

# Electrosynthesis and stabilization of $\alpha$ -cobalt hydroxide in the presence of trivalent cations

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## Abstract

Layered double hydroxides (LDHs) of cobalt with aluminium and chromium, isostructural with  $\alpha$ -cobalt(II) hydroxide, are electrosynthesized. This paves the way for their possible impregnation into porous metal plaques for ready use as electrodes in alkaline secondary cells. Unlike pure cobalt hydroxide, the LDHs of cobalt are not amphoteric and retain their  $\alpha$ -like structure in strong alkali, even after prolonged ageing. In addition, they exhibit electrochemical activity as shown by cyclic voltammetric studies.

*Keywords:* Layered double hydroxide; Cobalt hydroxide; Electrosynthesis; Aluminium; Chromium

## 1. Introduction

Cobalt(II) hydroxide and nickel(II) hydroxide exhibit many similarities in both structure and properties [1]. Despite this, cobalt(II) hydroxide has not been used as an electrode material in alkaline secondary cells, except as a minor component in the more widely used nickel hydroxide electrode [2]. The reasons are two-fold: (i) cobalt hydroxide is amphoteric and is not expected to be chemically stable in alkaline medium, and (ii) cobalt hydroxide has been found to yield an electrochemically resistive phase during anodic polarization in alkaline medium [3]. In addition, while nickel(II) hydroxide is known [4] to exist in two polymorphic forms, namely  $\alpha$  and  $\beta$  (the former has the higher electrochemical activity [5]), such polymorphism has not been unambiguously established in the case of cobalt(II) hydroxide.

Some promising work on cobalt hydroxide has recently been reported. For example, Ismail et al. [6] have used cyclic voltammetry to show that cobalt hydroxide can participate in a quasi-reversible charge-storage reaction similar to that of the nickel hydroxide electrode. An  $\alpha$ -form of cobalt hydroxide, isostructural with  $\alpha$ -Ni(OH)<sub>2</sub>, has also been successfully synthesized by an organic additive-mediated electrodeposition reaction [7]. Glemser and co-workers [8] have progressed a step further and overcome the problem of amphotericity of cobalt hydroxide by preparing layered dou-

ble hydroxides (LDHs) of cobalt with aluminium and iron, and have successfully employed them as electrodes in alkaline medium.

Hydroxide electrodes for battery applications are generally fabricated by electrochemical impregnation of porous metal plaques by a one-step, cathodic reduction reaction [9,10]. The motivation for the present study was to see if the LDHs of cobalt could be electrosynthesized in a similar fashion to pure [9,10] and doped [11] nickel hydroxides.

In this paper, we report the electrosynthesis of the LDHs of cobalt with aluminium and chromium. These LDHs are isostructural with  $\alpha$ -Co(OH)<sub>2</sub>, are stable in alkaline medium, and retain electrochemical activity.

Thus, the LDHs are important candidate electrode materials for alkaline secondary cells.

## 2. Experimental

All LDHs were prepared in a one-step, electrodeposition process by cathodic reduction of nitrate ions [9] from a mixed metal nitrate bath (total metal concentration 0.3 M) that contained cobalt and the trivalent ion in a 3:1 ratio. The synthesis was performed galvanostatically at a current density 65 mA cm<sup>-2</sup> in a divided electrochemical cell with a platinum flag (surface area 3 cm<sup>2</sup>) cathode. A 0.3 M potassium nitrate solution was placed in the anodic chamber and a platinum wire served as the anode. The deposition was carried out at ambient temperature (24 to 26 °C) for a period of 4 h. The

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material deposited in the cathodic chamber was filtered, washed with distilled water, and dried to constant weight at 55 °C. A control sample of pure  $\beta$ -cobalt hydroxide was prepared under identical conditions, but in the absence of any trivalent cations.  $\alpha$ -Cobalt hydroxide was prepared as reported in Ref. [7] by an additive-mediated electrosynthesis; 0.1 wt.% of fructose was used as the additive. The samples were characterized by powder X-ray diffractometry (XRD), infrared (IR) spectroscopy, and cyclic voltammetry (CV).

