# Cathodic reduction of different metal salt solutions Part I: synthesis of metal hydroxides by electrogeneration of base

G. H. ANNAL THERESE, P. VISHNU KAMATH*

*Department of Chemistry, Central College, Bangalore University, Bangalore 560001, India*

The yield of metal hydroxides obtained by electrolysis of chloride baths is greater than the yield obtained from nitrate baths showing that the hydrogen evolution reaction (HER) contributes as much to electrogeneration of base as the nitrate reduction reaction. This observation has implications for the fabrication of nickel hydroxide positive electrodes for alkaline secondary cells, and widens the scope of electrosynthesis to include chloride, sulphate and other anion containing α-nickel hydroxides and other layered hydroxides. Electrosynthesis of $Mg(OH)_2$ has been investigated as a model synthesis.

Keywords:   *alkaline cells, hydrogen evolution, nitrate bath, nitrate reduction, metal hydroxides*

## 1. Introduction

Deposition of nickel hydroxide by electrogeneration of base has been practised by electrochemists for many years [1]. Of late, this method has been extended to the synthesis of other unary and layered double hydroxides [2], simple and complex oxides [3–5] and hydrogenphosphates [6]. Switzer [7] and Matsumoto and others [8] have discussed the possible reactions that result in electrogeneration of base. One set of reactions concerns the stepwise reduction of the nitrate ion up to the formation of $NH_3$ or $NH_4^+$ which leads to generation of seven or nine hydroxyl ions per nitrate reduced. A second set of reactions concerns the hydrogen evolution reaction (HER). Of these, the former have been considered more important [9] and all successful cathodic electrodeposition reactions reported have been carried out in nitrate baths. To the best of our knowledge there has been no systematic study to determine the relative importance of the two classes of reactions.

In this paper, we have investigated the yields of electrodeposited hydroxides obtained from a nitrate bath and compared it with that obtained from a chloride bath. Since the chloride ion does not participate in any reduction reaction, the yield of hydroxide from a chloride bath should be entirely due to the HER. We have investigated the synthesis of $Mg(OH)_2$ as a model because it is a stoichiometric compound with a well defined structure and composition and then extended the results to the synthesis of nickel hydroxide. The latter has a rich polymorphism and exists in various forms designated as α and β [10]. Complete structural

and analytical investigations have been carried out to characterize the products and estimate the yields.

Our results show that the yields of metal hydroxides from chloride baths is comparable, if not actually in excess over the yields obtained from nitrate baths, showing that HER is as important as nitrate reduction for the purpose of electrogeneration of base.

## 2. Experimental details

### 2.1. Synthesis

Metal hydroxides were synthesized by cathodic reduction of their respective nitrate (or chloride) solutions (strength, 0.25 M) galvanostatically at current densities of 25 and 100 mA cm$^{-2}$ using Pt, Ni and Pb flag electrodes of surface area 2 cm$^2$ in a divided cell. A Pt flag dipped in $KNO_3$ (or KCl) solution of matching concentration was used as the counter electrode. Deposition was carried out for different times (1–4 h) and the product formed in the cathodic chamber was filtered off on a preweighed sintered glass crucible and dried to constant weight at 100 °C to estimate the yield. Synthesis was also carried out by varying the pH of the solution in the cathodic and anodic chambers from 2–6 by the use of $HNO_3$ (or HCl). The working electrode potential during electrolysis was measured with respect to a saturated calomel electrode (SCE). Coulombic efficiencies of the reactions were estimated as a ratio of the number of moles of hydroxide produced to the coulombs of charge input. However, unless otherwise stated, all data are presented in terms of absolute weight of the hydroxide produced. Synthesis of hydroxides from metal sulphate and metal perchlorates was also carried out.

* Author to whom correspondence should be addressed.

