

Short communication

Optimum conditions to prepare high yield, phase pure α -Ni(OH)₂ nanoparticles by urea hydrolysis and electrochemical ageing in alkali solutions

M. Jayalakshmi, N. Venugopal, B. Ramachandra Reddy, M. Mohan Rao*

^aInorganic Chemistry Division, Indian Institute of Chemical technology, Hyderabad 500007, India

Received 4 January 2005; accepted 21 February 2005

Available online 1 April 2005

Abstract

Phase pure alpha nickel hydroxide (α -Ni(OH)₂) is synthesized by a hydrothermal method using urea and nickel nitrate in an autoclave. Optimum conditions to obtain high yield and phase pure α -Ni(OH)₂ are identified by varying experimental parameters such as urea concentration, ramp time, and temperature. In a typical experiment, a 94% yield of phase pure α -Ni(OH)₂ is successfully prepared. The nickel content, analyzed by means of atomic absorption spectroscopy, is 44% in all samples. The α -Ni(OH)₂ nanoparticles are characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The BET surface area and tap density of the nickel hydroxide nanoparticles are also determined. Electrochemical characterization is undertaken via cyclic voltammetry for which the nanoparticles are immobilized on the surface of paraffin impregnated graphite electrodes in 1.0 M alkali solutions. The ageing of the alpha phase occurs within 27 min (30 cycles) of exposure in alkali solutions.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Alpha nickel hydroxide; Nanoparticles; Urea hydrolysis; Electrochemical ageing; Batteries

1. Introduction

Nickel hydroxide is widely used as an electrode material in Ni–Cd, Ni–Fe, Ni–Zn, Ni–MH cells. It has two polymorphs, namely, β and α , both of which consists of brucite-type layers with interlayer separations of 4.6 and 7.5 Å, respectively. The layers are well ordered and closely packed along the *c*-axis in the β -phase, but are randomly arranged along the *c*-axis with water and anionic species as intercalates in the α -phase. It has been established that alpha nickel hydroxide (α -Ni(OH)₂) has better electrochemical properties than β -Ni(OH)₂. Stabilized α -Ni(OH)₂ has a much higher charge capacity than β -Ni(OH)₂ and can be converted to γ -Ni(OH)₂ reversibly without any mechanical deformation and swelling of the electrode during cycling. Additionally, the number of electrons exchanged during the $\alpha \rightarrow \gamma$ transformation is

higher as the oxidation state of γ -phase is 3.5. In view of these advantages, the synthesis of phase pure α -Ni(OH)₂ and its stabilization in alkali solutions have attracted many researchers and mixed results have been reported. The formation of mixed phases by homogeneous precipitation of nickel salts in the presence of urea was reported [1,2]. Delahaye-Vidal and Figiarz [3] precipitated the α -phase from aqueous nickel nitrate solutions with ammonia. Dixit et al. [4] reported an ammonia-intercalated α -phase by the hydrolysis of urea at 120 °C [4]. Al-substituted α -Ni(OH)₂ was prepared by Zhao et al. [5] in the presence of surfactants such as Tween-20 and polyvinyl alcohol at 90 °C; the particles were 58–283 nm in size. Electrochemical impregnation of the α -phase into sintered nickel plates was shown to be temperature dependent [6]; α -Ni(OH)₂ forms below 60 °C, but a mixed phase with nickel oxyhydroxy nitrate above 60 °C. The most significant work has been reported by Akine et al. [7] who hydrothermally synthesized α -Ni(OH)₂ at 90 °C with a concentration of urea that was 30 times higher than that of nickel nitrate and

* Corresponding author. Tel.: +91 40 27193510; fax: +91 40 27160921.
E-mail address: mandapati@iict.res.in (M.M. Rao).

in presence of the dispersant HPMC (hydroxyl propyl methyl cellulose). The surface area of particles was good with a sub-micrometre range size and the yield was nominal.

