a Rigaku X-ray diffractometer (Model-2028, Cu Kα, $\lambda = 1.5418$ Å). The morphology of the product was determined by transmission electron microscopy (TEM) (JEOL-JEM 100SX microscope). The sample for TEM was prepared by placing a drop of the sample suspension on a copper grid coated with carbon film (400 mesh, Electron Microscopy Sciences) and allowing it to dry in air. The FT-IR spectrum was recorded on a Nicolet (Impact 410) infrared spectrophotometer with KBr pellets in the range 400−4000 cm^{-1}. The thermogravimetric analysis was done using a Mettler Toledo TGA/SDTA851 attached with a mass spectrometer (Balzers Instruments), in the temperature range 30−900 °C, at the rate of 10 °C/min, in a nitrogen atmosphere. The DSC pattern of the sample was recorded using a Mettler TC15 instrument over the temperarure range 30−550 °C under a nitrogen atmosphere. Elemental analysis was carried out using a Eager 200 CHN analyzer.

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