*Table 1. Results of wet chemical analyses of the metal hydroxides synthesized from their respective nitrate and chloride baths*

| $M(OH)_2$ obtained from | Composition/wt % | | | | Molecular formulae |
|---|---|---|---|---|---|
| | $M^{2+}$ | $OH^-$ | $A^-$ | $H_2O$ | |
| $MgCl_2$ | 24.3 | 34.0 | – | 1.9 | $Mg(OH)_2(H_2O)_{0.1}$ |
| $Ni(NO_3)_2$ | 51.2 | 26.9 | 11.2 | 10.7 | $Ni(OH)_{1.8}(NO_3)_{0.2}(H_2O)_{0.65}$ |
| $NiCl_2$ | 51.5 | 26.2 | 6.8 | 15.5 | $Ni(OH)_{1.8}Cl_{0.2}(H_2O)_{0.98}$ |
| $NiSO_4$ | 50.9 | 24.5 | 12.4 | 12.3 | $Ni(OH)_{1.7}(SO_4)_{0.15}(H_2O)_{0.79}$ |

## 2.2. *Wet chemical analysis*

To evaluate the number of moles of hydroxide pro-
duced, a complete wet chemical analysis of the
products was carried out. The metal content (Mg in
magnesium hydroxide and Ni in nickel hydroxides)
was estimated gravimetrically. The hydroxyl content
was estimated by dissolving an accurately weighed
amount of hydroxide in excess acid and estimating
the excess acid using a standard base, as described
elsewhere [11], by chemical titrations with the help of
a pH meter. The hydroxides of Ni were found to be
deficient in $OH^-$ ions. In such cases, charge neutrality
is restored by the intercalation of anions [12]. The
intercalated anion content was estimated gravimetri-
cally (chloride as AgCl and sulphate as $BaSO_4$).

## 2.3. *Physical characterization*

Powder diffraction data were acquired on a Jeol
JDX8P powder X-ray diffractometer. Infrared spec-
tra were recorded on a Nicolet Impact 400D FTIR
infrared spectrometer (KBr pellets, $4\,cm^{-1}$ resolution)
and TG data were recorded on a home-made system
(heating rate $2.5\,°C\,min^{-1}$).

## 3. Results

Within a few minutes of the electrolysis of a $MgCl_2$
solution, the formation of a white precipitate was
observed at the cathode exactly as in the case of a

$Mg(NO_3)_2$ solution. The products were analysed by
wet chemical analysis (Table 1) and X-ray diffract-
rometry (Fig. 1). The products of both reactions were
found to be $Mg(OH)_2$ showing that hydroxides can
be generated from non-nitrate baths also with equal
felicity. Figure 2 shows the yields of $Mg(OH)_2$ ob-
tained from both the nitrate and chloride solutions as
a function of $Q$ (charge input in A min) by using Pt,
Ni and Pb electrodes. It is found that in all three
cases, the yield of hydroxide from chloride baths is
nearly 150% of the yield from nitrate baths, espe-
cially at high $Q$. At low $Q$, the yields are comparable.
Further, the yields of magnesium hydroxide from all
three electrodes are almost identical for a given $Q$
value in both chloride and nitrate solutions.

In Fig. 3 the variation of the yield as a function of
pH of the bath is shown. At very low pH ($<2$) the
yields are low, and at moderate pH (4–6), the yields
reach a limiting value. Here again the yield from a
chloride bath is distinctly higher than the yield from
the nitrate bath.

Electrolysis of different nickel salt solutions
yielded green nickel hydroxides which, on analysis
(see Table 1 ), were found to be hydroxide-deficient
α-type hydroxides containing the respective anions.
The infrared spectra of the hydroxides clearly reveal
the characteristic absorptions of the α-type hydrox-
ides in the high (3700–3000 $cm^{-1}$) and low (800–
400 $cm^{-1}$) wavenumber regions. In the intermediate
(1600–1000 $cm^{-1}$) region, the spectra reveal the
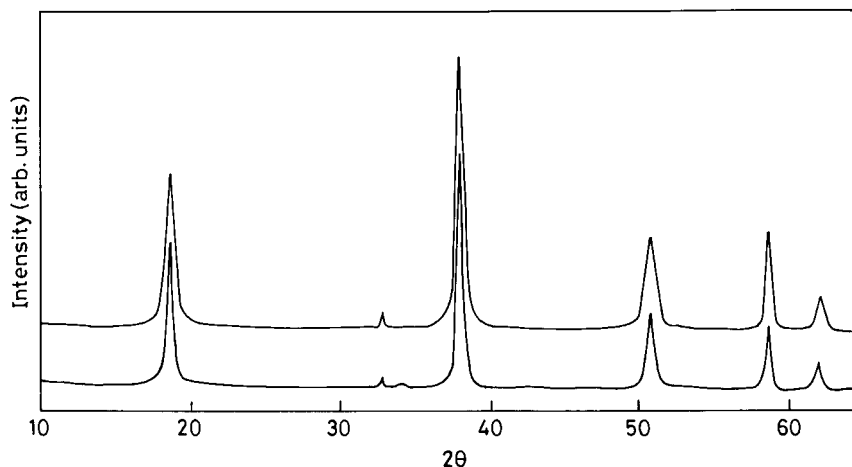presence of sulphate (1124 and 1047 $cm^{-1}$) and nitrate



