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Research Article

ELECTROCHEMICAL SUPERCAPACITOR BEHAVIOR OF β-PHASES OF NICKEL HYDROXIDE AND COBALT HYDROXIDE

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ABSTRACT

Crystalline β-nickel hydroxide was prepared by the addition of nickel nitrate to sodium hydroxide solution followed by ageing in mother liquor, while, β-cobalt hydroxide was procured from commercial source. The electrochemical performances of β-nickel hydroxide and β-cobalt hydroxide was investigated using cyclic voltammetry and charge–discharge studies. A specific capacitance of 150 F g^{-1} was obtained in aqueous KOH in the potential range of 0 to 0.6 V (vs. Hg/HgO) for β-nickel hydroxide. For cobalt hydroxide, the specific capacitance of 550 F g^{-1} in the potential range of -0.6 to 0.45 V (vs. Hg/HgO) was observed. The crystalline phase of β-cobalt hydroxide exhibits better electrochemical supercapacitor compared to β-nickel hydroxide.

Keywords: *Cobalt Hydroxide, Nickel Hydroxide, Supercapacitor, Cyclic Voltammogram*

INTRODUCTION

The active material used in the battery stores the charge during the redox reaction and the phenomena is Faradaic in nature. Most widely used active materials in alkaline and lithium batteries are transition metal oxides and metal hydroxides (where metal = Ni/Co/Mn/Cd/Fe) (Whittingham, 2004; McBreen, 2007). Nickel hydroxide, cobalt hydroxide and manganese hydroxide crystallize in lamellar structure and derivative their structure from brucite mineral i.e., $Mg(OH)_2$. hexagonal close packing of hydroxyl ions with divalent metal ions in their octahedral are observed in the crystal structure of metal hydroxide. This results in the stacking of charge neutral layers with an interlayer distance of 4.6 Å (Oswald and Asper, 1977). Nickel based metal hydroxide electrode reversibly exhibits 1 e^- exchange, while nickel aluminium layered double hydroxide exchanges 1.7 e^- (Kamath *et al.*, 1994; Ramesh *et al.*, 2005). Manganese dioxide reversibly exhibit 0.3 e^- exchange during the oxidation-reduction process (Kordesch and Weissenbacher, 1994). Cobalt hydroxide also crystallizes in the same structure as that of nickel hydroxide (Simon and Gogotsi, 2008). During oxidation of cobalt hydroxide, electrochemically inactive, irreversible and highly insulating phase of CoO_2/CoOOH is formed due to which cobalt hydroxide do not exhibit higher charge storage capacity. In a supercapacitor or an electric double-layer capacitor, the charge storage is achieved by an electrostatic non-Faradaic reaction without any charge transfer across the electrode interface. Also, supercapacitor does not induce any changes in the phase or composition during the charge-discharge, thus providing higher degree of cyclability. Few supercapacitors work on the principle of peudocapacitance, in which Faradic and double layer capacitor properties are combined (Pandolfo and Hollenkamp, 2006). Such a property is desirable for electronic devices and electric vehicles which demand higher power density. Therefore, electrochemical supercapacitors are classified based on the mechanism of energy storage i.e electrochemical double layer capacitors and redox supercapacitors. In redox supercapaciors, the energy is stored due to the separation of electronic and ionic species at the interface between the working electrode and the electrolyte solution. Carbon, metal oxide and polymers are used as electrode materials in electrochemical supercapacitors (Miller *et al.*, 1997; Wu, 2002; Pandolfo and Hollenkamp, 2006). Carbon-based active material exhibit high specific surface and are most widely used as negative electrodes. Activated carbon fabrics and activated carbon powder exhibit theoretical capacitance of 100-300 F g^{-1} and long-term cycling stability in different electrolytes (Niu *et al.*, 1997). Most of the transition metal oxides exhibit multiple oxidation state and are considered as promising electrochemical charge storage materials due to Faradaic reaction (Cottineau *et al.*, 2006). To enhance the energy density of electrochemical capacitors capacitors, metal oxides and metal hydroxides are considered as alternative materials. Ruthenium oxide is most widely used which exhibit specific capacitance 788 F g^{-1} 9 Min *et al.*, 2006). Even though RuO_2 is considered as a good pseudocapacitive electrode material with a high electrochemical stability, commercialization is not feasible due to higher cost (Min *et al.*, 2006). Lin *et al* reported that Co_3O_4 and CoO_x can be used as promising electrode materials for supercapacitor application due to intercalative pseudo-capacitance properties and a maximum capacitance of 291 F g^{-1} is reported (1999). The cobalt oxide electrode has good efficiency better performance and corrosion stability (Liu *et al.*, 1999). Co based xerogel electrode also exhibits capacitor-like behavior. Nanostructured transition metal oxides and hydroxides have been investigated for their application as supercapacitors due to the accessibility of i) large surface-to-volume ratio, ii) active sites and iii) interlayer region. Cobalt hydroxide is attracting increasing attention because of its novel electric and catalytic properties and important technological applications (Hosono *et al.*, 2005; Jeevanan *et al.*, 1999; Chen *et al.*, 2001). The irreversible behavior of cobalt hydroxide indicates i) electric double-layer capacitance and ii) pseudo-capacitance due to redox reaction and interfacial phenomena, promoting us to evaluate the supercapacitor behavior. Sheet-like structure of cobalt hydroxide provides inter-lamellar spacing for the transfer of ions between the active material and the electrolyte with the theoretical specific capacitance of 3460 F g^{-1} (Wang *et al.*, 2008). Cobalt hydroxide crystalllizes in two phases, i.e., α and β-form, both of them have hexagonal structure but differ in their interlamellar spacing. β-cobalt hydroxide comprises of perfectly stacked layers along the *c*-axis with an interlamellar distance of 4.6 Å, while α-cobalt hydroxide possess random orientation of layers due to the presence of intercalated water molecules and anions for charge neutrality with an interlamellar distance of 7.6 Å (Jayashree and Kamath, 1999). Chemical precipitation (Dixit *et al.*, 1996), hydrothermal (Shao *et al.*, 2009), solvothermal (Mehdizadeh *et al.*, 2013), radiation-induced (Kim *et al.*, 2010), ball-milling (Li *et al.*, 2010) and electrochemical methods (Yarger *et al.*, 2007) have been employed for the synthesis of the cobalt hydroxide. Wang and his coworkers reported that cobalt hydroxide exhibits 280 F g^{-1} (Wang *et al.*, 2006), while Zhao et al. has developed a simple N-methylpyrrolidone surfactant assisted electrochemical synthetic route to modify the packing density of the layered cobalt hydroxide (Zhao *et al.*, 2011). The as-prepared β-cobalt hydroxide has a high specific capacitance of 651 F g^{-1}, but after 500 cycles, 76% of initial capacitance is retained. Recently, graphene/cobalt oxide or hydroxide composite has been evaluated for the electrochemical supercapacitor behavior and the data shows that in presence of graphene, the performance is better compared to cobalt oxide/hydroxide without graphene (Wang *et al.*, 2011). Xia et al. prepared graphene sheet/porous NiO hybrid film by combining electrophoretic deposition and chemical-bath deposition methods. The hybrid film exhibits good cycling stability and 94% of initial capacitance is retained even after 2000 cycles, while nickel oxide capacitance retention is 87% only (Xia *et al.*, 2011). α and β-cobalt hydroxide thin films were prepared by potentiostatic cathodic electrodeposition from nitrate bath at 60 and 95°C, respectively (Brownson *et al.*, 2008). However, there are no reports on the comparison of electrochemical supercapacitor behavior of crystalline phases of β-phases of cobalt hydroxide and nickel hydroxide. The electrochemical properties of cobalt hydroxide are related to the structure and crystallinity. Also, very little attention has been paid towards understanding the nature of crystallinity and its relation to electrochemical supercapacitor behavior. In this article we have examined and compared the supercapacitor behavior of β-phases of cobalt hydroxide and nickel hydroxide samples using cyclic voltammetry and charge-discharge studies.

