

# Electrochemical precipitation of nickel hydroxide

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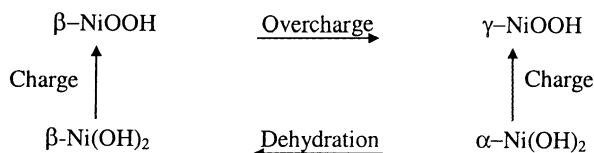
## Abstract

The electrochemical precipitation of nickel hydroxide is examined by varying nickel and nitrate ion concentration, pH, current density, and temperature. The particle size, crystallographic orientation and morphological patterns are studied. The grain size increases, but both current efficiency and tap density decrease with increase in current density. The tap density increases with increase in nickel concentration. XRD data show peaks at 39.0, 59.6 and 33.6°, which conforms that samples obtained by the electrochemical route after drying at 100 °C are β-Ni(OH)<sub>2</sub>. The charge and discharge characteristics are investigated to assess the capacity of the active nickel hydroxide material in 30% KOH solution. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Nickel hydroxide; Electrochemical; Precipitation; Discharge capacity; Current density; Preparation

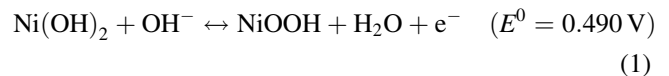
## 1. Introduction

Nickel hydroxide is an important material for nickel–cadmium and nickel–metal-hydride batteries. Nickel hydroxide is a complex crystalline material with a structure which depends on the method of preparation [1]. Bode et al. [2] reported that on electrochemical precipitation of nickel nitrate, the product α-Ni(OH)<sub>2</sub>·2H<sub>2</sub>O is formed in which the water of hydration is integral part of the crystal structure. An internal layer of water increases the lattice distance between the hydroxide layers in the α-Ni(OH)<sub>2</sub>. Two types of nickel hydroxides are formed: One has an anhydrous form with a brucite structure and is termed β-Ni(OH)<sub>2</sub>, the other hydrated form is called α-Ni(OH)<sub>2</sub>. Oxidation of β-Ni(OH)<sub>2</sub> produces β-NiOOH, while oxidation of α-Ni(OH)<sub>2</sub> produces γ-NiOOH. The α-Ni(OH)<sub>2</sub> dehydrates in concentrated alkali to form β-Ni(OH)<sub>2</sub> and β-NiOOH could be converted to γ-NiOOH. The overall reaction reported by Gomez et al. [3] is as follows:

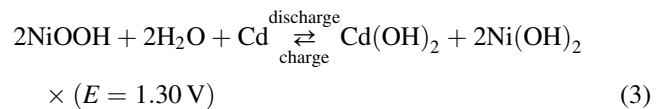


The following reactions take place in nickel–cadmium and nickel–metal-hydride batteries.

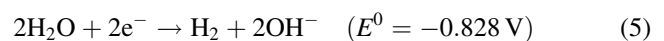
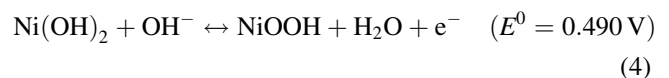
Ni–Cd:



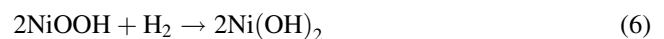
Overall reaction:



Ni–MH:



Overall reaction:



Briggs and Fleischman [4] showed that different oxidation processes could take place simultaneously at the solid/liquid interfaces of nickel hydroxide. On reduction: (i) NiOOH exists over a wide range of composition; (ii) a phase change occurs only at definite limiting compositions; (iii) electrochemical activity occurs not at phase boundaries but at the expanding interface between conducting NiOOH and non-conducting Ni(OH)<sub>2</sub>.

Several authors [5–9] have carried out extensive research on the preparation and physicochemical properties of nickel

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hydroxide. Faure et al. [5] obtained turbostatic  $\alpha$ -nickel hydroxide from nickel sulfate solution and chemical analysis and infrared studies showed that sulfate ions were adsorbed and intercalated between nickel hydroxide layers. Delahaye-Vidal et al. [6] characterized  $\alpha$ - and  $\beta$ -type nickel hydroxide, obtained chemically or electrochemically, by different techniques. The electrochemical impregnation of porous nickel sintered plates were investigated by Portemer et al. [7] to obtain a better understanding of the structure, texture and composition of the deposited active material. It was reported that the nature of the material depends on the temperature of impregnation bath. Below 60 °C,  $\alpha$ -nickel hydroxide formed, whereas above 60 °C the  $\alpha$ -phase appeared simultaneously with  $\beta$ -nickel hydroxide as well as with a crystallized phase in a major proportion which displayed structural features similar to those nickel oxyhydroxy nitrate. Qiangqing et al. [8] studied the conditions for preparation of highly activated nickel hydroxide and the effect of additives on the activity of nickel hydroxide. The tap density and activity of nickel hydroxide were determined by Hui et al. [9].

