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INTRODUCTION

Metal hydride electrodes are an attractive substitute for the cadmium electrode in Cd/Ni batteries because of their relatively benign environmental impact and higher energy density. However, even though MH_x/Ni batteries are currently competitive in certain applications, their full potential as cheap, reliable, energy storage devices is not yet realized: a severe penalty has been incurred in storage capacity and materials costs in order to inhibit corrosion and attain acceptable electrode cycle life. Currently there are two types of alloys which are useful as metal hydride electrodes, the AB₅ and the AB₂ classes of intermetallic compounds. The former have the hexagonal CaCu₅ structure where the A component comprises one or more rare earth elements and B consists of Ni, or another transition metal, or a transition metal combined with other metals. The AB₂ electrodes, which are not yet commonly used in batteries, are complicated, multiphase Laves type alloys with as many as nine metal components. Alloy formulation is primarily an empirical process where the composition is adjusted to provide one or more hydride forming phases in the bulk alloy particle with a surface that is presumed to be corrosion resistant because of the formation of semi-passivating oxide layers. Here we shall only be concerned with the AB₅ class of hydride electrodes.

The paradigm compound of the AB₅ intermetallics is LaNi₅, a compound which has been well investigated because of its utility in conventional hydrogen storage applications. Unfortunately LaNi₅ is too costly and corrosion sensitive to use as a battery electrode. Thus commercial AB₅ electrodes use mischmetal, a low cost combination of rare earth elements, as a substitute for La. The B₅ component remains primarily Ni but is substituted in part with Co, Mn, Al etc. The partial substitution of Ni increases thermodynamic stability of the hydride phase and corrosion resistance. Such an alloy is commonly written as MmB₅ where Mm represents the mischmetal component; the B₅ composition in commercial batteries is variable but electrodes consisting of MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3} have good storage capacity and cycle life (1) and most

AB₅ battery electrodes have a similar composition. We have been concerned with the function that individual components play in such an alloy with respect to lattice expansion, hydride stability, and surface passivation. Thus we have focused on the properties of a similar alloy, A(NiCoMnAl)₅ where A is La or La_{1-x}Ce_x. Some of our results noted here have previously appeared in separate publications; the purpose of this paper is to combine them with new data to give a more coherent and complete whole.

ELECTRODE CORROSION

The susceptibility of MH_x electrodes to corrosion is essentially determined by two factors, surface passivation due to the formation of surface oxides or hydroxides and the molar volume of hydrogen, V_H, in the hydride phase. As pointed out by Willems and Buschow(2), V_H is important since it governs alloy expansion and contraction during the charge - discharge cycle. Large volume changes increase the flushing action of the electrolyte through the pores and microcracks of the electrode during each charge and discharge cycle thereby increasing the rate of contact of the alloy surface with fresh electrolyte and, consequently, the corrosion rate. Thus, when examining the effect of various substituents upon electrode corrosion the question always arises whether an observed change is due to a change in lattice expansion or to a change in surface passivation, e.g., the formation of a corrosion resistant oxide layer.

CORROSION AND COMPOSITION

The long life of the complex MmB₅ battery electrodes stands in sharp contrast to that of other more simple formulations. This is illustrated in Figure 1 where electrode capacity, Q, is plotted as a function of charge discharge cycles for two electrodes, LaNi_{4.7}Al₃ and MmNi_{3.55}Co_{0.75}Mn_{0.4}Al₃. The former electrode rapidly corrodes and would not be suitable for battery applications. Obviously alloy composition is responsible for the observed behavior. However, while cycle life may differ dramatically, inspection of these plots reveals a common behavior which is found in almost all MH_x electrodes. There is an initial steep increase in capacity in the first few cycles which comprises the activation process. After activation a maximum in electrochemical storage capacity, Q_{max}, is reached. This is usually followed by an almost linear decrease in capacity which may be termed capacity decay. It is defined as the slope of the capacity vs. cycle curve, i.e., -dQ/dcycle.

Adzic et. al.(3) exploited such plots to quantitatively determine electrode behavior. The H content of the charged electrode, expressed as the

number of H atoms, n , per formula unit, was calculated from Q_{\max} via the Faraday equation,

$$n = e^- = \frac{3600}{9.65 \times 10^7} (mw)(Q_{\max}) \quad [1]$$

where mw is the molecular weight of the alloy and the units of Q are mAh/g. They assumed that after activation the remaining uncorroded alloy in each subsequent charge - discharge cycle is hydrided and dehydrided to the same degree and n is constant. The percent lattice expansion of the unit cell in each electrochemical cycle was calculated via the equation

$$\% \frac{\Delta V}{V} = \frac{V_H}{V} n \times 100 \quad [2]$$

where ΔV is the actual volume change of the unit cell in \AA^3 in each charge or discharge cycle, V is the initial unit cell volume and n is the number of H atoms inserted into the unit cell and subsequently discharged.