The XRD patterns were recorded on a Philips X-ray diffractometer with Co  $K\alpha$  ( $\lambda = 1.7902 \text{ \AA}$ ) radiation. The as-prepared, double hydroxide of cobalt with chromium was found to be X-ray amorphous. On ageing in 6 M KOH for 4 weeks at ambient temperature, however, it was found to order itself in the LDH structure.

IR spectra were recorded using a Perkin-Elmer 580 infrared spectrometer in KBr pellets at a resolution of  $3 \text{ cm}^{-1}$ .

CV measurements were conducted, as described in Refs. [6,11], with a PARC Model 362 scanning potentiostat hooked to a Digital Electronics (India) Omnigraph 2000 recorder. The CVs of pure and doped cobalt hydroxides were studied in two different ranges of switching potentials, viz.,  $-1.0$  to  $-0.3 \text{ V}$  and  $-0.2$  to  $0.65 \text{ V}$  with respect to a Hg/HgO (1 M KOH) reference electrode. The protocols used for electrolyte preparation, electrode cleaning and LDH film fabrication have been reported previously in Refs. [6,11,12]. The scan rate employed was  $10 \text{ mV s}^{-1}$ . Up to 10 scans were examined for each film, and 3 to 6 films were studied under each condition to establish reproducibility of the film behaviour.

### 3. Results

The powder XRD patterns of  $\alpha$ - and  $\beta$ -cobalt(II) hydroxides are presented in Fig. 1. While  $\beta$ -cobalt hydroxide displays major lines at 4.65, 2.75, 2.36 and 1.77  $\text{\AA}$ , respectively,  $\alpha$ -cobalt hydroxide shows a low angle reflexion at 7.73  $\text{\AA}$  followed by another at 3.95  $\text{\AA}$ . The latter pattern resembles very closely that of  $\alpha$ -Ni(OH)<sub>2</sub> [7] and can be indexed on a hexagonal cell with  $a = 3.09 \text{ \AA}$  and  $c = 23.3 \text{ \AA}$ .

The powder XRD patterns of the double hydroxide of cobalt with aluminium are given in Fig. 2. The data for the as-prepared sample is indicative of a poorly crystalline material. Nevertheless, the pattern clearly reveals a low angle reflexion at 7.79  $\text{\AA}$ , followed by another at 3.92  $\text{\AA}$ . On ageing in 6 M KOH for a month, the double hydroxide orders itself and shows sharp lines at 7.56, 3.82, 2.586, 2.31 and 1.938  $\text{\AA}$ . These  $d$  values have been listed alongside those of  $\alpha$ -cobalt hydroxide in Table 1 and are indexed on a hexagonal cell ( $a = 3.07 \text{ \AA}$ ,  $c = 22.92 \text{ \AA}$ ). It is evident that the LDH is isostructural with  $\alpha$ -cobalt hydroxide. It is further observed that while  $\alpha$ -cobalt hydroxide itself is amphoteric and dissolves rapidly in strong alkali, the LDH is not only stable in strong alkali but also organizes itself into a more ordered structure.

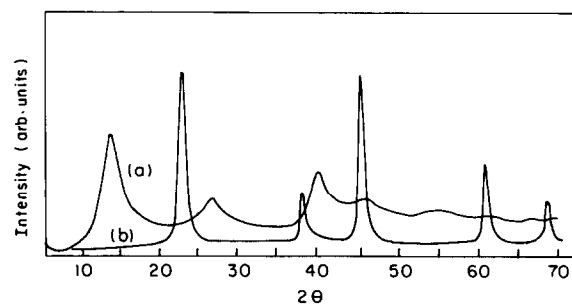


Fig. 1. Powder X-ray diffractograms for (a)  $\alpha$ - and (b)  $\beta$ -cobalt(II) hydroxides.

