

Cyclic voltammetric studies of pure and doped films of cobalt hydroxide in 1 M KOH

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Abstract

Cyclic voltammetric studies of electrosynthetically prepared pure and doped thin films of cobalt hydroxide (on a platinum foil substrate) in 1 M KOH show that $\text{Co}(\text{OH})_2$ undergoes a quasi-reversible redox reaction between a nearly quadrivalent black oxidic phase and a trivalent brown bronze-like phase. The coulombic efficiency is 60%. A common scheme is proposed for the electrode reactions of oxide electrodes in alkaline media, namely $\text{M}^{\text{II}}(\text{OH})_2 \rightleftharpoons \text{HM}^{\text{III}}\text{O}_2 \rightleftharpoons \text{M}^{\text{IV}}\text{O}_2$, where $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$. The three metals execute different steps in this two-electron redox reaction, either reversibly or quasi-reversibly. Based on this scheme, new compounds are suggested as possible electrode materials for secondary storage battery systems. The effect of eight, different, dopant metal ions on the redox reactions of $\text{Co}(\text{OH})_2$ is investigated. Only La^{3+} ions are found to influence favourably the performance of $\text{Co}(\text{OH})_2$ as an electrode material.

Introduction

Nickel hydroxide $[\text{Ni}(\text{OH})_2]$ has been widely studied and extensively used as an electrode material in secondary batteries [1–4]. By contrast, cobalt hydroxide $[\text{Co}(\text{OH})_2]$ has found little application. As with the nickel counterpart, $\text{Co}(\text{OH})_2$ adopts the hexagonal brucite structure [5] and exists in several forms of which the β polymorph is the most stable. Cobalt, like nickel, can exist in multiple oxidation states in the oxide–hydroxide matrix. While it is well known that the 3+ oxidation states of both metals are oxide–hydroxide phases [5], cobalt has been found to exist in a highly oxidized form in the 3.7+ state [6] and nickel in the 3.67+ state [7].

Despite the many similarities to $\text{Ni}(\text{OH})_2$ in terms of structure and chemistry, $\text{Co}(\text{OH})_2$ has not been used as an electrode material in alkaline batteries owing to its amphoteric nature [5] and instability in alkaline media. The latter results in the formation of an electrochemically inactive and highly resistive phase of CoHO_2 [8]. From studies of the structural and electrochemical properties of the redox products of the $\text{Co}(\text{OH})_2$ electrode, it has been reported [8] that the reactions of $\text{Co}(\text{OH})_2$ are irreversible. More recently, however, Bauer *et al.* [9] have overcome this difficulty by synthesizing electrodes of ternary hydroxy salts of cobalt with aluminium and iron.

The above work has encouraged the present cyclic voltammetric investigation of the reversibility of both pure and doped $\text{Co}(\text{OH})_2$ reactions in an alkaline medium. The dopants have included trivalent ions of the p-block (Al^{3+}), d-block (Cr^{3+} , Fe^{3+}) and rare earth (La^{3+}) elements, divalent ions of the s-block (Mg^{2+} , Zn^{2+}), d-block (Ni^{2+}) and p-block (Pb^{2+}) elements.

Experimental

Film preparation

Cobalt hydroxide films were prepared by cathodic deposition from 0.1 M $\text{Co}(\text{NO}_3)_2$, this is a convenient one-step synthesis [8, 10]. The substrate was a thin platinum foil of 1.5 cm² area. Prior to deposition, the foil was cleaned with detergent and then by an electrochemical procedure [11]. After this treatment, the foil was immersed in 0.1 M $\text{Co}(\text{NO}_3)_2$ and placed opposite a platinum counter electrode. Deposition was carried out for 1 min at 5 mA cm⁻². The resulting film was rinsed with water before further investigation.

Doped $\text{Co}(\text{OH})_2$ films were deposited from a mixed metal-nitrate bath containing cobalt and the dopant metal ion in the required concentration ratio. In order to provide a direct comparison of performance, the doped films were handled in a manner identical to that described above for undoped films.

