



Electrode reactions during electrolytic preparation of nickel hydroxide

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ABSTRACT

We investigate the electrode reactions involved in the electrolytic precipitation of nickel hydroxide from nickel nitrate through quantitative assessment of the reaction products using stainless steel cathode with Ti and Ni anodes. The nitrate ion is reduced at the cathode to form nitrite and ammonium ion, the later being the major product. The production of ammonium ion followed either directly via reduction of nitrate to ammonium ion or in steps via nitrate reduction to nitrite which further reduced to ammonium ion. Finally, we report XRD measurements, tap density, and the discharge capacity performed on the electrolytically precipitated Ni(OH)₂.

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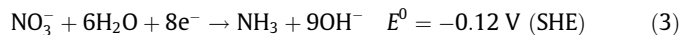
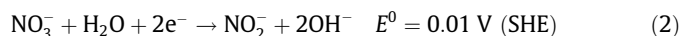
1. Introduction

Nickel hydroxide has been gaining importance because of its use as positive electrode in the nickel–metal hydride as well as other alkaline rechargeable batteries [1–3]. It is produced by employing chemical methods, which have been widely investigated and the characteristics of β-Ni(OH)₂ is well-understood [1–4]. On the other hand, electrochemical method of preparation of Ni(OH)₂ has not been investigated so well. Though it has been used to prepare thin films [5,6] and coatings [7,8], very limited work has been reported on bulk electrochemical production of Ni(OH)₂ [9,10]. Therefore, we have undertaken a systematic study to demonstrate electrochemical production of Ni(OH)₂ which will be reported in a series of papers. However, here we restrict the discussion to electrode reactions involved in the process.

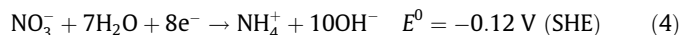
Nickel nitrate has been used as the electrolyte where the nitrate ion is reduced at the cathode to produce hydroxyl ion which raises the pH near the cathode. It makes the solubility product favorable to precipitate Ni(OH)₂:



However, nitrate reduction has not been studied extensively specifically in the context of Ni(OH)₂ preparation. In fact, it is known that this reaction is highly dependant on the cathode material and pH of the bath. Further, there are several references concerning the question of exact nature of the cathodic reaction. While, some researchers postulate nitrate reduction to nitrite [7,11], some others show generation of NH₃ according to the following reactions [8,12].



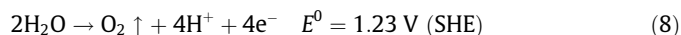
Furthermore, considering NH₃/NH₄⁺ equilibrium, some researchers have also reported following reactions to be dominant [5,6,8].



Lastly, it is also conceivable that nitrite reduction could take place leading to formation of NH₃ or NH₄⁺ according to the following reactions [8,12].



Compounding the issue the formation of N₂ and N₂O has also been reported. The anodic reactions depend on the anode material as shown below for nickel and inert anode



The aim of this paper is to bring clarity on the electrode reactions that take place during electrolytic precipitation of nickel hydroxide. A quantitative assessment of the reaction products in a galvanostatic precipitation study using Ti as well as Ni anodes is made. Stainless steel (SS) has been used as the cathode material and the initial pH was matched to the natural pH of nickel nitrate solution which is around 3. The important process parameters and properties of the product are discussed.

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2. Materials and methods

2.1. Electrolysis set-up

A 250 ml corning beaker with a micro porous polypropylene material fixed as diaphragm was used as the two compartment electrolytic cell. A SS cathode and two types of anode viz., iridium coated titanium (Ti) and nickel (99.9% Ni) were used in the experiments. Nickel nitrate solution in distilled water was used as the electrolyte. The electrolysis was carried out by applying direct current (DC) from a regulated power source. The cell voltage and individual electrode potentials were measured using digital multi-meters. Saturated calomel electrode was used as the reference electrode.

