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# Electrosynthesis of layered double hydroxides of nickel with trivalent cations

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## Abstract

Layered double hydroxides (LDHs) of nickel with aluminium, chromium, manganese and iron, with the same structure as  $\alpha$ -nickel hydroxide, have been electrosynthesized. This paves the way for their possible electrochemical impregnation in sintered nickel plaques for use as electrodes in nickel/cadmium batteries. All these LDHs stabilize the  $\alpha$ -nickel hydroxide structure in alkaline media and retain electrochemical activity, as evidenced by cyclic voltammetric studies. The nickel–aluminium LDH shows the highest coulombic efficiency, while the nickel–iron LDH may prove to be unsuitable as a battery electrode material as it catalyzes oxygen evolution by 50 mV, as compared with pure nickel hydroxide.

*Keywords:* Nickel hydroxides; Layered double nickel hydroxides; Electrosynthesis; Aluminium; Chromium; Manganese; Iron

## 1. Introduction

Among the polymorphs of nickel hydroxide, the  $\alpha$ -form has been shown [1] to have better electrochemical properties than the  $\beta$ -form. The  $\alpha/\gamma$ -couple is also known [2] to exhibit a higher charge capacity and better reversibility compared with the  $\beta(\text{II})/\beta(\text{III})$  couple. The  $\alpha$ -form is a metastable phase and rapidly ages to the  $\beta$ -form [3], and the advantages of the  $\alpha/\gamma$  couple have not been exploited in the nickel/cadmium batteries. Efforts to synthesize  $\alpha$ -nickel hydroxide [4–6] and stabilize it in alkaline media [7–10] have been a major endeavour of battery scientists and technologists for some time. It now appears that a structure similar to that of  $\alpha$ -nickel hydroxide can be stabilized in alkaline media by doping nickel hydroxide with trivalent cations such as aluminium and iron [10–12]. The doped materials are known as layered double hydroxides (LDHs) [13,14]. For the ready application of these new materials as electrodes in alkaline secondary batteries, it is of extreme technological importance to be able to impregnate them in sintered nickel plaques in the manner that nickel hydroxide electrodes are electrochemically fabricated [15–17]. As a background to these efforts, we have attempted to electrosynthesize LDHs of nickel with aluminium, chromium, manganese and iron by cathodic

reduction of nitrate ions from aqueous solution. In this paper, we report electrosynthesis and cyclic voltammetric studies on these LDHs.

## 2. Experimental

All LDHs were synthesized in a one-step deposition process by cathodic reduction of nitrate ions [18] from a mixed-metal nitrate bath (0.3 M total concentration) that contained nickel and the corresponding trivalent metal in a 3:1 ratio. The synthesis was done galvanostatically at a current density of 65 mA cm<sup>-2</sup> that used a platinum flag cathode (surface area 3 cm<sup>2</sup>) in a divided electrochemical cell. A 0.3 M potassium nitrate was used 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 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 nickel hydroxide was prepared under identical conditions, but in the absence of any trivalent cations. The samples were characterized by powder X-ray diffraction, infrared spectroscopy, and cyclic voltammetry.

Powder X-ray diffractograms (XRD) were recorded on a JEOL JDX 8P diffractometer using Cu K $\alpha$  ( $\lambda=1.541$  Å) or Fe K $\alpha$  ( $\lambda=1.937$  Å) radiation.

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The LDHs of nickel with chromium and iron were found to be X-ray amorphous. These were aged in 8 M KOH for fifteen days at ambient temperature [11]. On ageing they order themselves, although poorly, to give XRD patterns that are similar to those of the other LDHs.