Cyclic voltammetry

Freshly prepared films of pure and doped $\text{Co}(\text{OH})_2$ were immersed in a plastic tank containing 1 M KOH pre-electrolyzed using a method reported previously [12]. Cyclic voltammetric studies were performed using a platinum counter electrode and a Hg/HgO reference electrode (1 M KOH). All potentials are reported with respect to the latter electrode. Fresh electrolyte was used in each experiment.

A Princeton Applied Research Center potentiostat/galvanostat (model 362) was employed for the cyclic voltammetric studies. The potential was scanned anodically at 50 mV s⁻¹ from the hydrogen evolution region to the oxygen evolution region (i.e., -1.1 to +0.8 V) and the sweep was then reversed. The first and, when required, several successive scans were recorded for each film.

Preparation of model compounds

Electrosynthetically prepared $\text{Co}(\text{OH})_2$ was obtained in bulk after prolonged (2 to 3 h) cathodic deposition from a 0.1 M $\text{Co}(\text{NO}_3)_2$ solution. The compound which was blue during initial deposition turned rose-red in thicker deposits. The deposit was collected and analyzed. Model compounds, especially those described by Glemser [13] as $\text{Co}(\text{OH})_2$ and $\text{CoO}(\text{OH})$, were prepared in bulk by chemical means and then analyzed. These were used as reference samples for the analysis of the products from the $\text{Co}(\text{OH})_2$ redox reactions. The latter were obtained by holding freshly prepared $\text{Co}(\text{OH})_2$ films in 1 M

KOH at the potentials indicated by the cathodic and anodic peaks of the cyclic voltammogram. A black oxidic phase was obtained at +0.3 V and a brown phase at -0.5 V.

Characterization

The products of the redox reactions of the $\text{Co}(\text{OH})_2$ thin films and the model compounds were investigated by X-ray diffraction (XRD), IR spectroscopy, and 'ferrometry' (reaction with Fe^{2+}). The XRD patterns were obtained with a JEOL model JDX8P diffractometer that employed a Cu anode. The IR spectra were collected at a resolution of 3 cm^{-1} from KBr pellets with a Perkin-Elmer model 684 IR spectrometer.

The charge on the cobalt ion was estimated by reacting a known weight (10 mg) of the solid with an acidified solution of 0.01 M ferrous ammonium sulfate. On complete dissolution of the compound, the unreacted excess Fe^{2+} was estimated potentiometrically using a standard solution of 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7$. Determination of the end point is very accurate, and permits measurement of up to 1×10^{-4} equivalents of oxidizing power per mole of the compound.

Results and discussion

Cyclic voltammograms for five successive cycles of a thin film of $\text{Co}(\text{OH})_2$ are shown in Fig. 1. Clearly, during the first scan, $\text{Co}(\text{OH})_2$ undergoes a two-step oxidation (peaks I and II) at E_p values -0.62 and +0.36 V, respectively, and a one-step reduction (peak III) at 0.04 V. With further cycling, the first anodic peak shifts to cathodic potentials and gradually decreases in intensity to zero. The redox reactions associated with peaks II and III also reduce in intensity. These changes are highlighted in Fig. 2 where each step has been studied independently by narrowing the range of switching potentials. It is evident that the first of the anodic reactions is irreversible, while the second is quasi-reversible. The coulombic efficiency of the latter (measured as the ratio of cathodic to anodic peak area) is 60%. These results are in agreement with the polarization and coulometric studies on cobalt hydroxide reported by Benson *et al.* [8].

In order to identify the products of the redox reaction of $\text{Co}(\text{OH})_2$, freshly prepared films were potentiostatically held at -0.5, +0.3 and +0.1 V in 1 M KOH. The films were sonicated and the samples (labelled I, II and III, respectively) were collected and analyzed.

