

# Material Science and Engineering with Advanced Research

# Properties of Nickel Metal Hydride Battery Using Molybdenum-added Superlattice Metal Hydride Alloy

#### Kwo-Hsiung Young<sup>1,2\*</sup>, Xinting Lin<sup>3</sup>, Yu-Ling Lien<sup>4</sup> and Shigekasu Yasuoka<sup>5</sup>

<sup>1</sup>Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202, USA
 <sup>2</sup>BASF/Battery Materials-Ovonic, 2983 Waterview Drive, Rochester Hills, MI 48309, USA
 <sup>3</sup>Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA
 <sup>4</sup>Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA
 <sup>5</sup>Engineering Division, Ni-MH Group, FDK Corporation, 307-2, Koyagi-Machi, Takasaki, Gunma 370-0042, Japan

<sup>2</sup>Engineering Division, NI-WH Group, FDK Corporation, 307-2, Koyagi-Machi, Takasaki, Gunma 370-0042, Japan

\*Corresponding author: Kwo-Hsiung Young, Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202, USA

BASF/Battery Materials-Ovonic, 2983 Waterview Drive, Rochester Hills, MI 48309, USA; Tel: 01-248-273-7000; Fax: 01-248-299-4228; E mail: kwo.young@basf.com

Article Type: Research, Submission Date: 12 March 2018, Accepted Date: 02 April 2018, Published Date: 13 April 2018.

**Citation:** Kwo-Hsiung Young, Xinting Lin, Yu-Ling Lien and Shigekasu Yasuoka (2018) Properties of Nickel Metal Hydride Battery Using Molybdenum-added Superlattice Metal Hydride Alloy. Mater. Sci. Eng. Adv. Res 2(3): 1-14. https://doi.org/10.24218/msear.2018.27

**Copyright:** © **2018** Kwo-Hsiung Young, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

## Abstract

The performance of sealed cells comprising of a series of superlattice metal hydride (MH) alloys with compositions of  $Mm_{0.83}Mg_{0.17}Ni_{2.94-x}Al_{0.17}Co_{0.20}Mo_x$  (Mm is a mixture of La, Pr, and Nd, x = 0.00, 0.05, 0.10, 0.15, and 0.20) was evaluated and compared against other substitutional elements, such as Fe, Mn, and Co. The capacities of cells with Mo-containing alloys are higher than the ones using Mo-free alloy due to the former's higher active material utilization in positive electrodes. Cells with alloy of x = 0.10 showed the highest capacity and high-rate dischargeability, the best low-temperature (-10 and -20 °C), and the longest cycle performance (C-rates charge and discharge). This level of Mo (x = 0.10) is effective in protecting the alloy surface from oxidation. The main failure mechanism of the sudden capacity drop for cells in this study is the venting of gas/ electrolyte mixture from the build-up of internal pressure; this is caused by a dense surface oxide layer formed on the MH alloy blocking the path for gas-recombination during overcharge.

**Keywords:** Metal hydride, Nickel/metal hydride battery, Superlattice alloy, Hydrogen storage, Molybdenum, Electrochemistry.

## Introduction

Misch-metal based superlattice metal hydride (MH) alloy has been widely used as the substitution of the commonly used  $AB_5$  based alloys in nickel/metal hydride (Ni/MH) batteries in consumer [1–4], transportation [5], and stationary [6,7] applications as a result of its relatively high capacity, better high-temperature

[7] and low-temperature [8] performances, improved highrate dischargeability (HRD) [9], low self-discharge [10], and extended cycle life [11]. The name of the superlattice originates from the unique crystal structure comprising of alternating stacked  $A_{2}B_{4}$  and  $AB_{5}$  slabs along the *c*-axis [10]. In order to further enhance the performance of these superlattice MH alloy based Ni/MH batteries, continuous efforts are focused on both chemical composition and manufacturing. The superlattice MH alloy in the first commercial product contained only Ni and Al in the B-site atoms [10,12]. Mn and Co, two other commonly used B-site atoms in the AB<sub>2</sub> MH alloy, were not present in the original superlattice alloy to improve the self-discharge performance [10]. The influence on the hydrogen storage properties (both in the gaseous phase and electrochemistry) by elemental substitutions in Ni in the original formula with other transition metals, such as Mn [13], Fe [14], Co [15], and Mo [16] were reported. The cell performances of the first three substitutions were also evaluated and summarized as follows: Mn improves the HRD by increasing the reactive surface area [17]; Fe extends the cycle life by reducing the Al-leach from the negative electrode [18]; and Co facilitates the low-temperature discharge reaction [19]. In this paper, the cell performance of the Mo-substituted superlattice MH alloy are evaluated and compared to the results obtained from other substitutions. As only the failure modes of Ni/MH batteries made from AB<sub>e</sub> MH alloys were reviewed [20], a summary of failure modes of misch-metal based Ni/MH batteries with different chemical compositions is also included in this paper.