Nickel hydroxide can be prepared chemically, electrochemically or hydrothermally, and certain additives improve the characteristics of the material [1–34]. In our laboratory, extensive work has been performed on the precipitation of nickel hydroxide using a chemical method; the precipitate is washed thoroughly with distilled water till free of sulfate. Aqueous suspension of this precipitate is treated hydrothermally in an autoclave. Finally, the hydrothermally treated samples are cooled and allowed to age for 48 h [32]. The discharge capacity of this material is 165 mAh g<sup>-1</sup>. Efforts have also been made to precipitate nickel hydroxide using complexing agents [33] such as sodium succinate and tri-sodium citrate. The precipitate was aged for 72 h. The discharge capacity of the resulting nickel hydroxide is 107 mAh g<sup>-1</sup> in the case of sodium succinate and 131 mAh g<sup>-1</sup> in the case of tri-sodium citrate. Both these two methods take more time for preparation. Nickel hydroxide produced electrochemically is highly pure, gives high discharge capacity, and requires less washing for alkali removal. Aging of nickel hydroxide is not required in this method; and by controlling the operating conditions, the required quality of nickel hydroxide can be produced. In the study reported here, an attempt is made to correlate the conditions of preparation of nickel hydroxide, with apparent density, cell voltage and energy consumption. The effects of variables such as nickel concentration, nitrate ion concentration and current density on tap density and particle size are discussed.

## 2. Experimental

A 500-ml Corning beaker was made into compartments using a polypropylene diaphragm as a separator, and was used as an electrolytic cell. The anode was a titanium

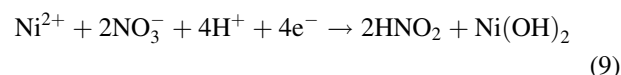
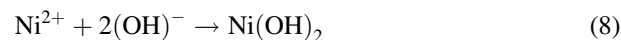
substrate, which had a thickness of 0.3 cm and dimensions of 10 cm (length) and 5 cm (width). The cathode was a stainless-steel sheet with dimensions of 10 cm (length) and 5 cm (width). Fresh electrodes were used for each experiment. The cathodes were carefully polished with fine (600 grade) emery paper, washed under running tap water, scrubbed with filter paper, rinsed with distilled water, and finally dried in air. The electrodes were placed in the cell and connected to the circuit for nickel hydroxide precipitation. Electrolysis was carried out by applying a dc voltage from a regulated power supply unit. All the reagents used in the present study were of analytical reagent grade. The electrolyte was prepared using nickel sulfate and distilled water. A pre-determined quantity of nitrate ion in the form of nitric acid was added to the electrolyte. The initial compositions of the catholyte and the anolyte were kept the same in all experiments. Physical properties such as tap density and apparent density were measured by standard methods, and the particle size was determined with a Malvern particle analyzer. The BET surface-area was measured with a Coulter SA 3100.

The charge and discharge characteristics were studied in 100 ml of 30% KOH solution using a Ni(OH)<sub>2</sub> pellet. The pellets were prepared by combining 4.34 g of active nickel hydroxide material with 2.27 g of graphite powder, 0.0276 g of nickel powder and 3 ml of 2% polyvinyl alcohol (PVA) as binding material at a pressure of 4 t m<sup>-2</sup> for 2 min. The nickel hydroxide pellet was used as the positive electrode and a cadmium hydroxide pellet as the negative electrode. The corresponding cell potentials were recorded at regular intervals of time. Charging was carried out at a current density of 15.9 mA cm<sup>-2</sup>, and discharging at 3.18 mA cm<sup>-2</sup>.

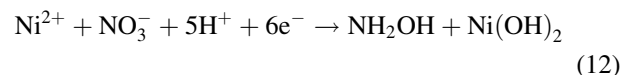
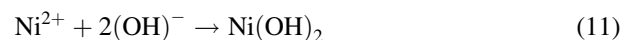
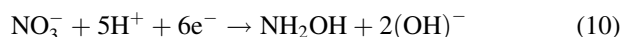
## 3. Results and discussion

MacArthur [10] has proposed four possible mechanisms for the reduction of nitrate ions at metal surfaces to either nitrite or hydroxylamine. This reduction reaction provides hydroxide for concurrent precipitation of nickel hydroxide from the solution.

