COMPOSITION AND FUNCTION IN AB₃ HYDRIDE ELECTRODES

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ABSTRACT

Multicomponent AB₃ hydrides are attractive replacements for the cadmium electrode in nickel - cadmium batteries. This paper is concerned with the differential effects of Ni substitution by cobalt, Mn and Al upon electrode corrosion and capacity, using alloys having the generic composition of La(NiCoMnAl)₃, and similar to those used for the preparation of commercial battery electrodes. The corrosion of metal hydride electrodes is determined by two factors, surface passivation due to the presence of surface oxides or hydroxides and crystal lattice expansion - contraction the charge - discharge process. Thus, in addition to determining the effects of Ni substitution we will also address the question of whether an observed change is due to a change lattice expansion or to a change in surface passivation, e.g. the formation a corrosion resistant oxide layer.

INTRODUCTION

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Currently there are two classes of metal hydride electrodes that are of interest for use as battery anodes, i.e. the AB₃ and AB₂ intermetallic compounds. The former have hexagonal CaCu₃ 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. As indicated in the title this paper will be concerned only with the AB₃ class of materials although the approach used would certainly applicable to the more complicated AB₂ alloys.

The paradigm intermetallic compound of AB₃ class is LaNi₃, which has been intensely studied because of its utility in conventional hydrogen storage applications. Unfortunately LaNi₃ is too costly for wide scale use in batteries and corrodes rapidly in the chemically

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aggressive battery environment. Thus commercial AB₅ electrodes use mischmetal, a low cost combination of rare earth elements, as a substitute for La. The B 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 Mm Ni_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3} have been reported to have good storage capacity and cycle life. (1) This paper will be primarily concerned with the effects on electrode lifetime (corrosion) and capacity as a function of the ratio of the various B components as compared to one having the standard composition1, i.e., ANi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3} where A is mischmetal or La.

The corrosion resistance of AB₅ electrodes is 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 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 a corrosion resistant oxide layer. Previous work has indicated that the presence of Ce (3) Al, Zr, and Si (4,2) in AB₅ electrodes reduce corrosion by the formation of a protective oxides (hydroxides) rather than by reducing lattice expansion. Here we report on the differential effects of Ni substitution by cobalt, Mn and Al upon electrode corrosion and capacity using alloys having the generic composition of La(NiCoMnAl)₅ and similar to those used commercially.

EXPERIMENTAL

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 1173K after which X-ray diffraction patterns were obtained for each alloy and its lattice parameters determined. The molar volume of hydrogen in the hydride phase was determined by preparing the hydride phase via the direct reaction with hydrogen gas under a H₂ pressure of ≈ 10 atm. The reactor was then cooled to 78K and evacuated. CO was introduced into the reactor and allowed to condense, after which it was slowly warmed to room temperature, venting CO as necessary to avoid excess pressurization. At 298K the system was vented and the sample removed. This procedure effectively poisoned the alloy surface and prevented hydride decomposition in air for at least several days (4) and permitted X-ray diffraction patterns of the hydride phase to be obtained in sample holders open to the atmosphere. After poisoning the alloy hydride was split into three portions; one used in the X-ray procedure and the other two were subjected to hydrogen analyses via thermal decomposition. Electrodes, containing 0.075 g of alloy, were

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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 or in some cases 30 ma, for two hours; once activated the charging rate did not significantly affect the storage capacity. The discharge current was constant at 10 ma ($\approx 0.5C$ rate); it was cutoff when the anodic voltage increased to -0.70 V vs. the Hg/HgO reference electrode.

RESULTS AND DISCUSSION

The composition, structural parameters and, for many alloys, V_H , are given in Table I. The effect of the substitution of Co, Al and Mn for nickel will be treated in sequence below. In all cases the performance of individual electrodes will be compared with that of the corresponding standard electrode, i.e., $ANi_{3.55}Co_{.75}Mn_4Al_3$.

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 low V_H . The increase of V_H in alloys containing no or little Co is illustrated in Table I exp #'s 132 and 195. Sakai et. al. (4) 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.

Initially we were concerned with the behavior of commercial type electrodes in which the rare earth component consists of mischmetal. Two types of mischmetal are available, normal mischmetal and cerium free mischmetal. In the present instance we prepared four electrodes two having the composition of $MmNi_{4.3-x}Co_xMn_4Al_3$ ($x = 0, 0.75$) and two of $Mm^*Ni_{4.3-x}Co_xMn_4Al_3$ ($x = 0, 0.75$) where Mm^* refers to Ce free mischmetal. Both the normal mischmetal and the cerium free mischmetal were analyzed at the Materials Preparation Center, Ames Laboratory, Ames IA; their respective compositions are given in Table II.

