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Bi_2O_3 modified cobalt hydroxide as an electrode for alkaline batteries

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Abstract

Manganese dioxide electrode shows reversible charge storage capacity, if the charge–discharge process is limited to $0.3e^-$ exchange. Addition of small amount of Bi_2O_3 to manganese dioxide induces reversibility with an exchange of $2e^-$/Mn. Nickel hydroxide is known to reversibly exchange $1e^-$. In spite of isostructural relationship between the cobalt hydroxide, nickel hydroxide and manganese dioxide, cobalt hydroxide does not show any electrochemical activity. Bi_2O_3 modified cobalt hydroxide electrodes exchanges $0.3–0.5e^-$/Co during the charge discharge process. The oxidation–reduction process in cobalt hydroxide and Bi_2O_3 modified cobalt hydroxide electrodes were monitored using the PXRD patterns.

Keywords: Cobalt hydroxide; Bi_2O_3; Electrode material; Alkaline batteries

1. Introduction

Transition metal oxides and hydroxides such as manganese dioxide and nickel hydroxide are extensively used as positive electrode materials in alkaline batteries [1,2]. Bivalent metal hydroxides such as nickel hydroxide, cobalt hydroxide and manganese hydroxide crystallize in brucite type structure, a mineral form of $Mg(OH)_2$. The crystal structure of cobalt hydroxide comprises of a hexagonal close packing of hydroxyl ions in which alternate layer of octahedral sites are occupied by divalent Co^{2+} ions. This results in the stacking of charge neutral layers with an interlayer distance of 4.6 Å [3,4].

Ismail et al. [5] proposed a common reaction mechanism for the reversible charge–discharge process in alkaline media:

$$\underset{\text{divalent hydroxide}}{M^{II}(OH)_2} \underset{d}{\overset{a}{\Leftrightarrow}} \underset{\text{trivalent bronze}}{HM^{III}O_2/M^{III}OOH} \underset{c}{\overset{b}{\Leftrightarrow}} \underset{\text{quadrivalent dioxide}}{M^{IV}O_2}$$

Nickel hydroxide electrode exhibits step (a)/(d) reversibly with $1e^-$ exchange, while nickel aluminium layered double hydroxide exhibits step (a and b)/(c and d) with $1.7e^-$ exchange [6,7]. MnO_2 exhibits steps (b)/(c) reversibly, if the discharge is limited to $0.3e^-$ exchange. Beyond this limit, Mn_3O_4 spinel is formed [8]. Cobalt hydroxide can also exist in multiple oxidation states similar to nickel hydroxide [9]. Cobalt hydroxide undergoes step (a) irreversibly resulting in the formation of an electrochemically inactive and highly resistive phase of $HCoO_2$/CoOOH. While step (b)/(c) are quasi-reversibly cycled between the nearly quadrivalent (conducting) oxide phase and the insulating trivalent oxyhydroxide [10]. Cyclic voltammetric study of cobalt hydroxide thin films during cathodic sweep clearly shows the formation of Co_3O_4 phase. Cyclic voltammetric studies of pure and doped cobalt hydroxide thin films with other divalent metals such as Mg^{2+}, Ni^{2+}, Zn^{2+}, did not show any beneficial effect on the first step (a) of cobalt hydroxide [10]. Therefore, the full potential scheme for reversible charge storage capacity of cobalt hydroxide bulk electrode was not observed. The study of Co-base electro-active materials can provide useful information for the understanding of limiting phenomena affecting redox mechanism in layered materials.

Buss et al. overcome the limitation of irreversible behaviour of cobalt hydroxide by synthesizing cobalt aluminum and cobalt iron layered double hydroxide [11,12]. These layered double hydroxide electrodes reversibly exchange $0.4e^-$/Co. Wroblowa and Gupta blended small amount of Bi_2O_3 with manganese oxide during electrode fabrication and succeeded in inducing $2e^-$ exchange reversibility in manganese dioxide electrode [13]. Bi_2O_3 coated cobalt hydroxide was used as additive to improve the electrochemical performance of nickel hydroxide electrode [14]. Bi_2O_3 coated cobalt hydroxide suppress Co_3O_4 formation during the charge–discharge process thereby increasing conductivity in the nickel hydroxide electrode. This clearly demonstrates that Bi_2O_3 will suppress the spinel formation

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in cobalt hydroxide and manganese oxide electrodes during charge–discharge studies. The fundamental aspects behind the irreversible behaviour of cobalt hydroxide are not investigated. In this paper, we have studied the electrochemical behaviour of bulk cobalt hydroxide electrodes with and without Bi_2O_3.

