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Effect of Substituents on the Electrochemical Reversible Discharge Capacity of Cobalt Hydroxide Electrodes

Thimmasandra Narayan Ramesh

Department of Studies and Research in Chemistry, Tumkur University, Tumkur 572 103, India

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Abstract: *Cobalt hydroxide, nickel hydroxide-cobalt hydroxide and zinc oxide-cobalt hydroxide biphasic mixtures were prepared by precipitation method. In spite of structural similarities exhibited by nickel hydroxide and cobalt hydroxide samples, former is a good electrode material and exchanges 1e-/Ni while latter does not show any reversibility. Presence of small amount of other metal ions such as nickel or zinc in the lattice of cobalt hydroxide or as a biphasic mixture of cobalt hydroxide-nickel hydroxide/cobalt hydroxide- zinc oxide, exchange up to 0.2 to 0.24e- exchange compared to pure cobalt hydroxide which shows 0.1 e^- exchange.*

Keywords: cobalt hydroxide, biphasic mixture, electrochemical performance, discharge capacity

1. INTRODUCTION

Among transition metal hydroxides, nickel hydroxide is extensively used as a positive electrode material in alkaline secondary batteries [1-2]. Nickel hydroxide and cobalt hydroxide crystallize in brucite structure and the structure comprises of hexagonal close packing of OH^- ions in which every alternate layer of octahedral sites are occupied by divalent metal ions resulting in the stacking of charge neutral layers with an interlayer distance of ≈ 4.6Å [3]. Cobalt like nickel can exist in multiple oxidation states in the hydroxide-oxide template [4] in which nickel hydroxide exchanges $1e^-$ on 100% charging [5]. On overcharging cobalt hydroxide will reach oxidation state of 3.7+, in which two step oxidation occurs.

$$Co(OH)_2 \leftrightarrow HCoO_2 \leftrightarrow H_{0.3}CoO_2 \quad (1)$$

$Co(OH)_2$ undergoes oxidation to cobalt oxyhydroxide irreversibly resulting in the formation of an electrochemically inactive and highly resistive phase of $HCoO_2$. Overcharging of cobalt hydroxide electrode leads to irreversibility due to the formation of Co_3O_4. Even though the structure of cobalt hydroxide is similar to that of nickel hydroxide, cobalt hydroxide has not been explored as an electrode material in alkaline batteries owing to its amphoteric nature in alkaline medium. Cyclic voltammetric studies on the reversibility of both pure and doped cobalt hydroxide have been reported by Ismail et al [5]. Doping of cobalt hydroxide with other divalent metals such as Mg^{2+}, Ni^{2+}, Zn^{2+} did not show any beneficial effect during the cyclic voltammetric measurements of $Co(OH)_2$ [5]. Bauer et al synthesized cobalt based layered double hydroxide which exhibits reversible charge storage capacity of 0.3 e^- exchange [6]. Addition or incorporation of cobalt metal powder/cobalt oxide or cobalt hydroxide was blended with the active material during electrode fabrication or coprecipitation along with nickel hydroxide during the synthesis enhances the electrochemical performance of nickel hydroxide [7-9]. We had earlier attempted to induce reversiblility in cobalt hydroxide by using bismuth oxide as additive [10]. The full potential scheme was therefore not realized in the cobalt hydroxide electrode. It is of interest to materials scientists and electrochemist to investigate whether similar enhancement of electrochemical behavior can be expected in cobalt hydroxide system by compositional tuning or isomorphous substitution of cobalt by zinc or nickel or in presence of biphasic mixtures due to similarities between nickel hydroxide and cobalt hydroxide. To the best of our knowledge there are no reports on the charge discharge studies of cobalt hydroxide and substituted or biphasic mixtures of cobalt hydroxide bulk electrodes. For the first time we have attempted to induce reversibility in cobalt hydroxide system by coprecipitation of cobalt hydroxide in presence of nickel or zinc ion. Plane cobalt hydroxide exchanges 0.1e- exchange while zinc oxide/nickel substituted biphasic mixtures of cobalt hydroxide exchanges 0.2 e- and 0.24 e-/Co respectively.

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*To whom correspondence should be addressed:
Email: adityaramesh77@yahoo.com,
Phone: +91-0816 2260220

2. EXPERIMENTAL

b-cobalt hydroxide was prepared by chemical coprecipitation method. Cobalt nitrate solution (1M, 25 mL) was added to ammonium hydroxide solution (2M, 50 mL) and the precipitate obtained was aged at RT for 18 h prior to filtration.

In separate experiments, nickel doped cobalt hydroxide and zinc doped cobalt hydroxides [M_{1-x} M^{I}_{x} $(OH)_2.zH_2O$; x=0.2] were obtained by the addition of mixed metal nitrates solution to sodium hydroxide solution and the obtained slurries were aged in mother liquor at room temperature for 18 h. The products were washed free of alkali and then dried at RT till constant weight is obtained.