Nanostructured $\text{Ni}(\text{OH})_2$ is expected to yield at least a 20% improvement in cathode energy content as reported by the US Nano Corp. Inc. If it is in the phase pure α form, the significance is enormous in terms of specific energy. For large-scale applications like electric and hybrid electric vehicles, the production cost of nickel hydroxide should be minimal. In this respect, the hydrothermal method is unique, as it involves a single, easy and cost-effective synthesis of the nanomaterial. No repetitive washings to remove unwanted ions as in conventional method are required. In this work, high yields of phase pure α - $\text{Ni}(\text{OH})_2$ nanoparticles have been obtained by urea hydrolysis without any added surfactant or dispersant and with a minimal amount of urea. Also, the optimum experimental parameters of temperature, reaction time, and urea concentration were established. The nanoparticles are characterized by X-ray diffraction (XRD) and by transmission electron microscopy (TEM). The electrochemical characterization of α - $\text{Ni}(\text{OH})_2$ is investigated by cyclic voltammetry.

2. Experimental

Typically, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.05 M) and urea (0.3 M) were dissolved in 200 ml of de-ionized water and the solution was transferred to a stainless steel autoclave. This was programmed to reach 130°C in 1 h (ramp time), and at this temperature, the reaction was kept for 2 h (soak time) with a stirring speed of 400 rpm. During the experiment, the in situ pressure of around 5–10 atm. developed. When the autoclave reached room temperature, the solution with precipitate was filtered, and washed with distilled water to neutral pH. The solid was dried overnight in oven at 120°C to obtain $\text{Ni}(\text{OH})_2$ nanoparticles. The experimental procedure was repeated for varying concentrations of urea, soak time, and at a constant temperature of 130°C .

Powder XRD data of the samples were obtained by means of a Siemens D 5000 X-ray diffractometer with Bragg-Brentano geometry and having $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned for 2θ values in the

range from 2° to 65° . The TEM images were obtained with a Tecnai-12 model, FEI instrument operated at an accelerating voltage of 100 kV. The $\text{Ni}(\text{OH})_2$ products were dissolved in dilute HCl and analyzed after proper dilution, by atomic absorption spectroscopy using a Perkin-Elmer Model. The pH was measured with a Digisun digital electronic pH meter, and the BET surface area with a Quantachrome Autosorb-1 Model. All electrochemical experiments were conducted with a PGSTAT 30 Autolab system (Ecochemie, Netherlands). Nanoparticles of α - $\text{Ni}(\text{OH})_2$ on paraffin impregnated graphite (PIGE) were prepared as the working electrodes, as described in earlier work [8]. The PIGEs were made by impregnating graphite rods with melted paraffin (melting point = 65°C) under vacuum.

3. Results and discussion

The XRD pattern and TEM image of α - $\text{Ni}(\text{OH})_2$ nanoparticles are presented in Figs. 1 and 2, respectively. The XRD pattern shows the formation of phase pure α -phase of nickel hydroxide, as demonstrated in earlier studies [7,9]. The peak around $2\theta = 12^\circ$, a characteristic peak for turbostratic nickel hydroxide, and an asymmetric broad peak at 2θ values about 32 – 35° , characteristic of the turbostratic disorder, confirm the formation of the pure α -phase in all the samples. The first two peaks at about 12° and 25° correspond to the (001) and (002) planes and the d values for the seven samples are listed in Table 1. There is a slight shift in both the d_{001} and d_{002} values, which is expected due to the intercalation of anions. The TEM image of sample 7 is given in Fig. 2. Some particles are of spherical shape, while many others are rod shaped. The agglomeration of some particles results in undefinable shapes. This is understandable, as the reaction has been carried out in the absence of any structure-directing agent.

