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Electrochemical synthesis of α-cobalt hydroxide

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Cathodic reduction of an aqueous solution of cobalt nitrate at low pH, high Co(II) ion concentration ($\geqslant 1$ M) and low current densities (<0.3 mA cm^{-2}) leads to the formation of a novel layered hydroxide of Co(II) with an interlayer spacing of 8.93 Å. This hydroxy deficient phase is structurally and compositionally related to α-nickel hydroxide, but likely contains Co(II) ions in a mixed octahedral/tetrahedral coordination. Under other deposition conditions, the better known β-cobalt hydroxide ($a = 3.17 \pm 0.01$ Å, $c = 4.61 \pm 0.02$ Å) is obtained.

Cobalt(II) hydroxide is isostructural with the mineral brucite [$Mg(OH)_2$] and consists of a hexagonal packing of hydroxy ions with Co(II) occupying alternate rows of octahedral sites.[1] Other bivalent hydroxides[2] also adopt this structure, most notable among them being β-nickel hydroxide.[3] Hydroxides of Co(II) and Ni(II) are widely employed as electrode materials in alkaline secondary batteries.[4–6]

The hydroxides of Ni(II) can be stabilized in different polymorphic modifications,[7,8] and important among these is α-nickel hydroxide. The α-hydroxide is a hydroxy deficient compound and consists of a stacking of positively charged layers of composition $[Ni(OH)_{2-x}(H_2O)_x]^{x+}$, which intercalate anions and water molecules in the interlayer region to restore charge neutrality.[9,10] Consequently, the α-hydroxides have a higher interlayer spacing (7.5–8 Å) compared to the brucite-like β-hydroxides (4.6 Å). The α-hydroxide of nickel, though unstable in an alkaline electrolyte, is theoretically expected to exhibit superior electrochemical properties compared to the β-form.[7] However, a corresponding α modification of the hydroxide of Co(II) has not been reported. Our earlier attempts[11,12] to synthesize α-cobalt hydroxide yielded poorly crystalline materials with the attendant problems of characterization.

Among the many synthetic routes[13,14] to α-nickel hydroxide, the electrochemical route[15] by the cathodic reduction of an aqueous nickel nitrate solution is the best known and is widely employed in the fabrication of battery electrodes.[16,17] In a recent investigation[18] of the factors governing the electrosynthesis of α-nickel hydroxide, we have found that conditions that promote chemical corrosion of the electrode, also promote the electrodeposition of α-nickel hydroxide. The product of chemical corrosion, which takes place simultaneously with the electrodeposition, is a poorly ordered layered phase which is structurally similar to α-hydroxide and provides nucleation sites for the deposition of the latter. One of the best ways to verify this hypothesis is to extend the corrosive electrosynthesis of α-hydroxide to a system where polymorphism is unknown. Here, we have chosen the hydroxides of Co(II) and report the electrochemical synthesis of the α-hydroxides of Co(II) from a corrosive cobalt nitrate bath having a low pH and high Co(II) concentration, by the use of a corrodable electrode such as mild steel or cobalt metal at low current densities. The products obtained are stable to aging and work up.

Experimental

Synthesis

All cobalt hydroxides were prepared electrochemically in a divided cell by cathodic reduction of a 1 M cobalt(II) nitrate solution (pH before electrolysis, 2.6) using mild steel, cobalt or platinum cathodes. The anode chamber was filled with a 1 M potasssium nitrate solution and a platinum foil was used as an anode. The synthesis was carried out galvanostatically at different current densities (0.1–20 mA cm^{-2}), for 17 h and the product electrodeposited at the cathode was scraped or filtered, washed and dried to constant weight at room temperature.

Wet chemical analysis

The cobalt content in the cobalt hydroxide was determined themogravimetrically. The total base content (OH^-) was estimated by dissolving a known quantity of the sample in excess hydrochloric acid and back titrating the excess acid with a standard solution of sodium hydroxide using a pH meter.[12] Analysis revealed that all samples were hydroxide deficient. The hydroxy deficiency was compensated by the inclusion of nitrate ions. The unaccounted mass was assigned to the water content to arrive at an approximate formula.

Characterization

All the samples were characterized by powder X-ray diffractometry (JEOL Model JDX 8P Powder diffractometer, CoKα radiation, $\lambda = 1.79$ Å), IR spectroscopy (Nicolet Model IMPACT 400D FTIR spectrometer, KBr pellets, 3 cm^{-1} resolution), UV–VIS spectroscopy (Pye Unicam spectrometer, reflectance mode) and themogravimetry (TG) (lab-built system; heating rate 2.5 °C min^{-1}).