#### **Methods**

Five batches of MH powder (Mo1-Mo5, 20 kg each) were prepared by Japan Metals & Chemicals Company (Tokyo, Japan) using the induction melting method with the design compositions of  $Mm_{0.83}Mg_{0.17}Ni_{2.94-x}Al_{0.17}Co_{0.20}Mo_x$  (Mm is a mixture of La, Pr, and Nd, x = 0.00, 0.05, 0.10, 0.15, and 0.20). The structural, gaseous phase hydrogen storage, and electrochemical properties of these multi-phase superlattice MH alloys previously reported [16] are summarized in Table 1. As the Mo-content in the alloy increased, both the electrochemical capacity and half-cell HRD decreased, and the surface chargetransfer resistance first decreased and then increased. Twentyfive C-sized cylindrical Ni/MH cells were assembled from each alloy in this study with a 1.5-1.7 negative-to-positive (N/P) capacity ratio cell design. The negative electrode was prepared by dry compacting the alloy powder onto nickel mesh substrates, and a counter positive electrode consisted of a mixture of 89% Ni<sub>0.91</sub>Co<sub>0.045</sub>Zn<sub>0.045</sub>(OH)<sub>2</sub> alloy, 5 wt% Co powder, and 6% CoO powder pasted onto a nickel foam substrate. The separator Scimat 700/79 (Freudenberg Group, Weinheim, Germany) made from acrylic acid grafted polypropylene/polyethylene was used, and the electrolyte was 30 wt% KOH solution with additional LiOH (1.5 wt%). Cells made from MH alloys Mo1, Mo2, Mo3, Mo4, and Mo5 are named Cell Mo1, Cell Mo2, Cell Mo3, Cell Mo4, and Cell Mo5, respectively. The electrodes/separator assembly was coiled into a bundle and inserted into an empty Ni-plated stainless steel can, which was then filled with the electrolyte to the top, and allowed to rest for 30 min. before removal of the un-absorbed electrolyte by a pipetting. Electrochemical tests were performed using a Maccor Battery Cycler (Maccor, Tulsa,

Oklahoma, USA). After the closing, the cells went through a formation process composed of six cycles of charging to 50%, 100%, 120%, 150%, 150%, and 150% of the calculated capacity at 0.1C rate and discharging to a cutoff cell voltage of 0.9V at C/5 discharge rate. A JEOL-JSM6320F scanning electron microscope (SEM, Tokyo, Japan) including energy dispersive spectroscopy (EDS) was used to study the failure modes of cells at the end of its cycle life.

# **Results and discussion**

## **Cell Performance**

**Capacity and Rate-capability:**Four different discharge rates (C/5, C/2, C, and 2C) were used to obtain the room temperature (RT) discharge voltage curves. For example, the curves for Cells Mo1 and Mo3 are presented in Figures 1 and 2, respectively. As the discharge current (i) increases, the voltage (V) is suppressed by the internal resistivity (*R*) in the cell roughly following the eq. (1):

$$V = V - iR \tag{1}$$

where  $V_{oc}$  is the open-circuit voltage.