Finally the loss of electrochemical capacity is directly proportional to the loss of the AB_5 alloy by corrosion and readily calculated as follows;

$$\frac{\% \text{wt. loss}}{\text{cycle}} = \frac{-dQ}{\text{cycle}} (Q_{\max}) \times 100 \quad [3]$$

The effects of Ce, Co, Al and Mn upon H content, lattice expansion and corrosion of $A(\text{NiCoMnAl})_5$ electrodes were determined employing the above equations which are discussed in the following sections.

Effect Of Cerium

The rare earth composition of commercial electrodes is also related to electrode corrosion. This was noted by Sakai et. al.(4) who found that the presence of Nd and Ce inhibited corrosion when substituted in part for La in $\text{La}_{1-x}\text{Z}_x(\text{NiCoAl})_5$ ($Z = \text{Ce}$ or Nd) electrodes. However no explanation for the effect was noted. Willems and Buschow(2) prepared an electrode having the composition of $\text{La}_{0.8}\text{Nd}_{0.2}\text{Ni}_{2.5}\text{Co}_{2.4}\text{Si}_{1.1}$ which retained 88% of its storage capacity after 400 cycles. He attributed its long cycle life to a low V_H of 2.7\AA^3 .

The case of cerium is of particular interest. Adzic et. al.(3) examined the properties of a homologous series of alloys with a composition corresponding to $\text{La}_{1-x}\text{Ce}_x\text{Ni}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_3$ and measured their comparative performance as battery electrodes. Cycle life plots for these electrodes are illustrated in Figure 2. The decreased charge capacity found in all $\text{La}_{1-x}\text{Ce}_xB_5$ alloys with $x > 0.35$ conforms to the increasing equilibrium dissociation plateau pressure (P_{pl}) and

decreasing H content as the Ce content increases as shown in figure 3. Note that P_{pH} of CeB_5H_i is 8 atm at 303K which accounts for its low electrochemical capacity in an open cell.

The corrosion rates for the $\text{La}_{1-x}\text{Ce}_x\text{B}_5$ electrodes are listed in Table 1. The results are summarized graphically in Figure 4 which plots lattice expansion, corrosion rate, and H content (n) vs. Ce content. The plot clearly shows the anti-correlation of lattice expansion with corrosion; thus one concludes that the corrosion inhibition stemming from the presence of Ce is due to a surface effect. This conclusion is supported by previous work reporting that a film of CeO_2 on metal surfaces inhibits corrosion(5). XAS (X-ray absorption spectroscopy) studies have confirmed the corrosion inhibition effect of Ce(6).

Table 1. Effect of Ce in $\text{La}_{1-x}\text{Ce}_x\text{Ni}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_3$ electrodes(3).

x value	V_{H} $\text{Å}^3/\text{atom}$	n <u>H atoms</u> unit cell	$\% \Delta V/V$	Q_{max} mAh/g	Corrosion wt.%/cyc.
1.0	1.6 ^a	0.8	1.4625	51	0
0.75	3.15	3.8	13.919	241	0.003
0.5	3.15	4.4	15.917	278	0.04
0.20	3.21	4.8	17.534	305	0.042
0.20	3.21	4.6	16.547	293	0.047
0.50	3.15	4.0	14.634	260	0.054
0.20	3.21	4.6	16.659	293	0.051
0.20	3.21	5.0	18.122	318	0.057
0.35	3.24	5.0	18.376	318	0.057
0.20	3.21	5.0	18.112	318	0.066
0.0	2.99 ^b	4.8	15.96	305	0.15
0.0	2.99 ^b	5.2	17.33	331	0.139
0.0	2.99 ^b	5.1	17.002	325	0.145
$\text{LaNi}_{4.7}\text{Al}_3$ ^c	3.47	4.5	17.943	285	0.291

^a α phase.

^b Average

^c Included for comparison.

Effect of Cobalt

Cobalt is invariably present in commercial MH_x battery electrodes. It tends to increase hydride thermodynamic stability and inhibit corrosion. However, it is also expensive and substantially increases battery costs; thus, the substitution of Co by a lower cost metal is desirable. Willems and Buschow (2) attributed reduced corrosion in $LaNi_{5-x}Co_x$ ($x=1$ to 5) to a reduction of V_H . Sakai et. al.(7) noted that $LaNi_{2.5}Co_{2.5}$ was the most durable of a number of substituted $LaNi_{5-x}Co_x$ alloys but it also had the lowest storage capacity.