MATERIALS AND METHODS

Crystalline brucite-like β-nickel hydroxide is prepared by the addition of nickel nitrate to 40% sodium hydroxide and the precipitated nickel hydroxide gel was aged for 96 h. The precipitate was filtered, washed free of alkali and dried at 65 °C till constant weight is attained. Cobalt hydroxide was procured from Sigma Aldrich and used as such.

Characterization

Nickel hydroxide and cobalt hydroxide samples were characterized by wet chemical analysis to obtain their approximate formula. The nickel content was estimated by the DMG method and cobalt content was determined by the decomposing cobalt hydroxide to obtain Co_3O_4 (a = 8.08 Å) and the weight changes were noted. The OH^- content was estimated by dissolving a known weight of the sample (nickel hydroxide/cobalt hydroxide) in excess acid and back titrating the excess against a standard NaOH solution using a pH meter.

In case of nickel hydroxide and cobalt hydroxide samples, the $[OH^-]/[Ni^{2+}]$ and $[OH^-]/[Co^{2+}]$ ratio was found to be 2. The unaccounted weight (1-2 wt%) was attributed to water molecules to arrive at an approximate formula. PXRD patterns of nickel hydroxide and cobalt hydroxide samples were obtained using a Bruker D8 Advanced powder X-ray diffractometer (Cu Kα source, $\lambda = 1{\cdot}5418$ Å).

