PII: S0955-2219(98)00034-X

Synthesis of Nickel Hydroxide Powders by Urea Decomposition

Mufit Akinc,[a] Nathalie Jongen,[b] Jacques Lemaître[b]* and Heinrich Hofmann[b]

[a]Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA
[b]Laboratoire de Technologie des Poudres, Département des Matériaux, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Abstract

Synthesis of nickel hydroxide from aqueous solutions by decomposition of urea was investigated. Spherical agglomerates of nanocrystalline particles were obtained. Precipitated powders show turbostratic α-phase with significant carbonate intercalated into the structure. Addition of dispersant HPMC increases the specific surface area and reduces the median agglomerate size, whereas increase in aging time increases the precipitation yield considerably. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Nickel hydroxide is employed as positive electrode in a number of secondary batteries including Ni–metal hydride (Ni–MH), nickel–cadmiun (Ni–Cd), and nickel–iron (Ni–Fe) in low power applications. Use of Ni-MH batteries in high power applications such as electric vehicles is limited by the discharge-charge rate which determines the vehicle acceleration and recharge rate of the battery.[1] During the course of operation, the positive electrode cycles between $Ni(OH)_2$ and $NiOOH$ forms, both of which have the same hexagonal structure. Overall electrode half-cell reaction is represented as:

$$Ni(OH)_2 + OH^- \Longleftrightarrow NiOOH + H_2O + e \quad (1)$$

Obviously, the rate of the above reaction is determined by diffusion of hydroxyl and water in and out of the electrode, reaction at the electrode, and ability to carry the electron through the electrode

material. $Ni(OH)_2$ is a poor conductor and the electrode material is usually doped with small amounts of trivalent cobalt to increase its conductivity. Cobalt ions remain in $+3$ state through the redox cycle providing improved electrical conductivity.[2]

Nickel hydroxide has two polymorphs: namely α- and β-$Ni(OH)_2$. These two phases have the same hexagonal structure with the exception that the β form exhibits well ordered brucite type hydroxide layers with an interlayer separation of 0·46 nm whereas the α form is known as hydrated nickel hydroxide with an interlayer separation of 0·8 to 0·9 nm depending on the type and extent of anion intercalated between the nickel hydroxide layers.[3] Significant quantities of carbonate ions are detected in α-phase and claimed to have been introduced from the atmospheric CO_2.[2,4] In addition, the α form exhibits turbostratic character, i.e. though the interlayer separation remains constant, the orientation of the layers is completely random.

It is generally agreed that the α-$Ni(OH)_2$ provides a higher electrochemical reactivity than the β form presumably due to higher mobility of OH and H_2O within the largely separated nickel hydroxide layers.[3] Unfortunately, the α-phase is metastable with respect to β-phase in alkaline solutions as is the case for battery electrolyte.[4]

A number of chemical and electrolytic methods were attempted to synthesize $Ni(OH)_2$ powders to be employed as positive electrode materials. Portemer *et al.*[4] electrolyzed $Ni(NO_3)_2$ solution to force precipitation of $Ni(OH)_2$ onto porous nickel electrode. They reported that below 50°C, the yield of the process was quite low. Also, at temperatures above 60°C, a mixture of α and β phases were observed. Rate of $Ni(OH)_2$ deposition was quite low at reasonable current densities. Ho[5] referring to electrochemical impregnation of nickel plated

*To whom correspondence should be addressed.

porous sintered plaques, under similar conditions, stated that the impregnation rate was initially high but leveled off quickly at high charge input values limiting applicability of this method as an industrial process. Leveling of impregnation rate was attributed to precipitation at the surface of the electrode and blocking the pores.

Kamath and Subbanna[6] tried several methods to prepare reactive nickel hydroxide electrode material including direct precipitation with KOH, electrolytic precipitation, and sol–gel method. In the latter, they complexed the nickel ions with trisodium citrate prior to precipitation with KOH. The sol–gel method produced fine powders with a specific surface area of $178 \, m^2 g^{-1}$. The XRD patterns of these powders exhibited characteristic peaks of β-Ni(OH)$_2$.