Fig. 1. Powder X-ray diffraction patterns of magnesium hydroxide electrosynthesized from magnesium nitrate (lower curve) and mag-
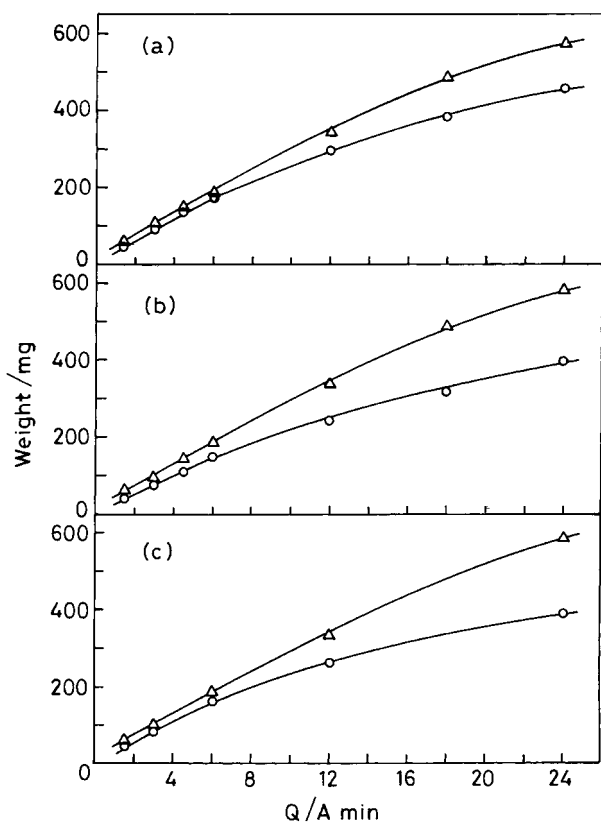nesium chloride (upper curve) baths.

Fig. 2. Yield of magnesium hydroxide as a function of charge passed from chloride ($\triangle$) and nitrate ($\bigcirc$) baths using Pb (a), Ni (b) and Pt (c) electrodes.

(1455, 1387, 1296 and 1051 cm$^{-1}$) ions in the hydroxides obtained from the respective salts. The hydroxide obtained from nickel chloride solution exhibits weak absorption from adsorbed carbonate
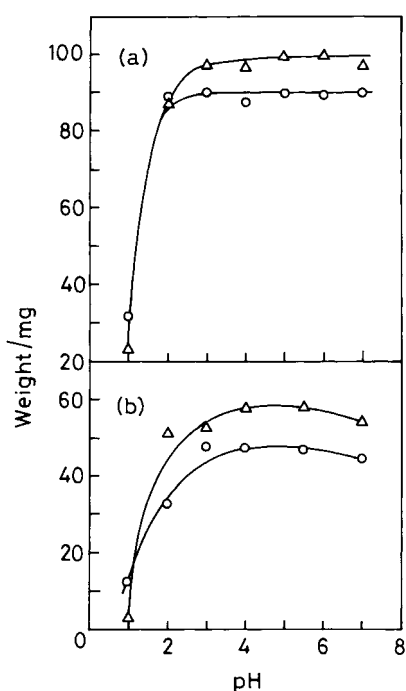