2.2. Assaying

The nickel content of the sample was determined by dissolving 0.5 g of nickel hydroxide sample in a known amount (excess) of hydrochloric acid. The solution was titrated against standard EDTA solution at pH 10 using murexide indicator to determine the nickel content. The hydroxyl ion content of the sample was determined by titrating excess acid in the above solution against a standard sodium hydroxide solution up to pH 7.0. The rest of the sample after deducting the Ni^{++} and OH^- ion contents determined in the above manner was assumed to be H_2O . The nitrite content in the electrolyte was determined by a Varian make UV–visible spectrophotometer which allows measurement of intensity of the color developed by nitrite ion at a wave length of 543 nm. The nitrate content of the nickel hydroxide sample was determined by reducing the nitrate in solution after passing it through a cadmium column; the nitrite content was determined in a similar manner. The ammonium ion content in the electrolyte was determined by Macro-Kjeldahl distillation method.

The precipitated $\text{Ni}(\text{OH})_2$ samples were characterized by a series of tests. First, the particle size was measured by Malvern particle size analyzer. The TG-DTA studies were carried out using a Mettler make thermal analyzer and the X-ray diffraction (XRD) of the powder sample was obtained using a Pan Analytical X-ray diffractometer using a copper target ($\lambda = 1.5404 \text{ \AA}$). Lastly, the discharge capacity was measured by charge–discharge equipment–Bitrode LCN1-25-24 supplied by Bitrode Corporation, Fenton, Missouri, USA.

3. Results and discussion

3.1. Galvanostatic deposition study with Ti anode

The galvanostatic study was conducted in an electrolyte solution containing 100 ml each of 1.02 M nickel nitrate solution as catholyte and anolyte. The initial pH was maintained at 3 and the tests were run for 6 h. The reaction products were evaluated at a cathodic current density of 200 Am^{-2} with SS cathode and Ti anode. The process parameters including the physical and electrochemical properties of $\text{Ni}(\text{OH})_2$ are presented in Table 1. During the experiments, it was observed that the anolyte pH changed from 3 to 0.1 after 6 h and the catholyte pH increased from 3 to 6 in 30 min and reached 6.4 after 6 h. The solubility product of nickel hydroxide is calculated as

$$K_{\text{sp}} = [\text{Ni}^{++}][\text{OH}^-]^2 \quad (9)$$

and the corresponding values at different times are recorded as 0.98×10^{-16} (0.5 h), 3.73×10^{-16} (3 h) and 3.41×10^{-16} (6 h). The K_{sp} of $\text{Ni}(\text{OH})_2$ range between 1.6×10^{-14} and 5.47×10^{-16} [4,5], which are close to those estimated here. However, it may be noted

Table 1

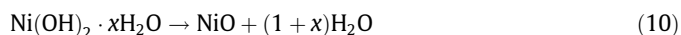
Comparison of process parameters and product properties in electrolytic preparation of nickel hydroxide using Ti and Ni anode. Initial $[\text{Ni}^{++}]$: 1.02 M, initial pH: 3, temperature: 25 °C, cathode current density: 200 A m^{-2} , duration of electrolysis: 6 h.

Sl no.	Parameter/property	Ti anode	Ni anode
1	Final pH	6.4	6.8
2	Final $[\text{Ni}^{++}]$ (M)	0.54	0.25
3	Final K_{sp}	3.41×10^{-16}	9.95×10^{-16}
4	Precipitate (g)	5.77	9.01
5	Ni content (%)	53.5	55.3
6	OH content (%)	31.2	32.3
7	H_2O content (%)	15.3	12.4
8	Approximate formula	$\text{Ni}(\text{OH})_2 \cdot 0.93\text{H}_2\text{O}$	$\text{Ni}(\text{OH})_2 \cdot 0.73\text{H}_2\text{O}$
9	Weight loss (%)	33.0 (31.9) ^a	31.8 (29.6) ^a
10	Average cell voltage (V)	3.41	1.80
11	Cathode current efficiency (%)	57.87	93.30
12	Anode current efficiency (%)	54.48	70.49
13	Energy consumption (kWh/kg)	2.30	0.78
14	Tap density (g/cc)	1.31	1.29
15	Particle size, (d_{50}) (μm)	21.56	5.99
16	Discharge capacity (mAh/g)	145	180

^a Values in the parenthesis are calculated on the basis of the approximate formula.

that even though the pH took sometime to reach 6, precipitation occurred immediately. This might have been due to a local increase in pH, and hence a higher K_{sp} , near the cathode surface where OH^- ion is generated. Also, it should be mentioned that the pH and K_{sp} values during six hours of electrolysis indicate a steady state situation for $\text{Ni}(\text{OH})_2$ precipitation.