Delahaye-Vidal and Figlarz[3] synthesized Ni(OH)$_2$ by precipitating from aqueous Ni(NO$_3$)$_2$ solutions with ammonia. The precipitated hydroxide was of the α form but quickly transformed to β after several oxidation–reduction cycles with concomitant reduction of charge capacity from 0·92 to 0·65 per nickel atom.

Transformation of turbostratic α-phase to β-phase was claimed to have proceeded by two separate but complimentary processes: chemical aging in concentrated KOH solution and electrochemical cycling between oxidized and reduced states.[3] It is not clear whether the electrochemical cycling actually contributes to phase transformation or not. It appears that substitution of Co^{3+} or similar trivalent cations assists in stabilization of phase α.[7] Although the mechanism of such stabilization has not been elucidated, it is likely that CO$_3^{2-}$ which is found in turbostratic α phase may be easier to retain between the nickel hydroxide layers in the presence of trivalent cations as these ions do not undergo reduction to divalent state as Ni ions do.

Review of the open literature indicates that pure α-Ni(OH)$_2$ can be formed by precipitation in moderately alkaline (pH$\leq$10) solutions but is unstable with respect to the β phase in contact with the battery electrolyte. It is also clear that large multivalent anions, in particular CO$_3^{2-}$, are necessary for α-phase formation and that these anions are retained intercalated if a fraction of the nickel ions are substituted with a trivalent cation such as Co^{3+}.

The primary purpose of this study is to explore the feasibility of an alternative route for the synthesis of α-Ni(OH)$_2$ from aqueous solutions. Homogeneous precipitation by urea decomposition provides excellent opportunity to synthesize phase pure α-Ni(OH)$_2$ as the pH of the solution remains relatively low throughout the process.[8] In addition, it generates one CO$_2$ per urea molecule

decomposed providing ample source of CO$_3^{2-}$ homogeneously according to following well established reaction:

$$(NH_2)_2CO + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \quad (2)$$
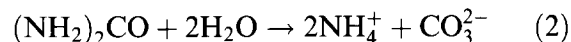
Furthermore, homogeneous precipitation by urea offers the opportunity to produce discrete, uniform particles as has been demonstrated for a number of other systems.[9] An additional advantage of urea process is that it offers an economically attractive and environmentally benign process as it is inexpensive and environmentally safe. A secondary goal of the present work is to assess the role of a common dispersant in modifying the morphology (i.e. particle size, shape, specific surface area) of the particles produced.

Although Avena *et al.*[10] have recently attempted to synthesise nickel hydroxide within the pores of porous nickel electrode by urea decomposition, the yield of the process was extremely low (0·44 mg Ni(OH)$_2$/g-Ni electrode) and no emphasis was given to morphological characteristics of the particles produced.

2 Experimental

All the reagents used in this study were analytical grade and used without further purification. Nickel source was either NiCl$_2$·6H$_2$O (Merck) or Ni(NO$_3$)$_2$·6H$_2$O (Fluka). Urea was >99% pure (Merck) and dispersant was hydroxy propyl methyl cellulose (HPMC) obtained from Sigma and designated as having a viscosity of 100 centipoise for 2% solution in water.

A stock solution of 0·1 M Ni^{2+} solution was prepared by dissolving an appropriate amount of nickel salt in deionized water ($\sigma = 0·055 \, \mu$S·cm). Urea stock solution of 6 M was prepared by dissolving 360 g urea in water to make one liter solution. Dispersant solution was prepared by dissolving 1·0 g of HPMC in water to make 200 ml solution. All the stock solutions were filtered through 0·2 μm cellulose membrane and stored in sealed bottles.

A 100 ml aliquot of 0·1 M Ni^{2+} solution was mixed with either 0, 5, or 10 ml of HPMC solution and appropriate amount of water (50, 45, or 40 ml, respectively) and immersed in ethylene glycol bath at 90 $\pm$ 1°C in sealed bottles and brought to reaction temperature prior to addition of 50 ml urea solution. The nucleation time was determined by visual detection of slight turbidity. Once the nucleation was detected, usually in 15 min, the solutions were aged for 30, 60, or 120 min. The