2. Experimental

β-Cobalt hydroxide and Bi_2O_3 were obtained from Aldrich Chemical Co and Loba Chemie India and used as such. Bismuth doped cobalt hydroxides were also prepared by means of chemical precipitation. Simultaneous addition of mixed metal nitrates solution [$Co(NO_3)_2$: 0.9, 0.8 mol% and $Bi(NO_3)_3$ 0.1, 0.2 mol%] and NaOH (1 M) to a beaker containing an aqueous solution of sodium carbonate (0.5 M) results in the precipitation of the solid. The precipitation was stopped at pH at 9 and the product was aged in mother liquor at 65 °C for 18 h prior to filtration [15]. The samples were filtered, washed with distilled water and dried at 25–30 °C to constant weight.

The samples were characterized by powder X-ray diffraction (PXRD) using a Philips X'pert pro diffractometer (Cu Kα source, λ = 1.5418 Å) with graphite as secondary monochromator.

2.1. Charge–discharge studies

Cyclic voltammetry studies (scan rate of 10 mV s^{-1}) and galvanostatic charge discharge studies were carried out by Versastat Model II A (EG&G PARC) scanning potentiostat. Graphite powder was obtained from scientific chemicals (Chennai) and nickel foam was obtained from Nitech (thickness: 1.8 mm and porosity: 500 μm). Electrodes were prepared by mixing the active material with graphite powder and an aqueous suspension of poly-tetrafluoroethylene in the ratio 6:3:1. The mixtures were thoroughly ground to obtain a paste-like consistency in a pestle and mortar. This paste was pressed at 75–120 kg cm^{-2} on both sides of a nickel foam (2.9 cm × 2.3 cm) support at the ambient temperature 25–30 °C.

Physically modified cobalt hydroxide electrodes were prepared by blending different ratios (2.5, 5, 10, 12 mol%) of Bi_2O_3 with the active material. As prepared cobalt hydroxide–Bi_2O_3 composites was used as an active material during electrode fabrication. An electrode comprising Bi_2O_3 without active material was also cycled to investigate its contribution to the charge storage capacity. All the electrodes were dried at 65 °C and soaked in 6 M KOH for 24 h before being galvanostatically charged at current density of 13 mA/cm^{-2} charged to 120% of the theoretical capacity computed for a $1e^-$ exchange. The excess charge is to compensate for the side reactions such as oxygen evolution occurring during the charging process. Nickel plates were used as counters, and all potentials were measured using an Hg/HgO/OH/reference electrode in 6 M KOH. These electrodes were then discharged at a current of 20 mA to a cutoff voltage of 0 V at the 25–30 °C. The discharge current was chosen to yield a C/4 rate for the expected theoretical capacity of the electrode. The discharge capacities of all the electrodes were normalized with respect to the weight of the active material. After cycling the electrodes were removed from the cell, rinsed with distilled water and dried at 25–30 °C in a dessicator.

3. Results and discussion

Fig. 1a shows the PXRD pattern of cobalt hydroxide. The PXRD patterns display sharp Bragg reflections with *d*-values of 1.78, 2.38 and 4.6 Å. The *d*-values match well with β-cobalt hydroxide (ICSD No. 88940). Cyclic voltammetric studies on cobalt hydroxide thin film exhibit two anodic peaks at 0.36, −0.64 V and one cathodic peak at 0.04 V versus Hg/HgO/OH^-, respectively [10]. Anodic peak at 0.36 V is due to irreversible oxidation of Co(II) to Co(III) and the second quasi-reversible −0.64 V peak is due to oxidation of Co(III) to Co(IV). Cyclic voltammogram of bulk cobalt hydroxide is given in Fig. 2. Cobalt hydroxide bulk electrodes show peaks at 0.33 mV due