The experimental parameters and final results obtained for the seven samples are given in Table 1. In each case, the final product is α - $\text{Ni}(\text{OH})_2$ in a phase pure form. In experiments 1–4, the urea concentration is increased from 0.1 to 0.4 M and the other parameters are kept constant. The maximum yield is given at a 0.2 M concentration of urea. The

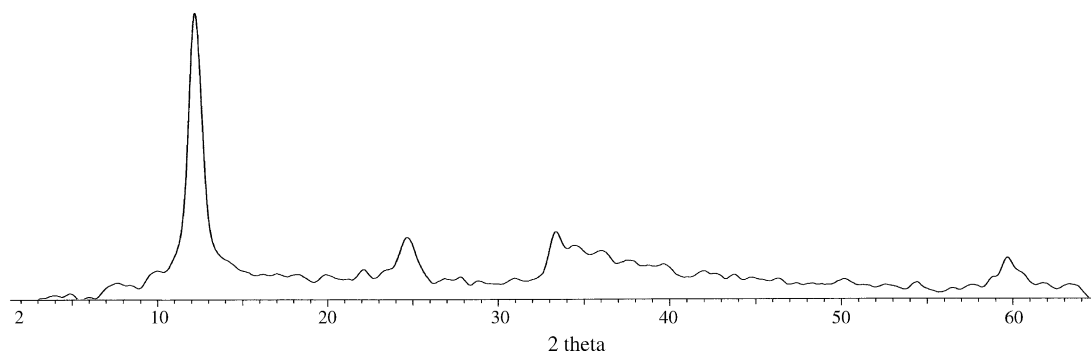


Fig. 1. XRD pattern of phase pure α - $\text{Ni}(\text{OH})_2$ (sample 7) synthesized by the hydrothermal method.

Table 1
Experimental parameters and end results of α -Ni(OH)₂ prepared by hydrothermal synthesis

Sample no.	Nickel nitrate (M)	Urea (M)	Time (min)	Initial pH	Final pH	Yield (%)	Ni (%)	Tap density (g cm ⁻³)	Specific-surface area (m ² g ⁻¹)	XRD peak, d_{001}	XRD peak, d_{002}
1	0.05	0.1	30	4.50	7.37	76.2	44.9	0.75	20.1	7.178	3.574
2	0.05	0.2	30	4.85	7.95	89.0	44.0	0.52	15.7	7.233	3.610
3	0.05	0.3	30	4.91	8.26	86.6	44.4	0.39	14.8	7.206	3.601
4	0.05	0.4	30	5.42	8.79	82.4	43.6	0.46	15.7	7.253	3.618
5	0.05	0.2	60	4.85	8.12	90.9	44.6	0.5	22.8	7.260	3.623
6	0.05	0.2	90	4.85	8.12	93.5	44.0	0.48	21.9	7.170	3.588
7	0.05	0.2	120	4.85	8.14	94.4	44.0	0.52	20.9	7.219	3.608

decrease in yield at higher concentrations of urea can be attributed to soluble nickel amine complexes. This competitive process at higher pH values imparts a blue colour to the final reaction solutions, and thereby confirms the formation of the complex formation. In experiments 5–7, the reaction time is increased to 2 h and a maximum yield is achieved within this timeframe. When the reaction temperature is increased, quite interestingly, the percent yield of nickel hydroxide decreases and a mixed form, but not phase pure α -form, is the resultant product (results not given). The nickel content, as estimated by atomic absorption spectroscopic measurements, is almost consistent. The highest tap density is found with sample 1 for which the urea concentration is minimum. The BET surface areas are in consistent with earlier work [7].

The observed acidic pH in all the experiments prior to hydrolysis is due to the fact that nickel nitrate in aqueous solutions forms Ni²⁺ and NO₃⁻ ions. While the nickel ions interact with hydroxide ions, the protons consume the nitrate ions turning the solution acidic. On heating, urea decomposes to give ammonia and HNCO. The latter is then converted to ammonium ions by taking up protons and CO₂. Both reactions consume protons and lead to an increase in the pH of the solution after hydrolysis.