suspension was quenched in ice-water bath at the end of the aging period. The precipitates were centrifuged twice with 200 ml water and once with ethanol at 4500 rpm for 15 min. They were then dried overnight in an air convection oven at 75°C. The resultant green-colored powder was weighed to determine the process yield. Combination of experimental variables used in these experiments and raw data are summarized in Table 1. Portions of the powder were analyzed using TGA (Mettler 4000), XRD (Siemens 5000), and SEM (Jeol JSM 6300F). Specific surface areas of the powders were also measured by nitrogen adsorption at liquid nitrogen temperature using a Micromeritics Gemini 2375 analyzer. Particle size distributions were measured using a Horiba CAPA 700 particle size analyzer. Chemical analyses were carried out by the Professional Service Industries, Pittsburgh, PA. Contents of Ni, C, N, O, and H were determined quantitatively.

The effects of two factors at three levels—A: HPMC concentration (0.00, 0.25 and $0.50 \, \mathrm{g \, l^{-1}}$), and B: aging time (30, 60 and 120 min)—were investigated in the fully randomized 3^2 factorial statistical design of nine experiments summarized in Table 1. In order to prevent any possible chronological drift from obscuring the interpretation of the data, the tests were effected in the randomized order indicated in the table. The data were analyzed using a statistical model including the linear and quadratic contributions of the factors and their interactions.[11] The significance of the regression coefficients were tested using the ANOVA method at the error risk, p, indicated in the figures: p is the probability that the regression coefficients are effectively equal to 0 (null hypothesis). The adjusted values presented in the figures were then calculated using the statistical models in which only the significant regression coefficients were retained. The adequacy of the statistical model was checked *post hoc* by residual analysis (i.e. by checking that the differences between experimental and calculated observations are unrelated to any other variable, including the order of experiments'

execution and the observations themselves, and that they are normally distributed).

3 Results and Discussion

As shown in Table 1, the initial pH of the solutions was constant at $\mathrm{pH} \cong 5.75$ that is, HPMC does not effect the pH of the starting solution. The final pH however, shows a weak dependence on aging time but not on HPMC concentration. Final pH for the 30 and 60 min of aging is around 7.25 ± 0.1 whereas for 120 min, the final pH is about 7.5 ± 0.1. The higher final pH value measured for longer aging times is anticipated as more nickel precipitates out with time, more $\mathrm{OH^-}$ needs to accumulate for further precipitation.

The precipitation yields were determined from the dried sample weights and weight losses observed by thermal decomposition of the powders to NiO. A typical TGA plot is shown in Fig. 1. The sample shows a continuous weight loss from room temperature to about 480°C with a weak event between 140 and 200°C and a sharp weight loss between 260 and 300°C. The former is attributed to tightly bonded water molecules and the latter to dehydroxylation and elimination of other anions.[4] A total weight loss of about 36% up to 500°C is observed for most samples indicating that no significant change in composition of the precipitate is brought about by either aging time or HPMC content. Slight weight gain above 500°C may be attributed to oxidation of NiO to $\mathrm{Ni_3O_4}$ in a flowing air atmosphere.

Combining the original mass of the powder with the TGA data gives the yield of the process expressed as percent of nickel precipitated. The results are shown in Table 1 and in Fig. 2. Data indicate that yield increases steadily with aging time: from 21 up to 57% from 30 to 120 min. No significant effect of the presence of HPMC can be observed. This observation is in agreement with the previous work[8] carried out in other systems that the decomposition of urea is the rate limiting step.

Table 1. Experimental conditions and physical characteristics of the powders[a]

Sample no.	Testing order no.	Concentration of HPMC $(g \, l^{-1})$	Aging time (min)	Initial pH	Final pH	Surface area $(m^2 \, g^{-1})$	Yield (%)	Median particle size (μm)
1	2	0.00	30	5.80	7.24	22.3	18.3	2.1
2	6	0.25	30	5.76	7.20	46.1	22.4	1.5
3	9	0.50	30	5.67	7.13	54.3	22.5	0.9
4	8	0.00	60	—	7.34	26.8	31.3	2.7
5	4	0.25	60	5.75	7.27	43.4	36.4	3.0
6	7	0.50	60	5.72	7.25	46.8	39.4	1.8
7	5	0.00	120	—	7.40	24.3	57.2	3.3
8	1	0.25	120	5.75	7.50	37.6	58.1	2.4
9	3	0.50	120	5.76	7.40	35.7	55.8	2.6

