

Layered double hydroxides of Ni with Cr and Mn as candidate electrode materials for alkaline secondary cells

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Abstract

Nickel-based layered double hydroxides (LDHs) having the composition $\text{Ni}_{1-x}\text{M}_x^{\text{III}}(\text{OH})_2(\text{A}^{n-})_{x/n} \cdot z\text{H}_2\text{O}$ ($x = 0.2\text{--}0.33$, $\text{M}^{\text{III}} = \text{Al, Fe, Co}$) are isostructural with α -nickel hydroxide, stable to aging in alkali and deliver reversible discharge capacities corresponding to the α/γ couple. The LDHs of Ni with Cr and Mn are also electrochemically active and deliver capacities of 500 (Ni–Cr), 400 (Ni–Mn, $x = 0.2$) and 430 (Ni–Mn, $x = 0.1$) mAh g^{-1} of Ni, respectively, while control electrodes of β_{bc} (bc: badly crystalline)-nickel hydroxide deliver only 335 mAh g^{-1} . © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nickel hydroxide, the positive electrode material of Ni-based alkaline secondary cells exists in two polymorphic modifications known as α and β [1]. α -Nickel hydroxide comprises positively charged nickel hydroxide slabs with anions intercalated for charge neutrality and stability [2]. This results in an increase in the interplanar distance from 4.6 Å observed in β -nickel hydroxide to 7.6 Å in α -nickel hydroxide.

The positive charge is due to the partial protonation of the hydroxyl slabs in the brucite structure according to the equilibrium:



The larger interplanar distance in the α -phase facilitates the easy intercalation and deintercalation of protons and alkali metal ions between the layers during electrochemical cycling. Thus, the α/γ couple which involves a 1.7 e^- exchange is superior to the β/β couple which involves only a 1 e^- exchange [1]. Since, α -nickel hydroxide ages to β -nickel hydroxide in the alkaline medium, the α/γ couple has not been utilized in nickel-based alkaline secondary cells.

Structurally as well as functionally, α -nickel hydroxide behaves as an anionic clay [2] and exchanges the intercalated anions for hydroxyl ions from the alkaline electrolyte.

In addition, the highly dehydrating nature of the concentrated alkali extracts the intercalated water from the interlayer region. This leads to a topotactic transformation of α to β modification. This transformation is evocative of the cation exchange reactions observed in the smectite family of clays.

In the smectite family of clays, when the negative charge on the layers is higher than a critical value, as seen in the micas, the Coulombic attraction between the layers and the intercalated cations becomes very large and the ion-exchange property is lost [3]. Using the same principle, stabilization of α -nickel hydroxide has been achieved by increasing the positive charge on the nickel hydroxide slabs by partial isomorphous substitution of Ni(II) with a suitable trivalent cation (M) to yield a layer composition of $[\text{Ni}_{1-x}\text{M}_x^{\text{III}}(\text{OH})_2]^{x+}$. Carbonates are generally included for charge compensation. Earlier work reported from this laboratory [4] has shown that when $x \geq 0.2$, carbonate exchange for hydroxyl ions from the alkaline electrolyte can be suppressed and this stabilizes the α -phase in concentrated alkali. The carbonates anchor the layers at an interlayer distance of 7.6 Å. Materials of this type with a composition of $\text{Ni}_{1-x}\text{M}_x^{\text{III}}(\text{OH})_2(\text{CO}_3)_{x/2} \cdot z\text{H}_2\text{O}$ ($x = 0.15\text{--}0.33$) are referred to as layered double hydroxides (LDHs).

A variety of Ni-based LDHs such as Ni–Al [4–7], Ni–Co [8–10], Ni–Fe [11–13] and Ni–Mn [14–16] have been studied as cathode materials. In each case, the LDHs have delivered superior charge storage capacities compared with β -nickel hydroxide.

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The motivation for the present work is the following.

- (1) Ni–Cr LDHs have been recently described by Ulibarri and co-workers [17]. We were interested in investigating the electrochemical properties of this new LDH and to determine its suitability as a candidate cathode material for nickel-based alkaline secondary cells.
- (2) In LDH materials, the trivalent ions replace 20% of the nickel ions and are electrochemically inactive and thus adversely affect the theoretical gravimetric capacity of the active material. If a tetravalent cation such as Mn could be employed, the requisite positive charge to impart stability to the α -phase could be generated by replacing only 10% of the nickel ions with Mn(IV), and thus the gravimetric capacity of the electrode material would be enhanced.