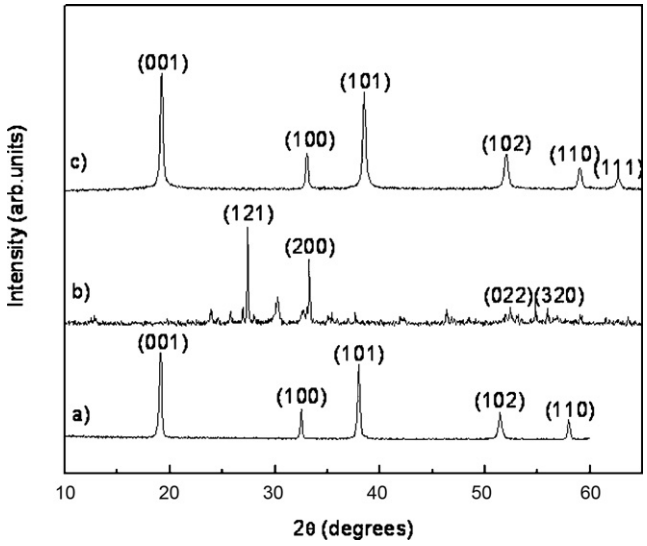

Fig. 1. PXRD patterns of (a) crystalline β-cobalt hydroxide, (b) commercial Bi_2O_3 and (c) crystalline β-nickel hydroxide samples.

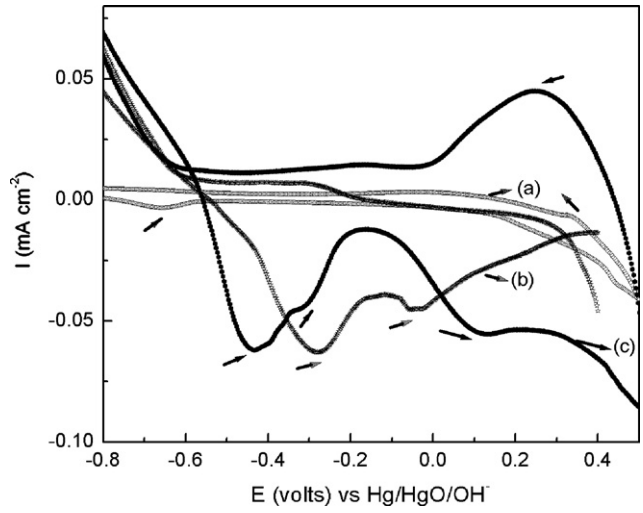

Fig. 2. Cyclic voltammogram of (a) cobalt hydroxide electrode, (b) Bi_2O_3 and (c) 12 mol% Bi_2O_3 blended cobalt hydroxide electrode at scan rate of 10 mV/s.

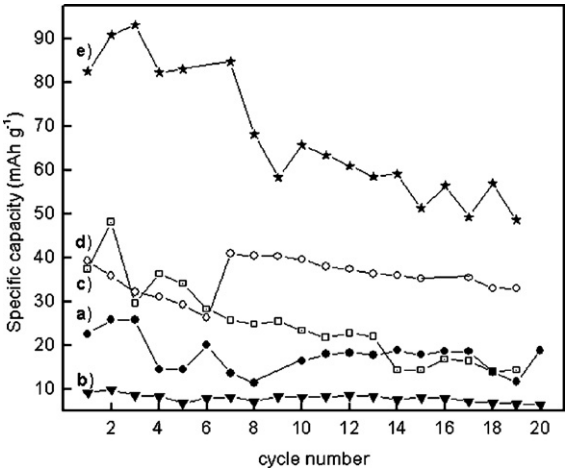

Fig. 3. Cycle life data of (a) cobalt hydroxide, (b) Bi_2O_3, cobalt hydroxide with (c) 2.5 mol% Bi_2O_3, (d) 5 mol% Bi_2O_3 and (e) 12 mol% Bi_2O_3.