[a]Other experimental conditions were: $(\mathrm{Ni^{2+}})_o = 0.05 \, \mathrm{M}$, $(\mathrm{Urea})_o = 1.5 \, \mathrm{M}$, aging temperature $= 90°C$.
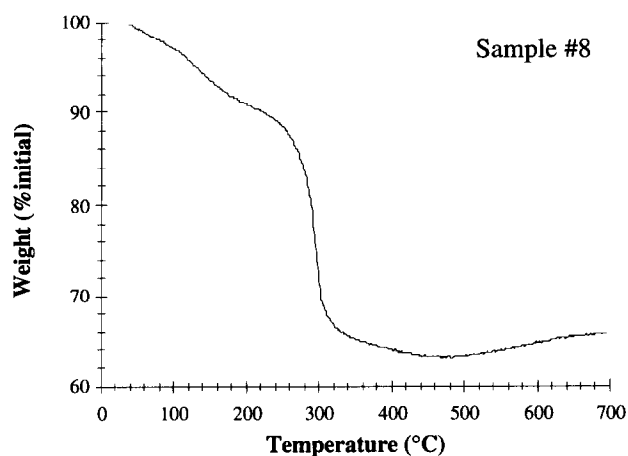
Fig. 1. Thermogravimetric Analysis of a typical nickel hydroxide precipitate (sample no. 8) in air atmosphere. Heating rate was $10°\,\mathrm{min}^{-1}$.
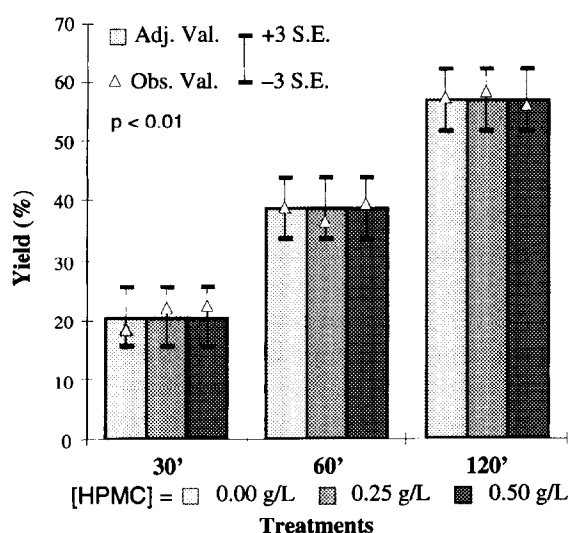

Fig. 2. Effect of HPMC concentration and aging time on Ni precipitation yield.

In fact, even after 120 min of aging, only 12% of the urea decomposes. An approximate calculation indicates that only 60% of the nickel should precipitate in 120 min of aging which agrees with about 57% yield obtained experimentally. If complete precipitation of nickel is required, the solutions should be aged either for longer times or at higher temperatures.

Chemical analysis of a typical sample indicates that the powder has an approximate composition of: Ni = 44·5%, C = 5·90%, H = 2·1%, N = 2·1% and O = 40·0%. As chemical analysis clearly demonstrates a significant amount of carbonaceous species (presumably in the form of carbonates) are incorporated into the precipitate. A few percent of the total is unaccounted for and was assumed to be weight loss occurred during sample conditioning prior to chemical analysis. Combining chemical analysis, TGA, and electrical neutrality requirement

leads to an approximate chemical composition of: $Ni_3(OH)_4(HCO_3)_{1.85}(NO_3)_{0.15}$.

X-ray diffraction pattern of a typical powder is shown in Fig. 3. The general features of all the diffraction patterns obtained for all the samples are the same and consistent with the patterns reported for α-Ni(OH)$_2$ and its derivatives.[8] The first two peaks at 7·307 and 3·645 Å correspond to (001) and (002) reflections. The broad asymmetric band with a peak at d = 2·68 Å is assigned to (10l) plane family and is characteristic of turbostratic Ni(OH)$_2$ due to random stacking of nickel hydroxide layers. All the peaks observed for the powders synthesized in this study can be indexed to that of α-Ni(OH)$_2$ with slight shift in the (001) and (002) peak positions. These shifts are attributable to the extent and type of the intercalating anions in the structure. No peaks due to β-Ni(OH)$_2$ were observed indicating that the precipitated powders are phase pure at least at the XRD detection level.