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

Cyclic voltammetric measurements were carried out as described elsewhere [19–21] using a PARC model 362 scanning potentiostat hooked on to a Digital Electronics (India) Omnigraph 2000 recorder. For cyclic voltammetric studies, a thin film of the LDH was deposited on a previously cleaned platinum flag ( $1.5 \text{ cm}^2$  surface area) at a current density of  $65 \text{ mA cm}^{-2}$  under exactly the same conditions at which the bulk synthesis was carried out, for a period of 5 to 10 s. The film was rinsed in distilled water and immersed in 50 ml of 1 M KOH in a plastic tank. A platinum flag was used as the counter electrode. Cyclic voltammetry was carried out between switching potentials of 0.0 and 0.7 V with respect to Hg/HgO (1 M KOH) as reference. Up to 40 cycles were recorded at a scan rate of  $5 \text{ mV s}^{-1}$  to check for reproducible behaviour of the film in successive scans, after which a scan was recorded at a rate of  $2 \text{ mV s}^{-1}$  for the purpose of analysis. Three to six fresh films were studied for each composition to establish reproducibility of the film behaviour. Where necessary, the oxygen evolution potential was estimated from the cyclic voltammogram by measuring the potential at a current density of  $6.0 \text{ mA cm}^{-2}$  in the positive-going scan.

### 3. Results

In Fig. 1, we give the powder XRD patterns of the double hydroxides of nickel with aluminium, chromium, manganese and iron and compare them with that of nickel hydroxide synthesized in the absence of any trivalent ions. The XRD pattern of pure nickel hydroxide shows lines at 4.6, 2.7, 2.3 and  $1.75 \text{ \AA}$ , respectively. This pattern matches well with that listed in PDF no. 14-117 and assigned to  $\beta\text{-Ni(OH)}_2$ . The co-deposited nickel–aluminium and nickel–manganese double hydroxides, on the other hand, have a completely different structure and show a low-angle reflexion close to  $8 \text{ \AA}$ , followed by another at around  $4 \text{ \AA}$ . This pattern is characteristic of the chemically prepared LDHs of the formula  $\text{Ni}_{1-x}\text{M}_x^{\text{III}}(\text{OH})_2\text{A}_{x/n}^{n-}\text{yH}_2\text{O}$  ( $\text{M} = \text{Al, Fe}$ ;  $x = 0.25$ ;  $\text{A} = \text{NO}_3^-, \text{CO}_3^{2-}$ , and  $y = 0.66$ ) [10–14]. The  $d$  values are listed in Table 1. The patterns can be indexed on a hexagonal cell of  $a = 3.12 \pm 0.09 \text{ \AA}$  and  $c = 24.84 \pm 1.2 \text{ \AA}$ . The as-prepared LDHs of nickel with chromium and iron were found to be X-ray amorphous.

Table 1  
X-ray powder diffraction data of layered double hydroxides of nickel with trivalent cations

$h k l^a$	$d_{\text{obs}}$ for binary hydroxide samples ( $\text{\AA}$ )			
	Ni–Al	Ni–Cr <sup>b</sup>	Ni–Mn	Ni–Fe <sup>b</sup>
0 0 3	8.309	8 925	7.708	7.836
0 0 6	4.175	4 327	3 948	3.920
1 0 2	2.574	2 736		
1 0 5			2 325	
1 1 0		1 596		
1 1 2	1.502		1 544	
$a$	3.037	3 20	3.115	
$c$	25.074	26 0	23.68	23.52

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

<sup>b</sup>Aged in 8 M KOH for 15 days

Table 2  
Cyclic voltammetric data for electro synthesized thin films of layered double hydroxides of nickel with trivalent cations

Sample	Peak potentials <sup>a</sup> (mV)		$E_{\text{rev}}$ (mV)	$\Delta E_{a,c}$ (mV)	Coulombic efficiency (%)
	Anodic	Cathodic			
Ni	470	390	430	80	77
Ni–Al	510(540)	440	475(490)	70(100)	74
Ni–Cr	455	375	415	80	63
Ni–Mn	425	340	383	85	56
Ni–Fe		445			

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

On ageing in 8 M KOH for 15 days, they were found to order themselves and show an XRD pattern similar to the other LDHs (see Fig. 1 and Table 1). The electro synthesized LDHs seem to have a structure similar to those of samples prepared by chemical synthesis [10–12] and also have a remarkable similarity with that of  $\alpha\text{-Ni(OH)}_2$  [5].