Results and discussion

Fig. 1 shows the powder X-ray diffractograms of the cobalt hydroxides electrosynthesized under different conditions. The sample obtained at a high current density (20 mA cm^{-2}) using an inert platinum electrode shows prominent reflections at 4.61, 2.74, 2.36, 1.77 and 1.59 Å, respectively. This pattern matches well with that assigned to brucite-like β-cobalt hydroxide (PDF: 30–0443) and can be indexed on a hexagonal cell ($a = 3.17 \pm 0.01$, $c = 4.61 \pm 0.02$ Å). The cobalt hydroxide obtained at a low current density (0.15 mA cm^{-2}) using a reactive cobalt electrode, on the other hand has prominent reflections at 8.93, 4.47, 2.70 and 1.56 Å, respectively. Of these, the first two reflections are sharp, and can be assigned to (00*l*) ($l = 1,2$). The reflections at 2.70 and 1.56 Å are both broad, with a sharp rise in intensity followed by a pronounced asymmetry on the higher angle side. These 'saw-tooth' reflections are typical of turbostratic phases which are ordered in two dimensions, but whose layers are orientationally disordered. They can be assigned to the 2-D (10) and (11) reflections respectively. Table 1, lists the prominent *d*-spacings. To the best of our knowledge there are no known phases of cobalt hydroxide having such a XRD pattern. However, these

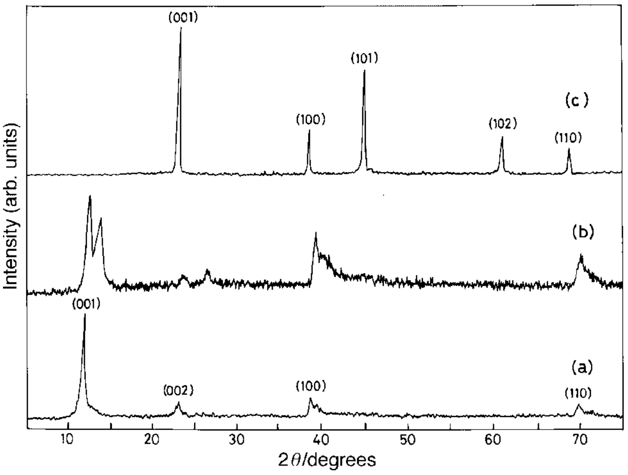

Fig. 1 PXRD patterns of cobalt(II) hydroxides electrosynthesized at (a) low, (b) moderate and (c) high current densities.

Table 1 Powder X-ray diffraction data for the electrosynthesized α- and β cobalt(II) hydroxides

	α-Co(OH)$_2$		β-Co(OH)$_2$	
hkl[a]	d_{calc}/Å	d_{obs}/Å	d_{calc}/Å	d_{obs}/Å
001	8.93	8.93	4.61	4.61
002	4.47	4.47	—	—
100	2.71	2.70	2.75	2.74
101	—	—	2.36	2.36
102	—	—	1.77	1.77
110	1.57	1.56	1.59	1.59
a/Å	3.12±0.01		3.17±0.01	
c/Å	8.93±0.08		4.61±0.02	

[a] The patterns were indexed according to these *hkl* values on a hexagonal cell.

characteristics are very similar to those observed for α-nickel hydroxide. Therefore we refer to this phase as α.

At intermediate current densities (0.3 mA cm^{-2}) an additional pair of lines are seen at 7.91 and 3.98 Å respectively, corresponding to another phase with a lower interlayer spacing. However no additional lines due to the (*hk*) reflections of this second phase can be seen. It was also not obtained as a single phase product.

Table 2 lists the results of wet chemical analysis of the α and β phases of cobalt(II) hydroxide. While the β-phase is stoichoimetric and corresponds to the formula Co(OH)$_2$; the α-phase is hydroxy deficient with an approximate empirical formula $Co(OH)_{1.8}(NO_3)_{0.2}\cdot 0.67H_2O$ which is very similar to that of α-nickel hydroxide.[10] Evidence for nitrate incorporation can be found in the IR spectra (Fig. 2). The α-phase shows strong absorptions at 1491(ν_4), 1393(ν_3) and 1357(ν_1) cm^{-1} together with a weak doublet at 825 and 880 cm^{-1}, which is characteristic of nitrate ion intercalated in C_{2v} symmetry. The β-phase does not show any significant absorption in this region in keeping with what is expected of its formula except for weak peaks due to trace amounts of adsorbed nitrate. Intercalated nitrate ions can be either grafted to the layers or hydrogen bonded. The former is a strong interaction, which causes a large (250 cm^{-1}) splitting between the ν_4 and ν_1 vibrations of the nitrate.[10] In the present instance, the splitting is smaller (135 cm^{-1}), which is characteristic of nitrate ions hydrogen bonded to the hydroxide slabs. The other absorptions in the high (3700–3000 cm^{-1}) and low (800–400 cm^{-1}) frequency regions are in keeping with the expectation of hydrogen bonded hydroxy groups in the α-phase and free hydroxy groups in the β-phase. Similar spectra are observed in the nickel system and detailed assignments are given elsewhere.[14]