In this paper, we report our investigations on the LDHs of Ni with Cr(III), Mn(III) and Mn(IV).

2. Experimental

All LDHs were prepared using Reichle's procedure [18]. Aqueous solutions of Cr(III) and Mn(II) nitrates were used as the sources of Cr(III) and Mn(III, IV), respectively. Stoichiometric mixtures of metal nitrates (Ni/Cr = 0.8/0.2, Ni/Mn = 0.8/0.2 and Ni/Mn = 0.9/0.1) were added to a mixture of NaOH and Na₂CO₃. In the case of Mn samples, 10 times the required quantity of 6% H₂O₂ was added to the mixed metal nitrate mixture to oxidize Mn(II) to its higher oxidation states. The stoichiometric requirement of NaOH together with three times the required quantity of Na₂CO₃ was used to provide the anions. The slurry obtained by the addition of mixed metal nitrates to alkali was aged in the mother liquor for 18 h at 65 °C. The precipitate was then washed free of alkali using large portions of distilled water and dried to constant weight.

All materials were characterized by powder X-ray diffraction (JEOL JDX 8P powder X-ray diffractometer, Co K α source, $\lambda = 1.79$ Å), infrared spectroscopy (Nicolet Impact 400D FT-IR spectrometer, KBR pellets, 4 cm⁻¹ resolution) and thermogravimetric studies (lab. built system, heating rate, 5 °C min⁻¹).

2.1. Wet chemical analysis

Estimation of chromium dissolved in electrolyte: The electrolyte was neutralized with 1:1 HNO₃, treated with 10 ml of acetate buffer (6 M in acetic acid + 0.6 M in sodium acetate), and then with 10 ml of 3.5% lead nitrate solution to precipitate chromate as PbCrO₄. The precipitate of PbCrO₄ was collected in a pre-weighed sintered crucible, washed, dried and weighed to constant weight at 120 °C.

Estimation of oxidation state of Mn: Accurately weighed portions of the LDHs were treated with ferrous ammonium sulfate (FAS) (strength, 0.1N) and the excess FAS was

potentiometrically titrated against a standard K₂Cr₂O₇ (0.1N) solution.

2.2. Electrochemical studies

The LDH was mixed with graphite, Co powder and PTFE (33% aqueous suspension) in the ratio 50:20:20:10 and thoroughly ground to a paste-like consistency. Control electrodes of highly active, poorly crystalline β -nickel hydroxide were prepared by mixing with the same ingredients in the ratio 60:15:15:10 [19]. LDH and control electrodes were also studied in the absence of Co by using a mix composition of 60:30:10. The above paste was pressed onto a nickel foam (2.9 cm \times 2.3 cm) at 120 kg cm⁻² pressure at room temperature. The electrodes were soaked in 6 M KOH for 24 h and galvanostatically charged (Spectrum Engineers, India, dc power supply; Optoprecision, India, milliammeter) to 200% overcharge of the theoretical capacity of 1.7 e⁻ exchange per Ni. This corresponds to the capacity of the α/γ couple. Nickel plates were used as counter electrodes and all potentials were measured using a Hg/HgO/OH⁻ (6 M KOH) reference electrode (Meco, India, high impedance voltmeter). The electrodes were discharged at approximately the C rate to a cut-off voltage of 0 V at ambient temperature (28–30 °C). All discharge capacities are reported normalized to the Ni content in the electrode materials.

3. Results and discussion

3.1. LDH of Ni with Cr(III)

The hydroxide of Cr(III) has not been well characterized. Strong alkali precipitation from solutions of Cr(III) salts yields a dirty green gel of Cr(III) oxide. It is therefore not surprising that the LDHs of divalent metals such as Mg, Co, Ni and Cu with Cr(III) had not been described until recently. Simple co-precipitation reactions result in X-ray amorphous gels. Such a material was obtained by precipitation from a mixed [Ni(II) and Cr(III)] metal nitrate solution. Since the electrochemical activity of electrode materials is enhanced by engineering structural disorder [20] into them, we used the as-prepared gel for electrochemical studies.