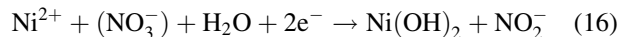
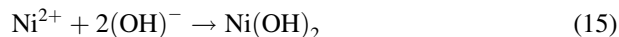
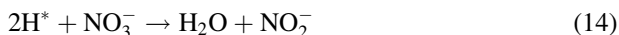
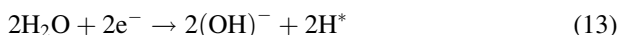
1. Direct nitrate reduction to nitrous acid:



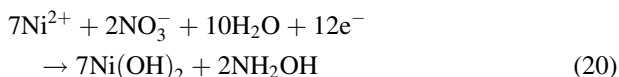
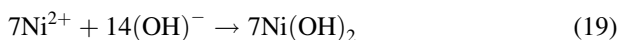
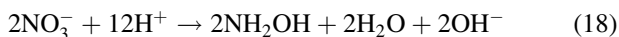
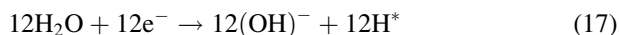
2. Direct reduction to hydroxylamine:



## 3. Indirect reduction to nitrite:



## 4. Indirect reduction to hydroxylamine:



All the four mechanisms will produce  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub>. These can be distinguished from the lattice positions.

## 3.1. Effect of nickel concentration

Haeussler [12] produced nickel hydroxide from 8.8 g dm<sup>-3</sup> nickel nitrate solution in HNO<sub>3</sub> adjusted to pH 2.3. In this system, the cathodic process is dominated by the reduction of nitrate ions. As H<sup>+</sup> ions are consumed, the pH in the immediate vicinity of the cathode increases and leads to the precipitation of nickel hydroxide. McHenry [13] used a larger concentration of 234.76 g dm<sup>-3</sup> Ni(NO<sub>3</sub>)<sub>2</sub>, a higher pH of 5.1 and higher current densities of 1750 A m<sup>-2</sup> to prepare nickel hydroxide electrochemically.

Kumar et al. [14] have studied the effect of nickel concentration during the electrowinning of nickel. They found that the current efficiency increased marginally from 79 to 82% and the power requirement decreased by 5% when the nickel concentration was increased from 60 to 140 g dm<sup>-3</sup> at

a current density of 200 A m<sup>-2</sup>. Cobalt behaves in a similar way to that of nickel. Das and Subbaiah [15] also observed an increase of current efficiency from 35 to 70% as the cobalt concentration was increased from 6 to 50 g dm<sup>-3</sup>. Above this concentration, the current efficiency remained almost same throughout the range studied. The same authors found similar behavior in the presence of additives [16] such as boric acid and sodium fluoride. Such additives also increase the current efficiency.

In the present study, the concentration of nickel in the catholyte was changed from 10 to 40 g dm<sup>-3</sup>. The initial pH of the catholyte was maintained at 4.5 and current density at 200 A m<sup>-2</sup>. The tap density was measured and was found to increase with increase in nickel concentration up to 15 g dm<sup>-3</sup>. The current efficiency decreased with increase in nickel concentration up to 15 g dm<sup>-3</sup>, and remained constant above this concentration. The effect of nickel concentration on current efficiency and tap density is shown in Fig. 1. The effect of nickel concentration on cell voltage, apparent density and energy consumption is listed in Table 1. The apparent density is the weight of a unit volume of loose powder, and the tap density is obtained by tapping of a mass of loose powder or, more specifically, the application of vibration to the powder mass. It is also observed that at higher nickel concentrations, a pasty and adhering type of

Table 1

Effect of nickel ion concentration on cell voltage, apparent density and energy consumption

Sample	Ni concentration (g dm <sup>-3</sup> )	Cell voltage (V)	Apparent density (g cm <sup>-3</sup> )	Energy consumption (kWh kg <sup>-1</sup> )
1	10	4.50	0.39	4.86
2	20	4.75	0.55	3.91
3	30	4.60	0.66	3.51
4	40	4.50	0.67	3.43

Current density = 200 A m<sup>-2</sup>; initial pH 4.5; HNO<sub>3</sub> concentration = 28.4 g dm<sup>-3</sup>; 30 ± 1 °C.

