HIGH CYCLE LIFE, COBALT FREE, AB₅ METAL HYDRIDE ELECTRODES

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HIGH CYCLE LIFE, COBALT FREE, AB5 METAL HYDRIDE ELECTRODES

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ABSTRACT

Cobalt-free La(Ni,Sn)X alloys have been identified as low cost, corrosion resistant electrodes for nickel-metal-hydride batteries. The structure of these alloys is similar to non-stoichiometric La(Ni,Cu)X compounds; i.e., they retain the P6/mmm space group while Ni dumbbells occupy La sites. Electrodes fabricated from some of these novel alloys have capacities and cycle lives equivalent to those made from commercial, battery grade, ABX alloys with cobalt.

INTRODUCTION

Currently cobalt is present in all AB5HX electrodes used in Ni-MH batteries. It increases hydride phase stability and extends electrode cycle life by inhibiting corrosion. However, cobalt is also expensive and substantially increases battery costs; thus the substitution of Co by a lower cost metal is desirable. At present the anodes of most NiMH batteries are based on the AB5 family of intermetallic compounds. They have the hexagonal CaCu5 structure where the A component is comprised of one or more rare earth elements and B consists of Ni, or other transition metals, or transition metals combined with main group metals. The parent compound of the AB5 alloys is LaNi5, a compound which has been thoroughly investigated due to its utility in conventional hydrogen storage applications. Unfortunately LaNi5 is too unstable and corrosion sensitive to be used 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 is comprised mostly of Ni in addition to Co, Mn and Al. The partial substitution of Ni increases the thermodynamic stability of the hydride phase and its 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 MmNi4.5Co7.5Mn4Al3 have good storage capacity and cycle life(1) and therefore most AB5 battery electrodes have similar compositions. However, cobalt is responsible for a large fraction of the total raw material cost. Thus, there is an intensive research effort underway to understand the beneficial role of cobalt and develop low-Co or Co-free AB5-type alloys without degrading the electrochemical performance (2,3,4,5,6,7,8).

This paper will present our results on cobalt-free, non-stoichiometric electrodes of the general formula La(Ni,Sn)X, which have cycle lives and storage capacities comparable to current commercial electrodes. The substitution of Sn onto the B sites in AB5 type alloys has been discussed earlier by Lambert et al.(9) and Bowman et al.(10). Both reported that the x-ray diffraction pattern indicated very good crystallinity of the stoichiometric and substoichiometric La(Ni,Sn)X.
compounds. Such Sn substituted alloys could be cycled thousands of time in gas solid systems without a significant change in pressure–composition–temperature (PCT) properties and hydrogen storage capacity, whereas the hydrogen storage capacity of LaNi$_5$ is reduced by more than 90% after 10,000 cycles in hydrogen$^{11}$. Sn modified, stoichiometric, AB$_5$ electrodes were also found to have initial storage capacities between 200- 320 mAh/g$^{(12, 13)}$. The crystal structure of stoichiometric LaNi$_{5-x}$Sn$_x$ has been investigated by Cantrell et. al. (14) and by Wasz et al.(15). The former report the alloys to crystallize in the space group P6/mmm as does LaNi$_5$ and suggested that Sn prefers the 2c sites with some occupation of the 3g sites. The latter also assign the P6/mmm space group to LaNi$_{5-x}$Sn$_x$ but place Sn only on the 3g sites.

EXPERIMENTAL

Alloy Preparation and Cycle Life Tests

A total of six alloys were examined and are listed in Table 1. One alloy was obtained from a commercial vendor, Tribacher Auermet Produktions, GmbH. Note that the La deficient alloys have a different unit cell structure than the others. We also give the stoichiometry normalized with respect to the rare earth component. All calculations for the La deficient alloys are based on the unit cell formulas as determined from their crystal structures as described in the section on Crystal Structure.

All starting elements used in the syntheses had purity grades higher than 99.9%. The preparation and testing procedure has been described in detail previously$^{16}$, but for the readers convenience we give a brief summary: the alloys were prepared in an arc furnace under inert gas and then annealed for 3 days at 1173K. In some cases the annealing temperature was increased to 1273K. After annealing each alloy was examined by x-ray diffraction, all the alloys were essentially single phase. We were not able to prepare single phase La deficient alloys with more than 5% of the A sites La deficient.

Electrodes, containing 0.075 g of active material were fabricated from each ingot. 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 30 mA for two hours. The discharge current was constant at 10 mA (=0.5C rate). It was cut off when the voltage became more anodic than -0.70 V vs. the Hg/HgO reference electrode.

In several cases the atomic volume of hydrogen in the hydride phase, $V_h$, was determined by analyzing the expansion of the unit cell after hydriding using X-ray diffraction$^{(16)}$.