The cycle lives of each of the four mischmetal electrodes (#24, 125, 195, 194) are illustrated in Figure 1 and their corrosion rates and other pertinent data are tabulated in Table III. The cycle lives of the Co free electrodes (#s 195 and 194) are surprisingly poor although their initial storage capacity was higher than the corresponding Co containing electrodes. It is of interest to note that V_H in e195 is the highest in this group as its lattice expansion (see below). However its corrosion rate is less than that of any Co free electrode. This may be attributed

to its high Ce content which is known to inhibit corrosion of AB₃ electrodes (3) even though it tends to increase V_H .

In view of the above results, the cycle life of each of an homologous series of electrodes (#51,192,167,132) of composition $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_4\text{Al}_3$, was determined as shown in Figure 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 which is shared by all AB₃ hydride electrodes. 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 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., $-dQ/d\text{cycle}$, and determined via a least squares fit of the data as shown in Figure 1.

In order to determine the causal relationship between the change in behavior and variation of Co content it is necessary to quantitatively determine lattice expansion. Thus Table III lists % expansion in addition to the H content, n , and capacity decay. The H content is expressed as the number of H atoms, n , per formula unit. n is calculated from Q_{max} via the Faraday equation,

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

where mw is the molecular weight of the alloy and the units of Q are mAh/g. It is 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. Note however that Q is usually not constant since it is a function of the weight of the uncorroded alloy in each cycle. The percent lattice expansion of the unit cell in each electrochemical cycle can be calculated via the equation

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

where ΔV is the actual volume change of the unit cell in $\text{\AA}^3$ 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.

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

$$\frac{\text{wt. loss } AB_5}{\text{cycle}} = \left(\frac{-dQ}{d\text{cycle}} \right) (Q_{\max})^{-1} \times 100 \quad [3]$$

The corrosion rates for all alloys are given in Table III.

The effect of Co content upon electrode corrosion is also clearly shown in Figure 3 which illustrates plots of alloy corrosion and % $\Delta V/V$ versus Co content for all the $LaNi_{4.3-x}Co_xMn_4Al_3$ 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 Figure 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 mechanism. In this connection Kanda et. al. (6) found evidence that Co suppresses the transport of Mn to the surface where it is readily oxidized causing rapid electrode deterioration. Recent x-ray absorption spectroscopy results (5) also suggest that Co inhibits corrosion by suppressing Ni migration to the surface and subsequent oxidation.

Effect of Aluminum

Aluminum appears to be present in all commercial AB_5 electrodes. Plots of storage capacity versus cycle life for three Al free electrodes (exp #'s 173, 202, 253) are shown in Figure 4 and may be compared with an electrode of standard composition. The Al free electrodes corrode at a greatly increased rate (see also Table III). It is of interest to note that e173 contains Ce and its lower corrosion rate is attributed to its presence. Further in an homologous series of Mm^*B_5 electrodes (#'s 210, 209, 206) an increase in Co content does not compensate for the absence of Al as shown Figure 5. The presence of Al not only decreases V_H it also decreases n (note that $Q_{\max}$ for Al free e202 is 366 mAh/g), thus lattice expansion is reduced relative to Al free electrodes. (2) However at this time it is not possible to differentiate between lattice expansion and surface passivation as the primary cause of corrosion inhibition in Al containing AB_5 electrodes because the necessary V_H values are lacking.

Effect of Manganese

Manganese is also present in most commercial electrodes. Its function is not so clear as that of Co or Al. It apparently increases V_H (in Mn free e199 V_H is the lowest of those measured, 3.02 A³/atom H). The cyclic behavior of a series of electrodes (exp #s 199, 256 and 254) of varying Mn content is shown in Figure 6. It appears that a slight reduction in Mn content (exp #254) to give a slightly rare earth rich, non stoichiometric composition, increases storage capacity without a severe penalty in corrosion rate. Unfortunately only V_H for one electrode in this series is available and a correlation between lattice expansion, composition and corrosion rate again is not possible.

Summary and Conclusions

The single most important parameter affecting the corrosion of metal hydride electrodes in repetitive cycles of charge and discharge is the degree lattice expansion and contraction in each full cycle. Large volume changes increase the flushing action of the electrolyte through the pores and fissures of the electrode thereby increasing corrosion by a mass action effect (2). Thus an electrode, in which V_H is large and has a high H storage capacity, will undergo large volume changes upon cycling and corrode relatively rapidly; therefore it is important to formulate alloy electrodes in which V_H is minimized. Another consequence of large volume changes is the increased mobility of metal atoms at the moving interface between the metal phase and the hydride phase during the charge - discharge process. This increases the possibility of transport of easily oxidized alloy components to the electrode surface (2). Indeed Kanda et. al. (6) suggest this is the mechanism by which Co inhibits corrosion in Mn containing electrodes.

