



# Influence of TiO<sub>2</sub> on the electrochemical performance of pasted type $\beta$ -nickel hydroxide electrode in alkaline electrolyte

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## ABSTRACT

Nickel hydroxide was used as the positive electrode material in rechargeable alkaline batteries, which plays a significant role in the field of electric energy storage devices.  $\beta$ -nickel hydroxide ( $\beta$ -Ni(OH)<sub>2</sub>) was prepared from nickel sulphate solution using potassium hydroxide as a precipitating agent. Pure  $\beta$ -phase of nickel hydroxide was confirmed from XRD and FT-IR studies. The effects of TiO<sub>2</sub> additive on the  $\beta$ -Ni(OH)<sub>2</sub> electrode performance are examined. The structure and property of the TiO<sub>2</sub> added  $\beta$ -Ni(OH)<sub>2</sub> were characterized by XRD, TG-DTA and SEM analysis. A pasted-type electrode is prepared using nickel hydroxide powder as the main active material on a nickel sheet as a current collector. Cyclic voltammetry and electrochemical impedance spectroscopy studies were performed to evaluate the electrochemical performance of the  $\beta$ -Ni(OH)<sub>2</sub> and TiO<sub>2</sub> added  $\beta$ -Ni(OH)<sub>2</sub> electrodes in 6 M KOH electrolyte. Anodic ( $E_{pa}$ ) and cathodic ( $E_{pc}$ ) peak potentials are found to decrease after the addition of TiO<sub>2</sub> into  $\beta$ -Ni(OH)<sub>2</sub> electrode material. Further, addition of TiO<sub>2</sub> is found to enhance the reversibility of the electrode reaction and also increase the separation of the oxidation current peak of the active material from the oxygen evolution current. Compared with pure  $\beta$ -Ni(OH)<sub>2</sub> electrode, TiO<sub>2</sub> added  $\beta$ -Ni(OH)<sub>2</sub> electrode is found to exhibit higher proton diffusion coefficient ( $D$ ) and lower charge transfer resistance. These findings suggest that the TiO<sub>2</sub> added  $\beta$ -Ni(OH)<sub>2</sub> electrode possess improved electrochemical properties and thus can be recognized as a promising candidate for the battery electrode applications.

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## 1. Introduction

Increasing energy demand and the limited availability of fossil fuels have stimulated the research on the development of clean and renewable energy sources. In the recent decades, much interest has focused on the development of new electrode materials for advanced energy conversion and storage devices [1–5]. Among them, Nickel/Metal hydride (Ni/MH) batteries are considered to be one of the most promising candidates due to their better combination of the output power, capacity, reliability, life and cost [6,7]. Nickel hydroxide is extensively used as the positive electrode material in rechargeable nickel-based batteries, which plays a substantial role in the field of electric energy storage devices. The storage and release of electrical energy depend mainly on how fast the electrons and ions move through the electrodes. In such conditions, the high proton diffusion coefficients and high electric conductivity of the active material are the crucial factors for improvement of the reliability and high rate

discharge properties of the batteries. Many studies have been made on different compositions of nickel hydroxide to achieve optimum performance [8–11].

The nickel hydroxide (Ni(OH)<sub>2</sub>) is found to occur in two polymorphic forms, namely  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub>, which are converted into  $\gamma$ -NiOOH and  $\beta$ -NiOOH, respectively during charging [12–14]. The  $\beta$ -phase exhibits superior stability compared to the  $\alpha$ -Ni(OH)<sub>2</sub>. Many studies have revealed that incorporation of compounds containing transition metal atom into the nickel electrode is an effective approach to improve active material utilization and cycle life [15–19]. Moreover, adding metallic compounds into the nickel electrode are reported to have beneficial effects such as inhibiting the swelling of the nickel electrode during charging and thus prolong the cycle-life of rechargeable batteries [20–22].