To further confirm this, Fig. 2 gives the infrared spectra of the electro synthesized LDHs. The infrared spectra are useful to probe the short-range structure, and it is seen that the electro synthesized LDHs can be characterized by the presence of: (i) a broad band centred about  $3400 \text{ cm}^{-1}$  due to OH stretching of hydrogen-bonded hydroxyl groups; (ii) strong absorption in the  $1600$  to  $1000 \text{ cm}^{-1}$  region due to the intercalated anions, and (iii) three bands in the  $800$  to  $200 \text{ cm}^{-1}$  region due to the OH in plane ( $620 \text{ cm}^{-1}$ ) and out-of-plane bending ( $370 \text{ cm}^{-1}$ ) and metal oxygen stretching ( $460 \text{ cm}^{-1}$ ) frequencies, respectively. These features are similar to those of chemically prepared LDHs [11] and of electrochemically impregnated  $\alpha\text{-Ni(OH)}_2$  [17].

Cyclic voltammograms for the LDHs are presented in Fig. 3. The LDHs retain electrochemical activity and

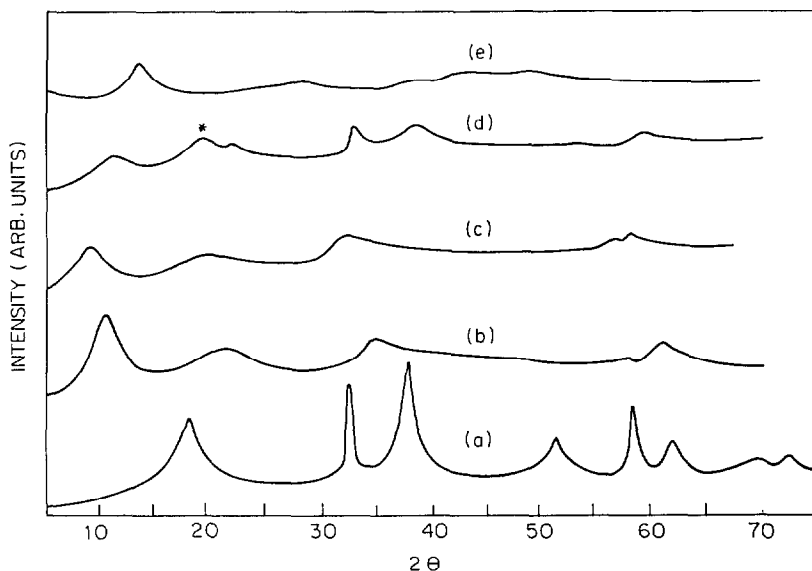


Fig. 1. Powder X-ray diffractograms of: (a)  $\beta$ -nickel hydroxide; double hydroxides of nickel with (b) aluminium, (c) chromium, (d) manganese, and (e) iron. Pattern for nickel-iron LDH recorded with Fe  $K\alpha$  source. Feature marked with asterisk is an impurity peak