The results of a systematic study(8) of the effect of Co in an alloy series corresponding to $LaNi_{4.3-x}Co_xMn_{.4}Al_{.3}$ is shown in Figure 5 and summarized in Table 2 and graphically in Figure 6. The correlation between expansion and corrosion is rather weak; e.g., at $x = 0.2-0.4$ corrosion is decreased while both H content and expansion is unchanged. It is thus likely that that corrosion inhibition by Co may also be due to a surface effect as with Ce. In this connection Kanda et. al. (9) put forward evidence that Co suppresses the transport of Mn to the surface where it is readily oxidized causing rapid electrode deterioration. Recent XAS results also suggest that Co inhibits

Table 2. Effect of Co in $LaNi_{4.3-x}Co_xMn_{.4}Al_{.3}$ electrodes(8)

x Value	V_H $\text{\AA}^3/\text{atom}$	Q_{max} mAh/g	n <u>H atoms</u> unit cell	$\Delta V/V\%$	corrosion wt.%/cycle
0.75	2.99	330	5.18	17.3	0.139
0.40	3.09	334	5.25	18.1	0.257
0.20	3.09	334	5.25	18.1	0.380
0.0	3.26	324	5.09	18.5	0.485

corrosion via a surface process which inhibits Ni oxidation(10).

Effect of Aluminum

Aluminum appears to be present in all commercial AB_5 electrodes. Sakai et. al.(11) noted that the incorporation of Al in $La(NiCoAl)_5$ alloys substantially reduced electrode corrosion; they attributed this to the formation of protective surface oxides. The corrosion inhibiting effect of Al

is clearly shown in figure 7 which plots of storage capacity versus cycle life for $\text{LaNi}_{3.85-x}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_x$ ($x = 0, 0.1, 0.2, 0.3$) electrodes(12); the Al free electrode corrodes at a greatly increased rate. As illustrated in Table 3 and Figure 8 the presence of even a small amount of Al substantially decreases V_H , n and, consequently, both lattice expansion and corrosion.

Table 3. Effect of Al in $\text{LaNi}_{3.85-x}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_x$ electrodes(12)

x Value	V_H \AA^3	Q_{\max} mAh/g	n <u>H atoms</u> unit cell	% $\Delta V/V$	corrosion wt. %/cyc
0.2	3.01	314	4.98	16.66	0.1274
0.3	2.99	330	5.18	17.33	0.1394
0.1	3.01	327	5.22	17.58	0.2905
0.0	3.20	353	5.66	20.39	0.4079
0.0	3.35	366	5.88	22.30	0.4126

Effect of Manganese

Manganese is also present in most commercial electrodes. In a series of experiments examining the cycle lives of the homologous alloys $\text{LaNi}_{5-x}\text{M}_x$ ($M = \text{Mn, Cu, Cr, Al}$ and Co) Sakai et. al.(11) noted that Mn was the least effective in extending cycle life. In the more complex alloy examined by Adzic et. al.(12) the function of Mn is still open to question. The cyclic behavior of a series of electrodes of varying Mn content is shown in Figure 9. It apparently increases V_H (Table 4) slightly and, although the correlation between lattice expansion, n , and the corrosion rate is fairly strong they are not a function of Mn content as shown in fig. 10.

Table 4. Effect of Mn in $\text{LaNi}_{3.95-x}\text{Co}_{0.75}\text{Mn}_x\text{Al}_3$ electrodes(12).

x Value	V_H $\text{\AA}^3/\text{atom}$	Q_{\max} mAh/g	n <u>H atoms</u> unit cell	% $\Delta V/V$	corr. wt. %/cyc
0.14	3.16	320	4.87	17.27	0.106
0.40	2.99	330	5.18	17.33	0.1394
0.0	3.02	340	5.37	18.38	0.1676
0.30	3.07	353	5.48	18.75	0.150

SUMMARY

Electrode corrosion is the critical problem associated with the use of metal hydride anodes in batteries. The extent of corrosion is essentially determined by two factors, alloy expansion and contraction in the charge - discharge cycle and chemical surface passivation via the formation of corrosion resistant oxides or hydroxides. Both factors are sensitive to alloy composition which can be adjusted to produce electrodes having an acceptable cycle life. In AB₅ alloys the effects of Ce, Co, Mn and Al upon cycle life in commercial type AB₅ electrodes were correlated with lattice expansion and charge capacity. Ce was shown to inhibit corrosion even though lattice expansion increases. Co and Al also inhibit corrosion.