Microscopic observation of the powders indicates that particles are spherical agglomerates of sheet-like nanometer scale crystallites (Fig. 4). Indeed, XRD peak widths confirm that the primary particles are nanocrystalline as shown in Fig. 3. These findings are corroborated by the specific surface area measurements, presented in Fig. 5. The lowest BET surface areas are observed for the precipitates obtained without HPMC (22 to $25\,\mathrm{m^2\,g^{-1}}$); in this series, no significant effect of aging time is observed. The presence of HPMC in the precipitation medium increases S_{BET} considerably after 30 min aging, the main increase occurring between 0 and $0.25\,\mathrm{g\,l^{-1}}$ of HPMC, with a maximum of $54.3\,\mathrm{m^2\,g^{-1}}$ for $0.50\,\mathrm{g\,l^{-1}}$ HPMC; S_{BET} decreases with aging times, a faster decrease being observed for the precipitates prepared with the highest HPMC concentration.
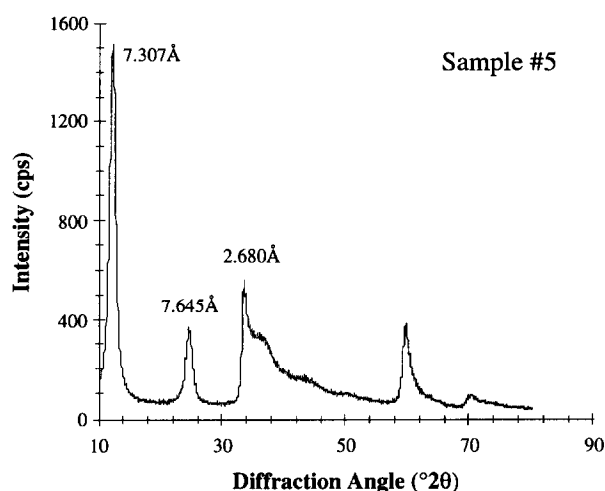