An amount of 5.77 g of precipitate was produced in a typical electrolysis test in 6 h. Its nickel and hydroxyl ion contents were 53.5% and 31.16%, respectively. The molar ratio of $[\text{OH}^-]$ to $[\text{Ni}^{++}]$ is close to 2. The nitrate content was 0.04% which is quite low and may be neglected. The rest may be water and thus, the approximate formula of the product is $[\text{Ni}(\text{OH})_2 \cdot 0.93 \text{H}_2\text{O}]$. With this composition the total loss according to reaction (10) should be 31.90%.



The total weight loss observed from the thermo-gravimetric study is 33%. This value is in reasonable agreement with the chemical analysis.

During the entire period of electrolysis, no trace of NH_3 or other gases of nitrogen were observed to escape. Analysis revealed 0.007 g of nitrite (NO_2^-) and 0.180 g of NH_4^+ ions in the final catholyte. These values account for 0.21% and 54.98% current efficiencies (CE) for (NO_2^-) and (NH_4^+) formations, respectively. It implies that two schemes i.e., reaction (2) + (6) or, reactions (4) might be taking place. In either scheme or in combination, the stoichiometry corresponds to reaction (4). It is difficult to estimate the exact contribution of each scheme to the overall reaction. However, the CE with respect to NH_4^+ formation which is equivalent to 10 OH^- formation as in Eq. (4) remains close to the CE of $\text{Ni}(\text{OH})_2$ formation. This indicates that most of the OH^- formed ends up in precipitated $\text{Ni}(\text{OH})_2$. The rest of the current might have been consumed to produce H_2 at the cathode according to reaction (11).



Table 2 presents a mass balance based on CE. It is observed that 1.025 g (42.13% CE) of OH^- is unaccounted in the catholyte after $\text{Ni}(\text{OH})_2$ was precipitated. It is also observed that the terminal pH in the anode chamber corresponds only to 54.48% of CE for the oxygen evolution according to reaction (8), leaving behind 0.066 g of H^+ (equivalent to 1.22 g of OH^-) unaccounted in the anode chamber. The unaccounted amounts – H^+ and OH^- formed in respective

Table 2
Mass balance in the cathode and anode chamber with respect to coulombs passed. Cathode current density = 200 A m⁻², initial [Ni²⁺] = 1.02 M, initial pH 3, temperature = 25 °C.

Cathode chamber			Anode chamber		
	OH ⁻ (g)	CE ^a (%)		H ⁺ (g)	CE ^a (%)
1. Reaction 2 NO ₂ ⁻ : 0.007 g ≡	0.005	00.21	1. Reaction 8 (assumed)	0.145	100
2. Reaction 4 NH ₄ ⁺ : 0.180 g ≡	1.700	54.98			
3. Reaction 11 (assumed) ≡	1.108	44.81			
Total	2.813	100.00	Total	0.145	100
4. Ni(OH) ₂ Precipitate: 5.77 g ≡	1.778	57.87	2. End pH 0.1 H ⁺ used	0.079	54.48
OH ⁻ unaccounted	1.025	42.13	H ⁺ unaccounted Equivalent to OH ⁻ : 1.122 g	0.066	45.52

^a CE, current efficiency.

chambers – might have been neutralized. The diffusivities of H⁺ and OH⁻ are 9.2×10^{-5} and 5.6×10^{-5} cm²/s, respectively [12], that are much higher than that for Ni²⁺ (0.69×10^{-5} cm²/s) and NO₃⁻ (1.84×10^{-5} cm²/s). Thus either or both of these species (H⁺ and OH⁻) might have diffused through the diaphragm and balanced each other. This explains the limitation on CE on account of Ni(OH)₂ precipitation at 57.87%.

In the overall process, the average cell voltage was 3.41 V and the energy consumption for production of nickel hydroxide was 2.30 kWh/kg.