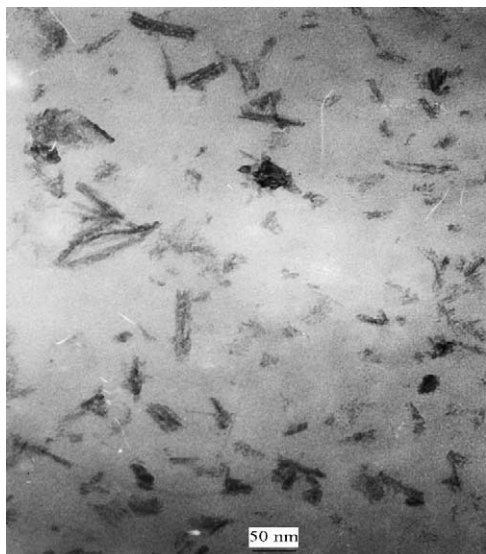


Fig. 2. TEM image of α -Ni(OH)₂ (sample 7) nanoparticles.

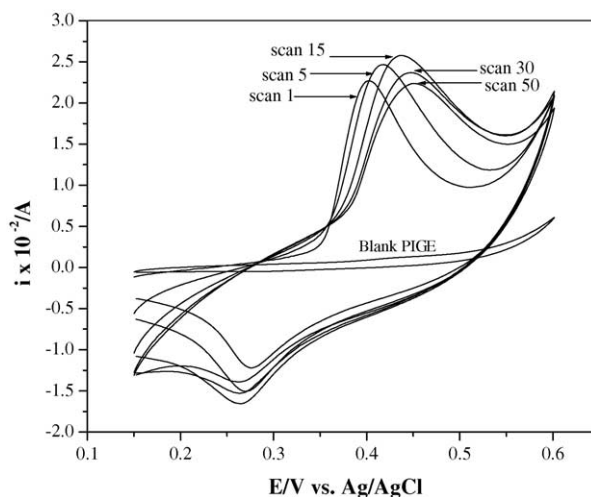
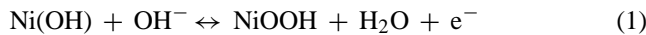


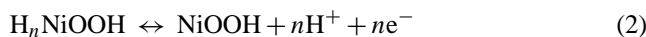
Fig. 3. Cyclic voltammograms of α -Ni(OH)₂ immobilized on a PIGE in 1.0 M NaOH solutions; continuous cycling up to 50 scans.

Cyclic voltammograms (CVs) recorded at a scan rate of 20 mV s⁻¹ for α -Ni(OH)₂ nanoparticles immobilized on a PIGE from the 1st to the 50th cycle are given in Fig. 3. From the CVs, it is clear that the anodic current peak shifts towards more positive potentials with continuous cycling from the 1st to the 30th cycle (0.401–0.441 V versus Ag/AgCl), which is expected for the ageing process. With further cycling, the peak potential remains constant up to the 50th cycle. As the α -phase is thermodynamically unstable, the conversion to the β -phase or a mixed phase is an energetically favourable process, as indicated by the shift of the anodic current peak towards positive potentials. The conversion of α -phase to β -phase has been a topic of considerable interest and several research papers have described the phenomenon. In general, it is claimed that the phase conversion proceeds by two separate, but complimentary, processes, namely, chemical ageing in concentrated KOH solution and electrochemical cycling between oxidized and reduced states. It was reported that nitrate ions were repelled within 5 min of ageing time in 5 M KOH, as confirmed by nuclear magnetic measurements and Raman spectroscopy. For charge balance, the α -phase was found to take up alkali metal cations during the oxidation process (mass gain) and to become stabilize within 30–45 s of cycling [10]. The observations are consistent with the results presented here.