The gel was aged in strong alkali (6 M KOH) for 15 days to study its chemical stability. The absence of the β -phase in the aged material clearly suggested the chemical stability of the gel in strong alkali. This encouraged us to employ the LDH gel as a candidate electrode material to stabilize the α/γ couple in alkaline cells. Pasted electrodes fabricated using Ni-foam, without using Co as an additive, yielded high initial capacities (470 mAh g⁻¹ of Ni; 1.03 e⁻ exchange), but deteriorated rapidly (Fig. 1a). After 10 cycles, the stabilized gravimetric capacity was the much less (335 mAh g⁻¹; 0.74 e⁻ exchange) than that observed for the control nickel hydroxide electrode (400 mAh g⁻¹;

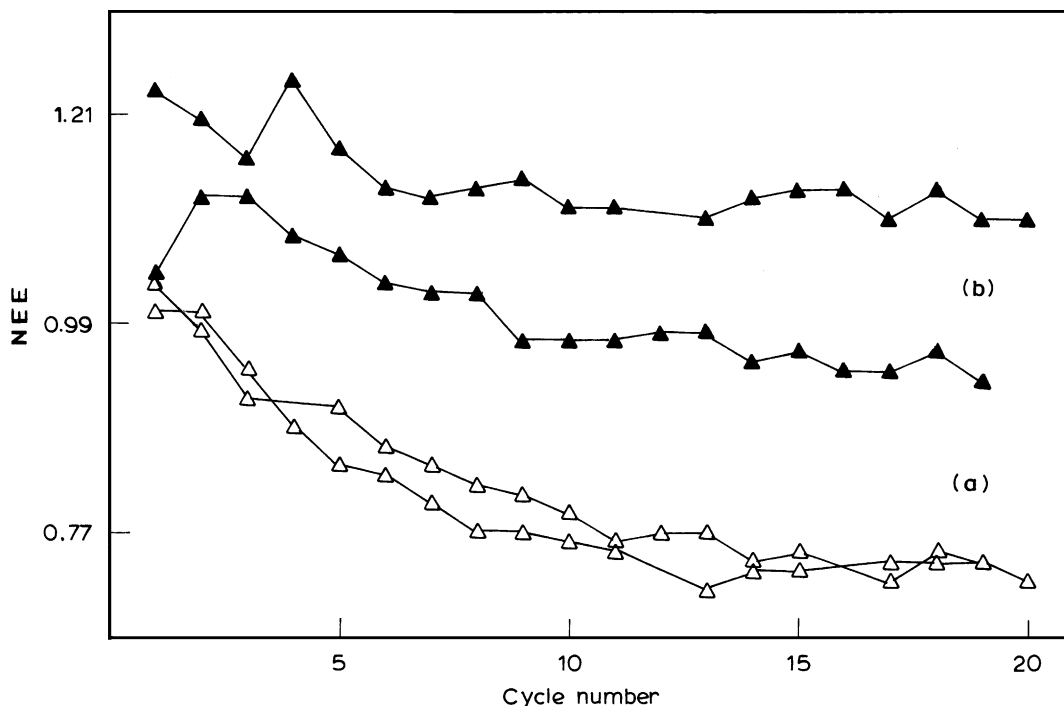


Fig. 1. Cycle-life data of Ni–Cr ($x = 0.2$) LDH electrodes without (a) and with (b) Co metal included as an additive.