The XRD pattern of electrosynthesized $\text{Co}(\text{OH})_2$ exhibited peaks at d values of 1.78, 2.38 and 4.66 Å. These data are a perfect match with the PDF pattern no. 2-1094 [14] assigned to $\beta\text{-Co}(\text{OH})_2$. By contrast, the products of $\text{Co}(\text{OH})_2$ oxidation gave ill-defined XRD patterns. This behaviour is indicative of highly disordered phases and no definitive information could be gathered. Nevertheless, the identity of the species I, II and III could be established from IR spectroscopic analysis as this technique is sensitive to the short-

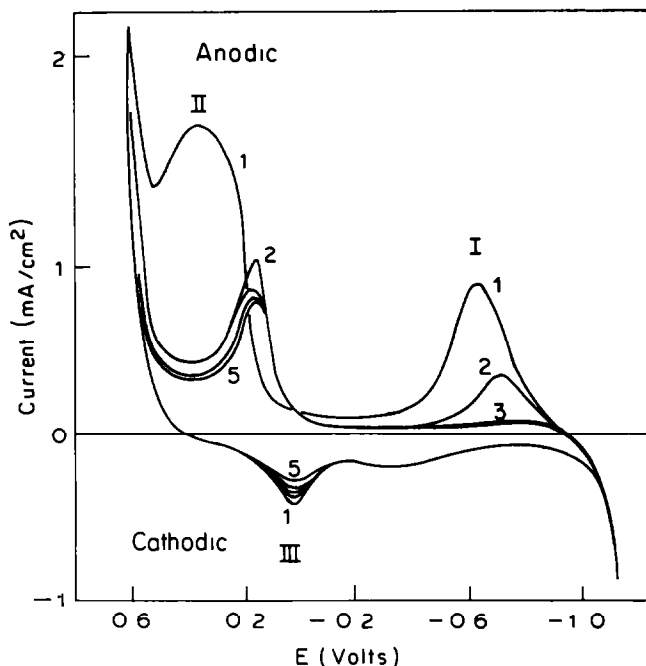


Fig 1 Cyclic voltammograms for first five cycles of Co(OH)_2 film in 1 M KOH

range structure. The resulting spectra for the three species are compared in Fig 3 with those for the model compounds Co(OH)_2 and CoO(OH) . While Co(OH)_2 exhibits a sharp OH-stretching peak at 3650 cm^{-1} , the CoO(OH) shows a broad, weak band in the range $3500\text{--}3300\text{ cm}^{-1}$ that clearly indicates the absence of free non-hydrogen-bonded hydroxyls in this compound. In the metal-oxygen stretching region, Co(OH)_2 displays the characteristic bands of the brucite coordination cage [1] at 480 , 430 and 300 cm^{-1} , respectively. On the other hand, CoO(OH) yields a simple one-band spectrum at 620 cm^{-1} . The products of the Co(OH)_2 oxidation, viz., species I and II, both produce a spectrum similar to that of the model compound CoO(OH) with no absorption in the energy range $3700\text{--}3000\text{ cm}^{-1}$. Species III gives weak absorption at 3650 cm^{-1} and at close to the 300 cm^{-1} region. Nevertheless, the predominant band still occurs at 620 cm^{-1} and this confirms that the phase is predominantly CoO(OH) .

The hydroxyl group in the brucite structure does not participate in any hydrogen bonding [5] and, in the IR spectrum, the OH-stretching energy appears as a well-defined peak for Co(OH)_2 . By contrast, a similar peak is not observed for the phase identified in the literature as CoO(OH) [13, 15]. This observation, together with the absence of both the intense peak at 300 cm^{-1} (assigned to out-of-plane OH bending) and the 480 cm^{-1} band (assigned to in-plane OH bending [1]) demonstrates that CoO(OH) is not a well-defined hydroxide. The single-peak spectrum is more indicative of a metal dioxide.