Acknowledgement

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TABLE I					
COMPOSITION	Exp #	a, Å	c, Å	$V_H, \text{\AA}^3$	% $\Delta V/V$
LaNi _{3.55} Co _{0.75} Mn _{0.4} Al _{0.3}	51	5.0615	4.0298		
LaNi _{3.55} Co _{0.75} Mn _{0.4} Al _{0.3} H _{0.01}	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 _{0.12}	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 _{0.53}	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 _{0.64}	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 _{0.73}	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 _{0.531}	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 _{0.514}	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 _{0.543}	195	5.3458	4.2793	3.51	23.05
LaNi _{3.85} Co _{0.75} Mn _{0.38}	253	5.0526	4.0195		
LaNi _{3.85} Co _{0.75} Mn _{0.38} H _{0.636}	253	5.4192	4.2829	3.15	22.57
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 _{0.566}	192	5.3894	4.2569	3.09	19.55

Mm* = Cerium free mischmetal

TABLE 2		
Composition of Mischmetal by Chemical Analysis ⁺		
Rare earth	Normal, Wt. %	Ce free, Wt. %
Ce	56.9	0.13
La	20.5	58.2
Nd	14.7	29.9
Pr	5.5	7.6
Fe	0.42	0.07
O	0.058	0.47
C	0.032	0.104
N	0.002	0.162
Y	<0.01	0.04
Ca	0.13	0.27

+ Analysed at Materials Preparation Center, Ames Lab. Ames Iowa

TABLE III

COMPOSITION	exp.#	$V_H, \text{\AA}^3$	$Q_{\max}$ mAh/g	dQ/dcyc	mw	n H/F.U.	%expan.	wt. % corr/cyc
MmNi _{3.55} Mn ₄ Al ₃ Co _{0.75}	24	3.13	247	0.00	423	3.90	14.27	0.001
Mm*Ni _{3.55} Co _{0.75} Al ₃ Mn ₄	125	3.05	295	0.12	422	4.64	16.03	0.041
LaNi _{3.55} Co _{0.75} Mn _{4.5} Al _{2.3}	250		316	0.31	422	4.97		0.098
LaNi _{3.55} Co _{0.75} Mn _{1.4} Al ₃	256		320	0.34	408	4.87		0.106
LaNi _{3.55} Mn ₄ Al ₃ Co _{0.75}	51	3.06	330	0.46	421	5.18	17.74	0.139
LaNi _{3.55} Co _{0.75} Mn _{3.0} Al ₃	254		353	0.53	416	5.48		0.150
LaNi _{3.95} Co _{0.75} Al ₃	199	3.02	340	0.57	423	5.37	18.38	0.168
Mm* Ni _{3.2} Co _{1.2} Mn _{0.6}	210		305	0.55	431	4.90		0.180
Mm*Ni _{3.4} Co _{1.0} Mn _{0.6}	209		312	0.68	431	5.02		0.218
La _{0.7} Ce _{0.3} Ni _{3.55} Co _{0.75} Mn ₇	173		315	1.41	430	5.05		0.248
LaNi _{3.9} Co _{0.4} Mn ₄ Al ₃	192	3.09	334	0.86	421	5.25	18.10	0.257
Mm*Ni _{3.65} Co _{0.75} Mn ₆	206		322	0.93	431	5.18		0.289
MmNi _{4.3} Mn ₄ Al ₃	195	3.51	314	1.11	423	4.96	20.14	0.354
LaNi _{4.1} Co _{0.2} Mn ₄ Al ₃	167	3.09	334	1.27	421	5.25	18.11	0.380
LaNi _{3.85} Co _{0.75} Mn _{3.8}	253	3.15	353	1.44	430	5.66	20.07	0.408
LaNi _{3.85} Co _{0.75} Mn ₄	202		366	1.51	431	5.88		0.413
LaNi _{4.3} Mn ₄ Al ₃	132	3.26	324	1.57	421	5.09	18.54	0.485
Mm*Ni _{4.3} Mn ₄ Al ₃	194	3.14	314	3.23	422	4.94	17.69	1.029

Figure 1: Co substitution in MmB5 electrodes, Q_{max} shown.
Slope calculated for linear region as shown for e125

Figure 2: Performance of $\text{LaNi}_{4.3-x}\text{Co}_x\text{Mn}_4\text{Al}_3$ electrodes ;
 x values and Q_{max} noted.

Figure 3: Lattice expansion and corrosion rate vs Co content.

Swiss

Figure 4: Comparison of Al free electrodes with $\text{LaNi}_{3.55}\text{Co}_{.75}\text{Mn}_4\text{Al}_3$.

Note $Q_{\max}$ for e202.

e206_10

Figure 5: Al free Mm*B5 electrodes with varying Co content
Compare e125 in figure 1.

nan/g6

Figure 6: Effect of Mn content on electrode cycle life.

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Swiss3

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Note $Q_{\max}$ for e202.

e206_10

Figure 5: Al free Mm*B5 electrodes with varying Co content
Compare e125 in figure 1.

san1g6

Figure 6: Effect of Mn content on electrode cycle life.