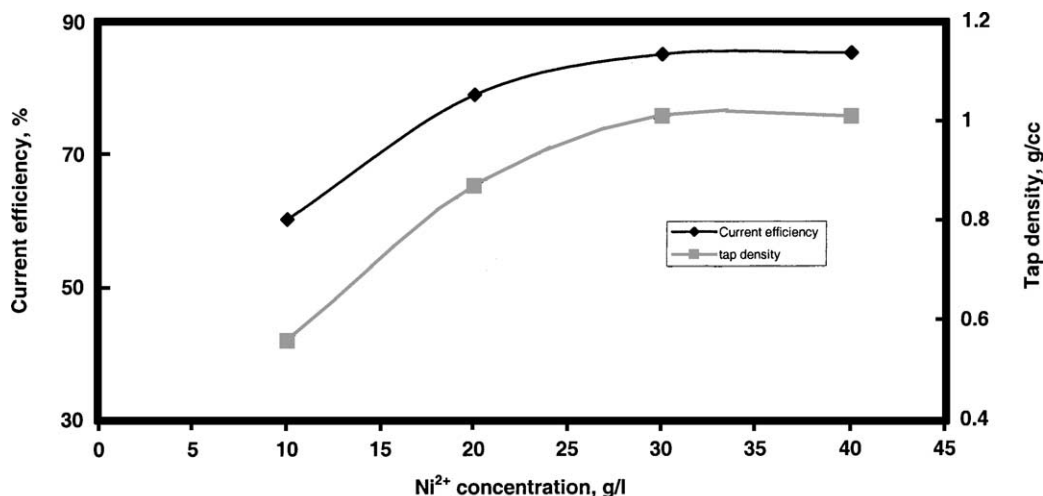


Fig. 1. Effect of Ni<sup>2+</sup> concentration on current efficiency and tap density.

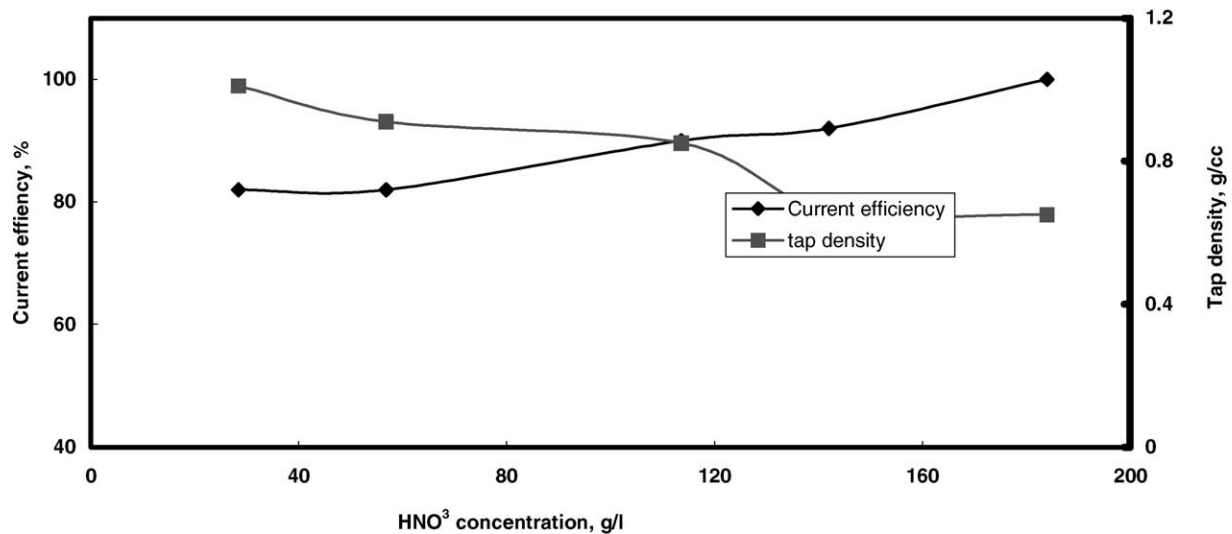


Fig. 2. Effect of nitrate ion concentration on current efficiency and tap density.

nickel hydroxide is deposited on the cathode. The apparent density also increases with nickel concentration. Further, it is found that there is little variation in cell voltage with increase in nickel concentration, and the energy consumption is greater at lower nickel concentration.

### 3.2. Nitrate ion concentration

The nickel concentration in the catholyte was maintained at  $40 \text{ g dm}^{-3}$  and nitrate ion in the form of  $\text{HNO}_3$  was added to the catholyte from 0 to  $284 \text{ g dm}^{-3}$ . A minimum of  $28.4 \text{ g dm}^{-3}$  nitrate is required for hydroxide precipitation, otherwise nickel metal is deposited. In the absence of nitrate ion, there is no nickel hydroxide precipitation. The effect of nitrate ion on current efficiency and tap density is shown in Fig. 2. The variation of current efficiency with increase in nitrate ion concentration is marginal, but the tap density decreases. A similar observation was made found by Christopher et al. [17]. The effect of nitrate ion on cell voltage, energy consumption, and apparent density is shown in Table 2. The results show that there is no change in cell voltage, and the change in both apparent density and energy consumption is also marginal.