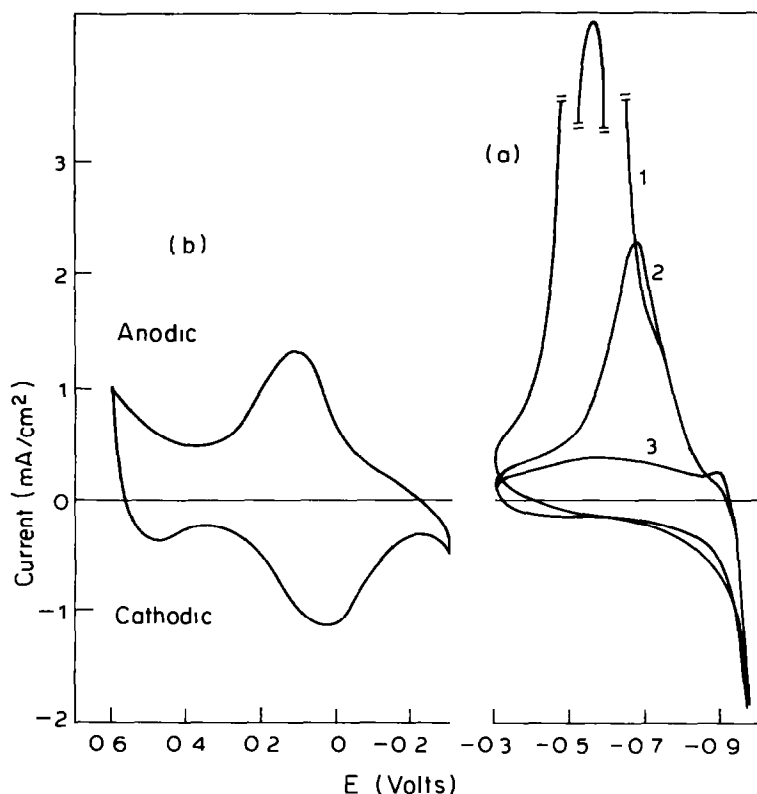


Fig 2 (a) Cyclic voltammogram for first anodic reaction of Co(OH)_2 showing its irreversible nature (b) Cyclic voltammogram for second anodic reaction of Co(OH)_2 after 25 cycles

[16] cage and suggests that the oxide-hydroxide, CoO(OH) , is actually a bronze of the quadrivalent oxide and should be represented as H_xCoO_2 ($x=1$). Consequently, the species I, II and III obtained by the oxidation of Co(OH)_2 are actually bronzes of composition H_xCoO_2 and differ from each other in the value of x . These findings are similar to those obtained for Ni(OH)_2 and MnO_2 electrode reactions [17, 18]

It is concluded, therefore, that Co(OH)_2 oxidation takes place through proton extraction from the interleaving space between the CoO_2 oxide slabs of the brucite structure. The charge on cobalt in species II is estimated to be $3.7+$, in which case, the two-step oxidation reaction can be represented by



A comparison of the above reactions with those for Ni(OH)_2 and MnO_2 electrodes suggests the following common reaction scheme for all three electrode types in alkaline media

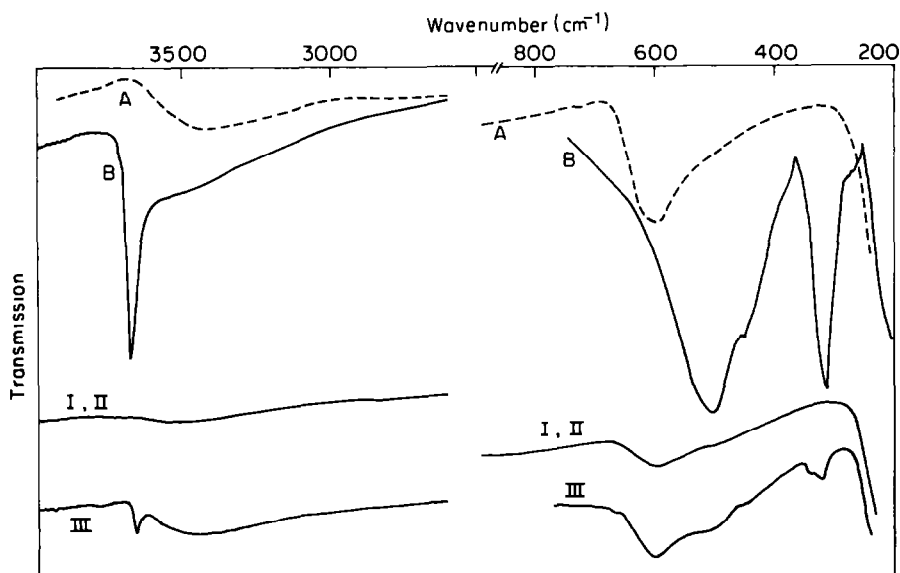


Fig 3 IR spectra for species I, II and III (see text) and model compounds (A) CoO(OH) (B) Co(OH)_2



divalent trivalent quadrivalent
hydroxide bronze dioxide

This scheme involves a divalent hydroxide at one end and a quadrivalent dioxide at the other end of the charge/discharge cycle. The complete reaction encompasses a two-electron change.