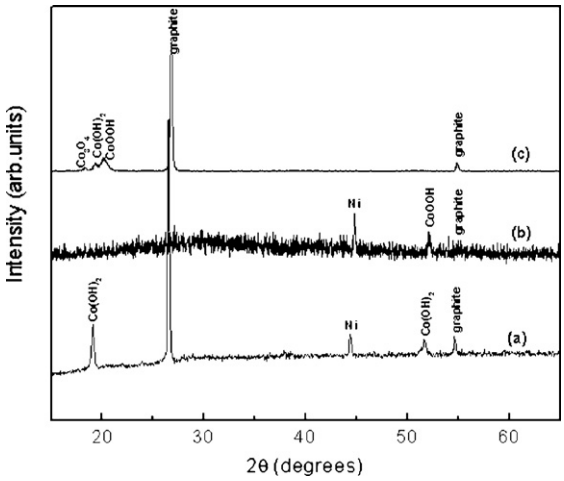

Fig. 5. PXRD patterns of (a) fresh cobalt hydroxide, (b) charged and (c) discharged cobalt hydroxide electrodes.

to oxidation of Co(II) to Co(III) and −0.65 mV due to reduction of Co(IV) to Co(III). We have restricted our studies from Co(II) to Co(III) region, during which highly resistive CoOOH/Co_3O_4 phase is formed.

Fig. 3a shows the cycle life data of cobalt hydroxide electrode and it exchanges 0.1e^-/Co. Similar results was also observed by Elumalai et al. [16]. The discharge profile of cobalt hydroxide does not show plateau potential in the range of 450–0 mV (see Fig. 4a). The PXRD patterns of as-prepared fresh cobalt hydroxide, charged and discharged electrodes are shown in Fig. 5. On charging, cobalt hydroxide electrode gets oxidized to CoOOH. CoOOH also crystallizes in the layered structure similar to β-cobalt hydroxide. The absence of reflections in the PXRD pattern of charged state of cobalt hydroxide is due to the amorphous nature (see Fig. 5b). On discharge, we observe (i) peaks due to CoOOH, Co_3O_4 and (ii) a less intense peak for cobalt hydroxide (see Fig. 5c). The PXRD patterns clearly show the structural changes that can take place during the charge discharge process of cobalt hydroxide. Cobalt hydroxide will also undergo oxidation in KOH to form highly insulating phase of $Co^{III}OOH$ [17]; $Co^{III}OOH$ further transforms to Co_3O_4 [14,17]. This is the cause of an irreversible electrochemical behaviour in cobalt hydroxide.

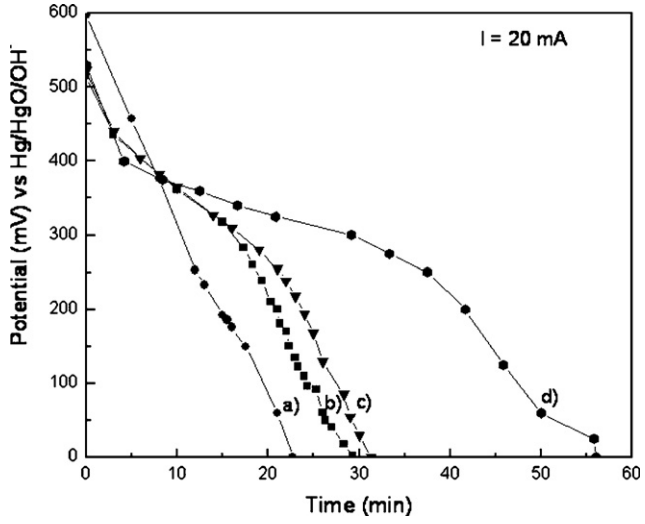

Fig. 4. Discharge profiles of (a) cobalt hydroxide, (b) with 2.5 mol% Bi_2O_3, (c) with 5 mol% Bi_2O_3 and (d) with 12 mol% Bi_2O_3.

In manganese dioxide, reversible electrochemical behaviour was achieved by two approaches [18]. In the first method, when the discharge of $MnO_2 \Leftrightarrow MnOOH$ was limited to 0.3e^-/Mn ($MnO_2 \Leftrightarrow Mn_{1-x-y}{}^{4+}Mn_y{}^{3+}O_{2-4x-y}O^{2-}OH_{4x+y}{}^-$: $y = 0.3$) it can be reversibly cycled. In second method, Wroblowa and Gupta could reversibly cycle manganese dioxide [$MnO_2 \Leftrightarrow MnOOH \Leftrightarrow Mn(OH)_2$] upto 2$e^-$ exchange by incorporating small percentage of Bi_2O_3. The latter result is a direct evidence for the common reaction mechanism proposed by Ismail et al. [5]. Cyclic voltammetric study shows that Bi_2O_3 doped manganese dioxide and Bi_2O_3 coated cobalt hydroxide prevents M_3O_4 (M = Co, Mn) formation [14,19]. Several authors report the formation of Mn–Bi complexes in alkaline medium [19–21]. Pralong et al. soaked cobalt hydroxide in KOH solution containing bismuth nitrate. After 10 days, the product was recovered. The PXRD pattern of the recovered product does not show any trace of Co_3O_4 formation [14]. The isostructural relationship between manganese dioxide and cobalt hydroxide promotes us to investigate the effect of Bi_2O_3, on cobalt hydroxide electrode from fundamental point of view.