Table 2  
Effect of nitrate ion concentration on cell voltage, apparent density and energy consumption

Sample	HNO <sub>3</sub> concentration (g dm <sup>-3</sup> )	Cell voltage (V)	Apparent density (g cm <sup>-3</sup> )	Energy consumption (kWh kg <sup>-1</sup> )
1	28.4	4.50	0.67	3.43
2	56.8	4.50	0.56	3.45
3	142	4.32	0.55	3.31
4	284	4.29	0.54	3.31

Current density =  $200 \text{ A m}^{-2}$ ; initial pH 4.5; Ni concentration =  $40 \text{ g dm}^{-3}$ ;  $30 \pm 1^\circ\text{C}$ .

### 3.3. Current density

The nickel concentration in the catholyte was maintained at  $40 \text{ g dm}^{-3}$ . The initial pH of the solution was 4.5 and the final pH was 6.5–7.0. The effect of current density was studied in the range  $200\text{--}600 \text{ A m}^{-2}$ . The effect of current density on current efficiency and tap density is given in Fig. 3. With increase in current density, current efficiency and tap density are decreased. The effect of current density on cell voltage, apparent density and energy consumption is listed in Table 3. As expected, the cell voltage and energy consumption are increased.

Das and Subbaiah [15] also observed that current efficiency decreases with increase in current density above  $100 \text{ A m}^{-2}$  in the case of cobalt electrowinning. This is probably due to a decrease in the effective metal ion concentration in the vicinity of the catholyte as a result of which hydrogen evolution increases.

Kang et al. [19] showed that it is far more efficient to form films using low current density and long deposition times than it is to increase the current density in order to cause nickel hydroxide precipitation to proceed more rapidly. Disordered

Table 3  
Effect of current density on cell voltage, apparent density and energy consumption

Sample	Current density (A m <sup>-2</sup> )	Cell voltage (V)	Apparent density (g cm <sup>-3</sup> )	Energy consumption (kWh kg <sup>-1</sup> )
1	200	4.50	0.67	3.43
2	300	4.60	0.60	3.98
3	400	4.67	0.43	5.70
4	500	6.40	0.48	8.50
5	600	7.35	0.49	12.30

Ni concentration =  $40 \text{ g dm}^{-3}$ ; initial pH 4.5; HNO<sub>3</sub> concentration =  $28.4 \text{ g dm}^{-3}$ ;  $30 \pm 1^\circ\text{C}$ .

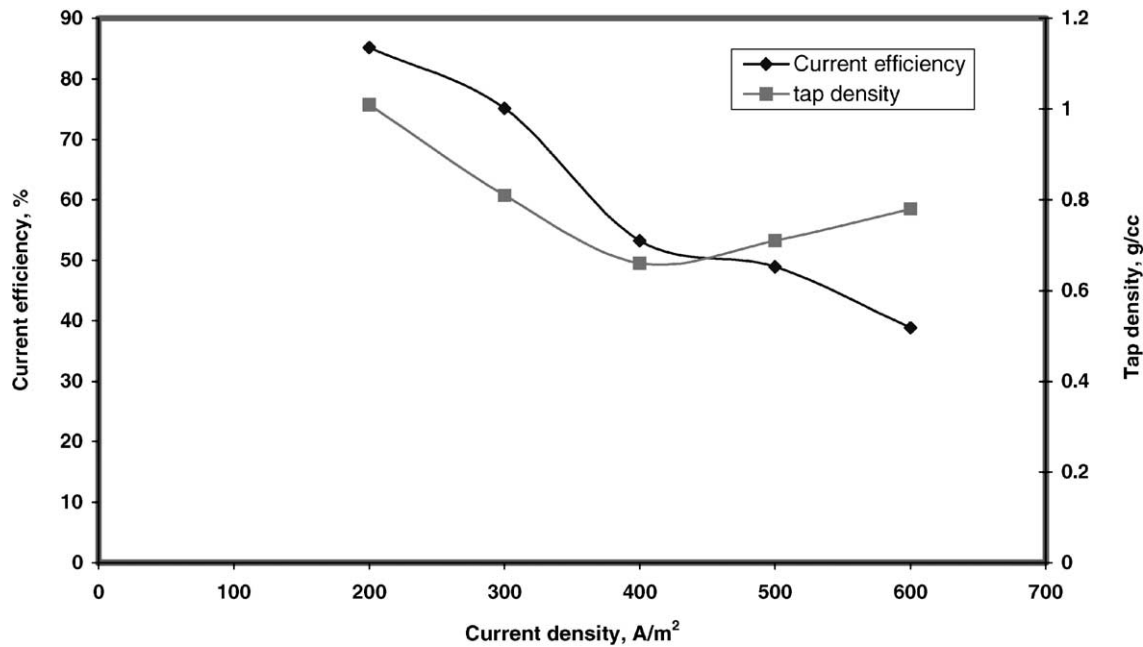


Fig. 3. Effect of current density on current efficiency and tap density.

films might impair conductivity and therefore might insulate the surface of the growing film sufficiently to reduce the quantity of nickel hydroxide precipitated during later stages of film formation. Homogeneous films with a relatively compact structure were obtained at  $30 \text{ A m}^{-2}$ . This suggests that there is a narrow range of optimum conditions.