In the recent years, many attempts have been made to improve the performance of the nickel hydroxide active material, among which the most commonly used approach is to add different metallic oxides and hydroxides directly into the electrodes [16,22,23]. One of the functions of the additive metal oxides is to aid in the electron and proton conduction. In particular, TiO<sub>2</sub>, as one of the most promising materials, has attracted much attention because of its superior

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characteristics [24,25]. It has been extensively reported that  $\text{TiO}_2$  is a promising candidate due to its multiple advantages of high abundance, low cost, structural stability, and excellent safety during cycling [26]. Photochemical and photoelectrochemical behavior of a  $\text{TiO}_2/\text{Ni}(\text{OH})_2$  electrode has been investigated [27]. Nickel oxide-embedded titania nanotube array electrodes, nickel oxide-titania nanocomposites and mesoporous Ni-Co oxides nanowire arrays on ordered  $\text{TiO}_2$  nanotubes with different morphologies and their capacitive properties have been studied [28–31]. Aqueous  $\text{TiO}_2/\text{Ni}(\text{OH})_2$  rechargeable battery with a high voltage based on proton and lithium insertion/extraction reaction was investigated [32].

Although structural and electrochemical performance of  $\beta$ - $\text{Ni}(\text{OH})_2$  with different additives have been studied, the effects of  $\text{TiO}_2$  on the electrochemical behavior of pasted type  $\beta$ - $\text{Ni}(\text{OH})_2$  electrode have not been studied in detail. In the present work,  $\beta$ - $\text{Ni}(\text{OH})_2$  was synthesized using precipitation method. Structural, thermal and electrochemical properties of pasted type  $\text{TiO}_2$  substituted  $\beta$ -nickel hydroxide electrode are investigated and the results are reported.

## 2. Experimental

### 2.1. Synthesis of $\beta$ -nickel hydroxide

The chemical synthesis of nickel hydroxide in the present studies was achieved in three steps viz. (i) addition of the reagents, (ii) digestion of the precipitate and (iii) drying and grinding of the precipitate. AR grade potassium hydroxide (KOH) and nickel sulphate ( $\text{NiSO}_4$ ) were used as reagents. A solution of 1 M KOH was added to 1 M  $\text{NiSO}_4$  solution by dripping at a flow rate of 10 mL/min with continuous stirring. The addition of the reagent was terminated when the pH of the suspension reaches around 13. Then the mixture was permitted to stand for 24 h for digestion of the precipitate. The separation of the precipitate from the excess reagent was done by centrifugation at 1500 rpm for 1 h. The precipitate was washed thoroughly with distilled water. Barium chloride ( $\text{BaCl}_2$ , 1 M) in excess was added to wash water, causing precipitation of barium sulphate ( $\text{BaSO}_4$ ). The washing of the precipitate was concluded when the white precipitate of  $\text{BaSO}_4$  was no more found in the wash water. This nickel hydroxide precipitate was dried at 60 °C for 48 h. Finally, the precipitate was pulverized.

### 2.2. Preparation of electrode and electrochemical testing

Following two compositions of the electrode materials were achieved viz. (i) pure  $\beta$ - $\text{Ni}(\text{OH})_2$  electrode with no additives having the composition: 85%  $\beta$ - $\text{Ni}(\text{OH})_2$  powder + 10% graphite powder + 5% PTFE as binder and (ii)  $\text{TiO}_2$  added  $\beta$ - $\text{Ni}(\text{OH})_2$  electrode having the composition: 80%  $\beta$ - $\text{Ni}(\text{OH})_2$  powder + 5%  $\text{TiO}_2$  powder + 10% graphite powder + 5% PTFE as binder [33].  $\text{TiO}_2$  powder was obtained from Sigma-Aldrich. The test electrode was made by first mixing the prepared sample  $\beta$ -nickel hydroxide powder with graphite powder, additives and PTFE solution in the form of slurry. The resulting slurry was pasted onto a nickel sheet. After being coated with the paste, the resulting electrode was dried at 80 °C for 1 h. The backside of the electrode and the wire were insulated with Teflon tape. The electrodes have the following dimensions: 1 cm × 1 cm area.

Structure of the electrode material was determined using X-ray diffraction analysis using Bruker AXS D8 Advance diffractometer. The FT-IR (Infra-red) spectrum (400–4000  $\text{cm}^{-1}$ ) of the nickel hydroxide was recorded on a Bruker Alpha spectrophotometer in KBr pellets. Thermal gravimetric-differential thermal analysis (TG-DTA) of  $\text{TiO}_2$  added  $\beta$ - $\text{Ni}(\text{OH})_2$  electrode was carried out by Perkin Elmer STA 6000 thermal analyzer. Morphological studies were carried out on the pure  $\beta$ - $\text{Ni}(\text{OH})_2$  and  $\text{TiO}_2$  added  $\beta$ - $\text{Ni}(\text{OH})_2$  electrodes using Scanning Electron Microscope (SEM) (Model: Leica S440i INCA X-sight).