Fig. 3. A representative plot of the yield of magnesium hydroxide at a nickel electrode as a function of the bath pH from chloride ($\triangle$) and nitrate ($\bigcirc$) baths for a deposition time of 2 h (a) and 1 h (b).

ions (1465 and 1382 cm$^{-1}$) (Fig. 4). This is because the intercalation of carbonate ions in layered hydroxides is unavoidable in view of their affinity for carbon dioxide of the atmosphere. Carbonate ions partially exchange for other intercalated ions [12]. The yield of nickel hydroxides as a function of $Q$ has been plotted in Fig. 5. When a nickel electrode is used, both chloride and nitrate baths yield identical quantities of the hydroxide. However the yield of nickel hydroxide from a Pb electrode is less than that obtained from a Pt electrode. The coulombic efficiencies of all the reactions in terms of the number of moles of hydroxides to the coulombs of charge passed have been given in Table 2.

Figure 6 shows the working electrode potential as a function of $Q$ for all the reactions described above. The potential at the Pt electrode varies continuously in all electrolytes showing that a single common reaction takes place at the Pt electrode in both nitrate and chloride baths. The potential of the Ni and Pb electrodes varies continuously in chloride baths, while in nitrate baths there is a sudden change at a $Q$ value 0.5 to 0.75 A min. The potential at high $Q$ is similar to that observed in the chloride bath, while at low $Q$, there is a large difference. It is evident that in the nitrate bath the nature of the reaction at the working electrode is different at low $Q$ compared to high $Q$, and there is a sudden change at an intermediate $Q$ value. The behaviour of a Pb electrode in the Mg system however is different. At low $Q$, the potential in nitrate as well as chloride baths is identical and the difference becomes large at high $Q$.

## 4. Discussion

Metal hydroxides can be electrosynthesized from a variety of baths and the yield from a chloride bath is higher than that from a nitrate bath. Unlike the other anions such as $SO_4^{2-}$, $NO_3^-$ and $ClO_4^-$ which can undergo cathodic reduction to $SO_3^{2-}$, $NO_2^-$ and $ClO_3^-$, respectively, and yield base, the chloride ion does not participate in any reduction reactions. In the chloride bath, the only reaction that can result in electrogeneration of base is HER:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \qquad E^\circ = -0.83\,V$$
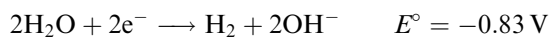
The fact that the hydroxide yield from chloride baths is higher than that from nitrate baths clearly shows that HER has as important a role in electrogeneration of base, as the nitrate reduction reaction. The hydroxides obtained from both baths are isostructural and are similar in composition.

If HER is indeed the major reaction leading to electrogeneration of base, the metal hydroxide yield should depend on the one hand upon the hydrogen overpotential of the electrode and on the other upon the nature and pH of the bath.

However, the present results are ambiguous. In the nickel chloride bath, the yield of nickel hydroxide at a Pb electrode (overpotential 0.64) is less than the yield at a Pt electrode (overpotential 0.0), as expected. But
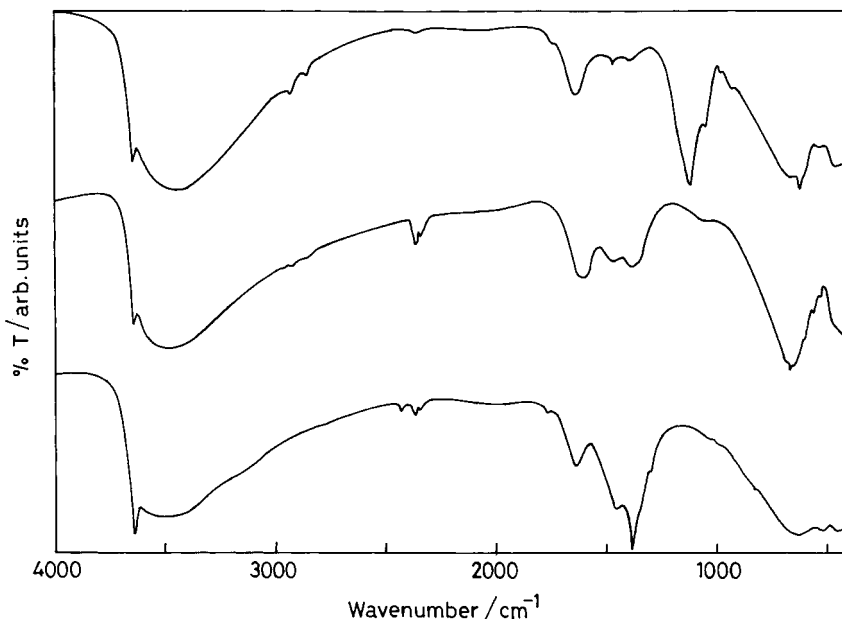
Fig. 4. Infrared spectra of α-type nickel hydroxide samples electrosynthesized from nitrate (bottom curve), chloride (middle curve) and sulphate (top curve) baths.