Charge–Discharge Studies

Electrodes were prepared by following the procedure reported in references.[4,10,13] The electrodes were galvanostatically (current, 5·5 mA; 21 h) charged and nickel plates were used as counters, all potentials were measured using Hg/HgO/OH–(6M KOH) reference. The electrodes were discharged at a current of 40 mA to a cut off voltage of -400 V for cobalt hydroxide and 0 V for nickel hydroxide at 28–30°C. Cyclic voltammetric studies were carried out for cobalt and nickel hydroxide electrodes at different scan rates (20, 40 and $60 mVs^{-1}$) in the potential window 0.4 to -0.6V.

RESULTS AND DISCUSSION

Figure 1 shows the PXRD patterns of β-cobalt hydroxide and β-nickel hydroxide respectively. The PXRD patterns display sharp Bragg reflections with d-values of 1.78, 2.38 and 4.6 Å and the diffraction peaks are indexed to β-nickel hydroxide and β-cobalt hydroxide respectively in accordance to JCPDS 14-0117 and ICSD No. 88940. Wet chemical analyses indicate that nickel hydroxide and cobalt hydroxide samples are stoichiometric in nature with the chemical formula to be $Co/Ni(OH)_2$ containing 1–2 weight % moisture. Cyclic voltammetric measurements evaluate the electrochemical properties and quantify the specific capacitance of nickel hydroxide and cobalt hydroxide electrodes. Electrodes used in the supercapacitor and their performances were tested using cyclic voltamogramm (CV) technique. The cyclic voltammograms with different scan rates indicates that the current under the curve increases with increase in the scan rate. Figure 2 (lower trace) shows the cyclic voltammetric curve of cobalt hydroxide electrode at the scan rate 50 mV/s within the potential range of 400 to -400 mV vs Hg/HgO/OH− in 6M KOH electrolyte. Cyclic voltammogram of β-cobalt hydroxide does not show redox peaks but the area of the quasi-reversible peak increases with increase in scan rate. This shows that voltammetric current is directly proportional to the scan rate indicating an ideally capacitance behavior. The shape of the cyclic voltammogram at different scan rates is similar suggesting high efficiency in the capacitive characteristics at the electrode/electrolyte interface. The maximum super capacitance of 462 $F\ g^{-1}$ is obtained during the charge-discharge studies (see Figure 3).

For β-phase of nickel hydroxide, faradaic reactions will proceed according to the reaction

$$Ni(OH)_2 \rightleftharpoons NiOOH + OH^-$$

Figure 2 shows the cyclic voltammetric curves for nickel hydroxide electrodes at different scan rates (20, 40, 60 $mV\ s^{-1}$) scan rate, two redox reaction peaks were observed due to pseudo capacitive capacitance (see upper trace of Figure 2). The anodic peak due to oxidation of $Ni(OH)_2$ to NiOOH and the cathodic peak is reduction of NiOOH to $Ni(OH)_2$. The shape of the cyclic voltammetric curves reveals that the capacitive characteristic is distinctive from that of electric double-layer capacitance in which case it is normally close to an ideal rectangular shape.[23] β-nickel hydroxide electrode exhibited the supercapacitance of 150 $F\ g^{-1}$ (see Figure 3). The peak current densities and peak potential of both peaks in curve 2 is higher than that in curve 1, revealing a higher charge storage capacity for β-nickel hydroxide nickel hydroxide. Cyclic voltammetric curve shows the typical electrochemical behavior of battery with charging in the higher potential region and discharge in a lower potential region, exhibiting redox reversibility for β-nickel hydroxide nickel hydroxide. The specific capacitance increases with increasing the scan rate of cyclic voltammogram. Based on the potential window the electrochemical charge storage capacitance of β-nickel hydroxide is shown to exhibit poor specific capacitance compared to β- cobalt hydroxide.

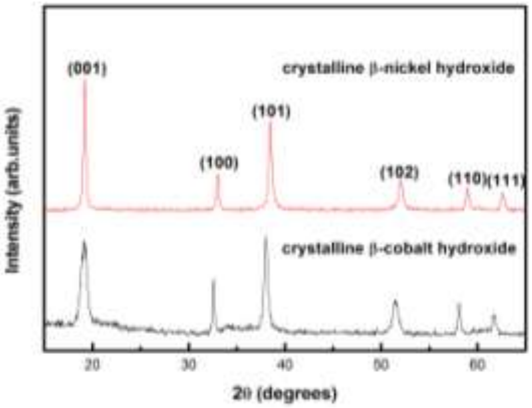

Figure 1: Powder X-ray diffraction patterns of a) cobalt hydroxide and b) nickel hydroxide respectively