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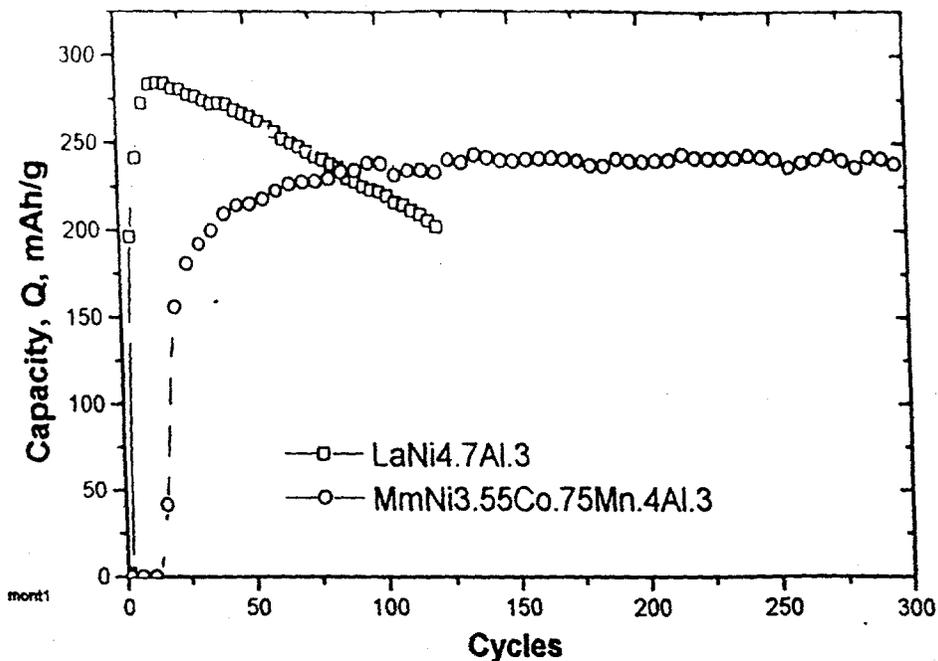


Figure 1: Capacity vs. charge - discharge cycles for