such a trend is not seen in the Mg system, where all three electrodes show comparable yields. What is unambiguous, however, is that the yield from a chloride bath is higher than, or equal to, that from a nitrate bath.

The results of pH variation show that the yield of hydroxides is low at low pH ( <2) because the electrogenerated base is consumed to neutralize the bath acidity. The coulombic efficiency peaks at interme-

diate pH values of 2–3 and remains constant up to pH 7 as observed by other authors [9]. Beyond pH 7, chemical precipitation vitiates the estimates of yield.

The potential measurements are more revealing. A continuous variation of potential with $Q$ is indicative of a single reaction, whereas sudden changes are indicative of a change in the dominant reaction taking place at the electrode. It therefore appears that at a Pt electrode, there is a single reaction taking place at nearly the same potential in both nitrate and chloride baths. The only reaction common to both baths is the HER. It is, therefore, clear that hydrogen evolution is the only reaction responsible for electrogeneration of base at a Pt electrode. In the case of Ni and Pb electrodes, the potential in nitrate baths approaches that of the chloride bath only at high $Q$, indicating that at high $Q$, electrogeneration of base is due to HER and at low $Q$ it is due to nitrate reduction.
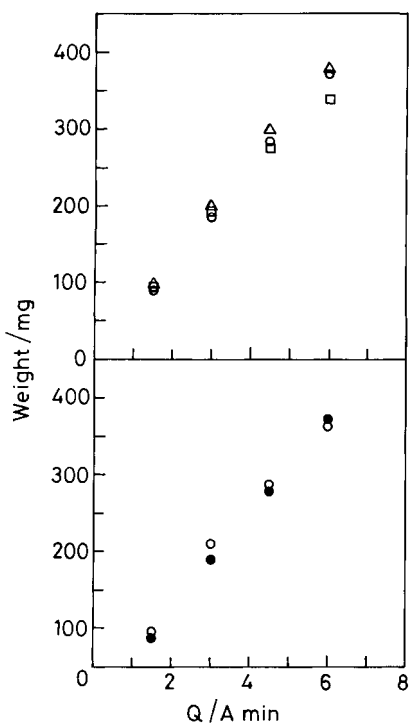


Fig. 5. Yield of nickel hydroxide at a nickel electrode as a function of $Q$ from chloride (●) and nitrate (○) baths (lower panel) and yield of nickel hydroxide from a chloride bath at Ni (○), Pt (△) and Pb (□) electrodes (upper panel).

Table 2. Coulombic efficiencies of electrosynthesis of nickel and magnesium hydroxides from their chloride and nitrate baths

| System | Charge input, $Q$ /A min cm$^{-2}$ | Efficiency/% | | |
|---|---|---|---|---|
| | | Pt | Ni | Pb |
| Mg$^{2+}$ | 12 | 77.4 (60.6) | 78.1 (55.2) | 78.5 (66.9) |
| Mg$^{2+}$ | 24 | 67.4 (44.5) | 66.6 (45.8) | 65.9 (52.2) |
| Ni$^{2+}$ | 3 | 97.6 | 91.7 (99.5) | 91.0 |
| Ni$^{2+}$ | 6 | 90.7 | 90.5 (85.3) | 81.7 |

