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Function of cobalt in AB_5H_x electrodes

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Abstract

The role of cobalt in the behavior of AB_5H_x electrodes has been investigated. Alloy compositions were as follows, $LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$ ($x=0$, 0.2, 0.4, 0.75) and $MmNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$ ($x=0$, 0.75). Cobalt was found to decrease the molar volume of hydrogen, V_H, in the hydride phase. Both $LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$ and $MmNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$ alloy electrodes were subjected to repeated electrochemical cycling and corrosion rates measured. The corrosion rate was found to be inversely proportional to the cobalt content of the electrode.

Keywords: Metal hydride electrodes; AB_5

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1. 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 high end 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 AB_5 and the AB_2 classes of intermetallic compounds; this discussion will be confined to the former.

The paradigm compound of the AB_5 alloys is $LaNi_5$ which has been well investigated because of its utility in conventional hydrogen storage applications. Unfortunately $LaNi_5$ is too costly and corrosion sensitive to use as a battery electrode. Thus commercial AB_5 electrodes use mischmetal, a low cost combination of rare earth elements, as a substitute for La. The B_5 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 MmB_5 where Mm represents the mischmetal component; the B_5 composition in commercial batteries is variable but electrodes consisting of $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ have been reported to have good storage capacity and cycle life [1]; here we will examine the effect of variable Co content in $ANi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$ alloys where A is La or Mm.

The corrosion resistance of AB_5 electrodes is primarily determined by two factors, surface passivation due to the presence of surface oxides or hydroxides and the molar volume of hydrogen, V_H, in the hydride phase. The value of V_H is most important as it governs alloy expansion and contraction during the charge–discharge cycle, a process that has been directly correlated to electrode corrosion [2]. 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. Previous work has indicated that the presence of Ce [3], Al, Zr, and Si [4,2] in AB_5 electrodes reduce corrosion by the formation of protective oxides (hydroxides) rather than by reducing lattice expansion. Here we report on the differential effect of cobalt upon electrode corrosion using alloys of composition similar to those used commercially.

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 low V_H. Sakai et al. [5] noted that $LaNi_{2.5}Co_{2.5}$ was the most durable of a number of

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substituted LaN$_{5-x}$Co$_x$ alloys but it also had the lowest storage capacity.

2. Experimental

A total of eight alloys were prepared; four consisted of LaNi$_{4.3-x}$Co$_x$Mn$_{0.4}$Al$_{0.3}$ (x=0, 0.2, 0.4, 0.75); two were of MmNi$_{4.3-x}$Co$_x$Mn$_{0.4}$Al$_{0.3}$ (x=0, 0.75) and two were Mm*Ni$_{4.3-x}$Co$_x$Mn$_{0.4}$Al$_{0.3}$ (x=0, 0.75) where Mm* refers to Ce free mischmetal. All starting elemental metals had a purity specification of >99.9%.

The entire experimental procedure has been described in detail previously [3], but for the readers convenience we give a brief summary. Alloys were prepared in an arc furnace under inert gas and were then annealed for 3 days at 1173 K. V_H was determined by measuring lattice expansion as a function of H content using X-ray diffraction. Electrodes, containing 0.075 g of alloy, were fabricated from each ingot sample. Cycle life measurements were carried out using an open cell containing 6 M KOH. The counter electrode was Pt and the reference electrode was Hg/HgO. The electrode was activated in situ via successive electrochemical charge and discharge cycles. After activation the charging rate was kept constant at 15 mA for two hours, which is approximately equivalent to a rate of ≈0.66 C. The discharge current was constant at 10 mA (≈0.5 C rate); it was cutoff when the anodic voltage decreased to −0.70 V vs. the Hg/HgO reference electrode.

3. Results and discussion

The composition, structural data and V_H values for all alloys are listed in Table 1. Note the relatively high values of V_H for the Co free alloys 195 and 132.

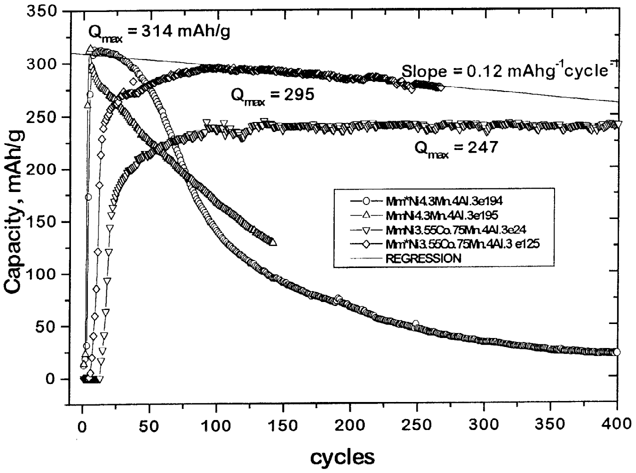

Fig. 1. Effect of Co substitution in MmB$_5$ electrodes, Q_{max} shown. Slopes are calculated for linear region as shown for e125.