$0.9 e^-$ exchange). This clearly suggests that the LDH rapidly transforms to β -nickel hydroxide on cycling. The Cr(III) was found to have leached into the alkaline electrolyte as the CrO_4^{2-} ion. Although, the LDH structure permits the exchange of a greater number of electrons, it is evident that Cr(III) oxidation to Cr(VI) takes place simultaneously with charging of the electrode. Cr(VI), being a soluble species, leaches out of the lattice and leaves behind β -nickel hydroxide. In contrast to the LDHs of Ni with other trivalent cations such as Al, Fe and Co, the Ni–Cr LDH has no electrochemical stability and ages during charge–discharge cycling. A wet chemical estimation of the dissolved CrO_4^{2-} matched with the Cr(III) content of the electrode material. This indicates that the Cr(III) had been completely extracted from the electrode. This rapid degradation could be suppressed, however, by including Co metal as an additive during electrode fabrication (see Fig. 1b) and a stabilized reversible discharge capacity which ranged from 425 to 500 mAh g^{-1} (0.9 – $1.1 e^-$ exchange) was obtained. This observation gives rise to the possibility that the improved performance of the Co-containing electrodes is due to the addition of Co and is not associated with the LDH material. We therefore compared the discharge capacities of β -nickel hydroxide electrodes fabricated with and without Co. With Co metal included as an additive during electrode fabrication, the reversible discharge capacity of the poorly crystalline control sample of β -nickel hydroxide is found to decrease from 400 mAh g^{-1} ($0.9 e^-$ exchange) to 335 mAh g^{-1} ($0.74 e^-$ exchange) [19]. This clearly shows that the improvement in the performance of the Ni–Cr LDH electrodes on the inclusion of Co is only due to the LDH

structure. In addition, the LDH electrodes deliver 50% higher capacity than the control electrodes.

Although a high capacity with good retention is observed by the inclusion of Co as an additive, the entire Cr is found to leach out into the electrolyte. It is likely that Co metal is oxidized to Co(III) [21–23] and incorporated in the nickel hydroxide lattice in place of Cr(III) to retain the α -structure.

3.2. LDHs of Ni with Mn

Mn in alkaline medium can exist in either the Mn(III) or Mn(IV) states. Mn(III) (d^4) ions in LDHs are present in the high spin state as hydroxyl ions act as weak field ligands. High spin d^4 systems are susceptible to Jahn–Teller distortions, a factor that introduces lattice instability in the LDH. This lattice instability can be overcome in two ways, namely: (i) oxidation of Mn(III) to Mn(IV); (ii) hybridization of the Mn (3d) orbitals with the Ni (3d) orbitals to yield an average d electron configuration per metal atom greater than 4.

Wet chemical analysis (see Table 1) of the LDHs indicates that a majority of the Mn ions are in the 4+ state and yield an average oxidation state in the range 3.6–3.8. It appears that mechanism (ii) above does not come into play in this system. On aging in KOH, Mn^{4+} is further stabilized due to the effect of the alkaline electrolyte, which favors the 4+ oxidation state [14–16].

The presence of Mn in the 4+ state results in some difficulties. While a large number of LDHs of divalent cations with trivalent cations are reported, there are few, if any, reports of LDHs which comprise quadrivalent ions. In

Table 1
Oxidation state (OS) of Mn in as-prepared Ni–Mn LDHs

| Composition (x) | Average OS of Mn | Average OS of Ni + Mn | Composition of cation sublattice |
|---------------------|------------------|-----------------------|---|
| 0.1 | 3.59 | 2.16 | $\text{Ni}_{0.9}\text{Mn}_{0.04}^{3+}\text{Mn}_{0.06}^{4+}$ |
| 0.2 | 3.80 | 2.36 | $\text{Ni}_{0.9}\text{Mn}_{0.04}^{3+}\text{Mn}_{0.16}^{4+}$ |

instances where quadrivalent ions have been introduced in the LDH matrix, they have been incorporated in very small proportions of $x \sim 0.01$ and, partially substitute for the trivalent ions of the LDH. The main difficulty in incorporating $4+$ ions in the LDH could be the enhanced cation–cation repulsions which a monovalent anion lattice, such as that of hydroxyl ions cannot adequately screen. In such an event, the hydroxyl ions lose protons and turn into oxide ions, which on account of their higher negative charge can accommodate quadrivalent cations.

Proton loss results in: (i) extinction of the positive charge on the layers and the consequent loss of the α -like structure as seen in the oxide–hydroxides of trivalent ions such as Mn(III), Co(III) and Ni(III); (ii) as the number of protons that can be potentially exchanged falls, there is loss of charge storage capacity.

