Journal of Power Sources 275 (2015) 55–63

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Electrochemical studies on electrolytic preparation of battery grade nickel hydroxide – Effect of $(OH)^-$ to Ni^{2+} ratio

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HIGHLIGHTS

- Cathodic reactions supported by values of open-circuit potential.
- Catholyte pH and solubility product play important role.
- Ratio of $(OH)^-/Ni^{++}$ decides specific phase which is regulated by $(OH)^-$ supply through current density.
- $(OH)^-/Ni^{++}$ ratio also has direct relationship with adsorbed/intercalated water content and surface area.

ARTICLE INFO

Article history:
Received 25 July 2014
Received in revised form
22 October 2014
Accepted 26 October 2014
Available online 28 October 2014

Keywords:
Polarization
Nickel hydroxide
Phase control
Battery grade

ABSTRACT

Polarization studies have indicated occurrence of three reactions on the cathode surface during precipitation of nickel hydroxide. Out of the three reactions, the nitrite forming reaction followed by conversion to ammonium ion might be the reaction path. The reaction scheme is well supported by the trends in variations in open-circuit potential. Detail prolonged galvanostatic precipitation studies have shown that $(OH)^-/Ni^{2+}$ ratio plays an important role in determining the phase of the nickel hydroxide. A ratio of $(OH)^-/Ni^{2+}$ higher than 6 with sufficient nickel ion in bath ensures β-nickel hydroxide with bigger particles and lesser H_2O molecules within. Maintaining these ratios at lesser levels forms α-nickel hydroxide with finer size and more H_2O molecules within. The mechanism of these products formations has been explained in this paper. It is also observed that finer size with higher surface area and higher H_2O molecules in crystal structure results in higher discharge capacity.

1. Introduction

The impetus on study of precipitation of nickel hydroxide is mainly due to its use as positive electrode of alkaline rechargeable batteries [1–3]. At present the entire demand of nickel hydroxide is met through chemical precipitation technique. Therefore, this method of preparation has been widely investigated and there are also several studies on the characteristics of nickel hydroxide [1–8]. The electrochemical method of preparation of nickel hydroxide provides comparatively better advantages such as high power density, high energy, low cost, high volumetric energy density, well-defined electrochemical redox activity, low toxicity, and environment friendliness [9–15]. Not much work on electrochemical preparation has been reported so far and for this reason, a systematic study has been undertaken to demonstrate electrochemical preparation of nickel hydroxide.

In the electrochemical method, reaction (1) is allowed to take place chemically, whereas, the reactant OH^- is generated electrochemically at the cathode.

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2\downarrow \quad (1)$$

Even, the other reactant, Ni^{2+}, can also be generated simultaneously at the anode. The anodic reactions on different electrode surfaces are as follows:

Consumable nickel sheet anode:

$$Ni \rightarrow Ni^{2+} + 2e^- \; E^0 = 0.257\ (SHE) \quad (2)$$

inert anode:

$$2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^- E^0 = 1.23\ V\ (SHE) \quad (3)$$

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http://dx.doi.org/10.1016/j.jpowsour.2014.10.141
0378-7753/© 2014 Published by Elsevier B.V.

Usually nickel nitrate is used as the electrolyte and the nitrate ion is reduced at the cathode to produce hydroxyl ions which raise the pH near the cathode to make the solubility product favorable to precipitate nickel hydroxide as per reaction (1). Though there are various reports on the possible reaction schemes on the cathode [16–21], recent reports [22] and [23], as part of the series of earlier studies from this laboratory have established that the cathodic reaction may be one of the three plausible routes: (a) reaction (4), (b) combination of reactions (5) and (6), or (c) a mixed route which is a combination of (a) and (b). In any case, the ultimate stoichiometry follows reaction (4).

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10OH^- \quad E^0 = -0.12V\,(SHE) \tag{4}$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad E^0 = 0.01V\,(SHE) \tag{5}$$

$$NO_2^- + 6H_2O + 6e^- \rightarrow NH_4^+ + 8OH^- \quad E^0 = -0.165V\,(SHE) \tag{6}$$

It was apparent from the Tafel plot that there are two discontinuities in the cathodic part which corresponds to reactions (5), (4) and (6), respectively [23]. Further, it has also been established that besides the nitrate reduction, hydrogen reaction occurs. The replacement of Ti-anode by consumable Ni-anode decrease occurrence of hydrogen generation, increases nitrate reduction, and hence improves the (OH^-) utilization. The current efficiency and energy consumption for electrolytic precipitation of $Ni(OH)_2$ also improved considerably [22].