Fig. 1b shows the PXRD pattern of commercial Bi_2O_3. The Bragg reflections in the PXRD pattern were indexed to α-phase of Bi_2O_3. Cobalt hydroxide was physically mixed with various proportions of (2.5–12 mol%) Bi_2O_3 during electrode fabrication. Cyclic voltammogram of Bi_2O_3 is shown in Fig. 2b. We observe peaks at −0.54, −278 and −26 mV due to reduction of Bi_2O_3 to Bi. Cyclic voltammogram of 12 mol% Bi_2O_3 modified cobalt hydroxide is shown in Fig. 2c. We observe peaks at 270 (due to the oxidation of cobalt hydroxide), −440, −320, −122 (reduction of Bi_2O_3 to Bi) and 125 mV (due to reduction of CoOOH), respectively. Cyclic voltammogram clearly shows that the presence of Bi_2O_3 induces reversibility in cobalt hydroxide electrode. The cyclic voltammograms presented in this article are the representative profiles for the samples tested.

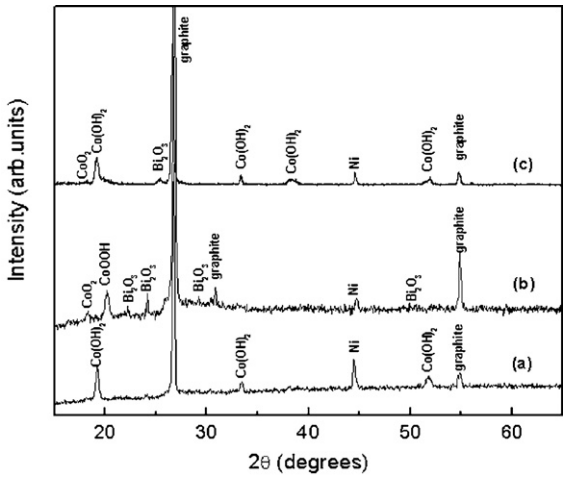

Fig. 6. PXRD patterns of (a) fresh Bi_2O_3 modified cobalt hydroxide, (b) charged Bi_2O_3 modified cobalt hydroxide and (c) discharged Bi_2O_3 modified cobalt hydroxide.

Fig. 3a shows the cycle life data of plane cobalt hydroxide. In Fig. 3c–e is shown the cycle life data of cobalt hydroxide with 2.5, 5 and 12 mol% of Bi_2O_3 (physically mixed), respectively. At 12 mol% Bi_2O_3 addition (see Fig. 3e), cobalt hydroxide exchanges 0.3–0.4e^-. Since the cutoff voltage during the discharge process in cobalt hydroxide is limited to 0 V, the reduction of Bi_2O_3 to Bi is not feasible. In Fig. 4b–d are shown the discharge plateaus of cobalt hydroxide with 2.5, 5 and 12 mol% Bi_2O_3. The redox couple of Co^{3+}/Co^{2+} is expected to be in the range of 0.35–0.20 mV. 12 mol% Bi_2O_3, modified cobalt hydroxide shows a plateau in the range of 0.32–0.29 mV.

