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Conf-941063--10

BNL-60533

COMPOSITION AND CYCLE LIFE OF MULTICOMPONENT AB_5 HYDRIDE ELECTRODES

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Multicomponent AB_5 hydrides are attractive replacements for the cadmium electrode in nickel - cadmium batteries. The archetype compound of the AB_5 alloy class is $LaNi_5$, but in a typical battery electrode mischmetal is substituted for La and Ni is substituted in part by variety of metals. While the effects of Ni substitution have been widely studied, relatively little effort has focused on the effect of La substitution. This paper deals with the effect on cycle life due to the increasing presence of Ce in the alloy series $La_{1-x}Ce_xNi_{3.55}Co_{.75}Mn_{.4}Al_{.3}$. Alloys were characterized by the determination of pressure-composition relationships, molar volume of H and electrode cycle life. The effects due to lattice expansion are taken into account. It was concluded that the rate of loss of electrochemical capacity per charge/discharge cycle was significantly decreased due to the presence of Ce.

Multicomponent AB_5 hydrides are attractive as replacements for the cadmium electrode in nickel - cadmium batteries from both an environmental and performance viewpoint. However the paradigm compound of the AB_5 class of alloys, $LaNi_5$, is not a suitable electrode because it corrodes rapidly in the chemically aggressive battery environment. This problem can be ameliorated by partial substitution of Ni by a variety of metals such as Co, Al, Si etc. The efficacy of this remedy has been attributed primarily to the reduction of the molar volume of hydrogen, V_H, in the hydride phase thereby reducing alloy expansion and contraction during the charge - discharge cycle which leads to a reduction of the flushing action of the electrolyte through the small pores and fissures of the alloy produced in the activation process. Consequently corrosion of the electrode is reduced.[1] While the effects of Ni substitution has been widely studied, relatively little effort has focused on the effect of La substitution. This neglect is probably due to the good performance and low cost of mischmetal (Mm) B_5 battery electrodes. The rare earth composition of mischmetal corresponds to that of the ore body from which it is recovered; in bastnasite, the most common ore, it corresponds

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to (in atom%) 50-55 Ce, 18-28 La, 12-18 Nd, 4-6 Pr, <0.1 Sm, <2 others. The major component of mischmetal is cerium and this paper is concerned with the determination of the effect of increasing Ce content upon electrode cycle life. In pursuit of this goal we have examined the properties of a series of alloys with a composition corresponding to $La_{1-x}Ce_xNi_{3.55}Co_{.75}Mn_{.4}Al_{.3}$ and their performance as battery electrodes. In doing so we endeavored to discriminate between the effects due to lattice expansion and Ce substitution. Henceforth, for the sake of brevity, alloys with this B_5 composition will written as rare earths B_5, e.g., $La_{1-x}Ce_xB_5$.

EXPERIMENTAL

All the alloys were prepared from high purity, >99.9%, starting components with two exceptions, mischmetal and cerium, which were of commercial purity. Alloys were prepared by arc melting under helium. After the first melt the ingot was turned over and re-melted twice. Each ingot was annealed at 1173K for 3 days after which X-ray diffraction patterns were obtained for each alloy and its lattice parameters determined. Pressure - composition (P-C) isotherms were measured for all alloys according to the usual procedure.[2] The molar volume of hydrogen in the hydride phase was determined by preparing the hydride phase via the gas - solid reaction under a H_2 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.[3] This 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 two portions; one used in the X-ray procedure and the other was subjected to hydrogen analysis via thermal decomposition.

Electrodes were fabricated from a portion of each alloy and subjected to electrochemical cycling studies. Each electrode was prepared by mixing -100 mesh alloy particles with a mixture of teflon and carbon black (Vulcan -XC-72) in the weight ratio of 17% teflon, 33% carbon black and 50% alloy.[4] The weight of the AB_5 intermetallic alloy was 0.075 g. The mixture was then mechanically pressed onto a nickel mesh screen attached to a Ni wire connection. The active electrode surface area was 2 cm^2. Each electrode was introduced into an electrochemical cell, open to the atmosphere and containing 6 m KOH electrolyte. The electrode was activated *in situ* via electrochemical charge and discharge. The cycle life measurements were carried out using a computer controlled battery cycler (Arbin Corp., College Station, Texas). The discharge cycle was cutoff when the anodic voltage increased to -0.70 V vs. a Hg/HgO reference electrode.