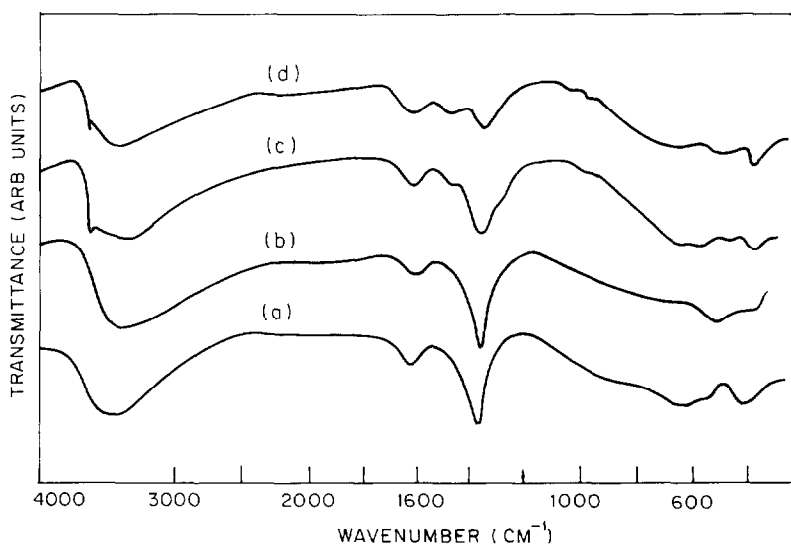


Fig. 2. Infrared spectra of electrosynthesized LDHs of nickel with (a) aluminium, (b) chromium, (c) manganese, and (d) iron. Curve (d) is for an aged sample.

as in case of pure nickel hydroxide [1,21], exhibit one anodic and one cathodic peak. The peak positions, the difference in the anodic and cathodic peak potentials ( $\Delta E_{a,c}$ ),  $E_{rev}$  (estimated as the average of anodic and cathodic peak potentials) and the coulombic efficiency (defined as ratio of the cathodic to anodic peak areas [22]) are listed in Table 2, and compared with that of pure nickel hydroxide. The peak potentials of the electrosynthesized LDHs are considerably shifted when compared with that of pure nickel hydroxide. The nickel-aluminium LDH shows a split anodic peak and the features are shifted by about 50 to 70 mV to more positive potentials compared with pure nickel hydroxide. In the nickel-manganese case, the shift is towards more negative potentials by a similar amount. In the

nickel-chromium LDH, the features appear at potentials similar to that of pure nickel hydroxide. With the nickel-iron LDH, the anodic peak could not be identified due to catalysis of the oxygen-evolution reaction and the merging of the two features in the cyclic voltammogram. The coulombic efficiencies are also considerably different in the LDHs compared with pure nickel hydroxide. The nickel-aluminium hydroxide exhibits an efficiency of more than 70%, while the LDHs of nickel with chromium and manganese show lower efficiencies. The coulombic efficiency of the nickel-iron LDH cannot be estimated due to the overlapping of the oxygen evolution current with that of the anodic peak current. The nickel-aluminium LDH has an  $E_{rev}$  positive with respect to that of pure nickel hydroxide and a coulombic

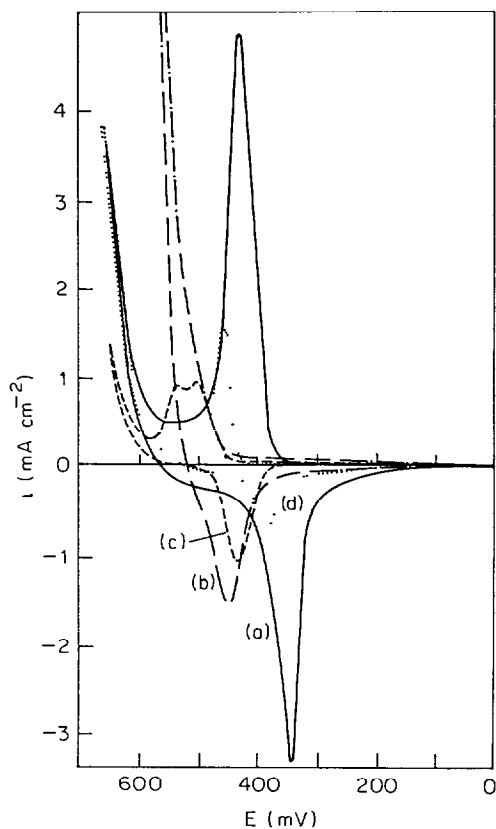


Fig 3 Cyclic voltammograms for films of electrosynthesized LDHs of nickel with: (a) manganese, (b) iron, (c) aluminium, and (d) chromium