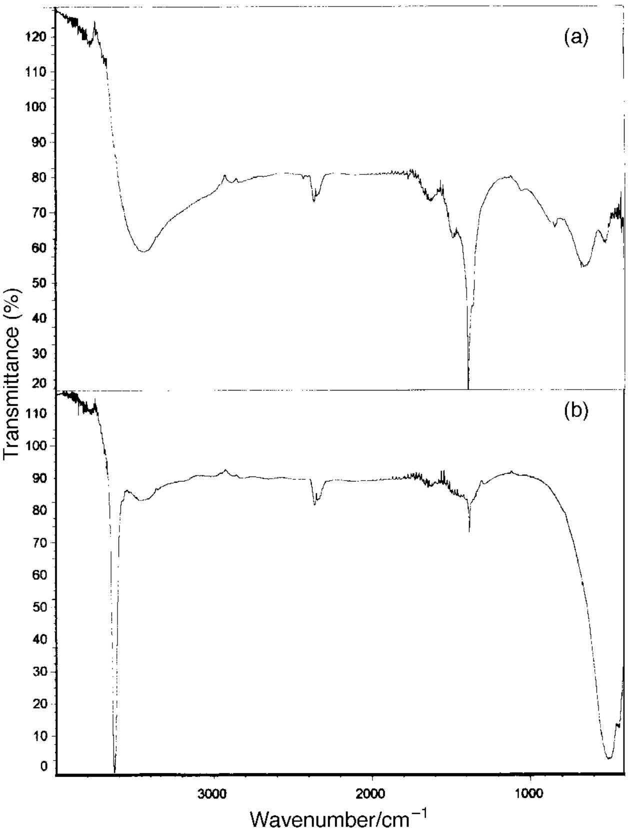

Fig. 2 IR spectra of electrosynthesized (a) α- and (b) β-cobalt(II) hydroxides, respectively.

Fig. 3 shows the TG data for α- and β-cobalt hydroxides.

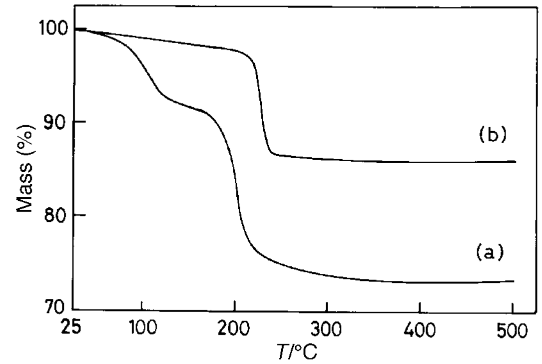

Fig. 3 Thermogravimetric data of electrosynthesized (a) α- and (b) β-cobalt(II) hydroxides, respectively.

Table 2 Chemical compositions of electrosynthesized α- and β-cobalt(II) hydroxides

Electrodes used for synthesis	Current density/ mA cm^{-2}	Approximate formulae[a]	Total weight loss (%)	
			Expected	Observed[b]
Cobalt	0.15	$Co(OH)_{1.8}(NO_3)_{0.2}\cdot 0.67H_2O$	29.6	29.5
Platinum	20	Co(OH)$_2$	13.6	13.4

[a] Results from wet chemical analysis. [b] From TG analysis.

In both cases the final product of decomposition is Co_3O_4 ($a = 8.1$ Å). The β-phase undergoes a single step weight loss (expected: 13.6%; observed: 13.4%), while the α-phase undergoes a two step weight loss due to dehydration and decomposition respectively. The net weight loss observed (29.5%) is consistent with what is expected (29.6%) on the basis of the approximate empirical formula.

Structurally and compositionally, the α-sample electrosynthesized by us is similar to α-nickel hydroxide. There is however one major difference. The c parameter of the sample reported here is 8.93 Å, while the c parameter of nickel hydroxide is only 7.6 Å.