RESULTS

Pressure - composition isotherms for a series of samples of composition $La_{1-x}Ce_xB_5$ are shown in Fig. 1. There is very little hysteresis in these systems and only absorption isotherms are shown for the sake of clarity. The maximum H content is achieved when $x = 0.2$; however, at $x > 0.2$ there is a decrease in the H storage capacity and hydride stability. This trend towards decreased stability is not unexpected as the desorption plateau pressure for $CeNi_5H_x$ is 90 atm @295K.[5] In figure 2 we show PC isotherms for MmB_5H_x and $LaNi_5H_x$ in which the latter exhibits a significant hysteresis effect. It may be mentioned that the lack of hysteresis near room temperature in multicomponent AB_5 hydrides is not unusual, but it is almost always present in the less complex binary and ternary systems. It is also noteworthy that, with one exception ($x = 0.2$ in $La_{1-x}Ce_xB_5$), all the multicomponent alloys have significantly less hydrogen storage capacity than $LaNi_5H_x$, a consequence of the substitution of Ni and La by other metals.

The lattice parameters of the starting alloys, their respective hydride phases and the molar volume of hydrogen, V_H, in the latter are listed in Table 1. All of the phases could be indexed as having hexagonal symmetry. For the calculation of V_H the unit cell is assumed to contain one formula unit for both the metal and the hydride phases. V_H is based on the expansion of the hexagonal unit cell per H atom inserted. It is of interest to note that the substitution of Ce increases V_H slightly.

The cycle life of $La_{1-x}Ce_xB_5$ and MmB_5 electrodes are illustrated graphically in Figure 3 by plotting the electrochemical discharge capacity, Q, vs. cycles. 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 electro-chemical storage capacity, Q_{max}, is reached. This is usually followed by a linear curve with a constant negative slope, -dQ/dcycle, which may be termed capacity decay. The low capacity of the $La_{.25}Ce_{.75}B_5$ electrode is attributed to a plateau pressure of >2 atm at 303K (Fig. 1) causing consequent diversion of hydrogen to form gaseous H_2. Two cycle life experiments were carried using $La_{.8}Ce_{.2}B_5$ because of its rather large storage capacity and extended cycle life. Further, in order to confirm the behavior of the LaB_5 two separate alloys (1 and 2) were prepared although the Ni content in one is slightly lower than usual (see Tables); however, both behaved similarly, i.e., they exhibited high decay rates.

The cycle life data is summarized in Table 2. In order to determine the effect of Ce substitution it is necessary to account quantitatively for effects of lattice expansion. Thus Table 2 lists a new parameter, $\Delta\epsilon$, in addition to Q_{max}, and capacity decay. $\Delta\epsilon$ is a function of V_H and the number of H atoms per formula unit, n, calculated from Q_{max}, it is determined via the Faraday equation,

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

where mw is the molecular weight of the unhydrided alloy (the error involved in the use of mw for the unhydrided alloy is negligible) and the units of Q are mAh/g. It is assumed that after activation the remaining alloy in each subsequent charge - discharge cycle is hydrided and dehydrided to the same degree and n is constant. Note however that Q is not constant since it is a function of the weight of the uncorroded alloy in each cycle. Thus for a unit cell, which contains one formula unit, undergoing the phase conversion process,

$$\Delta\epsilon = V_H \times n \qquad [2]$$

and gives the actual volume change of the unit cell in $Å^3$ in each charge or discharge cycle.

In the series $La_{1-x}Ce_xB_5$ the greatest values of $\Delta\epsilon$ corresponds to the two samples where $x = 0.2$, yet the capacity decay, -dQ/dcycle, is significantly less than that for the unsubstituted alloys where $x = 0$. For $x = 0.5$ n is significantly reduced as is, consequently, $\Delta\epsilon$. The MmB_5 electrode has a very low decay rate, but it also has a low capacity and it seems quite likely that a battery incorporating a $La_{1-x}Ce_xB_5$ electrode would have a better overall performance than one with MmB_5 electrode. The decay rate is 0.0 for $x = .75$, a low value due to the low electrochemical storage capacity which is a consequence of the decreased stability of the hydride phase (Fig. 1).

We note that $\Delta\epsilon$ of $LaNi_5$ exceeds that for any other alloy by a large margin and it is not surprising that it is reported to have a very high decay rate.[1]

CONCLUSION

From the above considerations we have concluded that the accelerated decay in storage capacity of the electrodes containing only La as the A component, relative to those alloys which contain Ce is not solely a function of the volume change per cycle, $\Delta\epsilon$, but also the absence of Ce. A possible explanation for this finding lies in the fact that Ce can form a protective oxide film on metal surfaces (Al, mild steel and others).[6] It has been shown via XANES (X-ray Near Edge Absorption Structure) studies that Ce in the film is present as four valent CeO_2.[7] Recent work reported in this conference has shown that Ce in the unhydrided bulk alloy of $La_{.8}Ce_{.2}Ni_{4.8}Sn_{.2}$ is present as a four valent atom.[8] Thus, it is quite possible that any Ce on the alloy surface will be readily oxidized to CeO_2 in the battery environment thereby enhancing corrosion resistance and electrode lifetime.