two AB₅ electrodes.

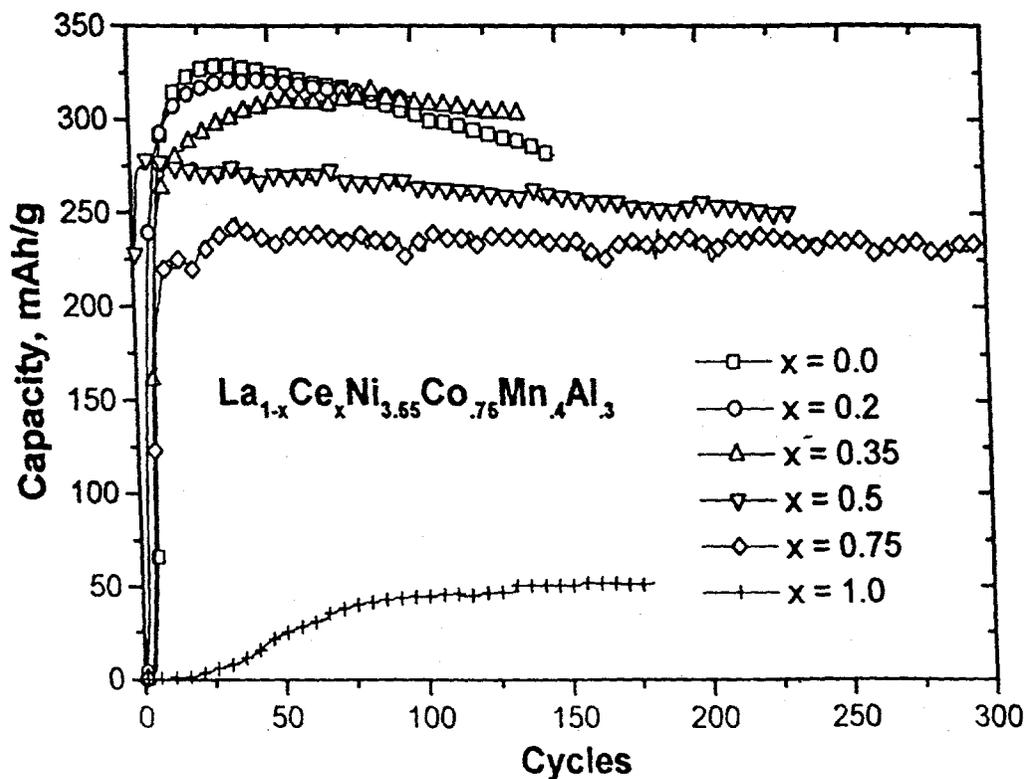
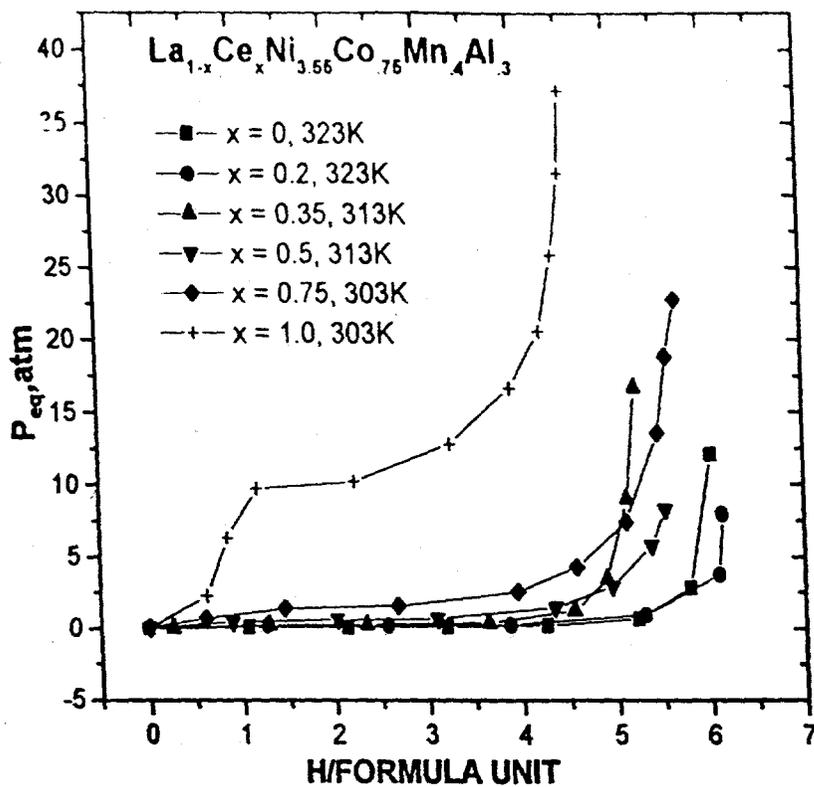
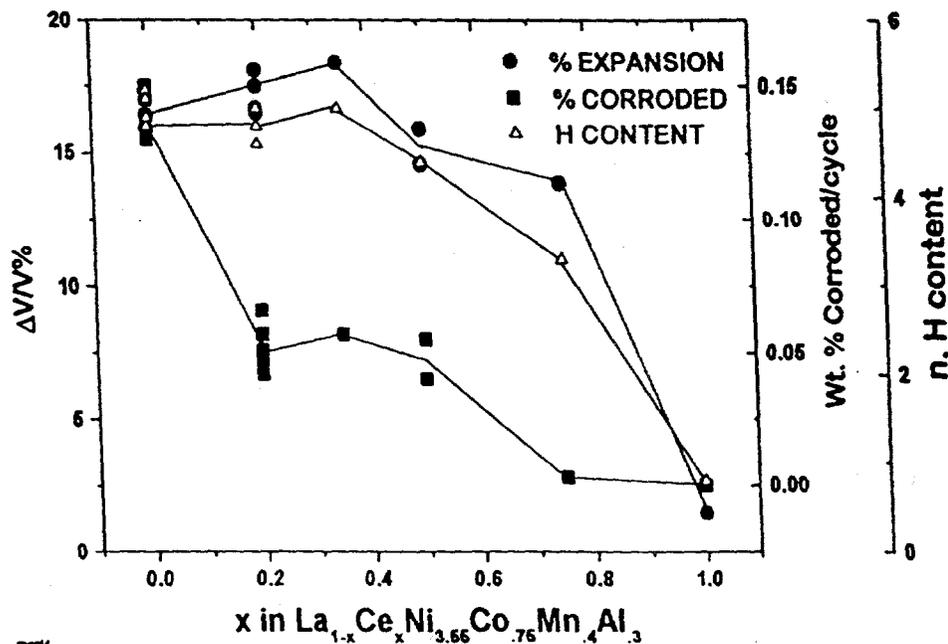


