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Synthesis, spectroscopic and electrochemical performance of pasted β-nickel hydroxide electrode in alkaline electrolyte

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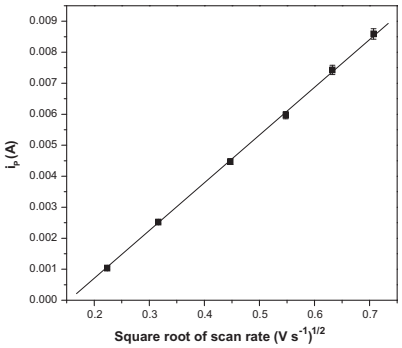
HIGHLIGHTS

- β-Nickel hydroxide (β-Ni(OH)$_2$) was synthesized using precipitation method.
- FT-IR and TG–DTA studies show that the β-Ni(OH)$_2$ contains water molecules and anions.
- Electrochemical performance of β-Ni(OH)$_2$ was investigated using CV and EIS.
- The proton diffusion coefficient (D) for β-Ni(OH)$_2$ is found to be 1.44×10^{-12} cm^2 s^{-1}.
- EIS studies confirmed that the electrode reaction processes are diffusion controlled.

GRAPHICAL ABSTRACT

Relationship between the anodic peak current (i_p) and the square root of the scan rate (υ½).



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ABSTRACT

β-Nickel hydroxide (β-Ni(OH)$_2$) was successfully synthesized using precipitation method. The structure and property of the β-Ni(OH)$_2$ were characterized by X-ray diffraction (XRD), Fourier Transform infra-red (FT-IR), Raman spectra and thermal gravimetric–differential thermal analysis (TG–DTA). The results of the FTIR spectroscopy and TG–DTA studies indicate that the β-Ni(OH)$_2$ contains water molecules and anions. The microstructural and composition studies have been performed using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis. A pasted-type electrode is prepared using β-Ni(OH)$_2$ powder as the active material on a nickel sheet as a current collector. Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS) studies were performed to evaluate the electrochemical performance of the β-Ni(OH)$_2$ electrode in 6 M KOH electrolyte. CV curves showed a pair of strong redox peaks as a result of the Faradaic redox reactions of β-Ni(OH)$_2$. The proton diffusion coefficient (D) for the present β-Ni(OH)$_2$ electrode material is found to be 1.44×10^{-12} cm^2 s^{-1}. Further, electrochemical impedance studies confirmed that the β-Ni(OH)$_2$ electrode reaction processes are diffusion controlled.

Introduction

With the increasing demand for portable electronic devices and electric vehicle applications, significant attention is focused on the development of alkaline batteries with higher specific energies in which battery chemistry plays a vital role [1–5]. In particular, the development and commercialization of nickel/metal hydride (Ni-MH) technology afford the possibility of producing secondary batteries with high specific energy. The positive nickel electrode strongly influences the performance of the alkaline batteries [6–8]. Nickel hydroxide is extensively used in rechargeable

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nickel-based batteries as a positive electrode material [9,10]. Normally, it exists in two polymorphic forms, namely α-$Ni(OH)_2$ and β-$Ni(OH)_2$, which are transformed into γ-NiOOH and β-NiOOH, respectively, during charging [11–13]. Owing to the instability of α-$Ni(OH)_2$ in alkaline media, β-$Ni(OH)_2$ is usually used as a precursor material in alkaline batteries.

Synthesis of nickel hydroxide has been extensively investigated due to the prominence of nickel hydroxide to the battery industry. Several authors [14–25] have carried out extensive research on the preparation and physicochemical properties of nickel hydroxide. Cheng Shao-an et al. [14] studied the electrochemical properties of the surface modified $Ni(OH)_2$ powder. Microstructural control of the nickel hydroxide is being researched to obtain optimum performance of the NiOOH/$Ni(OH)_2$ electrode [15–19]. Luo et al. [20] synthesized flower-like β-$Ni(OH)_2$ nanoarchitectures through a one-step mild hydrothermal reaction with the aid of ethylenediamine in $NiCl_2$ aqueous solution. Bernard et al. [21] investigated the relationship between structural defects and electrochemical reactivity of β-$Ni(OH)_2$. Ramesh and Kamath [22] investigated the effect of synthesis temperature on the phase selection among nickel hydroxide and found that low temperature induced the precipitation of α-$Ni(OH)_2$ while at high temperature β-$Ni(OH)_2$ was formed. Enbo Shangguan et al. [23] have synthesized the high density non-spherical $Ni(OH)_2$ cathode material for Ni-MH batteries. Effect of reaction conditions on size and morphology of ultrasonically prepared $Ni(OH)_2$ powders has been studied by Cabanas-Polo et al. [24]. Recently, a detailed account of the synthesis, characterization, and electrochemical properties of ultrafine β-$Ni(OH)_2$ nanoparticles have been studied by Mustafa Aghazadeh et al. [25].