The cycle lives of the four mischmetal electrodes (Nos. 24, 125, 195, 194) are illustrated in Fig. 1. The cycle life of both Co free electrodes is surprisingly poor although their initial storage capacity was higher than the corresponding Co containing electrodes.

In view of the above results, the cycle life of the homologous series of electrodes (Nos. 51, 192, 167, 132) of composition LaNi$_{4.3-x}$Co$_x$Mn$_{0.4}$Al$_{0.3}$, was determined as shown in Fig. 2. Mm was replaced with La to assure reproducibility since the composition of mischmetal varies from vendor to vendor. Inspection of the individual plots reveals the following general behavior. There is an initial steep increase in capacity in the first few cycles; this comprises the activation process which consists of particle size reduction and surface reconstruction. After activation a maximum in electrochemical storage capacity, Q_{max}, is reached. This is usually followed by a linear decrease in

Table 1

Composition	Exp No.	a (Å)	c (Å)	V_H (Å^3)	%$\Delta V/V$
LaNi$_{3.55}$Co$_{0.75}$Mn$_{0.4}$Al$_{0.3}$	51	5.0615	4.0298		
LaNi$_{3.55}$C$_{0.75}$Mn$_{0.4}$Al$_{0.3}$H$_{6.01}$	51	5.3947	4.2681	3.06	20.55
MmNi$_{3.55}$Co$_{0.75}$Mn$_{0.4}$Al$_{0.3}$	24	4.9626	4.056		
MmNi$_{3.55}$Co$_{0.75}$Mn$_{0.4}$Al$_{0.3}$H$_{3.12}$	24	5.1853	4.1335	3.13	11.27
Mm*Ni$_{3.55}$Co$_{0.75}$Al$_{0.3}$Mn$_{0.4}$	125	5.0318	4.0309		
Mm*Ni$_{3.55}$Co$_{0.75}$Al$_{0.3}$Mn$_{0.4}$H$_{5.3}$	125	5.3381	4.2356	3.05	18.26
LaNi$_{4.3}$Mn$_{0.4}$Al$_{0.3}$	132	5.0591	4.037		
LaNi$_{4.3}$Mn$_{0.4}$Al$_{0.3}$H$_{5.64}$	132	5.3900	4.2877	3.26	20.55
LaCo$_{0.2}$Ni$_{4.1}$Mn$_{0.4}$Al$_{0.3}$	167	5.0609	4.0361		
LaCo$_{0.2}$Ni$_{4.1}$Al$_{0.3}$Mn$_{0.4}$H$_{5.73}$	167	5.3907	4.2597	3.09	19.75
Mm*Ni$_{4.3}$Mn$_{0.4}$Al$_{0.3}$	194	5.0186	4.0233		
Mm*Ni$_{4.3}$Mn$_{0.4}$Al$_{0.3}$H$_{5.31}$	194	5.3381	4.2308	3.14	18.97
LaNi$_{3.95}$Co$_{0.75}$Al$_{0.3}$	199	5.0378	4.0107		
LaNi$_{3.95}$Co$_{0.75}$Al$_{0.3}$H$_{5.14}$	199	5.3613	4.1653	3.02	17.62
MmNi$_{4.3}$Mn$_{0.4}$Al$_{0.3}$	195	4.9652	4.0453		
MmNi$_{4.3}$Mn$_{0.4}$Al$_{0.3}$H$_{5.43}$	195	5.3458	4.2793	3.51	23.05
LaNi$_{3.9}$Co$_{0.4}$Mn$_{0.4}$Al$_{0.3}$	192	5.0629	4.0349		
LaCo$_{0.4}$Ni$_{3.9}$Al$_{0.3}$Mn$_{0.4}$H$_{5.66}$	192	5.3894	4.2569	3.09	19.55