Finally we note that the mischmetal electrode exhibits a low decay rate and $\Delta\epsilon = 11.6$ Å^3, a relatively low value due to its modest storage capacity. Nevertheless, because of their low decay rates MmB_5 electrodes are useful because of their extended lifetimes. In this connection it is of interest to point out that two other major components of mischmetal, Pr and Nd, also form four valent oxides and which have been reported to form protective oxide films.[6] Thus the use of mischmetal in the formulation of battery electrodes, chosen because of cost considerations, is also desirable in terms of electrode stability and lifetime.

ACKNOWLEDGEMENTS

This work was supported by the Chemical Sciences Division, Office of Basic Energy Sciences, U. S. Department of Energy, under contract No. DE-AC02-76CH00016 and DE-FG03-93ER14381.

REFERENCES

1. J. J. G. Willems and K. H. J. Buschow, J. Less-Common Metals 129, 13 (1987).

2. J. J. Reilly and R. H. Wiswall, Inorganic Chem. 13, 218 (1974).

3. J. R. Johnson and J. J. Reilly, Inorganic Chem. 17, 3103 (1978).

4. K. Petrov, A. A. Rostami, A. Visintin and S. Srinivasan, J. Electrochem. Soc. 141, No.7, 1747 (1994).

5. S. N. Klyamkin and V. N. Verbetsky, J. of Alloys and Compounds 194, 41-45 (1992).

6. D. R. Arnott, B. R. W. Hutton and N. E. Ryan, Corrosion 45, 12 (1989).

7. A. J. Davenport, H. S. Isaacs and M. W. Kendig, Corrosion Science 32, No.5/6, 653-663 (1991).

8. S. Mukerjee, J. McBreen, J. J. Reilly, J. R. Johnson and G. Adzic, Effect of Ce Composition on the Structural and Electronic Characteristics of Some Metal Hydride Electrodes: an *In-Situ* XANES and EXAFS Investigation, This Conference.

DISCLAIMER

TABLE 1

LATTICE PARAMETERS AND V_H

COMPOSITION	ALLOY #	a, Å	c, Å	CELL VOL Å^3	V_H Å^3/H atom
$LaNi_{3.5}Mn_{.4}Al_{.3}Co_{.75}$	1	5.0699	4.0392	89.91	
$LaNi_{3.5}Mn_{.4}Al_{.3}Co_{.75}H_{6.11}$	1	5.4074	4.2743	108.23	3.00
$LaNi_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	2	5.0642	4.0777	89.56	
$LaNi_{3.55}Mn_{.4}Al_{.3}Co_{.75}H_{5.84}$	2	5.3911	4.2387	108.56	2.93
$La_{.8}Ce_{.2}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	3	5.038	4.0416	88.84	
$La_{.8}Ce_{.2}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}H_{5.91}$	3	5.3985	4.2728	107.84	3.21
$La_{.5}Ce_{.5}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	4	4.9934	4.0446	87.33	
$La_{.5}Ce_{.5}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}H_{5.55}$	4	5.353	4.2229	104.79	3.15
$La_{.25}Ce_{.75}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	5	4.9538	4.0559	86.19	
$La_{.25}Ce_{.75}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}H_{2.84}$	5	5.1546	4.1358	95.16	3.15
$MmNi_{3.50}Mn_{.4}Al_{.3}Co_{.75}$	6	4.9623	4.0456	86.27	
$MmNi_{3.50}Mn_{.4}Al_{.3}Co_{.75}H_{3.34}$	6	5.209	4.1309	97.07	3.23

TABLE 2
CYCLE LIFE OF MODIFIED AB_5 ELECTRODES

ELECTRODE	ALLOY #	n * H atoms unit cell	$\Delta\varepsilon$ A^3/unit cell	DECAY -dQ/dcyc mAh/g·c
$La_{.25}Ce_{.75}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	5	1.3	4.1	0
$MmNi_{3.5}Mn_{.4}Al_{.3}Co_{.75}$	6	3.6	11.6	0.041
$La_{.5}Ce_{.5}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	4	4.3	13.5	0.11
$La_{.8}Ce_{.2}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	3	5.0	16.1	0.18
$La_{.8}Ce_{.2}Ni_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	3	5.4	17.3	0.25
$LaNi_{3.50}Mn_{.4}Al_{.3}Co_{.75}$	1	4.9	14.7	0.41
$LaNi_{3.55}Mn_{.4}Al_{.3}Co_{.75}$	2	4.8	14.1	0.46
$LaNi_5$ (ref. 1)		6.0	21	45%/100+

*Based on initial electrochemical capacity, Q_{max}, after activation and one formula unit per unit cell, i.e., AB_5H_n

+Decay curve was not linear; 45% capacity loss after 100 cycles.

