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Mn in misch-metal based superlattice metal hydride alloy – Part 2 Ni/MH battery performance and failure mechanism

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HIGHLIGHTS

- The battery performances of misch-metal superlattice alloys were compared to those from AB_5.
- Mn-free superlattice alloy shows better low temperature and high power performance when compared to AB_5.
- Mn in the superlattice improves cell voltage and high-rate dischargeability.
- The main degradation mode for misch-metal based superlattice alloy is pulverization and loss in electrolyte.
- MnxO debris was found in the separator and separator/positive electrode interface.

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ABSTRACT

The performance and failure mode of Ni/MH batteries made from a series of Mn-modified A_2B_7 superlattice and a commercially available AB_5 metal hydride alloys were studied and reported. Cells with the Mn-free A_2B_7 alloy generally show improved low-temperature, higher peak power, and similar charge-retention behavior over those with a conventional AB_5 alloy. As Mn-additive amount increased, cell voltage and high-rate capacity improved, low temperature, charge retention, and cycle life first improved, but then deteriorated, and peak power and high temperature voltage stand deteriorated. Analysis of battery performance test results show the use of a superlattice alloy containing 2.3% Mn as the best overall alloy composition. Failure analysis of the highly cycled AB_5 alloy containing cells indicate a balanced degradation in negative, positive, separator, and a moderate loss of electrolyte. Same analysis on cells containing the various superlattice alloys suffered from a high degree of pulverization and oxidation of its negative electrode (with the 9.3% Mn content experiencing the worst amount of pulverization/oxidation) and a high degree of electrolyte loss.

1. Introduction

Nickel/metal hydride (Ni/MH) rechargeable batteries mainly power portable electronics, store the energy during braking in a hybrid electrical vehicles, and serve as an energy back-up unit in the stationary applications. Misch metal based AB_5 metal hydride (MH) alloy with reversible hydrogen storage capability is the most widely used active material in the negative electrode of Ni/MH batteries due to its good balance among storage capacity, high rate performance, charge retention, and cycle stability. In 2005, a new type of Mg-containing superlattice MH alloy with a higher energy density and a prolonged service cycle was introduced in the low self-discharge Ni/MH battery [1–3]. Although many research papers in the electrochemical application of the superlattice alloy family can be found (for a recent review, see Ref. [4]), direct battery performance comparisons between the superlattice and the conventional AB_5 MH alloys are very rare [5,6]; therefore, a systematic study in a series of Mn-modified superlattice MH alloy was conducted in a collaboration between FDK and BASF. The characteristics of the superlattice alloys in the powder form, such as structural, gaseous phase hydrogen storage, electrochemical, and surface magnetic properties are reported in Part 1 of this two-part publication [7]. The battery performance in sealed cells and subsequent failure modes are presented in this paper.

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2. Experimental setup

Six MH alloys were compared in this study. The design chemical compositions are listed in Table 1. The La-rich AB_5 alloy used for comparison was supplied by Great Western Technologies Inc. (Troy, Michigan). Five superlattice alloys (F1–F5) were supplied by Japan Metals and Chemicals Co. C-size Ni/MH batteries were made with the dry compacted negative electrodes, wet pasted CoOOH-coated (2 wt.%) $Ni_{0.91}Co_{0.045}Zn_{0.045}(OH)_2$ as counter electrodes containing 5% Co metal powder and 1% Y_2O_3 additives in the paste, 6 M NaOH electrolyte with a small amount of LiOH added, and Scimat 700/79 acrylic acid grafted polypropylene/polyethylene separators (supplied by Freudenberg). The negative-to-positive capacity ratio design was 2.0 to maintain a good balance between the over-charge reservoir and the over-discharge reservoir [5]. After the batteries were sealed, they were loaded onto a Maccor battery cycler for electrical formation. The formation consists of 6 cycles with an increasing amount of charge input for the first 4 cycles (50%–100%–120%–150%) at C/10 charge and C/5 discharge rates. The following 2 capacity grading cycles consist of 150% C/10 charging, C/5 (cycle 5) and C/2 (cycle 6) discharge to 0.9 V.

Specific power of these sealed Ni/MH batteries was measured as a function of cycle life using a pulse-discharge method. During cycle 1 of life testing, the specific power is measured at 50 and 80% depth of discharge (DOD) using a discharge pulse method. This method involves discharging the cell at a C/3 to the indicated depth of discharge following by a 2C/3 pulse for a period of 30 s. This method is then repeated at cycle 50 and at 50 cycle increments thereafter until the cell reaches end of life.

Charge retention was measured by taking the full discharge capacity at C/5 rate after fully charging at C/10 rate first, then storing at room temperature (RT) for a specific time period (7, 14, 30 days). This remaining capacity at C/5 rate was normalized by the original capacity measured at C/5 discharge rate before the storage. Shelf life was measured by first discharging the cell at C/5 to 100% DOD and measuring the open circuit voltage. The battery was then placed in an oven at 45 °C and removed every 15 days to record any decay in open circuit voltage. When the open circuit voltage reaches 0 V, the cell is then removed from the test, allowed to cool to RT, and then tested for capacity loss. Capacity loss verification consists of 3 cycles at C/10 charge to 150% SOC followed by a C/5 discharge to 0.9 V. Cycle 3 capacity is then compared to the original formation capacity and the amount of loss is determined.