2.1. Characterization

Samples were characterized by powder X-ray diffraction (PXRD) using a Philips powder X-ray diffractometer (CuKa source, l = 1.5418 Å) fitted with a graphite monochromator. Infrared spectra were recorded using a Nicolet Model Impact 400D FTIR spectrometer (KBr pellets, 4 cm^{-1} resolution).

2.2. Charge-discharge studies

Electrodes were prepared by mixing the active material with graphite powder and an aqueous suspension of polytetrafluoroethylene in the ratio 0.6:0.3:0.1. The mixtures were thoroughly ground to obtain a paste-like consistency using isopropyl alcohol. The paste was placed on both sides of a nickel foam (2.9 ´ 2.3 cm) support and pressed at 75-120 kg cm^{-2} at ambient temperature. The electrodes were dried at 65°C till constant weight is attained and soaked in 6 M KOH for 24 h before being galvanostatically charged at ~ 5.6 mA to 120% of the expected capacity which has been computed for 1e^- exchange. The potentials were measured using mercuric oxide/mercury reference electrode with nickel plates as counter electrode. The electrodes were discharged to a cutoff voltage of 0 V at the ~25-30°C. This discharge current was chosen to yield a C/4 rate for the expected theoretical capacity of the electrode. The discharge capacities reported for all the electrodes were normalized with respect to the weight of the active material.

3. RESULTS AND DISCUSSION

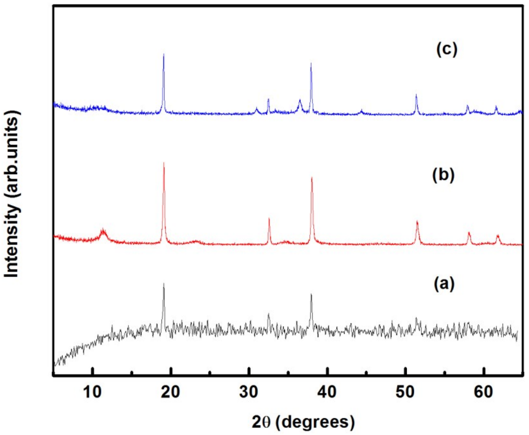

Figure 1. Powder X-ray diffraction patterns of a) cobalt hydroxide, b) biphasic mixtures of cobalt hydroxide-nickel hydroxide, c) cobalt hydroxide-zinc oxide respectively.

Figure 1 shows the PXRD pattern of cobalt hydroxide and sharp Bragg reflections were observed with the d-values of 1.78, 2.38 and 4.66 Å. These data match well with β phase of cobalt hydroxide (JCPDS No.2-1094). We attempted to induce reversibility by compositional tuning of cobalt hydroxide using isomorphic substitution. We chose nickel, which has 1e^- less than cobalt d orbitals and zinc in which d-orbitals are full. We can alter the total number of electron count to less than or greater than 3 on charging. The strong perturbation that nickel ion or zinc ion imposing on structure and electrochemical performance of cobalt hydroxide was investigated. Figure 1(b) shows the PXRD pattern of nickel substituted cobalt hydroxide and we observe two phases i.e α-phase with an interplanar distance of 7.6 Å and β-phase with 4.6 Å respectively indicating formation of biphasic mixture. Figure 1c shows the PXRD pattern of cobalt hydroxide obtained when cobalt and zinc salts were used for precipitation. The PXRD pattern also shows two phases i.e β phase of cobalt hydroxide and zinc oxide phase (minor). Use of strong alkali results in the oxidation of Co^{2+} to Co^{3+} in cobalt system, hence we get either biphasic mixture or highly ordered b-cobalt hydroxide. From the above data, it is clearly evident that biphasic mixture formation is more favoured in case of cobalt hydroxide system.

Infra red spectroscopic data of cobalt hydroxide and biphasic mixture of cobalt hydroxide- nickel hydroxide are shown in Table 1. b-phase of cobalt hydroxide shows a sharp non-hydrogen bonded OH stretched at 3633 cm^{-1} and 520 cm^{-1} and 460 cm^{-1} in the low wave number region. a-phase of cobalt hydroxide-nickel hydroxide shows broad OH stretching peak due to hydrogen bonding with the water molecules present in the interlayer region and the bands are observed at 640 cm^{-1}, 509 $cm^{-1}$and 447 cm^{-1}. The presence of interlayer nitrate is obserbed in 1600 to 1000 cm^{-1}.