In the present study, β-nickel hydroxide was synthesized using the precipitation method. The structure of the synthesized sample was characterized using XRD, FT-IR, Raman spectra and thermal gravimetric analysis. The microstructural and composition studies have been performed on β-$Ni(OH)_2$ using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis respectively. The electrochemical performance of the synthesized sample was tested by cyclic voltammetry and electrochemical impedance studies.

Experimental

Synthesis of β-nickel hydroxide

Nickel hydroxide was synthesized using precipitation method. Analar grade potassium hydroxide (KOH) and nickel sulphate ($NiSO_4$) were used as reagents. Triple distilled water was used for the solution preparation and washing of the precipitate. A solution of 1 M KOH was added to 1 M $NiSO_4$ solution by dripping at a flow rate of 10 ml min^{-1} with constant stirring. The addition of the reagent was terminated when the pH of the suspension reaches 13. Then the mixture was allowed 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 triple distilled water. Barium chloride ($BaCl_2$ (1 M)) in excess was added to wash water, causing precipitation of barium sulphate ($BaSO_4$). The washing of the precipitate was concluded when the white precipitate of $BaSO_4$ was no more found in the wash water. This nickel hydroxide precipitate was dried at 60 °C for 48 h.

Characterization of β-nickel hydroxide

Crystal structure of the synthesized nickel hydroxide was determined using X-ray diffraction analysis, with a Cu Kα radiation source (λ = 1.4581 Å) using Bruker AXS D8 Advance diffractometer. The FT-IR (Infra-red) spectrum (400–4000 cm^{-1}) of the nickel hydroxide was recorded on a Bruker Alpha spectrophotometer in KBr pellets. Raman spectra were obtained using BRUKER RFS 27 FT-Raman spectrometer. Thermal gravimetric–differential thermal analysis (TG–DTA) was carried out by Perkin Elmer STA 6000 thermal analyzer. The microstructure of the sample was taken by JEOL Model JSM – 6390LV Scanning Electron Microscope (SEM) and composition studies were obtained using JEOL Model JED – 2300 Energy Dispersive X-ray Spectrometer (EDS).

Preparation of nickel electrode and electrochemical testing

In the present studies, following composition of the electrode material was attained viz. β-$Ni(OH)_2$ (85 wt.%) + graphite (10 wt.%) + PTFE (5 wt.%) as binder. The test electrode was made by first mixing the prepared sample nickel hydroxide powder with graphite powder 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.

Cyclic voltammetry (CV) and AC impedance 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; Ag/AgCl 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 room temperature.

Electrochemical impedance spectroscopy (EIS) is an effective technique for analyzing the internal structures and structural change during cycling [26]. An AC impedance study of β-nickel hydroxide electrode was carried out at different applied DC potentials.

Results and discussion

Fig. 1 represents the XRD pattern of the as prepared nickel hydroxide. All of the diffraction peaks can be indexed entirely to a (space group: P3m1) crystal phase of β-$Ni(OH)_2$, with the lattice constants of a = 3.130 Å and c = 4.630 Å, which are well matched with the reported standard values (JCPDS card 74-2075). No other

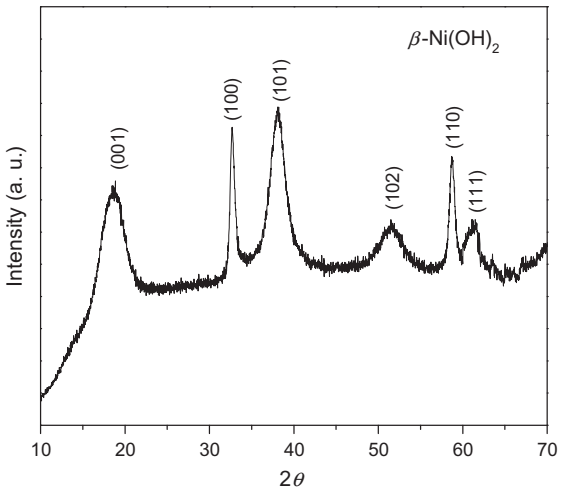

Fig. 1. XRD pattern of as-prepared nickel hydroxide.