The expansion of the c parameter from the value observed in the β-hydroxide (4.6 Å) takes place owing to intercalation of anions. Anions are intercalated to neutralize the positive charge on the hydroxide layers. There are many mechanisms by which a positive charge can be created in the hydroxide layers. The two most relevant to the present context are:

(1) by partial protonation of the hydroxy groups according to the equilibrium

$$Co(OH)_2 + xH^+ \leftrightarrow [Co(OH)_{2-x}(H_2O)_x]^+$$

(2) By partial substitution of an octahedrally coordinated cation by two tetrahedrally coordinated ions on either sides of the octahedral vacancy (see graphical abstract) leading to a layer composition $[(Co^{octa})_{1-x}(Co^{tetra})_{2x}(OH)_2]^{2x+}$ **I**. This model differs from the earlier one in that all crystallographically defined anion sites in the hydroxide layers are occupied by hydroxy ions.

The former mechanism has been invoked in the case of α-nickel hydroxide.[9] Since Co(II) has a relatively strong tetrahedral site preference, stabilization of α-cobalt(II) hydroxide with a mixed octahedral–tetrahedral site occupancy can be envisaged. If this were true, the hydroxide layer would be thicker as the tetrahedral sites would lie outside the layer, leading to a larger c-parameter. A model compound of this type already exists in hydrozincite-like $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$, where 40% of Zn(II) ions ($x = 0.25$ in **I**) occupy tetrahedral sites above and below the hydroxide layers.

The apparent inconsistency between the hydroxy-deficient empirical formula determined in Table 2 and the formula of the hydrozincite-like phase which has no vacancies on the hydroxy sub-lattice can be resolved by formulating the α-hydroxide as $Co_{10}(OH)_{18}(NO_3)_2{\cdot}7H_2O$ where 20% of the Co(II) ions ($x = 0.11$ in **I** above) occupy tetrahedral sites implying a lower occupancy of the tetrahedral sites compared to the mineral hydrozincite.

The partial occupation of tetrahedral sites by the Co(II) ions in the α-hydroxide is indicated by the UV–VIS absorption spectrum (Fig. 4) which shows the signature absorption of tetrahedral Co(II) above 620 nm, while the β-hydroxide exhibits an absorption maximum at 470 nm. The synthesis of a α-cobalt hydroxide with Co(II) in octahedral coordination, isostructural with α-nickel hydroxide is an important synthetic challenge. Such a material would have a lower interlayer spacing in the range 7.6–8.0 Å. Indeed, reflections corresponding to such a phase are obtained along with the α product at intermediate current densities, but this phase could not be obtained in the pure form.

As observed in our earlier study on the nickel system, the electrodeposition of α-cobalt hydroxide is promoted by the chemical corrosion of the electrode simultaneously with the electrochemical deposition. Chemical corrosion[10,18] leads to the formation of basic salts[19,20] which are structurally related[21] to the α-hydroxides and thereby help to nucleate the growth of the latter. When chemical corrosion of the electrode is suppressed, as at high current densities (when hydrogen evolution provides a protective blanket to the electrode), rose red β-$Co(OH)_2$ is electrodeposited.

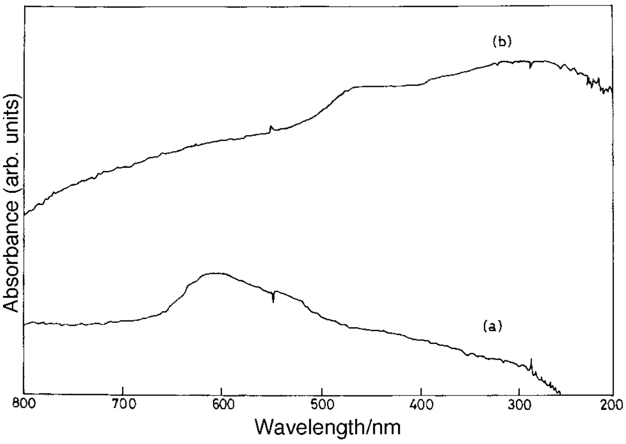

Fig. 4 UV–VIS spectra of electrosynthesized (a) α- and (b) β-cobalt(II) hydroxides, respectively.

In conclusion, we have succeeded in electrosynthesizing α-cobalt hydroxide. In as much as the synthetic conditions were chosen based on the factors governing the electrosynthesis of α-nickel hydroxide, our hypothesis that simultaneous chemical corrosion of the electrode nucleates the growth of α-hydroxides stands vindicated.

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