In the LDHs of Ni with Mn partial proton loss results in a phase with the composition $\text{Ni}_{1-x}^{2+}\text{Mn}_x^{4+}(\text{OH})_{2-2x}(\text{O})_{2x} \cdot y\text{H}_2\text{O}$. This can also be formulated as a composite $(1-x)\text{Ni}(\text{OH})_2 \cdot x\text{MnO}_2 \cdot y\text{H}_2\text{O}$. Since the PXRD pattern does not reveal the reflections of the constituent phases, namely, $\text{Ni}(\text{OH})_2$ and MnO_2 , we prefer to treat this phase as an X-ray amorphous solid solution. The IR spectra (data not shown) do not indicate the presence of intercalated anions in support of the above formula.

In this instance too, no attempts were made to synthesize ordered phases, as disorder has been shown to promote electrochemical activity [24]. Pasted electrodes were fabricated with either $x = 0.2$ or 0.1 composition and cycled in 6 M KOH. Both compositions yield higher charge storage

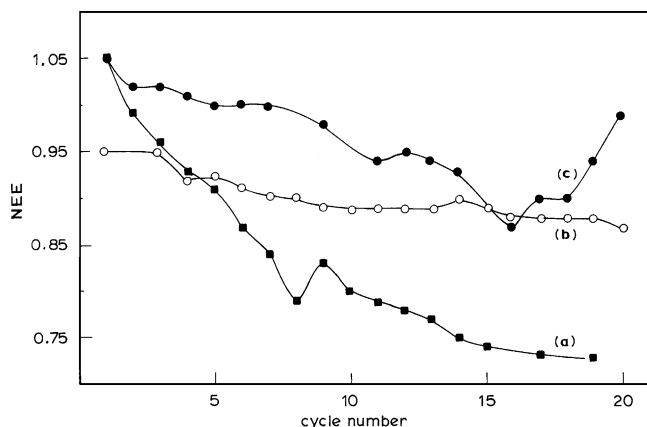


Fig. 2. Cycle-life data of β_{bc} -nickel hydroxide (a), Ni–Mn ($x = 0.2$) (b) and Ni–Mn ($x = 0.1$) LDH electrodes (all electrodes were prepared with Co metal included as an additive).

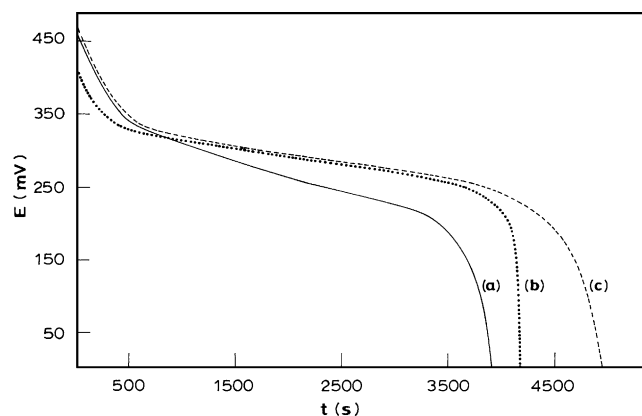


Fig. 3. Discharge profiles of Ni–Mn ($x = 0.2$) (a), Ni–Cr ($x = 0.2$) (b) and Ni–Mn ($x = 0.1$) (c) LDH electrodes.

capacities compared with the control electrodes of β -nickel hydroxide. The $x = 0.2$ composition with a capacity of 400 mAh g^{-1} ($0.89 e^-$ exchange) was slightly inferior to the $x = 0.1$ composition (capacity: 430 mAh g^{-1} ; $0.94 e^-$ exchange) (see Fig. 2). It is doubtful if this LDH can be said to stabilize the α/γ couple. The discharge curves of Ni–Cr, Ni–Mn ($x = 0.1, 0.2$) are shown in Fig. 3.

4. Conclusions

This paper reports the electrochemical performance of unconventional X-ray amorphous LDH systems. We still refer to these phases as LDHs, as the presence of Cr and Mn suppresses β -nickel hydroxide formation, which indicates their strong influence on the precipitation behavior of Ni^{2+} . While both systems perform better than β_{bc} -nickel hydroxide electrodes fabricated under similar conditions as controls, their performance is not as good as that of other LDHs, notably the LDH of Ni with Al. The latter in addition to chemical and electrochemical stability [19] also delivers a higher gravimetric capacity due to the lower weight of Al.

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