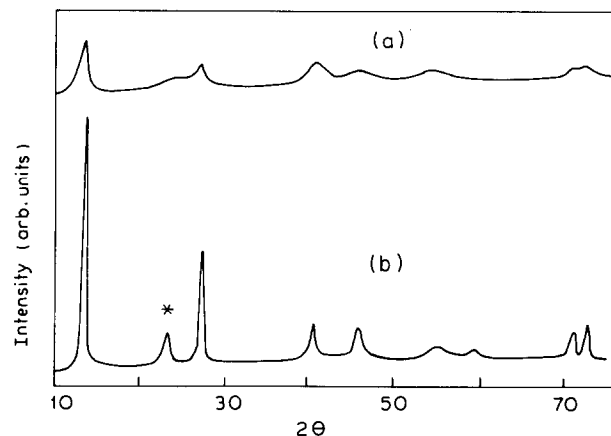


Fig. 2. Powder X-ray diffractograms for (a) as-prepared and (b) aged layered double hydroxide of cobalt with aluminium. Feature marked by asterisk is an impurity peak due to  $\beta$ -cobalt(II) hydroxide.

Similar observations are made with the cobalt–chromium system. The as-prepared double hydroxide is X-ray amorphous, but on ageing, a more ordered structure develops (Fig. 3). The major reflexions are listed in Table 1 and are indexed on a hexagonal cell ( $a = 3.09 \text{ \AA}$ ,  $c = 22.68 \text{ \AA}$ ). The double

Table 1  
Powder X-ray diffraction data for LDHs of cobalt with aluminium or chromium compared with that of  $\alpha$ -cobalt hydroxide

$hkl^a$	$d$ ( $\text{\AA}$ )	$d$ ( $\text{\AA}$ )			
		$\alpha$ -Co(OH) <sub>2</sub>	Co–Al LDH		Co–Cr LDH
			Fresh	Aged	Aged
0 0 3	7.73	7.79	7.56	7.56	
0 0 6	3.95	3.92	3.82	3.78	
1 0 1	2.60(b)			2.742	
0 1 2		2.605	2.586	2.60	
0 1 5	2.319	2.339	2.310	2.46	
0 1 8		1.972	1.938		
1 1 0		1.545	1.537		
1 1 3		1.522	1.491		
Cell parameters ( $\text{\AA}$ )	$a = 3.09$ $c = 23.3$	$a = 3.09$ $c = 23.52$	$a = 3.07$ $c = 22.92$	$a = 3.09$ $c = 22.68$	

<sup>a</sup> The data were indexed according to these  $hkl$  values on a hexagonal cell.

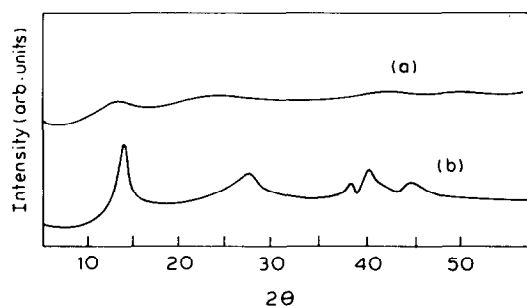


Fig. 3. Powder X-ray diffractogram of (a) as-prepared and (b) aged layered double hydroxide of cobalt with chromium.

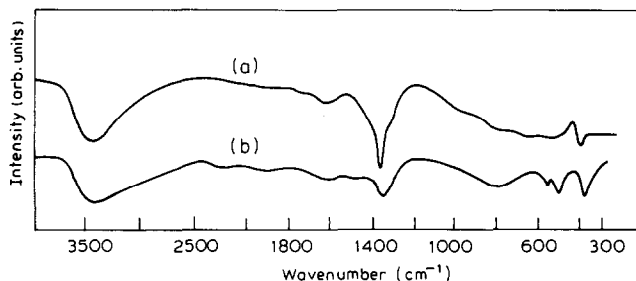


Fig. 4. Infrared spectra of the layered double hydroxides of cobalt with (a) aluminium and (b) chromium.

hydroxides of cobalt with iron and manganese could not be characterized unambiguously.