It has been suggested that $[OH^-]/[Ni^{2+}]$ ratio plays an important role in formation of specific phase (α- or β-) in the product [4,23–26]. It is pertinent to compare the properties of α- and β-nickel hydroxide with respect to their use in rechargeable nickel batteries. Table 1 presents some of the physical, chemical and crystallographic properties of α- or β-nickel hydroxide. At present, chemically produced β-nickel hydroxide attains a tap density of 2.1–2.2 g cm^{-3}, which results in a volume energy capacity of 620–640 mA h cm^{-3}. It would be interesting from practical standpoint if formation of specific phases can be regulated through parametric control.

The aim of this paper is to explore in further detail how current density regulates the $[OH^-]/[Ni^{2+}]$ ratio which in turn influences the formation of specific phase of the nickel hydroxide product. Polarization measurements as well as prolonged galvanostatic electrolysis, at varying initial Ni^{2+} and $(OH)^-$ ions concentration in the bath and current density, were employed in this study. Furthermore, a detailed analysis of galvanostatic precipitation studies have been carried out to determine the threshold level of $[OH^-]/[Ni^{2+}]$ for the exact phase formation of the nickel hydroxide.

Table 1
Comparison of physical, crystallographic and chemical properties of typical alpha and beta nickel hydroxide [27].

Parameter	β-nickel hydroxide	α-nickel hydroxide
Theoretical bulk density, g cm^{-3}	3.97	2.82
On charging converted to	β-NiOOH	γ-NiOOH
Theoretical capacity, mA h g^{-1}	289	482
Hydration	Not hydrated	Hydrated (0.5–0.7H_2O)
Crystal structure	Hexagonal	Hexagonal
	Brucite C-6 type structure	Turbostratic structure
a_0, Å	3.070–3.119	5.42
c_0, Å	4.610–4.686	7.60–8.51

2. Experiment

2.1. Electrolysis set-up

The experimental set up used here is similar to that used in the previous studies where potentiostatic polarization measurements were carried out using Princeton Applied Research Potentiostat/Galvanostat Model 273A [22] and [23]. Both cathodic and anodic polarization curves were drawn, taking cathode or anode as the working electrode. A 250 ml Corning™ beaker with a micro porous polypropylene material fixed as diaphragm makes it a two compartment electrolytic cell. Here the anode material is iridium coated titanium (Ti) and the cathode material is stainless steel (SS). Nickel nitrate solution (Fisher scientific India Pvt. Ltd.) in distilled water is used as the electrolyte. A DC current supply to the cell via a regulated power source supplied by APLAB India Pvt. Ltd. sets the electrolytic process. The cell voltage and individual electrode potentials are measured using digital multi-meters and saturated calomel electrode (SCE) as reference electrode. During the experiment, it was observed that the rest potentials of the cathode and anode take finite time before stabilizing. Approximately, it takes 15 min for the rest potential to stabilize. All the measured data reported here are the average values of three observations. The observed scatter in the values of the rest potentials was probably due to lack of reproducibility in preparing the electrode surface and solution in each measurement.

2.2. Determination of nickel and hydroxyl ion content in the sample

The nickel content of the sample as well as the electrolyte was determined by wet chemical method. A known amount of the nickel hydroxide sample (0.5 g) was dissolved in a known amount (excess) of hydrochloric acid. This solution was titrated against standard EDTA solution at pH 10, using murexide indicator to determine nickel content. The hydroxyl ion content of the sample was determined by titrating the excess acid in the solution against a standard sodium hydroxide solution up to pH 7.0. The rest of the sample after deducting the Ni^{2+} and OH^- ion contents as determined above was assumed to be H_2O.

2.3. Analysis of nickel hydroxide sample

The physical and electrochemical properties of the nickel hydroxide sample were determined. TG-DTA studies were carried out by using a thermal analyzer provided by M/s Mettler Toledo, Model No. TGA/SDTA851. The particle size of the nickel hydroxide sample was measured by Malvern Particle Size Analyser (Mastersizer Hydro *2000MU*). The X-ray diffractograms (XRD) of the nickel hydroxide samples were taken using an X-ray diffractometer of Pan Alytical make (PW 1830). The diffracted X-ray intensities were recorded as a function of 2θ by using a Ni filtered copper target [Cu Kα radiation with $\lambda = 1.5404$ Å]. The discharge capacity of the nickel hydroxide was measured by a charge–discharge equipment “Bitrode LCN1-25-24” supplied by BITRODE Corporation Fenton Missouri, USA. Nickel hydroxide pellet of 2.5 cm diameter (surface area 4.91 cm^2) were prepared by compacting a mixture of nickel hydroxide (2 g), graphite powder (1 g) and 3 drops of 5% PVA (polyvinyl alcohol) binder, at a pressure of 13–14 tons cm^{-2} for 2 min inside a stainless steel mesh. Before compacting, the mixture of nickel hydroxide with graphite powder and PVA was manually ground in a mortar and pastel to mix thoroughly. The pellets were made by keeping all the material inside a suitable die and by