Cycle life of each battery was tested by repeating a charge/discharge cycling performed at RT. Charging was completed at a C/2 rate with a $-\Delta V$ termination method. With this method, the charging process was terminated when a 3 mV decrease from the maximum cell voltage was detected, indicating the completion of charge and the start of hydrogen–oxygen recombination. Discharge was completed at a C/2 rate with the cut-off voltage set at 0.9 V. End of life is determined to have been reached when the cell capacity falls below 70% of its initial capacity.

For the failure analysis, a Varian *Liberty* 100 inductively-coupled plasma (ICP) system was used to determine the chemical composition, a Philips *X'Pert Pro* X-ray diffractometer (XRD) was used to study the structure of the negative electrode, and a JEOL-*JSM6320F* scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) capability was used to study the morphology and composition. JEOL JSM7100 field-emission SEM with EDS capability was also used to identify metal oxides imbedded in the separator.

3. Results and discussion

3.1. Alloy properties

The composition and hydrogen storage capacities from both the gaseous phase and electrochemistry and the high-rate dischargeability (HRD) of the six MH alloys used in this experiment are listed in Table 1. To summarize: while the AB5 alloy has only one major phase with a $CaCu_5$ crystal structure, the superlattice alloys are composed of the combination of AB_2, AB_3, A_2B_7, A_5B_{19}, and AB_5 phases made from alternating AB_5 and A_2B_4 slabs stacking along *c*-axis [7]. In the gaseous phase, AB5 alloy has a higher maximum hydrogen storage capacity (1.41 wt.%) than those from other superlattice alloys which decrease with increasing Mn-content. In the electrochemical capacity measurement, the discharge capacities of the superlattice alloys measured with a discharge current of 8 mA g^{-1} and a cut-off voltage of 0.9 V vs. $Ni(OH)_2$ electrode are closer to (even higher than in cases of F4 and F5) their gaseous phase storage capacities measured at 6 MPa hydrogen pressure. In the case of AB5, its electrochemical discharge capacity (331 mAh g^{-1}) is only 88% of its equivalent discharge capacity converted from the 1.41 wt.% gaseous phase storage capacity. The difference may arise from the multi-phase nature of the superlattice MH alloys which is similar to Zr_xNi_y-based MH alloys [8,9]. The half-cell HRD is defined as the ratio between capacities measured at 100 and 8 mA g^{-1} rates in half-cell flooded configuration. The half-cell HRD of the Mn-free base alloy is lower than that from the AB5 MH alloy and it decreases as the Mn-content increases due to reduction both in the bulk diffusion of hydrogen and surface reaction activity [7].

3.2. Cell capacity at room temperature and low temperatures

Benchmark rate performance test results on cells using alloys AB5, F1, F2, and F3 at four different discharge rates (C/5, C/2, C, and 2C) are plotted in Fig. 1. A comparison of the data shows similar capacities (4.2–4.4 Ah) for all four alloys at the C/5 discharge rate; however, as the discharge rate is increased, there is a corresponding decrease in rate performance as demonstrated by the lower mid-point voltage of the discharge curve and subsequent discharge capacity. Of particular note is the rate performance of Alloys F1 and F2. These alloys have a relatively lower mid-point voltage measured at 1C rate (listed in Table 2) and thus very low discharge capacities

Table 1

Summary of the composition and properties of alloys used in this study [7,21]. The electrochemical capacity was taken from the 2nd cycle at a discharge current of 8 mA $g^{-1}$with a cut-off voltage of 0.9 V against a standard $Ni(OH)_2$ positive electrode. The gaseous phase maximum capacity was obtained at 6 MPa hydrogen pressure. HRD is the ratio of discharge capacities measured with discharge current of 100 and 8 mA g^{-1}.

Alloy	Composition	Structure	Max. H-storage (wt.%)	Discharge capacity @8 mA g^{-1} (mAh g^{-1})	Ratio between electrochemical and gaseous phase capacity (%)	HRD (%)
AB5	$Mm_{16.7}Ni_{60.0}Co_{12.7}Al_{4.7}Mn_{5.9}$	$CaCu_5$	1.41	331	88	99.3
F1	$Mm_{19.3}Mg_{3.9}Ni_{72.8}Al_{4.0}$	Superlattice	1.39	354	95	97.6
F2	$Mm_{19.3}Mg_{3.9}Ni_{70.5}Al_{4.0}Mn_{2.3}$	Superlattice	1.37	346	94	96.5
F3	$Mm_{19.3}Mg_{3.9}Ni_{68.1}Al_{4.0}Mn_{4.7}$	Superlattice	1.25	332	99	95.6
F4	$Mm_{19.3}Mg_{3.9}Ni_{65.8}Al_{4.0}Mn_{7.0}$	Superlattice	1.21	328	101	94.3
F5	$Mm_{19.3}Mg_{3.9}Ni_{63.5}Al_{4.0}Mn_{9.3}$	Superlattice	1.15	317	103	95.4