Cyclic voltammetric studies of cobalt hydroxide display anodic peak at 0.28 V and cathodic peak at 0.15V vs Hg/HgO/OH^- respectively [5]. Anodic peak at 0.28V arises due to irreversible oxidation of Co(II) to Co(III). The redox couple of Co^{2+}/Co^{3+} is in the range of 0.3-0.35mV and that of Co_3O_4/Co_2O_3 ($Co^{2.67}/Co^{3+}$) is at + 90mV

Table 1. Infrared spectral data of cobalt hydroxide and cobalt hydroxide-nickel hydroxide biphasic mixture

β-cobalt hydroxide	wave number (cm^{-1})	Assignment	β-cobalt hydroxide-nickel hydroxide biphasic mixture	wave number (cm^{-1})	Assignment
	3650	O-H stretch		3633	O-H stretch
	-	-		3441	Hydrogen bonded O-H stretch
	-	-		1641	Bending mode of water molecule
	-	-		1388	Adsorbed nitrates
	-	-		640	Co/Ni-O-H α-phase
	520	Co-O-H bend		509	Co-OH bend
	460	Co-O stretch		447	Co-O stretch

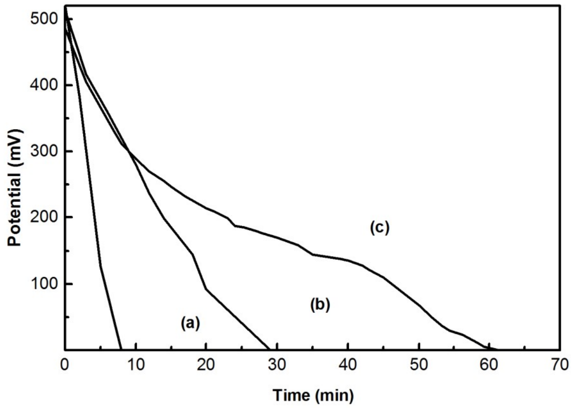

Figure 2. discharge profiles of a) cobalt hydroxide, b) cobalt hydroxide-zinc oxide biphasic mixture and c) biphasic mixtures of cobalt hydroxide-nickel hydroxide electrodes respectively.

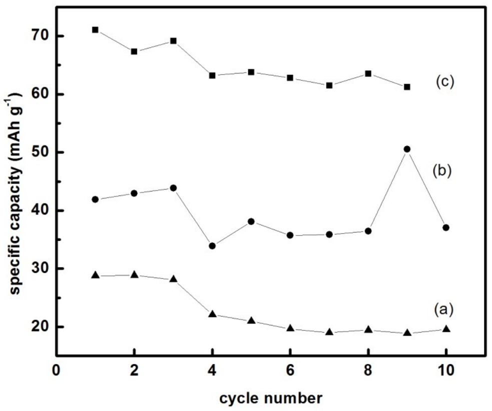

Figure 3. Cycle life data of a) cobalt hydroxide, b) cobalt hydroxide-zinc oxide biphasic mixture and c) biphasic mixtures of cobalt hydroxide-nickel hydroxide electrodes respectively.

versus Hg/HgO/OH^- respectively. Therefore we have restricted electrochemical studies of cobalt hydroxide electrode and biphasic mixture of cobalt hydroxides (zinc and nickel hydroxide) in the potential window of 0 to 550 mV [5].

Figure 2(a,b) shows a slope in the potential range of 550-0 mV for cobalt hydroxide and biphasic mixtures of cobalt hydroxide-zinc oxide. Figure 2(c) shows the discharge plateau around 150 mV for biphasic mixture of cobalt hydroxide-nickel hydroxide. Figure 3(a) shows the cycle life data of cobalt hydroxide electrode. It is clearly evident from Figure 3(b, c) that presence of nickel or zinc in cobalt hydroxide marginally improves the reversibility in cobalt hydroxide samples. Irrespective of the mode of modifying cobalt hydroxide, the reversibility of cobalt hydroxide observed is in the range of 0.2-0.24e exchange. Cobalt hydroxide undergoes oxidation easily compared to its nickel counterpart.

In Figure 3(b and c) is shown the cycle life data of nickel and zinc substituted cobalt hydroxides. Biphasic mixture of cobalt hydroxide and nickel hydroxide exchanges 0.4e exchange while that of cobalt hydroxide with zinc hydroxide exchanges 0.2 e- exchange. Nickel hydroxide being an active material in the material can also reversibly get cycled, therefore, in cobalt hydroxide-nickel hydroxide biphasic mixture, the contribution of nickel hydroxide was also taken into account and the sample shows reversibility of 0.24 e- exchange. It clearly indicates that presence of nickel hydroxide can slightly enhance the reversibility in cobalt hydroxide. To rule out the contribution of substituent on the reversible discharge capacity, we have investigated biphasic mixture of cobalt hydroxide with zinc oxide and the electrode show 0.2e- exchange.

Pasted electrodes comprising of cobalt hydroxide, biphasic mixtures of cobalt hydroxide with zinc oxide and nickel hydroxide display reversible discharge capacities of 20, 35 and 65 mAh g^{-1} respectively. Therefore, presence of nickel hydroxide or zinc hydroxide contributes towards marginal improvement in the electrochemical property of cobalt hydroxide. We conclude that the presence of nickel ion in cobalt hydroxide medium can slightly enhance the reversibility of cobalt hydroxide electrode. This clearly demonstrates that modifications due to the presence other transition metal ions either by physical mixture or chemical method has better chance to induce reversibility in cobalt hydroxide thus providing opportunity to exploit its potential usage in rechargeable batteries.

4. ACKNOWLEDGMENTS

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