Mm* = Cerium free mischmetal

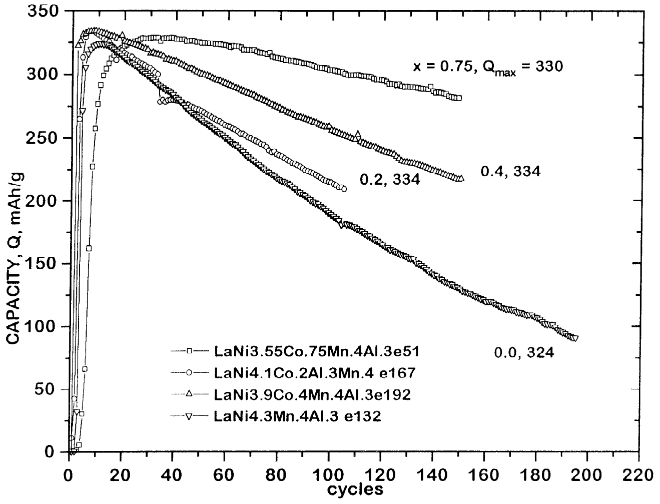

Fig. 2. Performance of $LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$ electrodes; x values and Q_{max} noted.

capacity as a function of cycles which is termed capacity decay. It is defined as the slope of the capacity vs. cycle curve, i.e., $-dQ/dcycle$, and determined via a least squares fit of the data as shown in Fig. 1. The percent lattice expansion of the unit cell in each electrochemical cycle can be calculated via the equation

$$\%\frac{\Delta V}{V} = \frac{V_H}{V} n \times 100 \qquad (1)$$

where ΔV is the actual volume change of the unit cell in $Å^3$ 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; n is calculated from Q_{max} (discharge) via Faraday's Law. It is assumed that in the linear decay region that the remaining uncorroded alloy is hydrided and dehydrided to the same extent in each cycle and therefore n is constant.

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

$$\%\frac{\text{wt. loss}AB_5}{\text{cycle}} = \left(\frac{-dQ}{dcycle}\right)(Q_{max})^{-1} \times 100 \qquad (2)$$

The corrosion rates for all alloys are given in Table 2. The effect of Co content upon electrode corrosion is also clearly shown in Fig. 3 which illustrates plots of alloy corrosion and $\%\Delta V/V$ versus Co content for all the $LaNi_{4.3-x}Co_xMn_{0.4}Al_{0.3}$ electrodes. Corrosion increases as Co content decreases and $\Delta V/V$ increases. This is particularly true at the extremities of the range, as well illustrated by the mischmetal electrodes shown in Fig. 1. In the range for $x=0.4–0.2$ there was no change in $\Delta V/V$ though corrosion increased. This suggests that corrosion inhibition by Co may also be occurring via a surface

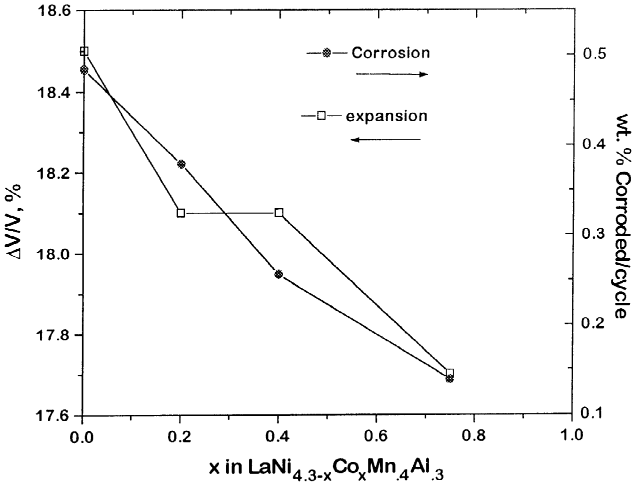

Fig. 3. Lattice expansion and corrosion rate vs. Co content.

Table 2

Composition	Exp. No.	V_H ($Å^3$)	Q_{max}	$dQ/dcycle$	n	$\%\Delta V/V$	% Corrosion/cycle
$MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$	24	3.13	247	0.002	3.90	14.3	0.001
$Mm^*Ni_{3.55}Co_{0.75}Al_{0.3}Mn_{0.4}$	125	3.05	295	0.12	4.64	16.0	0.041
$LaNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$	51	3.06	330	0.46	5.18	17.7	0.139
$LaNi_{3.9}Co_{0.4}Mn_{0.4}Al_{0.3}$	192	3.09	334	0.86	5.25	18.1	0.257
$MmNi_{4.3}Mn_{0.4}Al_{0.3}$	195	3.51	314	1.11	4.96	20.1	0.354
$LaNi_{4.1}Co_{0.2}Mn_{0.4}Al_{0.3}$	167	3.09	334	1.27	5.25	18.1	0.380
$LaNi_{4.3}Mn_{0.4}Al_{0.3}$	132	3.26	324	1.57	5.09	18.5	0.485
$Mm^*Ni_{4.3}Mn_{0.4}Al_{0.3}$	194	3.14	314	3.23	4.94	17.7	1.029

Mm* = Cerium free mischmetal

mechanism; a supposition which is supported by recent X-ray absorption spectroscopy results [6].

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