The IR spectra of the LDHs of cobalt with aluminium or chromium are given in Fig. 4. The spectra show absorptions in three regions that are characteristic of  $\alpha$ -cobalt hydroxide [7], i.e.: (i) a broad band centred around  $3400\text{ cm}^{-1}$  due to OH-stretching of the hydrogen bonded hydroxyl groups; (ii) strong absorption in the  $1600$  to  $1000\text{ cm}^{-1}$  region due to intercalated anions, and (iii) bands in the  $800$  to  $200\text{ cm}^{-1}$  region due to the in-plane and out-of-plane OH-bending vibrations and the metal–oxygen stretching. The IR spectrum of  $\beta$ - $\text{Co}(\text{OH})_2$  is quite different [7]. The hydroxyl groups are not hydrogen bonded and there are no vibrations due to intercalated anions. It is therefore evident that, even in terms of a short-range structure, the LDHs of cobalt with aluminium or chromium are closely related to  $\alpha$ - $\text{Co}(\text{OH})_2$ .

CVs for thin films of the LDHs of cobalt with aluminium or chromium, together with that of pure cobalt hydroxide, are presented in Fig. 5. In the  $-1.0$  to  $-0.3\text{ V}$  range of switching potentials (not shown here), pure and doped hydroxides of cobalt display an irreversible anodic peak. In the  $-0.2$  to  $0.65\text{ V}$  range, however, there is one anodic and one cathodic peak. This is in keeping with earlier studies [12]. While the peak positions of the cobalt–chromium LDH are similar to those of pure cobalt hydroxide, the anodic and cathodic peaks of the cobalt–aluminium LDH are shifted to positive potentials by about  $300\text{ mV}$  (Table 2). The reversible potential,  $E_{\text{rev}}$  (estimated as an average of the anodic and cathodic peak potentials), is  $468\text{ mV}$  for the cobalt–aluminium electrode compared with  $150\text{ mV}$  for the pure cobalt hydroxide electrode. The redox reactions of the LDHs of cobalt are quasi-

reversible, as demonstrated by the large difference in the anodic and cathodic peak potentials.

As doping with aluminium causes a significant change in the electrochemical properties of cobalt hydroxide, the CVs of the resulting LDHs were studied as a function of aluminium composition (Fig. 6). The  $10\text{ wt.}\%$  aluminium-substituted LDH has two anodic peaks; the first at  $200\text{ mV}$  corresponds to that of pure cobalt hydroxide; the second is at  $425\text{ mV}$ . The  $20\text{ wt.}\%$  aluminium-substituted LDH shows a major peak at  $520\text{ mV}$  and corresponds to the LDH phase.

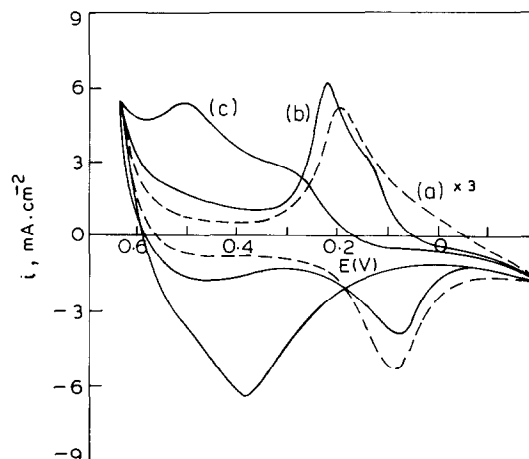


Fig. 5. Cyclic voltammograms of electrosynthesized thin films of (a) cobalt hydroxide, (b) cobalt–chromium and (c) cobalt–aluminium LDHs.

Table 2  
Cyclic voltammetric data of pure and layered double hydroxides of cobalt

Sample	Peak potentials <sup>a</sup> (mV)		$E_{\text{rev}}$ (mV)	$\Delta E_{\text{a,c}}$ (mV)
	Anodic	Cathodic		
Co	210	90	150	120
Co–Al	525	410	468	115
Co–Cr	235	100	168	135

<sup>a</sup> All potentials are with respect to a Hg/HgO (1 M KOH) reference electrode.