Fig. 3. X-ray diffraction pattern of a typical nickel hydroxide precipitate. The peak around $2\Theta = 12°$ and the broad asymmetric band around $2\Theta = 32 - 36°$ are typical for turbostratic α-Ni(OH)$_2$ phase.
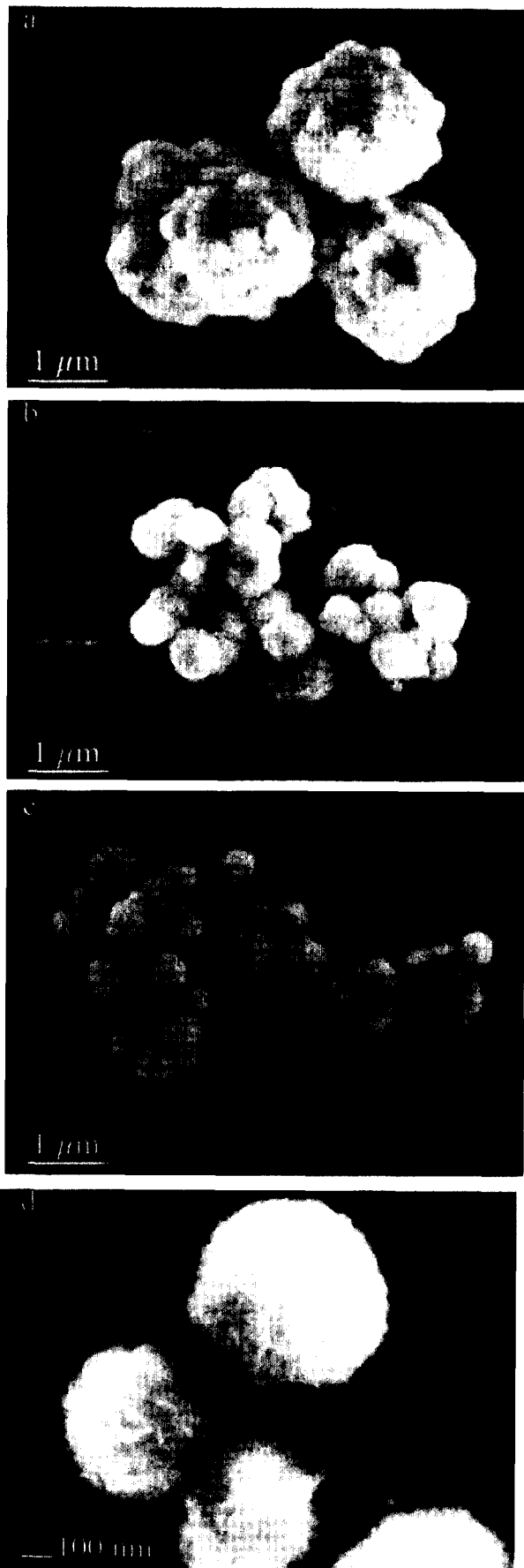
Fig. 4. Scanning electron micrographs of (a) sample no. 1, (b) sample no. 2, (c) sample no. 3 showing the change in particle size with addition of HPMC and (d) sample no. 2 showing the sheet-like nanocrystalline primary particle morphology.
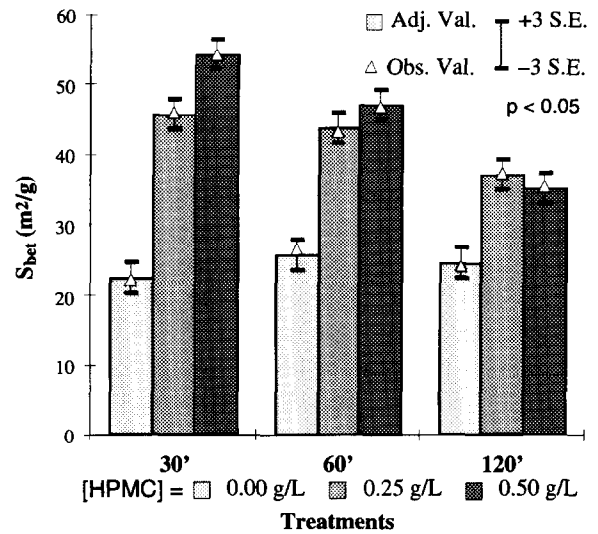

Fig. 5. Effect of HPMC concentration and aging time on the specific surface area of the precipitate.

The spherical agglomerates are typically sub-micron in size. These agglomerates in turn form secondary agglomerates on the order of couple of microns. Aging time and concentration of HPMC have a distinct influence on the degree of agglomeration. As the aging time increases, the degree of agglomeration increases as well. Similarly, as the concentration of HPMC increases for a given aging time (especially for short aging times) the size of the agglomerates decreases (Fig. 4). As Fig. 4 demonstrates, the size of the particles decreases from 1–2 μm to less than 0.5 μm as the concentration of HPMC is increased from 0.0 to 0.5 gl^{-1}.

Median particle size, D_{50}, values are presented in Fig. 6. They give an approximate measure of secondary agglomeration. A preliminary analysis of the data revealed that the result of experiment no. 5 was an outlier; therefore, the analysis was
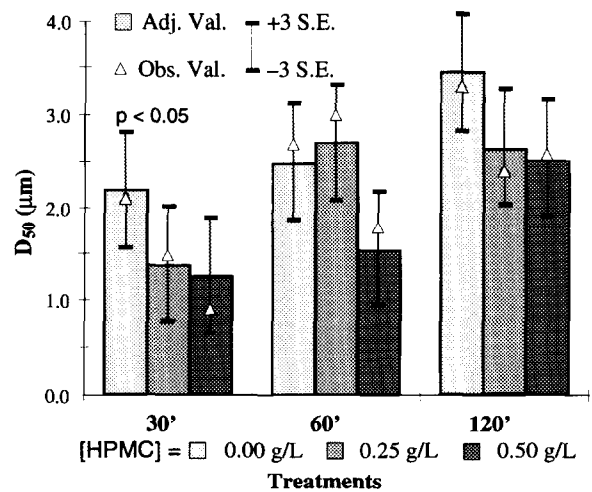

Fig. 6. Effect of HPMC concentration and aging time on the median agglomerate size of the precipitate.

repeated with a set of data where the result of experiment no. 5 has been replaced by the average value of experiment nos. 2 and 8 (i.e. $D_{50} = 1.95 \, \mu m$). The data indicate that the degree of agglomeration decreases with increasing HPMC concentrations, especially at shorter aging times. As aging time increases, the degree of secondary agglomeration increases as well irrespective of the presence of HPMC. However, the rate of secondary agglomeration depends on the HPMC concentration in the precipitation medium: the lowest at $0.25 \, g \, l^{-1}$ HPMC, and the highest at the $0.5 \, g \, l^{-1}$ HPMC concentration.