### 3.3.1. Particle size

Increase in current density causes variation in particle size. Watanabe et al. [21] studied the physical properties of several

hydroxide powders by laser diffractometry, BET, X-ray diffraction, thermal analysis, and SEM. It was reported that nickel hydroxide powder with a smaller crystalline size showed better charge–discharge characteristics. The individual and cumulative particle-size distribution at 200 and  $600 \text{ A m}^{-2}$ , are shown in Figs. 4 and 5, respectively. At a current density of  $200 \text{ A m}^{-2}$ , the particle size for  $D_{V,0.5} = 2.92$  and  $D_{V,0.9} = 6.08 \mu\text{m}$ . The specific surface-area of this material is  $2.7594 \text{ m}^2 \text{ cm}^{-3}$ . The same particle size is measured with BET analysis, the value is  $14.084 \text{ m}^2 \text{ g}^{-1}$ .

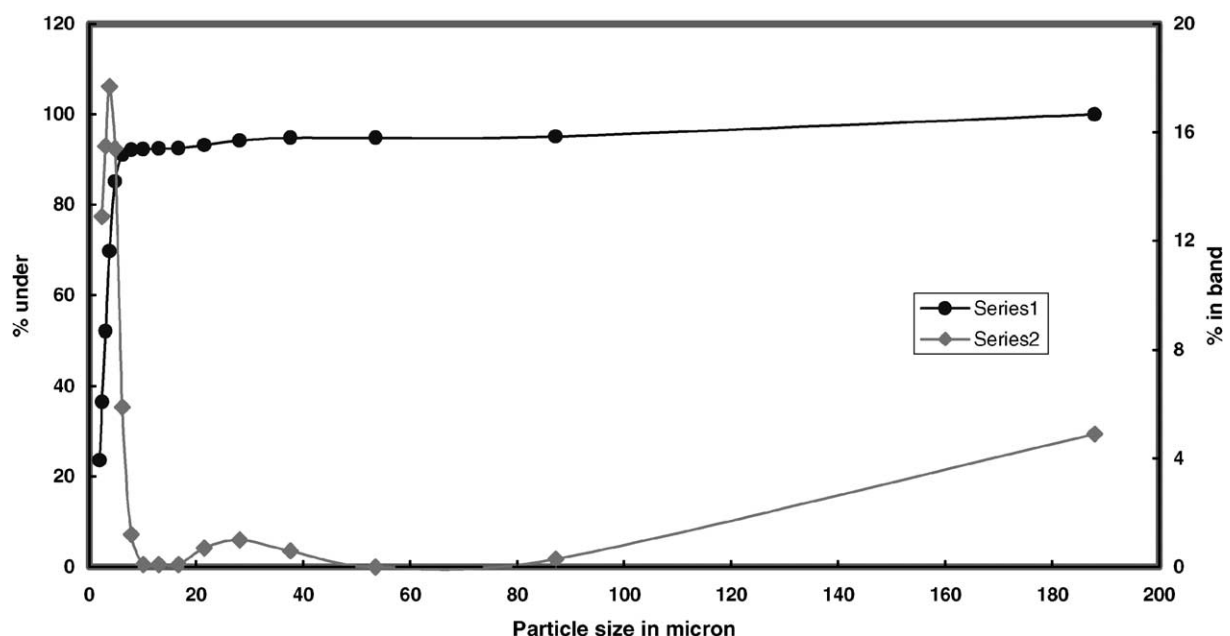


Fig. 4. Individual and cumulative particle-size distribution at current density of  $200 \text{ A m}^{-2}$ .