Figure 2: Q vs. cycles for La_{1-x}Ce_xB₅ electrodes(3)



mont3 Figure 3: P-C isotherms for $\text{La}_{1-x}\text{Ce}_x\text{B}_5\text{-H}$ system(3)



mont4 Figure 4: Expansion, corrosion and H content vs. Ce content

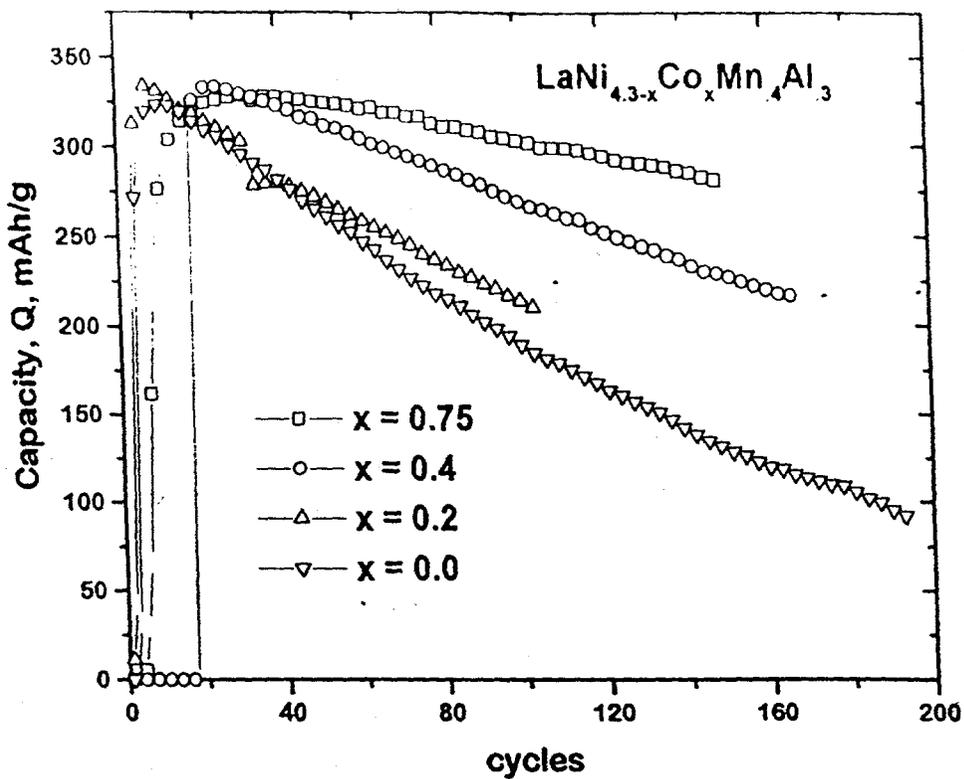


Figure 5: Q vs. charge - discharge cycles for electrodes of varying Co content(8). mont5