3.2. Galvanostatic deposition study with Ni anode

Further galvanostatic study was conducted by replacing Ti anode with Ni and all other parameters remained same as described in Section 3.1. The objective is to see the effect of reaction (7) over (8) at the anode, which is expected to bring down the cell voltage as well as the H⁺ in anode chamber. The results are also presented in Table 1. Precipitation of Ni(OH)₂ occurred in a similar way as discussed in Section 3.1. The terminal pH and K_{sp} reached 6.8 and 9.95×10^{-16} respectively after 6 h of electrolysis. The striking point is the production of 9.01 g of Ni(OH)₂ with a CE of 93.30% for OH⁻ utilization which is much higher in comparison to 57.87% as in case of Ti anode. This supports the idea that H⁺ generation in anode chamber was the reason for low utilization of OH⁻ in the cathode chamber. In addition, there was remarkable decrease in cell voltage and power consumption inasmuch as the later coming

down to 0.78 kWh/kg in case of Ni anode from 2.30 kWh/kg with Ti anode.

3.3. Physical and electrochemical properties of the Ni(OH)₂ produced

A series of optimization and characterization tests have been carried out encompassing all aspects of electrochemical production of Ni(OH)₂ as a battery grade material. However, for the sake of brevity, here we report properties of Ni(OH)₂ obtained in this study (Table 1). The Ni(OH)₂ precipitated using Ni anode is finer in size with higher discharge capacity (180 mAh/g) compared to Ni(OH)₂ precipitated with Ti anode (145 mAh/g). The respective tap densities – 1.29 and 1.31 g/cc, make the charge density 232 and 190 mAh/cc, respectively. These values may appear much lower than the presently achievable charge density of 400–450 mAh/cc. However, optimization of parameters is expected to produce the desired results. Fig. 1 shows the XRD pattern of the two samples. Both the samples contain α- and β-Ni(OH)₂ though the crystallinity of the sample particularly with respect to β-Ni(OH)₂ collected with Ni anode is relatively better.

4. Conclusions

The following conclusions may be drawn from this investigation.

1. Ammonium and nitrite ions formed with 54.98 and 0.21% current efficiency (CE), respectively, during electrolytic preparation of Ni(OH)₂ from nitrate bath using Ti anode. It formed in three plausible routes: (a) by reaction (4), (b) by reaction (2) + (6), or (c) by a mixed route which is a combination of (a) and (b). In either case the ultimate stoichiometry follows reaction (4). Ni(OH)₂ formation corresponds to 57.87% CE.
2. The CE for OH⁻ utilization never reached 100% in the cathode chamber which was probably due to H⁺ generation in the anode chamber according to reaction (8). Replacement of Ti anode with Ni replaced reaction (8) with (7) which reduced H⁺ generation in the anode chamber. This improved the CE for OH⁻ utilization in the cathode chamber to a level of 93.30%.
3. Electrolysis with Ni anode produced Ni(OH)₂ of finer size and higher discharge capacity in comparison to Ni(OH)₂ produced with Ti anode.
4. The product is a mixture of α- and β-Ni(OH)₂.

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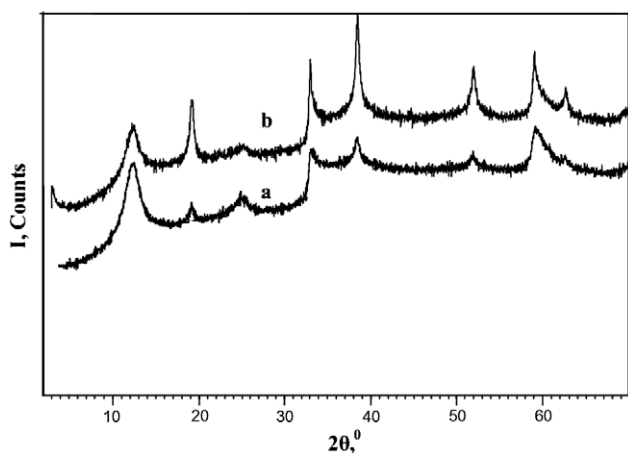


Fig. 1. XRD patterns of nickel hydroxide samples prepared using (a) Ti (b) Ni anodes. Cathode current density: 200 A m⁻², initial [Ni²⁺]: 1.02 M, initial pH: 3, temperature: 25 °C.

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