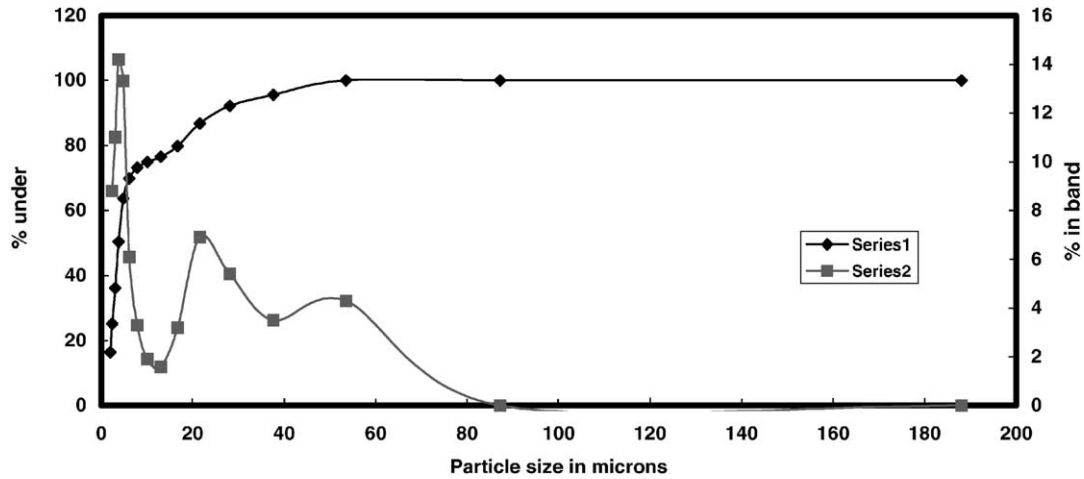


Fig. 5. Individual and cumulative particle-size distribution at current density of 600 A m<sup>2</sup>.

Spherical nickel hydroxide produced at UMEX Inc. (Canada) has a specific surface-area of 12–20 m<sup>2</sup> g<sup>-1</sup>. It is observed that at higher current density,  $D_{50}$  and  $D_{90}$  values are higher. At 600 A m<sup>-2</sup>,  $D_{V,0.5} = 3.80$  and  $D_{V,0.9} = 25.48$  μm.

3.3.2. XRD

XRD patterns indicate that α-Ni(OH)<sub>2</sub> forms peaks at 2 (Cu Kα) 11, 22, 33.5 and 60° [22]. The peaks at 44.5 and 51.7° correspond to the Ni metal of the sinter support. The β-Ni(OH)<sub>2</sub> peaks are at 2, 19.1, 33.2, 38.5 and 59.2°. The XRD data of the present sample has peaks at 39, 59.6 and 33.6° which shows the samples obtained by electrochemical precipitation and after drying at 100 °C are β-Ni(OH)<sub>2</sub>. Portemer et al. [7] reported that α-Ni(OH)<sub>2</sub> is formed when electrochemical precipitation takes place below 60 °C; the α-phase appeared simultaneously with β-Ni(OH)<sub>2</sub>.

Table 4

Effect of temperature on cell voltage, apparent density and energy consumption

Sample	Temperature (°C)	Cell voltage (V)	Apparent density (g cm <sup>-3</sup> )	Energy consumption (kWh kg <sup>-1</sup> )
1	30	4.50	0.66	3.43
2	40	4.40	0.66	3.85
3	50	4.39	0.68	3.93
4	60	4.17	0.72	3.74
5	70	3.99	0.77	3.61

Current density = 200 A m<sup>-2</sup>; initial pH 4.5; HNO<sub>3</sub> concentration = 28.4 g dm<sup>-3</sup>; Ni concentration = 40 g dm<sup>-3</sup>.

3.4. Effect of temperature

The catholyte concentration was maintained at 40 g dm<sup>-3</sup> and the temperature was varied from 30 to 70 °C. With