Structure Determination

High-resolution x-ray powder diffraction patterns were collected on beam line X7A at the National Synchrotron Light Source at Brookhaven National Laboratory. Monochromatic radiation, with a wavelength of 0.77842 Å, was obtained by using a channel-cut double crystal Ge(111) monochromator. After sieving through a −200 mesh (U.S. Sieve size), the samples were loaded into 0.2 mm diameter glass capillaries which were oriented and mounted on a goniometer that rotated (1-2Hz) during data collection to eliminate any preferred orientation effects. The sample density was measured when filling the capillaries and used to correct for absorption. A linear position-sensitive detector (PSD)$^{(17)}$ was used to collect data during runs of approximately 4 hours per sample. Structural
refinements were performed using the Rietveld refinement program PROFIL written by J.K. Cockcroft (anonymous ftp @ gordon.cryst.bbk.ac.uk). The background was determined by linearly interpolating between fixed points.

RESULTS

Electrode Cycle Life

Figure 1 presents plots of electrochemical storage capacity, Q, versus the charge–discharge cycles for three electrodes, e594, e132 and an electrode made from the commercial alloy, e564. (Mm refers to mischmetal which in this case has the composition 53 wt.% La, 32% Ce, 10% Nd and 5% Pr). Inspection of the cycle life plots reveals a common behavior of most MHx 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, Qmax, is reached. This is usually followed by an almost linear decrease in capacity due to corrosion. Note that the initial capacity of electrode e594 is slightly greater than e564 but decays at almost the same rate. Significantly the stoichiometric, Co free electrode, e132, loses capacity rapidly.

Figure 2 shows the performance of electrodes with varying La content, i.e., e594, e601, e600, e492. Note that the stoichiometric electrode e492, even though it has a slightly higher initial capacity, decays at a substantially higher rate than the non–stoichiometric ones. This is likely due, at least in part, to the increased expansion and contraction of the unit cell during the charge/discharge process.

The results of these experiments are summarized in Table 2. The corrosion rate is based on the slope of the linear portion of the capacity vs. cycle life plots. The number of hydrogen atoms/unit cell, n, is calculated from the maximum uptake, Qmax. The procedures are described in detail by Adziec et. al. (18)

Crystal Structure

Notten et. al.(19,20) reported that the electrochemical cycling stability can be improved dramatically when using non-stoichiometric La(Ni,Cu)x. alloys. They attributed the improvement to an alteration of the crystal structure in which the excess of B-type atoms is accommodated in the AB5 lattice by the occupation of A (La) sites by dumbbell pairs of Ni atoms elongated along the c-axis. This explained an observed anisotropic lattice deformation in these alloys where the a axis decreases while the c-axis increases. The authors also concluded from their studies of the La(Ni,Cu)x (5.0<x< 6.0) system that Cu (atomic radius: 126 pm) was not included in the dumbbells and that it primarily substitutes for Ni (atomic radius: 125 pm) in the basal plane 2c sites.

Figure 3 presents the observed X – ray diffraction pattern of LaNi4.84Sn32 (La0.9781(Ni0.0219)2Ni4.692 Sn0.338 #e594) and the residual differences with the calculated pattern based on Rietveld refinement. The crystallographic parameters are given in Table 3. The pattern indicates that the sample is highly crystalline. There are no indications of preferred orientation or evidence of the presence of stacking faults or strain. The P6/mmm space group of stoichiometric LaNi4.78Sn0.30 was preserved, as in the case of La(Ni,Cu)5x. The B(3,3) atomic displacement parameter (Table 3) indicates a large displacement of La along the c axis compared to the in-plane displacement. Aligning dumbbells along the c-axis in a random fashion will lead to this type of displacement parameter for the disordered dumbbell A-sites. The refinement also indicates that the electron density of the B site in the basal plane (2c) can be fully accounted for by Ni occupation. Placing Sn on this site would lead to vacancies, which in view of the stoichiometry is not very likely. As observed in the La(Ni,Cu)x. alloys(19), there is a substantial increase in the c axis and a decrease of the a axis of LaNi4.84Sn32.
(La_{0.978}Ni_{0.0219})_{2}Ni_{4.692}Sn_{0.308}) relative to the stoichiometric LaNi_{4.7}Sn_{0.3}. Again, the contraction of the a axis indicates that the bigger Sn atom (atomic radius of 163 pm) does not occupy the basal plane 2c sites. The mid-plane 3g sites are occupied by Ni and all of the Sn. Note that if dumbbells of Sn-Ni or Sn-Sn were present, one would expect much larger amounts of strain within the AB_{5} host structure. However, the very good crystallinity of the alloys militates against such atomic size mismatches. No indications of long range superstructures could be found. The same was observed by Coene et al. (21) in a transmission electron microscopy study of non-stoichiometric LaNi_{5+x} and LaNi_{4+x}Cu_{x} alloys. According to Notten's formalism (19), the fraction of Ni substituted A sites, \( y \), is given by