To further confirm that Bi_2O_3 induces reversibility in cobalt hydroxide and does not get reduced during the course of the discharge process; we have recorded the PXRD patterns of 12 mol% Bi_2O_3 modified cobalt hydroxide: (i) fresh electrode, (ii) on charging and (iii) after it was discharged (see Fig. 6a–c). On charging Bi_2O_3 blended cobalt hydroxide, the electrode will display a peak at 4.39 Å in the PXRD pattern due to the formation of CoOOH in addition to Bi_2O_3 peaks (see Fig. 6b). On discharge, the *d*-value increases from 4.39 to 4.6 Å due to the reduction of CoOOH to cobalt hydroxide ($d = 4.6$ Å) (see Fig. 6c). The PXRD patterns of charged and discharged electrodes observed in Fig. 6 were recorded after 20 cycles. This clearly shows that Bi_2O_3 induces reversibility in cobalt hydroxide without being reduced. Several authors have reported the cyclic voltammogram and show that the Bi_2O_3 reduction takes place in the negative potential [14,19]. In order to rule out the possible contribution of Bi_2O_3 in the positive potential window, we cycled Bi_2O_3 bulk electrode and the cycle life data is shown in Fig. 3b. It exchanges less than 0.1e^-/Bi_2O_3.

Layered double hydroxides derive their structure from magnesium hydroxide $Mg(OH)_2$. Partial substitution of divalent metal ion by trivalent creates positive charge on the layer $[Mg^{II}_{1-x}Al^{II}_x(OH)_{2-x}]$. To balance the positive charge on the layers, anions and water molecules get intercalated in the interlayer region resulting in an increase in the inter lamellar spacing from 4.6 to 7.6 Å [22]. Layered double hydroxides (Ni–Al, Ni–Co, Ni–Mn, Ni–Zn) are extensively used as electrode materials and are known to perform better than nickel hydroxide electrodes [7,23–25]. Our attempt to prepare Co–Bi layered double hydroxides $[Co_{1-x}Bi_x(OH)_{2-y}(A_y)^{n-}\cdot zH_2O$ where $x = 0.1$ and 0.2] failed, since the ionic radii of Bi is larger than the octahedral void present within the layer. The Bragg reflections in the PXRD pattern of chemically prepared Co–Bi (10 and 20 mol%) compounds could be indexed to mixture of Co–Bi layered double hydroxide, β-cobalt hydroxide and Bi_2O_3 (see Table 1). The cycle life data of 10 and 20 mol% chemically prepared Bi_2O_3 doped cobalt hydroxide are shown in Fig. 7b and c. In Fig. 8a and b are shown the discharge plateaus of 10 and 20 mol% of chemically prepared Bi_2O_3 cobalt hydroxide. Chemically modified cobalt hydroxide with Bi_2O_3 shows slightly higher reversible discharge capacity (0.5e^-/Co) compared to physical mixture due to the formation of Co–Bi layered double hydroxide and intimate mixing of cobalt hydroxide and Bi_2O_3 during precipitation. Solid solution of cobalt substituted nickel hydroxide obtained by co precipitation performs electrochemically better than the nickel hydroxide with post treat of

Table 1
The *d*-values in the PXRD pattern of chemically prepared Co–Bi (Bi = 10 and 20 mol%) samples

Co–Bi (10 mol%)	*d* (Å)	Co–Bi (20 mol%)	*d* (Å)
(0 0 3)	6.99	(0 0 3)	6.99
(0 0 6)	3.67	(0 0 1)[a]	4.63
(0 1 2)	2.94	(0 0 6)	3.67
(0 1 5)	2.70	(0 1 2)	2.98
–	2.12	(0 1 5)	2.70
Bi_2O_3	1.86	(1 0 1)[a]	2.36
Bi_2O_3	1.76	Bi_2O_3	1.90
Bi_2O_3	1.69	Bi_2O_3	1.76
Bi_2O_3	1.66	Bi_2O_3	1.60
Bi_2O_3	1.60		

[a] Peaks due to β-cobalt hydroxide.

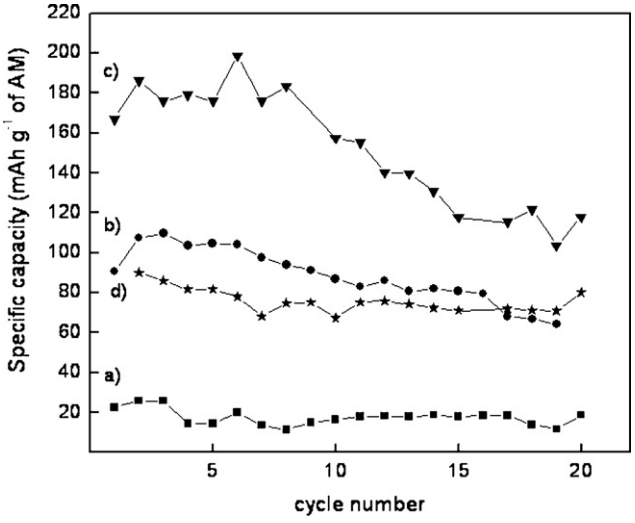

Fig. 7. Cycle life data of (a) cobalt hydroxide, (b) 10 mol% bismuth doped cobalt hydroxide, (c) 20 mol% bismuth doped cobalt hydroxide and (d) crystalline β-nickel hydroxide electrodes.