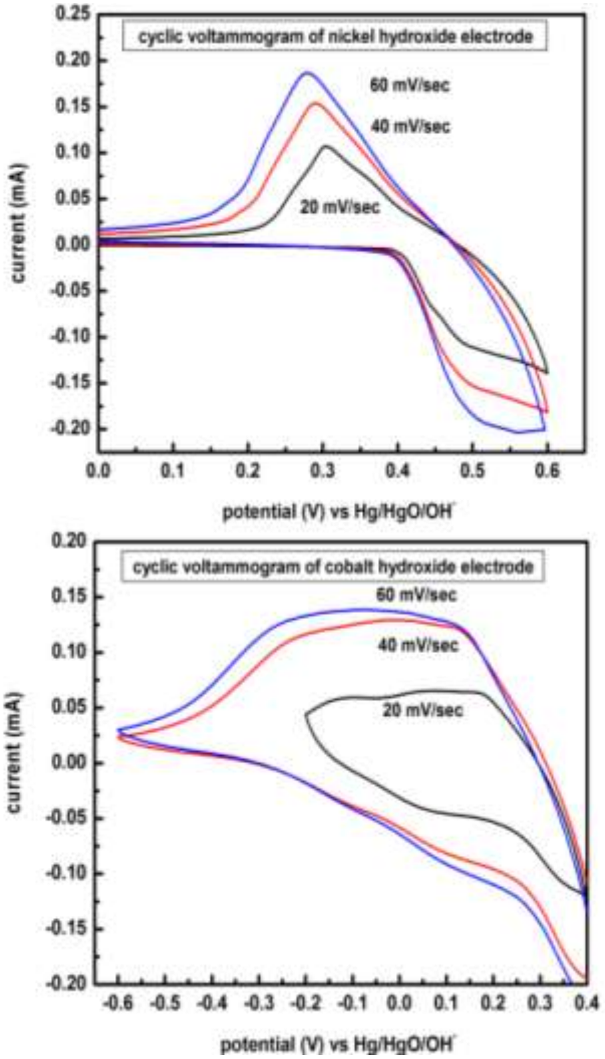

Figure 2: Cyclic voltammograms of a) cobalt hydroxide electrode and b) nickel hydroxide respectively

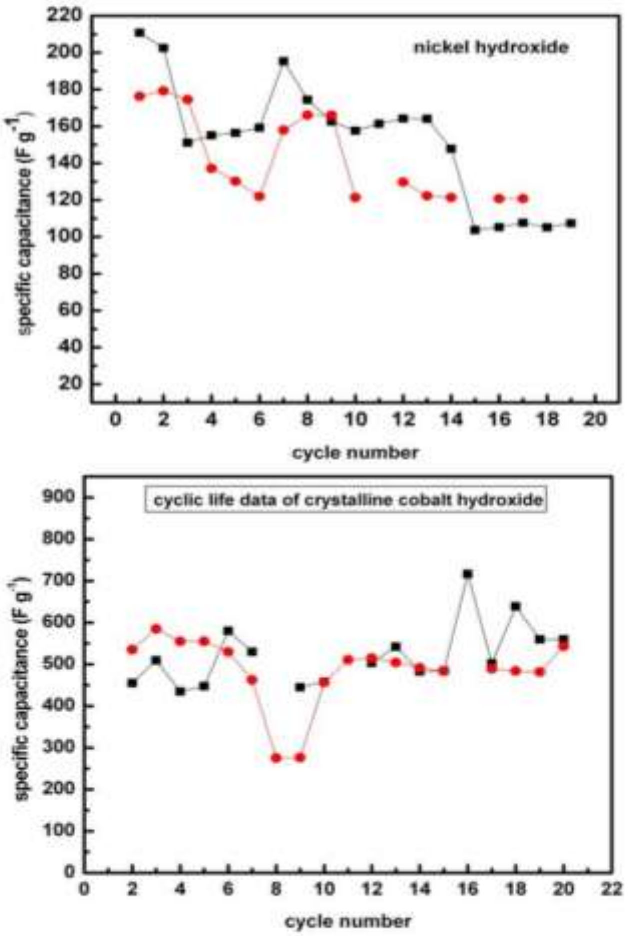

Figure 3: Charge-discharge cycles of a) cobalt hydroxide electrode and b) nickel hydroxide respectively

Conclusion

The effect of crystallinity on the electrochemical capacitance of β-phases of cobalt hydroxide and nickel hydroxide is reported. The specific capacitance values obtained from the charge-discharge studies reveals that of cobalt hydroxide exhibits around 462 F g^{-1} while nickel hydroxide has 150 F g^{-1}. The results demonstrate that the specific capacity of the active material not only depends on the morphology but also on the nature of crystallinity and the metal ion.

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