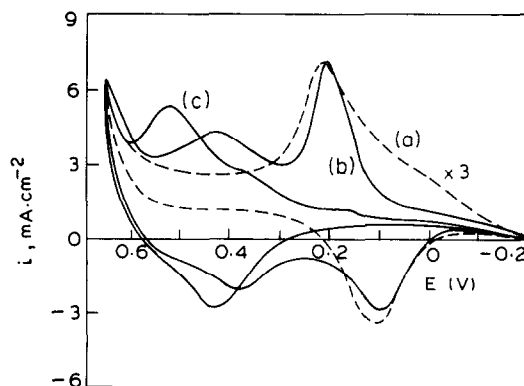


Fig. 6. Cyclic voltammograms for layered double hydroxides of cobalt with (a) 0, (b) 10, (c) 20 mol% aluminium, respectively.

#### 4. Discussion

Hydroxides of cobalt are receiving increased attention following the work of Glemser and co-workers [8] who have chemically stabilized cobalt hydroxide doped with aluminium or iron in strong alkali. Glemser's compound,  $[\text{Co}_4\text{Al}(\text{OH})_{10}\text{Cl}] \cdot 4\text{H}_2\text{O}$ , is one of a series of LDHs of the general formula  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2\text{A}_{x/n}{}^{n-}] \cdot m\text{H}_2\text{O}$  with  $x=0.2$ . Several minerals, such as hydrotalcite, pyroaurite, reevesite, takovite [13], belong to this series and differ from one another in the identity of the metals involved and the value of  $x$ .

Glemser and co-workers [8] have reported significant charge capacity and cycle life for the double hydroxides of cobalt with aluminium or iron. This suggests the possibility of using these materials as positive electrodes in alkaline secondary cells. It is practically important that some of these LDHs can be electrosynthesized in a single-step, nitrate reduction reaction [9]. Electrode fabrication by electrochemical impregnation of porous metal plaques can now be attempted for the widespread use of these candidate electrode materials. Unfortunately, our attempts to prepare the LDH of cobalt with iron have not proved successful, although others have reported a synthesis by chemical precipitation [14].

The LDHs of cobalt are isostructural with  $\alpha$ -cobalt hydroxide, but have the advantage of being resistant to both dissolution and ageing in strong alkali. A similar observation has been made for the nickel system [15]. The LDHs can therefore be called stabilized  $\alpha$ -forms of cobalt hydroxide. The stabilization is brought about by the intercalation of anions with enhanced strength between the positively charged hydroxide layers. The anions anchor the layers together and, thereby, prevent both dissolution and ageing. The anions can be identified by their fingerprint absorptions in the IR spectra [16]. On the other hand, no anions are intercalated in  $\beta$ -cobalt hydroxide and the anion content of the  $\alpha$ -form is expected to be less than 5 mol%.

It is particularly promising that the electrosynthesized LDHs are electrochemically active and exhibit peaks due to a quasi-reversible charge-storage reaction in their CV. As with pure cobalt hydroxide, all these LDHs, show two anodic peaks and one cathodic peak. The first anodic peak ( $-665$  mV) is irreversible in all hydroxides of cobalt and, hence, has not been discussed here. It is therefore anticipated that the LDHs of cobalt will exhibit poorer charge capacities compared with their nickel counterparts. This expectation has been vindicated by a comparison of Glemser's data with those for the LDHs of nickel [15].

#### 5. Conclusions

The above study has shown that:

1. Layered double hydroxides of cobalt with aluminium and chromium can be electrosynthesized by a simple one-step nitrate reduction reaction.
2. The layered materials are isostructural with  $\alpha$ -cobalt hydroxide and exhibit chemical and structural stability to ageing in strong alkali.
3. The layered materials retain electrochemical activity and are candidate electrode materials for alkaline secondary cells.

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