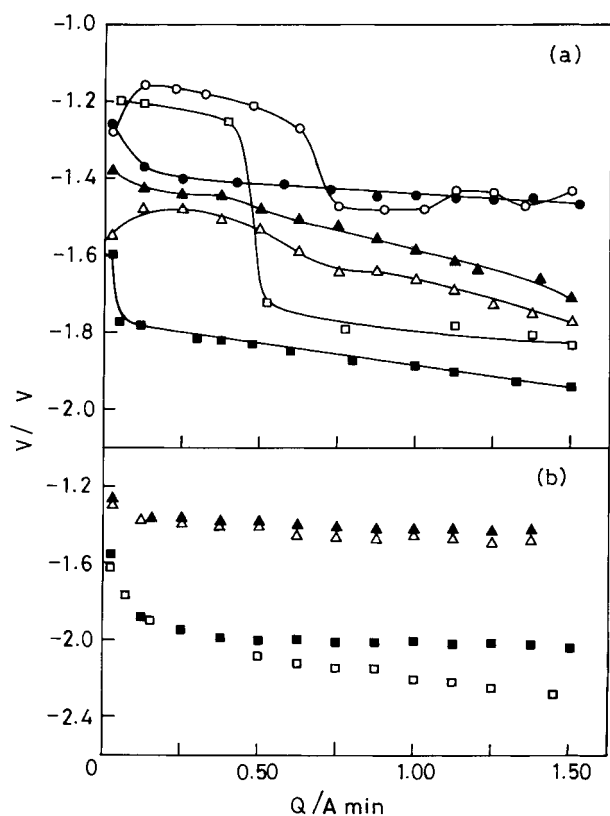Note: Values given inside parantheses correspond to the nitrate system.

Fig. 6. (a) Working electrode potentials in nickel chloride (closed symbols) and nickel nitrate (open symbols) baths for Ni (circles), Pt (triangles) and Pb (squares) electrodes. (b) Working electrode potentials in magnesium chloride (closed symbols) and magnesium nitrate (open symbols) baths for Pt (triangles) and Pb (squares) electrodes.

In conclusion we show that HER makes a significant contribution to electrogeneration of base during cathodic reduction of metal salt solutions. The demonstration of hydroxide synthesis by electrolysis of different metal salt solutions widens the scope of electrosynthesis greatly [13].

## References

[1]  E. J. McHenry, *Electrochem.Technol.* **5** (1967) 275.
[2]  L. Indira and P. V. Kamath, *J. Mater. Chem.* **4** (1994) 1487.
[3]  L. Gal-Or, I. Silberman and R. Chaim, *J. Electrochem. Soc.* **138** (1991) 1939.
[4]  H. Konno, M. Tokita, A. Furusaki and R. Furuichi, *Electrochim. Acta* **37** (1992) 2421.
[5]  I. Zhitomirsky, L. Gal-Or, A. Kohn and H. W. Hennicke, *J. Mater. Sci.* **30** (1995) 5307.
[6]  G. H. A. Therese, P. V. Kamath and G. N. Subbanna, *J. Mater. Chem.* (accepted).
[7]  J. A. Switzer, *Amer. Ceram. Soc. Bull.* **66** (1987) 1521.
[8]  Y. Matsumoto, T. Morikawa, H. Adachi and J. Hombo, *Mat. Res. Bull.* **27** (1992) 1319.
[9]  C. C. Streinz, A. P. Hartman, S. Motupally and J. W. Weidner, *J. Electrochem. Soc.* 142 (1995) 1084; C. C. Streinz, S. Motupally and J. W. Weidner, *ibid.* **142** (1995) 4051.
[10]  P. Oliva, J. Leonardi, J. F. Laurent, C. Delmas, J.J. Braconnier, M. Figlarz and F. Fievet, *J. Power Sources* **8** (1982) 229.
[11]  M. Dixit, G. N. Subbanna and P. V. Kamath, *J. Mater. Chem.* **6** (1996)
[12]  F. Portemer, A. Delahaye-Vidal and M. Figlarz, *J. Electrochem. Soc.* **139** (1992) 671.
[13]  G. H. A. Therese and P. V. Kamath, *J. Appl. Electrochem.* (to be communicated).