4 Summary

The present study has demonstrated that nickel hydroxide can be precipitated from aqueous solutions using urea as the precipitating agent. The precipitated powders exhibit turbostratic α-$Ni(OH)_2$ structure with a chemical composition of $Ni_3(OH)_4(HCO_3)_{1.85}(NO_3)_{0.15}$. Particles were found to be sub-micrometer size agglomerates of sheet-like nano-scale primary crystallites. The specific surface area of the powders is strongly affected by the presence of HPMC, especially for short aging times; it increases by more than two-fold from 22.3 to $54.3 \, m^2 \, g^{-1}$ with $0.5 \, g \, l^{-1}$ HPMC addition for 30 min aging times. The precipitation yield is primarily controlled by the aging time under the range of experimental conditions investigated; it increases from about 22 to 57% upon increasing the aging time from 30 to 120 min.

This investigation has shown that the urea process is an attractive method for producing uniform, nano-crystalline, turbostratic nickel carboxyhydroxide particles which may have a higher electrochemical reactivity than the powders obtained by other chemical methods. The stability in strongly alkaline solutions, and electrochemical behavior of the powders have yet to be investigated.

References

1. Ovshinsky, S. R., Fetcenko, M. A. and Ross, J., A nickel metal hydride battery for electric vehicles. *Science*, 1993, **260**, 176–181.
2. Faure, C., Delmas, C. and Willman, P., Preparation and characterization of cobalt substituted α-nickel hydroxide stable in KOH medium Part II. α-Hydroxide with a turbostratic structure. *Journal of Power Sources*, 1991, **35**, 263–277.
3. Delahaye-Vidal, A. and Figlarz, M., Textural and structural studies on nickel hydroxide electrodes. II. Turbostratic nickel (II) hydroxide submitted to electrochemical redox cycling. *Journal of Applied Electrochemistry*, 1987, **17**, 589–599.
4. Portemer, F., Delahaye-Vidal, A. and Figlarz, M., Characterization of active material deposited at the nickel hydroxide electrode by electrochemical impregnation. *Journal of the Electrochemical Society*, 1992, **139**(3), 671–678.
5. Ho, K. -C., Electrochemical precipitation of nickel hydroxide. *Journal of the Electrochemical Society, (Reviews and News)*, 1987, **134**(2), 52C–55C.
6. Kamath, P. V. and Subbanna, G. N., Electroless nickel hydroxide: synthesis and characterization. *Journal of Applied Electrochemistry*, 1992, **22**, 478–482.
7. Faure, C., Delmas, C., Fouassier, M. and Willmann, P., Preparation and characterization of cobalt-substituted α-nickel hydroxides stable in KOH medium part I. α'-Hydroxide with an ordered packing. *Journal of Power Sources*, 1991, **35**, 249–261.
8. Sordelet, D. and Akinc, M., Preparation of spherical, monosized Y_2O_3 precursor particles. *Journal of Colloid and Interface Science*, 1988, **122**(1), 47–59.
9. Akinc, M. and Sordelet, D., Preparation of yttrium, lanthanum, cerium and neodymium basic carbonate particles by homogeneous precipitation. *Advanced Ceramic Materials*, 1987, **2**(3A), 232–238.
10. Avena, M. J., Vasquez, M. V., Carbonio, R. E., DePauli, C. P. and Macagno, V. A., A simple and novel method for preparing $Ni(OH)_2$ part I. Structural studies and voltametric response. *Journal of Applied Electrochemistry*, 1994, **24**, 256–260.
11. Montgomery, D. C., *Design and Analysis of Experiments*. John Wiley & Sons, New York, 1991, pp. 387–398.