



# Partial substitution of cobalt for nickel in mixed rare earth metal based superlattice hydrogen absorbing alloy – Part 2 battery performance and failure mechanism



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## ABSTRACT

The electrochemical properties of Ni/MH batteries with a series of Co-substituted superlattice alloys as the negative electrodes in sealed cells were investigated and compared to those of a conventional AB<sub>5</sub> alloy. A small amount of Co (<5 at%) in the superlattice alloys is found to improve the discharge capacity, increase the discharge voltage, improve the low-temperature performance, and extend the cycle life. However, it is also responsible for the deteriorations in charge retention, 45 °C voltage stand, and high-temperature performance. Alloy C3 with 4.7 at% Co shows well-balanced properties – superior performance at low temperature and in cell capacity, charge retention, cycle stability, but is inferior at high-temperature when compared to the AB<sub>5</sub> alloy. The failure mechanisms of the cells were investigated with scanning electron microscopy, inductively coupled plasma and X-ray diffraction analysis. The failure mechanisms of alloy C3 were identified as a combination of electrolyte dry-out and positive electrode swelling.

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## 1. Introduction

Superlattice hydrogen-absorbing alloys (HAAs) have been intensively investigated since Sanyo first commercialized them [1–3] in 2005. Compared to the conventional AB<sub>5</sub> HAAs, their lower self-discharge, higher capacity and better power performance makes superlattice HAAs competitive in commercial products. This prompts the active research topic of battery failure mechanism (see review articles [4,5]).

It has been proven in the conventional AB<sub>5</sub> HAAs that the B-site atoms affect the crystal lattice parameters, hydride formation enthalpy, pressure-concentration-temperature (PCT) isotherm hysteresis, and plateau pressure [6–12], as well as sealed-cell capacity performance, cycle life and failure mechanism [13,14]. The additions of Co [15] and Co<sub>3</sub>O<sub>4</sub> [16] powder to the AB<sub>5</sub> HAAs were reported to have a synergistic effect on discharge capacity in a significant manner.

In AB<sub>2</sub> HAAs, Co was used as a B-site modifier to increase the PCT plateau pressure, reduce PCT hysteresis and extend the cycle life [17–20]. It was also reported to have a negative effect on both the gas phase and electrochemical capacity [21,22]. In an AB<sub>2</sub> alloy containing both C14 and C15 phases, it has been demonstrated that Co improves the activation properties, specific power, cycle life and low-temperature performance [23–25]. Co-addition in C14 Laves phase alloys also has a synergetic effect that improves the charge retention more than Mn-addition alone [26].

Given that the B-site modifier can effectively improve the electrochemical performances of AB<sub>5</sub> and AB<sub>2</sub> alloys, the effects of Mn-substitution on the physical and electrochemical performances, as well as the failure mechanisms of the cells with superlattice alloy negative electrodes, have been discussed before [27,28]. The effects of Co-substitution on the phase abundance, crystal structure, metallic nickel distribution in the surface oxide layer, and the electrochemical properties of the mixed rare earth (MRE) metal based superlattice alloys were discussed in Part 1 of this two-part paper [29]. This second part completes the investigation of Co-substitution on the electrochemical performance and failure mechanism of the sealed-cells made from the Co-substituted superlattice HAAs.