Cyclic voltammetry (CV) measurements were carried out using CHI604D electrochemical workstation. For cyclic voltammetric studies, the test electrode prepared as described above was used as a working electrode. The platinum foil was used as a counter electrode; Hg/HgO electrode was used as a reference electrode and 6 M KOH solution was used as an electrolyte. Prior to CV studies the electrodes were activated in 6 M KOH solution. After resting for 30 min, the cyclic voltammograms were obtained. All measurements were carried out at  $298 \pm 2$  K.

Electrochemical impedance spectroscopy (EIS) measurements were performed using a CHI604D electrochemical workstation. The test electrode prepared as described above was used as a working electrode. The platinum foil was used as a counter electrode; Hg/HgO electrode was used as a reference electrode and 6 M KOH solution was used as an electrolyte. The impedance spectra were recorded at 0.025V amplitude in a frequency range from 30 kHz to 1 Hz.

## 3. Results and discussion

Fig. 1 represents the XRD pattern of the synthesized nickel hydroxide. The characteristic diffraction peaks at (001), (100), (101), (102), (110) and (111) show that the sample has a crystal phase of  $\beta$ - $\text{Ni}(\text{OH})_2$ . No other peaks for the impurities such as  $\alpha$ - $\text{Ni}(\text{OH})_2$  or other phases are noticed in the pattern. This shows that pure  $\beta$ - $\text{Ni}(\text{OH})_2$  was attained under the present synthetic conditions [34,35]. Some disorders in the crystal lattice, which are characterized by the full-width at half maximum (FWHM) intensity of the (001), (101) and (102) reflection lines can also be found. This indicates that the as-prepared sample is poorly crystallized. A larger degree of broadening (FWHM) of the peaks corresponding to the (001), (101) and (102) reflections is obtained, while the broadening for the peaks corresponding to the (100) and (110) is smaller. The considerable broadening of the (001), (101) and (102) reflection lines in the XRD patterns of nickel hydroxide materials may be ascribed to: (i) crystallite size effects; (ii) increased degree of disorder due to the existence of crystalline defects and structural micro distortions such as stacking faults/growth faults and proton vacancies, or the adsorption of the inorganic species such as water and anions; and (iii) presence of other polymorphic alterations as interstratified phases [36–41].

To further support the XRD study, Fig. 2 provides the infrared spectrum of the as-prepared nickel hydroxide. The FT-IR spectrum

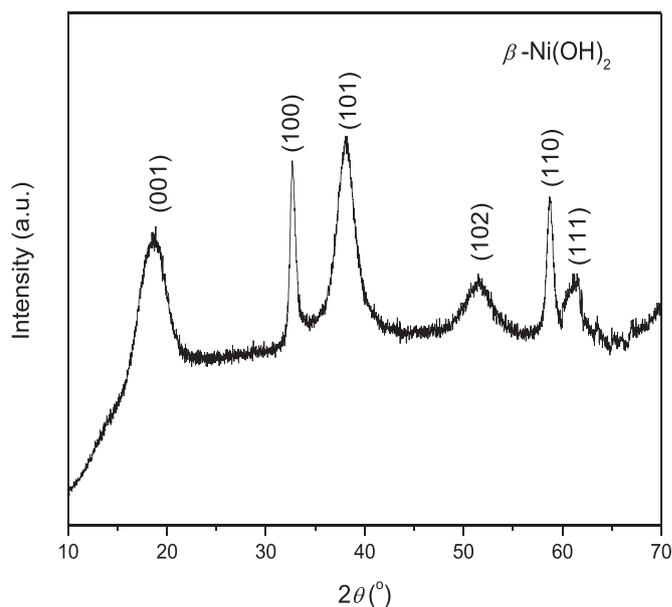


Fig. 1. XRD pattern of  $\beta$ -nickel hydroxide.

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