Transformation of turbostratic α -phase to β -phase occurs via the loss of water molecules in the crystal structure. In fact, the higher electrochemical activity of the α -phase has been attributed to the water activity in the crystal structure. It is well known that the Ni^{2+} to Ni^{3+} conversion is essentially a solid-state proton intercalation and de-intercalation process and it is usually accompanied by two competitive processes, viz., expulsion of alkali metal cations and nitrate ions and expulsion of hydroxyl ions/protons along with free water molecules. The nickel hydroxide undergoes the following redox reaction in 1.0 M alkali solutions:



This redox reaction can be rewritten as:



A significant and interesting fact is the increase in anodic peak current from the first (2.2×10^{-3} A) to the 15th scan (2.57×10^{-3} A) and the decrease at the 30th scan (2.36×10^{-3} A). This increase in peak current may be attributed to the electrochemical activity of water molecules associated with protons and the process can be described as follows.

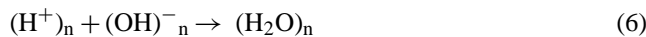
On anodic polarization, OH^- ions move towards the film vertical line/solution interface as:



where B represents the bulk of the solution and S represents the surface of the film. Depending on the local electrical field and the film thickness, diffusion of OH^- ions from the surface to some site in the interior of the film occurs, i.e.,



The oxidation of the divalent hydroxide species releases protons that diffuse away from the electrode to sites in the oxide, where they combine with OH^- ions to form water, i.e.,



where n is the neutralization site. As oxidation proceeds, the neutralization site moves towards the solution site and this progress ceases on reaching the solution phase. This explains the presence of a water concentration gradient in the film and that the variation in the electrochemical activity can be associated with water activity in the solid phase [11]. After the 30th scan, the concentration gradient between the solid and the solution ceases and an equilibrium is established with

a decrease in water concentration in the solid phase (beta-phase), which thus explains the constancy of the peak current and potential up to the 50th scan.

4. Conclusions

Phase pure alpha nickel hydroxide in high yields (94%), with comparable tap density and BET surface area, has been synthesized by a hydrothermal method that uses urea as a hydrolytic agent. The non-use of surfactants or dispersant makes this method very attractive for bulk synthesis. Furthermore, it does not require repeated washings (conventional method) to remove alkali metal cations, which is a tedious process. The particles are of non-uniform size and shape and are in the nanoscale range. Optimum conditions to obtain the best yields are identified. The decrease in electrochemical activity by ageing in alkali solutions has been assigned to change in water activity in the solid and solution phases.

Acknowledgements

This work was conducted under the CSIR task force project (CMM0006). One of the authors M. Jayalakshmi thanks CSIR, India for providing a fellowship.

References

- [1] X. Wang, H. Luo, P.V. Parkhutik, A. Millan, E. Matveeva, J. Power Sources 115 (2003) 153.
- [2] R. Acharya, T. Subbaiah, S. Anand, R.P. Das, Mater. Chem. Phys. 81 (2003) 45.
- [3] A. Delahaye-Vidal, M. Figiarz, J. Appl. Electrochem. 17 (1987) 589.
- [4] M. Dixit, G.N. Subbanna, P.V. Kamath, J. Mater. Chem. 6 (1996) 1429.
- [5] Y.L. Zhao, J.M. Wang, H. Chen, T. Pan, J.Q. Zhang, C.N. Cao, Int. J. Hydrogen Energy 29 (2004) 889.
- [6] F. Portemer, A. Delahaye-Vidal, M. Figiarz, J. Electrochem. Soc. 139 (1992) 671.
- [7] M. Akine, N. Jongen, J. Lemaitre, H. Hofmann, J. Eur. Ceram. Soc. 18 (1998) 1559.
- [8] M. Jayalakshmi, M. Mohan Rao, B.M. Choudary, Electrochem. Commun. 6 (2004) 1119.
- [9] J. Dai, S.F.Y. Li, T.D. Xiao, D.M. Wang, D.E. Reisner, J. Power Sources 89 (2000) 40.
- [10] M.C. Bernard, P. Bernard, M. Keddah, S. Senyarich, H. Takenouti, Electrochim. Acta 41 (1996) 91.
- [11] P. Mageswari, N. Jayalakshmi, V.S. Muralidharan, Bull. Electrochem. 7 (1991) 355.