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## 2. Experimental setup

Five superlattice HAAs ( $\text{Mm}_{0.83}\text{Mg}_{0.17}\text{Ni}_{3.14-x}\text{Al}_{0.17}\text{Co}_x$ ,  $x = 0, 0.1, 0.2, 0.3$ , and  $0.4$ ) were designed and their compositions are listed in Table 1. Japan Metals and Chemicals Co. (Tokyo, Japan) supplied these alloys. The chemical composition of the MRE metal (Mm) is 19.6 wt% lanthanum (La), 40.2 wt% praseodymium (Pr) and 40.2 wt% neodymium (Nd). In addition, alloy AB5 (a commercially available La-rich AB<sub>5</sub> HAA supplied by Eutectix, Troy, MI, USA) was used for comparison purposes. The same alloy has been used in our previous study of the Mn-substituted superlattice HAAs [28]. C-size Ni/MH batteries were assembled for electrochemical testing. The powders of the six different alloys were dry-compacted onto nickel mesh current collectors as negative electrodes. 95 wt% CoOOH-coated  $\text{Ni}_{0.91}\text{Co}_{0.045}\text{Zn}_{0.045}(\text{OH})_2$  (containing ~ 2 wt% CoOOH) and 5 wt% Co powder on nickel foam substrates were used as positive electrodes.  $\text{Y}_2\text{O}_3$  (1 wt%) additive was added into the positive electrode paste to raise the open-circuit voltage, reduce the impedance and extend the cycle life [30]. Scimat 700/79 acrylic acid grafted polypropylene/polyethylene separators were supplied by the Freudenberg Group, Weinheim, Germany. NaOH electrolyte (26.8 wt%) with LiOH (1.5 wt%) additive was used as the electrolyte. The negative-to-positive capacity ratio was set at 2.0 to maintain a good balance between the over-charge and over-discharge reservoirs [31]. C-sized Ni/MH batteries were assembled for electrochemical testing. A six-cycle electrochemical formation process was performed using a Maccor Battery Cycler after the batteries were sealed. The batteries were charged to 50%, 100%, 120% and 150% capacity in the first four cycles and then the 150% charge input was repeated for two more cycles. A 0.2C discharge rate was used in the first five cycles and 0.5C in the sixth cycle to discharge the cells to a cutoff voltage of 0.9 V.

The peak power of each of the sealed Ni/MH batteries was measured every 50 cycles at 50% depth of discharge (DOD) using a pulse-discharge method until the cell reached end of life. This method involves discharging the cell at a rate of 0.33C rate to 50% DOD followed by a 0.67C pulse for a period of 30 s.

The charge retention of each cell was measured at 7, 14 and 30 days at room temperature (RT) after being fully charged at a 0.1C rate on day one. The remaining capacity after 30 days was discharged at a 0.2C rate and was normalized by the 0.2C discharge capacity before the charge retention experiment. Shelf life was measured by placing a 100% state-of-charge (SOC) battery (charged at 0.2C) in an oven at 45 °C and recording the open circuit voltage decay every 15 days until the open-circuit voltage (OCV) dropped to 0 V. The cells were cooled to RT to test the capacity loss after 3 cycles of charge to 150% SOC at 0.1C followed by discharge to 0.9 V at 0.2C. The capacity at cycle 3 was compared to the original formation capacity to determine the amount of capacity loss.

The cycle life of each battery was tested under a 0.5C rate

charge/discharge cycling at RT with a discharge cut-off voltage of 0.9 V. The charging process was terminated when a 3 mV voltage drop from the maximum cell voltage was detected. The voltage drop indicates the end of the charging process, when oxygen begins to evolve from the positive electrode. The recombination of oxygen from the positive electrode with hydrogen from the negative electrode releases heat and causes the voltage to drop according to the Nernst equation. A capacity drop below 70% of the first discharge capacity after the formation process was considered as the end of life.

For the failure mechanism analysis, a JEOL-JSM6320F scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) capability was used to study the morphology and composition of the electrodes after cycling. A Philips X'Pert Pro X-ray diffractometer (XRD) was used to study the crystal structure of the negative electrode after cycling. A Varian Liberty 100 inductively coupled plasma (ICP) system was used to determine the composition of the Soxhlet extraction solution, and a JEOL JSM7100 field-emission SEM with EDS capability was used to map metal oxides migrated into the separator.