efficiency of more than 70%. It is evident that this LDH holds great promise as an electrode material [10], while the nickel–chromium behaves somewhat similar to pure nickel hydroxide. The nickel–manganese LDH has a lower  $E_{rev}$  value and can be charged at a lower potential. The nickel–iron LDH is found to catalyse dramatically the oxygen-evolution reaction by 50 mV compared with  $\beta$ -nickel hydroxide at a oxygen-evolution current of  $6.0 \text{ mA cm}^{-2}$ . This material is currently being studied in detail for possible application as an electrode material for water electrolysis. It is unlikely to be of much use as an electrode material for nickel/cadmium battery applications.

#### 4. Discussion

Electrogeneration of the base by cathodic reduction of nitrate ions has been widely used for electrochemical impregnation of  $\alpha$ -nickel hydroxide for electrode fabrication [15–17,23]. In an earlier study, we extended this technique for the synthesis of numerous simple and complex hydroxides [18] including the synthetic hydrotalcites. We also reported the electrosynthesis of  $\text{Al}(\text{OH})_3$ ,  $\gamma\text{-Mn}_2\text{O}_3$  and green  $\text{Cr}(\text{OH})_3$  by the electroreduction of the corresponding nitrates. The green

chromium hydroxide was found to be completely X-ray amorphous, while electroreduction of ferric nitrate did not yield any solid product.

On co-deposition with nickel from a mixed-metal nitrate bath, aluminium, chromium, manganese and iron can be nearly quantitatively precipitated out. The resultant products in the case of aluminium and manganese are found to stabilize in the LDH structure, similar to that of chemically prepared samples [10–12] and of  $\alpha$ -nickel hydroxide. The nickel–chromium and nickel–iron double hydroxides are X-ray amorphous. It has been observed [18] that if one of the components is X-ray amorphous, the complex hydroxide will also be X-ray amorphous. On ageing, however, poorly ordered materials develop with XRD patterns similar to those of the other LDHs. It is thus observed that while  $\alpha$ -nickel hydroxide decomposes to the  $\beta$ -form on ageing in alkaline media [3], the LDHs order themselves better in the  $\alpha$ -nickel hydroxide structure on ageing under similar conditions. This phenomenon can be attributed to the presence of adequate intercalated anions in the LDHs that serve to anchor the brucite-like hydroxide layers together [10]. Nevertheless, all of these phases are poorly ordered, as is evident from the broad peaks in the XRD patterns.

The infrared spectra of the electrosynthesized LDHs show all the essential features observed in the chemically prepared LDHs [11]. The as-prepared LDHs exhibit characteristic absorptions due to nitrate ions intercalated in the  $C_{2v}$  symmetry [11] ( $1470, 1380, 1300, 980 \text{ cm}^{-1}$ ). After ageing, the samples intercalate carbonate ions ( $1460, 1350 \text{ cm}^{-1}$ ) that have absorptions with a different peak shape.

It is significant that the electrosynthesized LDHs are electrochemically active. The shift towards positive potential of the  $E_{rev}$  in the case of the nickel–aluminium LDH is slightly disappointing, but its high coulombic efficiency is a sign of greater reversibility in electrode reactions. The nickel–manganese LDH has a negative shift in  $E_{rev}$ , and therefore can be charged at a lower potential. On the other hand, it has a poorer coulombic efficiency. The behaviour of the nickel–chromium LDH is somewhat similar to that of pure  $\beta$ -nickel hydroxide. The nickel–iron LDH catalyses oxygen evolution and is therefore of greater use in electrolyzers and is unsuitable as an electrode material for nickel/cadmium batteries.

#### 5. Conclusions

The above studies have shown that:

1. The double hydroxides of nickel with aluminium, chromium, manganese and iron can be electrosynthesized and, therefore, it is possible to electrochemically impregnate sintered nickel plaques with these materials.