MnO_2 exhibits a single-step irreversible discharge (step c, scheme (2)) [18, 19], while Co(OH)_2 undergoes step (a) irreversibly and steps (b) and (c) quasi-reversibly. Formation of CoO_2 has also been suggested by Burke *et al* [20] in a study of cobalt metal in alkaline medium. The MnO_2 electrode can also be reversibly recharged if the discharge is limited to 30% of the charge capacity [19]. With discharge beyond this limit, Mn_3O_4 is said to form. Because the latter compound is a poor conductor, the MnO_2 electrode is essentially irreversible on deep discharge. Similar behaviour has also been found with the cobalt system; Co_3O_4 formation has been held responsible for "difficulties in reactivating cobalt metal electrodes in the cathodic sweep" [21]. Since the Co(OH)_2 can be quasi-reversibly cycled between the nearly quadrivalent black oxidic phase and the trivalent brown bronze under conditions of deeper discharge than the MnO_2 electrodes, its performance is correspondingly superior to that of the MnO_2 electrode. The Ni(OH)_2 electrode, on the other hand, is closest to the ideal model given by scheme (2), and undergoes a 1.67 electron change reversibly. This explains the wide application

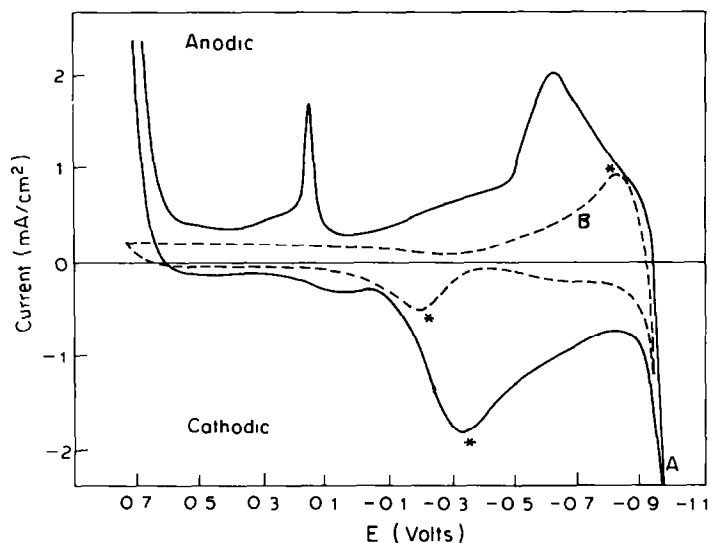


Fig 4 Cyclic voltammograms for Co(OH)_2 films doped with (A) Al^{3+} , (B) Fe^{3+} Starred features are peaks due to platinum substrate

TABLE 1

Electrochemical data from doped films of cobalt hydroxide

Dopant	Concentration for complete poisoning (mol %)	Concentration studied (mol %)	Peak potential (V)		Coulombic efficiency of step (b) (%)
			anodic	cathodic	
		Pure Co(OH)_2	-0.62 0.36	0.04	60
La	33	10	-0.58 0.16	0.08	68
Al	10	0.5	-0.62 0.15	0.08	10
Cr	10				
Fe	10				
Ni		10	-0.70 0.34		0
Mg	25	10	-0.66 0.37		0
Zn	25	10	-0.68 0.35		0
Pb	10				