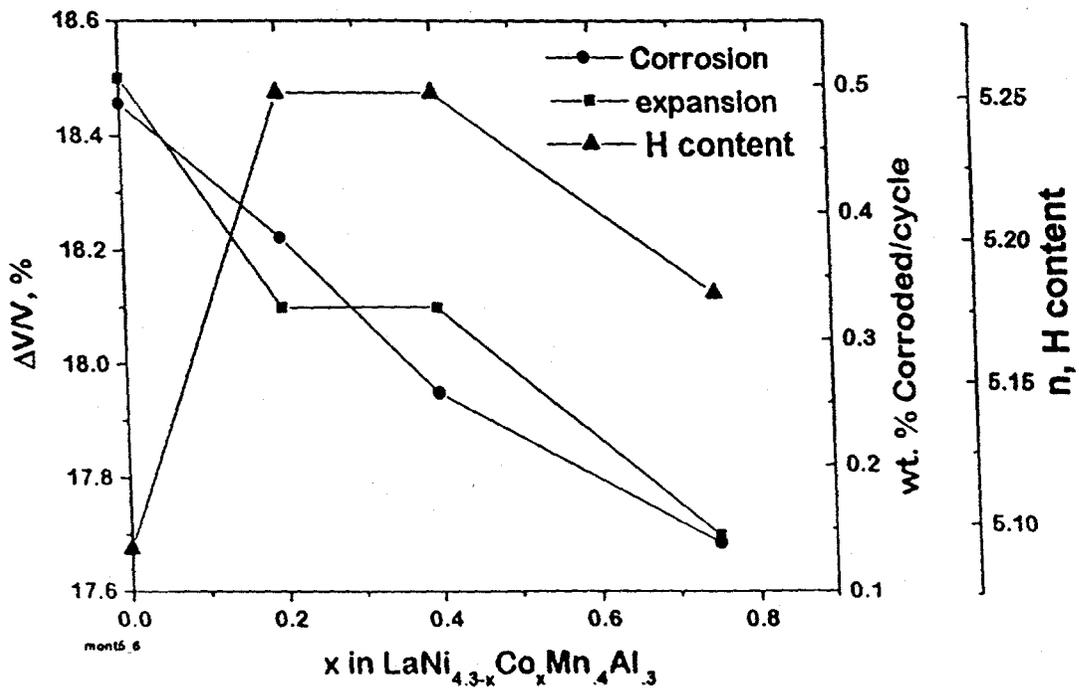


Figure 6: % $\Delta V/V$, corrosion & H content vs. Co content. mont5.6

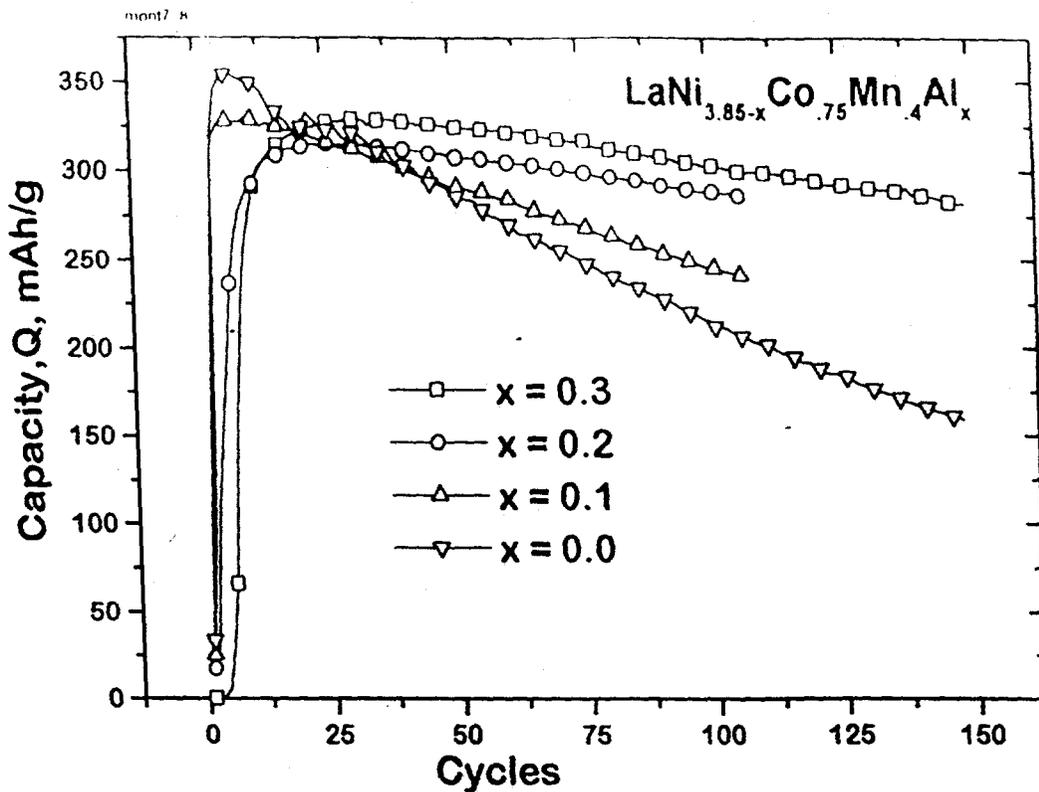


Figure 7: Capacity vs. cycles for electrodes of varying Al content

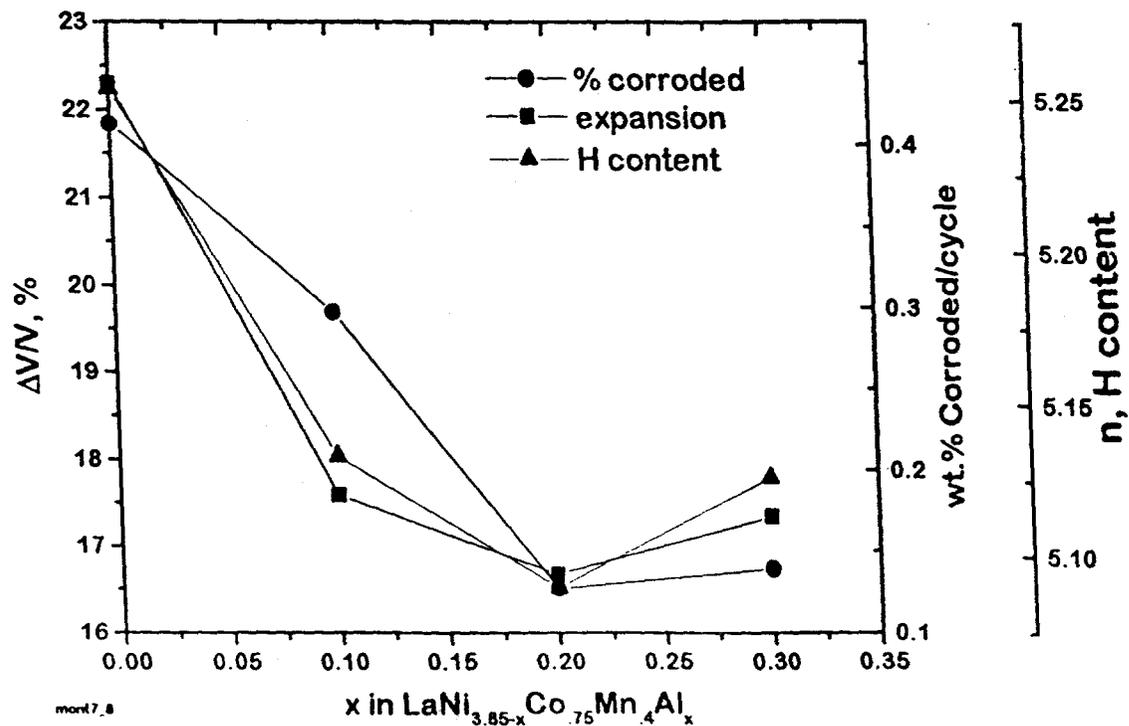


Figure 8: $\% \Delta V/V$, corrosion and H content vs. Al content.