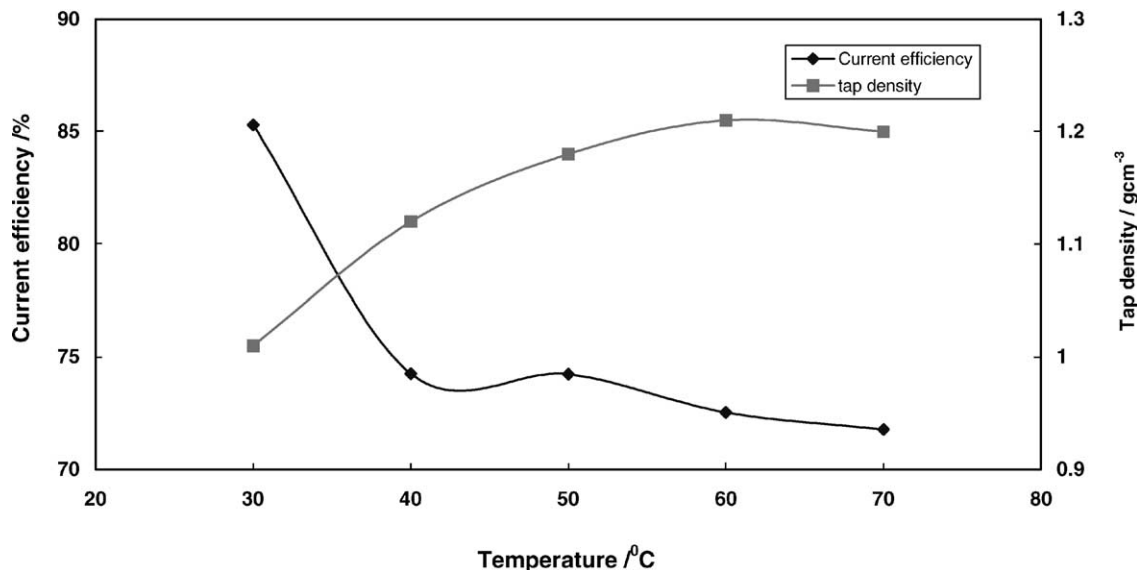


Fig. 6. Effect on temperature on current efficiency and tap density.

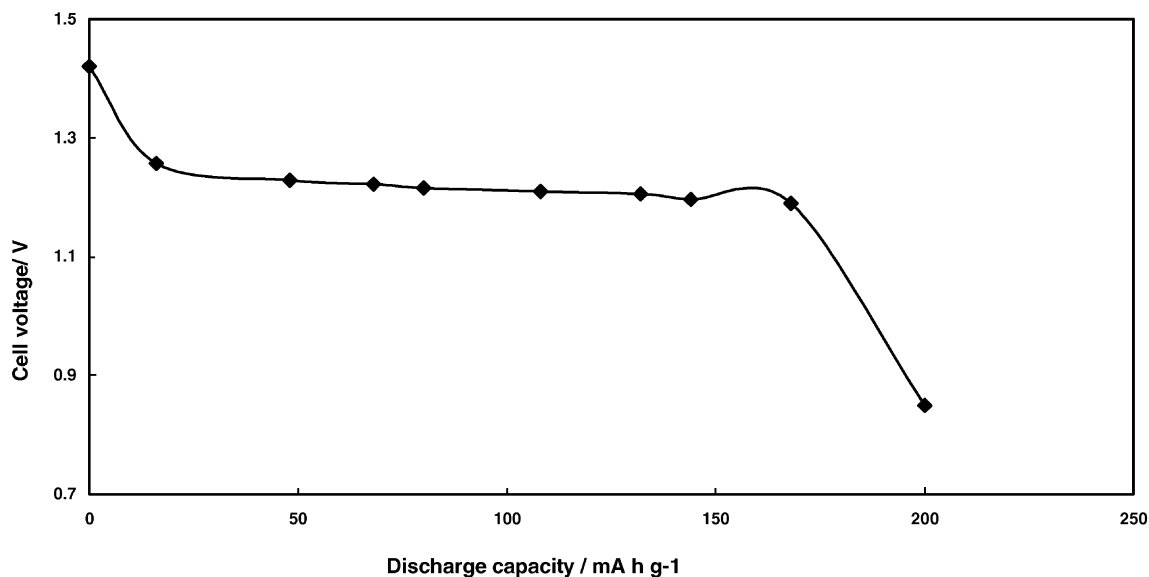


Fig. 7. Discharge characteristics of nickel hydroxide electrode.

increase in temperature, the current efficiency utilized for producing nickel hydroxide is decreased; the effect of temperature on current efficiency and tap density is shown in Fig. 6. The effect of temperature on cell voltage, apparent density and energy consumption is given in Table 4. Cell voltage is reduced marginally, and the changes in apparent density and energy consumption are also marginal. With increase in temperature, however, the tap density is increased. Christopher et al. [27] also observed that the molecular weight of the deposited film increases with temperature. This was attributed to a combination of increased rate of deposition and an increase in the lattice spacing of the active material.

### 3.5. Discharge characteristics of nickel hydroxide

The electrochemical properties of nickel hydroxide are generally characterized by the charge and discharge characteristics. Typical discharge characteristics of nickel hydroxide pellets in presence of ethanol on the second cycle are presented in Fig. 7. The capacity of the nickel hydroxide pellets is 200 mAh g<sup>-1</sup> and thus the discharge capacity and the discharge potential values are comparable with the values reported by others [31–34].

## 4. Conclusions

1. With increase in nickel concentration, the current efficiency of nickel hydroxide precipitation and the tap density of the compound both increase within the range studied (10–40 g l<sup>-1</sup> Ni<sup>2+</sup>).
2. In the absence of nitrate ions, there is no precipitation of nickel hydroxide.
3. With increase in current density, the current efficiency and the tap density both decrease.

4. The particle size of nickel hydroxide increases with increase in current density.
5. With increase of temperature, current efficiency of nickel hydroxide precipitation decreases.
6. The discharge capacity of nickel hydroxide is 200 mAh g<sup>-1</sup> of active material.

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