## 3. Results and discussion

### 3.1. Alloy properties

The composition, structure, maximum hydrogen storage capacity, electrochemical discharge capacity (tested in a flooded half-cell), ratio between electrochemical and gaseous phase capacity and the high-rate dischargeability (HRD) of the six HAAs are summarized in Table 1 and details of measurement can be found in Part 1 of this paper [29]. While the major phase in the AB5 alloy is a  $\text{CaCu}_5$  crystal structure [27], the superlattice HAAs are mainly composed of  $\text{Ce}_2\text{Ni}_7$  and  $\text{NdNi}_3$  superlattice crystal structures and a  $\text{CaCu}_5$  crystal structure. The lattice constants, unit cell volumes and phase abundances were previously reported [29]. The maximum gaseous phase hydrogen storage capability of the Co-substituted alloys demonstrated a stepwise increasing trend from 1.38 wt% at 0 at% Co-substitution to 1.41 wt% at 9.3 at% Co-substitution. The Mn addition into a similar base superlattice HAA showed an opposite trend, with a decreasing maximum hydrogen storage capacity [27]. The electrochemical discharge capacities of the superlattice alloys were all higher than that of the AB5 alloy, although the AB5 alloy demonstrated a higher gaseous phase capacity than both the Co- and Mn-substituted superlattice alloys. The capacities of the superlattice alloys had stepwise increases in both electrochemical and gaseous phase hydrogen storage tests. The maximum gaseous phase capacity can be converted to electrochemical capacity according to  $1 \text{ wt\% H} = 268 \text{ mAh g}^{-1}$ . This value converted from maximum gaseous phase capacity is considered to be the maximum electrochemical capacity that can possibly be reached

**Table 1**  
Summary of the composition and properties of alloys used in this study. The electrochemical capacity was taken from the 2nd cycle at a discharge current of 5 mA g<sup>-1</sup> with a cut-off voltage of 0.9 V against a standard Ni(OH)<sub>2</sub> 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 200 and 5 mA g<sup>-1</sup>.  $M_s$  is the saturated magnetic susceptibility reflecting the amount of metallic nickel in an activated surface.

| Alloy | Composition  | Structure       | Max. H-storage (wt%) | Discharge capacity @5 mA g <sup>-1</sup> (mAh g <sup>-1</sup> ) | Ratio between electrochemical and gaseous phase capacity (%) | HRD (%) | $M_s$ (emu g <sup>-1</sup> ) |
|-------|--|-----------------|----------------------|---|--|---------|------------------------------|
| C1    | $\text{Mm}_{19.3}\text{Mg}_{3.9}\text{Ni}_{72.8}\text{Al}_{4.0}$                 | superlattice    | 1.38                 | 346   | 94   | 93.6    | 3.52                         |
| C2    | $\text{Mm}_{19.3}\text{Mg}_{3.9}\text{Ni}_{70.5}\text{Al}_{4.0}\text{Co}_{2.3}$  | superlattice    | 1.39                 | 351   | 94   | 92.0    | 4.65                         |
| C3    | $\text{Mm}_{19.3}\text{Mg}_{3.9}\text{Ni}_{68.1}\text{Al}_{4.0}\text{Co}_{4.7}$  | superlattice    | 1.40                 | 354   | 94   | 93.8    | 6.36                         |
| C4    | $\text{Mm}_{19.3}\text{Mg}_{3.9}\text{Ni}_{65.8}\text{Al}_{4.0}\text{Co}_{7.0}$  | superlattice    | 1.40                 | 356   | 95   | 95.2    | 6.77                         |
| C5    | $\text{Mm}_{19.3}\text{Mg}_{3.9}\text{Ni}_{63.5}\text{Al}_{4.0}\text{Co}_{9.3}$  | superlattice    | 1.41                 | 360   | 95   | 91.4    | 7.49                         |
| AB5   | $\text{Mm}_{16.7}\text{Ni}_{60.0}\text{Co}_{12.7}\text{Al}_{4.7}\text{Mn}_{5.9}$ | $\text{CaCu}_5$ | 1.41                 | 334   | 88   | 98.6    | 5.17                         |

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