\[
y = \frac{(z-5)}{(z+2)} \tag{1}
\]

where \( z \) is the number of B atoms per La. Thus the actual chemical formula of LaNi_{4.94}Sn_{0.06} (AB_{5.157}, c594) is La_{0.978}Ni_{0.0219}Ni_{4.692}Sn_{0.308} indicating that 2.19% of the La atoms are substituted by Ni dumbbells. A representation of the structure is shown in Figure 4. Transition metal dumbbells have been found in other rare earth–transition metal compounds, i.e., RE_{2}Fe_{7}C_{x} (A_{2}B_{17} type) which have an ordered superstructure of the CaCu_{5} lattice (22,23). The crystal structures of the other La deficient alloys were also determined and were found to similarly substitute Ni dumbbells on vacant A sites.

**STRUCTURE AND CORROSION**

Electrode corrosion is a complex process depending on several factors (18), one of them being related to the cyclic expansion and contraction the hydride forming alloy undergoes with each charge/discharge cycle. Notten et al. (19) have suggested that the increased cycle life of non-stoichiometric La(Ni,Cu)_{5+x} alloys are in part due to reduced decrepitation that decreases the electrode surface area. The same could be true in the case of La(Ni,Sn)_{5+x} alloys. As noted above, Sn substituted stoichiometric alloys are remarkably resistant to thermodynamically driven degradation when cycled in hydrogen gas compared to LaNi_{5} which tends to lose its crystalline properties rapidly (10,11). On a microscopic level, reduced decrepitation could be the result of the partial relief of accumulated stress, created by repetitive charge/discharge cycles, via the motion of dislocations. Inue et al. (24) showed that in thin foils of LaNi_{5} only dislocations perpendicular to the basal plane are observed to move whereas the in-plane dislocations tend to accumulate and build up stress. It is possible that the presence of Ni dumbbells on the A site influences the motion of in-plane dislocations thereby reducing the stresses that ultimately leads to cracking. However, a definitive determination of the relationship between the dumbbell AB_{5+x} structure, Sn content and electrode performance must be deferred to future investigations.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the support by the Office of Chemical Sciences, Office of Basic Energy Sciences and the Exploratory Technology Research Program of the Office of Transportation Technologies, all of the U.S. Department of Energy under contract DE-AC02-98CH10886. We also thank Dr. Zamir Gavra, Nuclear Research Center, Negev, Israel, for alloy analyses.

**REFERENCES**
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<th>TABLE 1: ALLOY COMPOSITIONS</th>
<th>TABLE 2: ELECTRODE PERFORMANCE</th>
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<tr>
<td>Element Ratio</td>
<td>Structural Formula</td>
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<td>LaNi&lt;sub&gt;0.92&lt;/sub&gt;Sn&lt;sub&gt;0.08&lt;/sub&gt;</td>
<td>LaNi&lt;sub&gt;0.92&lt;/sub&gt;Sn&lt;sub&gt;0.08&lt;/sub&gt;</td>
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<td>LaNi&lt;sub&gt;3.55&lt;/sub&gt;Co&lt;sub&gt;0.75&lt;/sub&gt;Mn&lt;sub&gt;0.4&lt;/sub&gt;Al&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>LaNi&lt;sub&gt;4.33&lt;/sub&gt;Mn&lt;sub&gt;4.43&lt;/sub&gt;Al&lt;sub&gt;3&lt;/sub&gt;</td>
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*Mn refers to metallic, which in this case has the composition 30 wt.% La, 40% Co, 15% Nd, and 6% Pt.

**Atomic volume of D in hydride phase**
Experimental data: the calculated intensity at the fourth step of the pattern. See Figure 3 for a plot of the refined model versus the calculated intensity.

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<th>Atom</th>
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Table 3: Structural parameters of La₄Sn₂Ni₃F₁₈ Sn₄Ni₂F₁₈. Including anisotropic displacement parameters (ADP) in Å².
Commercial battery grade alloy

FIGURE 1: Cycle life of complex $AB_5$ alloys with and without cobalt.

Figure 2: Capacity vs. cycles for $La(NiSn)_{5+x}$ electrodes, where $x = 0.0, 0.08, 0.16, 0.33$. 
Figure 3: X-ray diffraction pattern of $\text{La}_{0.978}\text{Ni}_{0.02192}\text{Ni}_{4.692}\text{Sn}_{0.308}$ ($\text{LaNi}_{4.84}\text{Sn}_{0.32}$, e594); lower plot is the difference between the observed (above) and calculated intensities.

Figure 4: Representation of unit cell of $\text{La}(\text{NiSn})_{5+x}$ showing Ni dumbells. Sn, shown in the $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ 3g site, is actually disordered among all 3g sites.