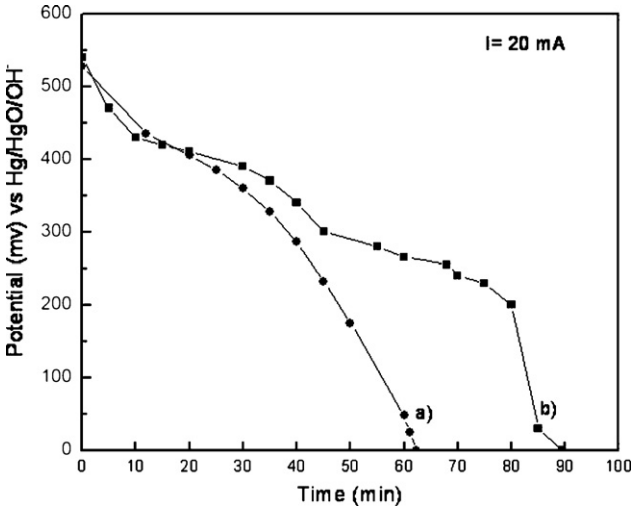

Fig. 8. Discharge profiles of (a) 10 mol% bismuth doped cobalt hydroxide and (b) 20 mol% bismuth doped cobalt hydroxide, respectively.

cobalt [26]. Several studies concerning relationship between the insertion/substitution of Co by other transition elements and the structural/conductivity properties of Co oxides have been previously reported [27]. Pralong et al. show that, highly conducting phase of $Co_x^{4+}Co_{1-x}^{3+}OOH_{1-x}$ phase is formed in the presence of Bi [14].

The amphoteric nature of cobalt hydroxide leads to a dissolution in alkaline medium resulting in the shedding of the material. Bi_2O_3 modified cobalt hydroxide to some extent prevents the dissolution of cobalt hydroxide. The surface area of cobalt hydroxide and chemically prepared Bi_2O_3 modified cobalt hydroxide are given in Table 2.

In Fig. 1c is shown the PXRD pattern of crystalline β-nickel hydroxide. In case of nickel hydroxide, crystalline samples deliver very low discharge capacity compared to disordered samples [28]. In Fig. 7d is shown the cycle life data of crystalline β-nickel hydroxide which exchanges $0.3e^-$/Ni. Disordered samples show better electrochemical activity and the discharge capacity is close to the theoretical expected value [29]. Crystalline cobalt hydroxide (see Fig. 7a) also delivers low discharge capacity but the disordered form of cobalt hydroxide does not exist. Addition of nickel nitrate to strong alkali produces highly disordered material [28] whereas in case of cobalt system, use of strong alkali results in the oxidation of Co^{2+} to Co^{3+}. Weak base such as ammonia, precipitates α-cobalt hydroxide, which immediately transforms into crystalline phase of β-cobalt hydroxide [30]. Hence, we get either biphasic mixture or highly ordered cobalt hydroxide. Therefore, disordered phase of β-cobalt hydroxide is not reported.

Table 2
BET surface area measurements

Sample	Surface area ($m^2\ g^{-1}$)
β-Cobalt hydroxide	16.9
Co–Bi (20 mol%) composite	19.3

4. Conclusion

Cobalt hydroxide electrode exchanges $0.1e^-$ while Bi_2O_3 modified cobalt hydroxide electrode (chemically and physically) reversibly exchanges $0.3–0.5e^-$. Bi_2O_3 prevents the Co_3O_4 formation in cobalt hydroxide during the charge–discharge process. We demonstrate that Bi_2O_3 modified cobalt hydroxide induces reversibility providing some insights into the charge discharge process of cobalt hydroxide.

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