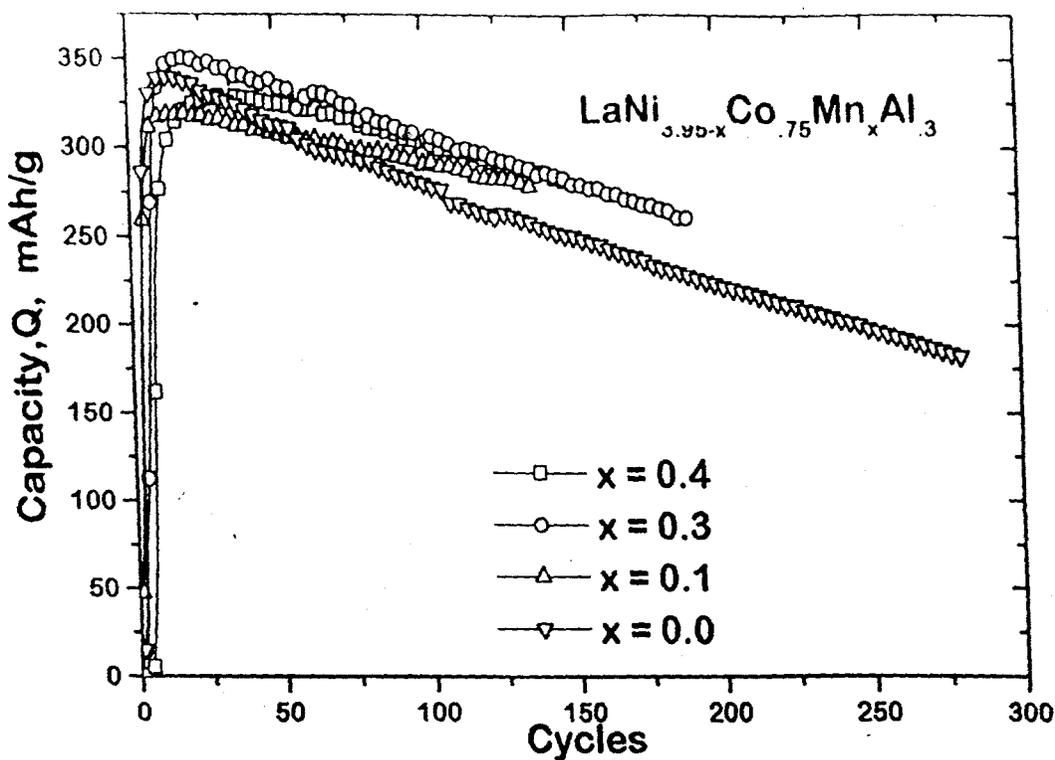


Fig 9: Capacity vs. cycles for electrodes of varying Mn content(12).

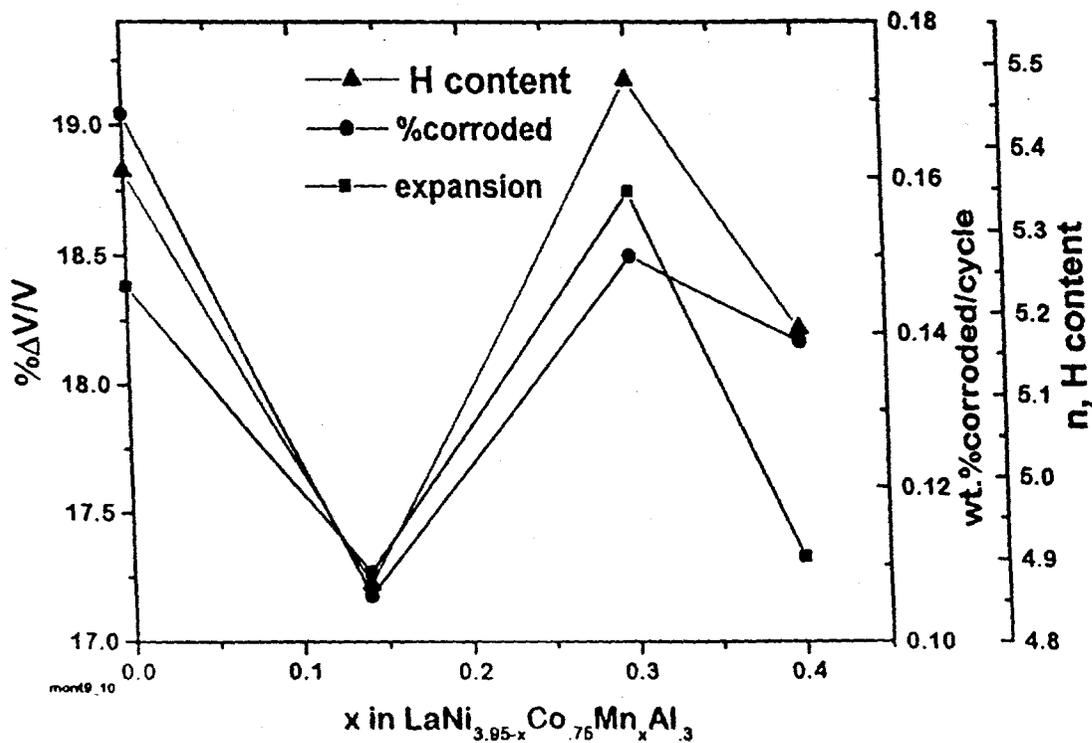


Figure 10: $\% \Delta V/V$, corrosion and H content vs. Mn content.