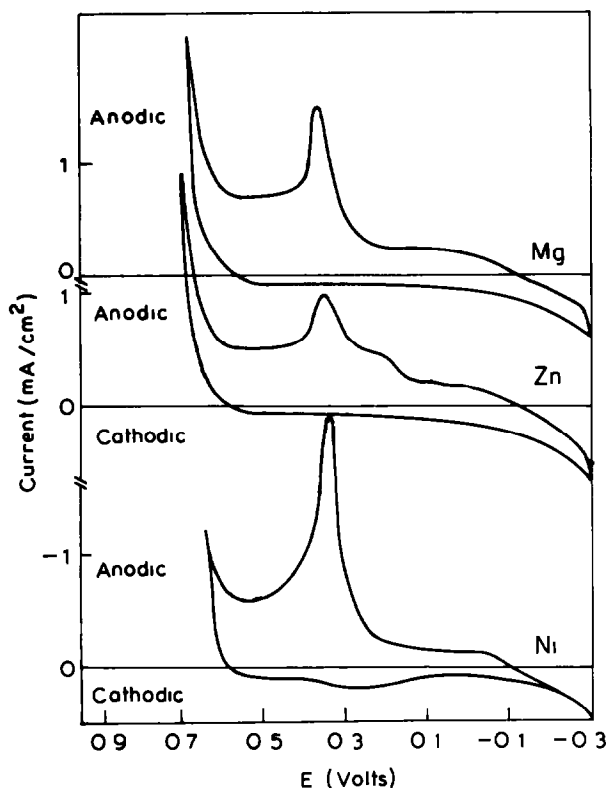


Fig 5 Cyclic voltammograms for second anodic reaction of Co(OH)_2 films doped with Ni^{2+} , Zn^{2+} or Mg^{2+}

of Ni(OH)_2 as an electrode material in secondary batteries. The hydroxide goes through intermediate phases, characterized as $\text{Ni}_3\text{O}_2(\text{OH})_4$ [3], that can be reformulated as bronzes of type $\text{H}_{1.33}\text{NiO}_2$, in keeping with scheme (2) proposed above.

The irreversible nature of the Co(OH)_2 reactions has been attributed to the high lattice stability of the 'CoO(OH)' phase [8]. It is therefore of interest to determine whether the reactions of Co(OH)_2 can be extended to the full potential of scheme (2) by chemical modification. Accordingly, eight different metal atoms (varying widely in charge, ionic radii and electron configuration) were selected and doped in the Co(OH)_2 film, with the hope that incorporation of dissimilar ions would produce lattice instability in the cobalt hydroxide matrix and thus lead to improved electrode reactions. The results of these studies are presented in Figs. 4 and 5 and summarized in Table 1.

In general, the dopants exerted unfavourable effects on the cobalt hydroxide reactions. Indeed, the dopants tended to poison the reactions of Co(OH)_2 . Trivalent metals such as Al^{3+} , Cr^{3+} and Fe^{3+} exhibited the greatest suppression of the Co(OH)_2 redox reactions, even at 10 mol % concentration. At lower concentrations (for example, 0.5 mol % Al) both the intensity and

the coulombic efficiency of the second anodic reaction were reduced (Fig 4) Lanthanum trivalent ions proved to be an exception and La-doped $\text{Co}(\text{OH})_2$ films displayed electrochemical activity up to 33 mol % La At 10 mol % La, the coulombic efficiency of the second anodic reaction was enhanced to 68% The suppression of the second anodic reaction by trivalent dopants may be associated with the stabilization of the trivalent phase as a result of the iso-structural nature of all the $\text{M}^{\text{III}}\text{O}(\text{OH})$ phases [22]

Doping of $\text{Co}(\text{OH})_2$ with divalent metals such as Mg^{2+} , Ni^{2+} and Zn^{2+} rendered the second anodic reaction completely irreversible (see Fig 5) This is due to the possible stabilization of the quadrivalent phase Such behaviour is to be expected as the substitution of Co^{3+} by divalent ions in the trivalent bronze would require the stabilization of the Co^{4+} ions in order to preserve charge neutrality Substitution by Pb^{2+} at a concentration of 10 mol % resulted in a complete inhibition of the electrode reaction

None of the dopants studied here provided a beneficial effect upon the first anodic reaction of $\text{Co}(\text{OH})_2$ The full potential of scheme (2) was therefore not realized in the $\text{Co}(\text{OH})_2$ electrode

Conclusions

1 Cobalt hydroxide undergoes a quasi-reversible redox reaction between a black oxidic phase, H_0CoO_2 , and a brown phase, HCoO_2 , with a coulombic efficiency of 60%

2 Both trivalent and divalent dopants do not influence favourably the performance of the $\text{Co}(\text{OH})_2$ electrode

3 A common reaction scheme for cobalt, manganese and nickel oxide electrodes in alkaline media has been proposed

4 Trivalent oxide-hydroxides [22] are a new class of compounds that may be explored further as possible electrode materials

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