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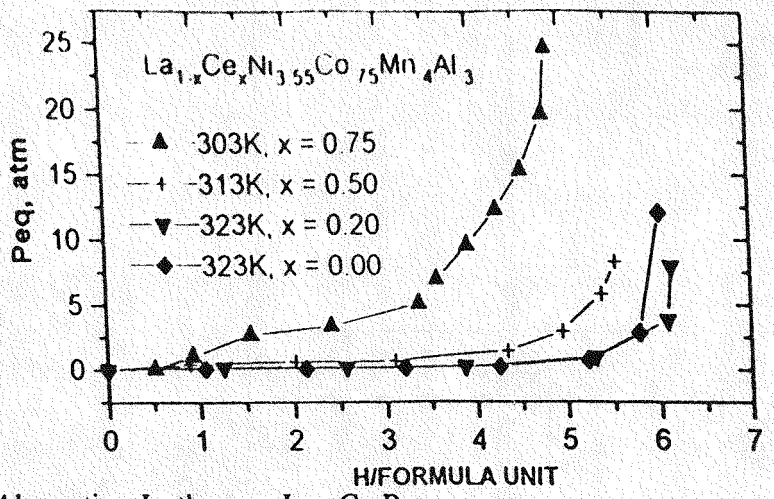

Fig. 1: Absorption Isotherms, $La_{1-x}Ce_xB_5$.

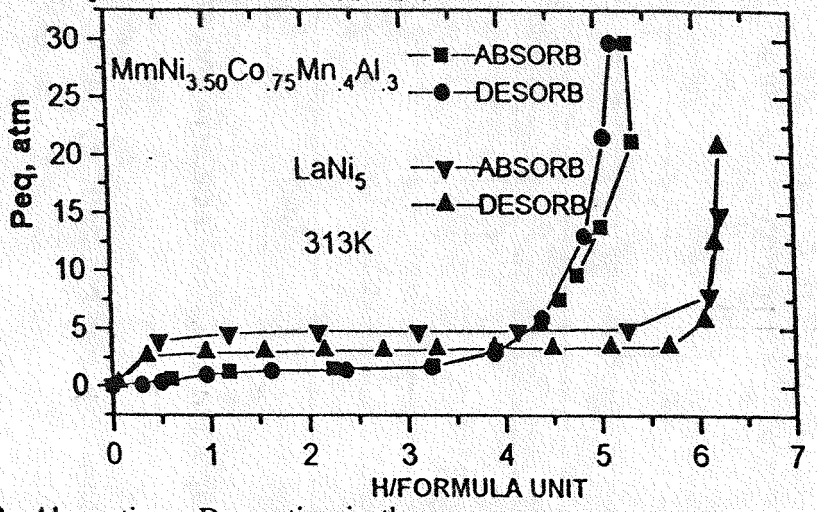

Fig. 2: Absorption - Desorption isotherms.

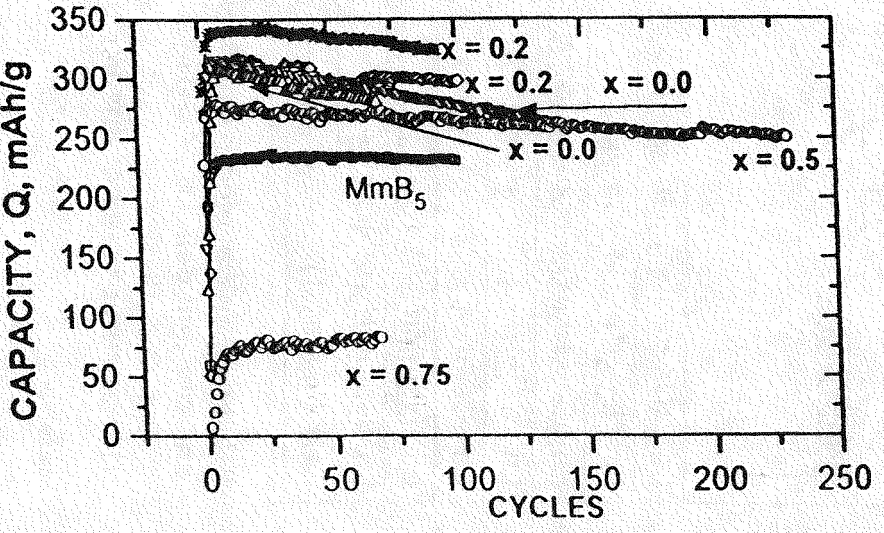

Fig. 3: Capacity vs cycles, MmB_5 and $La_{1-x}Ce_xB_5$. Value of x as shown.