2. The electrosynthesized double hydroxides have structural features that are similar both to the chemically synthesized double hydroxides and to  $\alpha$ -nickel hydroxide.

3. The electrosynthesized LDHs are electrochemically active, stable in alkaline media and are candidate materials for nickel/cadmium battery applications.

4. Among the electrosynthesized materials, the nickel–aluminium LDH is a promising material as an electrode for nickel/cadmium batteries, while the nickel–iron LDH holds promise as an electrode for electrolysis of water.

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### References

- [1] P. Oliva, J. Leonardi, J.F. Laurent, C. Delmas, J.J. Braconnier, M. Figlarz and F. Fievet, *J. Power Sources*, **8** (1982) 229.
- [2] R. Barnard, C.F. Randall and F.L. Tye, *J. Appl. Electrochem.*, **10** (1980) 109.
- [3] A. Delahaye-Vidal and M. Figlarz, *J. Appl. Electrochem.*, **17** (1987) 589.
- [4] S. Le Bihan, J. Guenot and M. Figlarz, *C R Acad. Sci., Ser C*, **270** (1970) 2131.
- [5] J.J. Braconnier, C. Delmas, C. Fouassier, M. Figlarz, B. Beaudouin and P. Hagenmuller, *Rev. Chim. Miner.*, **21** (1984) 496.
- [6] P. Genin, A. Delahaye-Vidal, F. Portemer, K. Tekia-Elhissen and M. Figlarz, *Eur J Solid State Inorg Chem.*, **28** (1991) 505.
- [7] P.V. Kamath, J. Ismail, M.F. Ahmed, G.N. Subbanna and J. Gopalakrishnan, *J. Mater. Chem.*, **3** (1993) 1285.
- [8] C. Faure, C. Delmas, M. Fouassier and P. Willmann, *J. Power Sources*, **35** (1991) 249.
- [9] C. Faure, C. Delmas, M. Fouassier and P. Willmann, *J. Power Sources*, **35** (1991) 291.
- [10] C. Faure, C. Delmas and P. Willmann, *J. Power Sources*, **35** (1991) 263.
- [11] P.V. Kamath, M. Dixit, L. Indra, A.K. Shukla, V.G. Kumar and N. Munichandriah, *J. Electrochem. Soc.*, in communication.
- [12] K.T. Ehlissen, A. Delahaye-Vidal, P. Genin, M. Figlarz and P. Willmann, *J. Mater. Chem.*, **3** (1993) 883.
- [13] L. Demauges-Guerlou, J.J. Braconnier and C. Delmas, *J. Solid State Chem.*, **104** (1993) 359.
- [14] W.T. Reichle, *J. Catal.*, **101** (1986) 547.
- [15] W.T. Reichle, *Solid State Ionics*, **22** (1986) 135.
- [16] K.C. Ho, *J. Electrochem. Soc.*, **134** (1987) 52C.
- [17] K.C. Ho and J. Jorne, *J. Electrochem. Soc.*, **137** (1990) 149.
- [18] F. Portemer, A. Delahaye-Vidal and M. Figlarz, *J. Electrochem. Soc.*, **139** (1992) 671.
- [19] L. Indra and P.V. Kamath, *J. Mater. Chem.*, **4** (1994) in press.
- [20] J. Ismail, M.F. Ahmed and P.V. Kamath, *J. Power Sources*, **36** (1991) 507.
- [21] J. Ismail, M.F. Ahmed and P.V. Kamath, *J. Power Sources*, **41** (1993) 223.
- [22] P.V. Kamath and M.F. Ahmed, *J. Appl. Electrochem.*, **23** (1993) 225.
- [23] D.A. Corrigan and R.M. Bendert, *J. Electrochem. Soc.*, **136** (1989) 723.
- [24] B. Mani and J.P. de Neufville, *J. Electrochem. Soc.*, **135** (1988) 800.