Concurrently, the discharge capacity obtained at the fixed cutoff voltage (0.8 V) decreases. In this batch of cell-builds, the weights of the positive electrode active materials remained unchanged. The utilization rate of the positive electrode active material is the highest in Cell Mo3 as observed from the highest discharge capacity obtained with the slowest rate (C/5), which is listed in the first data row in Table 2. The capacities obtained at different discharge rates are plotted in Figure 3 and show higher values for cells made from Mo-containing alloys. The addition of Mo in

Properties	Unit	Mo1	Mo2	Mo3	Mo4	Mo5
Main Nd <sub>2</sub> Ni <sub>7</sub> phase abundance	wt%	72.2	51.6	48.3	44.3	48.0
LaMgNi <sub>4</sub> phase abundance	wt%	23.1	19.7	14.9	12.7	17.6
Mo phase abundance	wt%	0.0	5.0	8.6	12.9	14.8
Maximum capacity	wt%	1.36	1.35	1.29	1.26	1.17
Reversible capacity	wt%	1.29	1.00	1.01	0.94	0.81
Desorption pressure	MPa	0.010	0.005	0.006	0.004	0.009
PCT Slope factor	%	80	56	58	46	52
PCT Hysteresis		0.29	0.31	0.20	0.64	0.44
Discharge Capacity	mAhg <sup>-1</sup>	347	346	332	327	302
Half-cell HRD at the 3rd cycle	%	97	97	97	93	95
Diffusion coefficient, D	10 <sup>-10</sup> cm <sup>2</sup> s <sup>-1</sup>	2.1	2.9	2.9	2.8	2.4
Surface reaction current, I <sub>0</sub>	mAg⁻¹	24.7	24.5	24.5	24.0	24.1
Charge-transfer resistance, R	Ωg	0.100	0.085	0.101	0.095	0.122
Double-layer capacitance, C	F g <sup>-1</sup>	0.40	0.50	0.33	0.41	0.39
Surfacecatalytic, RC	s	0.04	0.04	0.03	0.04	0.05

 Table 1: Summary of Structure, Gaseous Phase and Half-cell Electrochemical Hydrogen-Storage Properties of Alloys Mo1–Mo5 Measured at Room Temperature (Date from a previous study [16])

Note: PCT and HRD stand for pressure-concentration-temperature and high-rate dischargeability, respectively





Figure 1: Discharge voltage profiles for Cell Mo1 at four different discharge rates

Figure 2: Discharge voltage profiles for Cell Mo3 at four different discharge rates

C-cell Results	Unit	Mo1	Mo2	Mo3	Mo4	Mo5
C/5 at RT capacity	Ah	4.28	4.46	4.51	4.50	4.49
2C at RT capacity/0.2C at RT capacity	%	77	75	82	80	79
Mid-point voltage at 2C rate	V	0.99	0.95	1.00	1.00	1.00
1C at -10 °C capacity/0.2C atRT capacity	%	83	83	85	82	83
1C at -30 °C capacity/0.2C atRT capacity	%	15	17	14	15	22
30 days charge retention	%	90.8	83.0	85.6	89.7	91.4
0.5C/0.5C cycle life (reaching 3 Ah)	-	560	575	595	645	535
C/C cycle life (reaching 3 Ah)	-	240	240	275	255	195

Table 2: Summary of C-cell Testing Results

the negative electrode appears to increase the utilization rate of  $Ni(OH)_2$  in the positive electrode. The full-cell HRD is defined by the ratio of capacities obtained from the highest (2C) and the lowest discharge rate (C/5), and is listed in the second data row in Table 2. The highest and lowest HRD values are from Cells Mo3 and Mo2, respectively, which show a similar trend to that for the

mid-point voltage at a 2C rate (third row in Table 2). The initial decrease in the mid-point voltage from Cell Mo1 to Cell Mo2 is due to the lower gaseous phase desorption pressure for the latter (third row in Table 1). All cells except Cell Mo2 show similar mid-point voltages at different discharge rates (Figure 4). The increase in mid-point voltage (and the related HRD) in Cell Mo3



Figure 3: Discharge capacity comparison at different discharge rates for cells using alloys in this study



Figure 4: Mid-point voltage comparison at different discharge rates among cells using alloys in this study

is due to the increase in the  $Nd_5Co_{19}$  phase abundance, which contributes to a higher reactive surface area [16]. The decrease in HRD of Cell Mo4 and Cell Mo5 are due to their relatively low gaseous phase reversible capacities (second row in Table 1). To comparatively study different substitutional elements, in Figure 5 the full-cell HRDs are plotted against the amount of substitution, and show 4.7 at% Co, 4.7 at% Mn, and 2.3 at% Mo are the most effective in increasing the HRD.

The full-cell HRDs corresponding to the half-cell HRDs (seventh row in Table 1) in the superlattice alloys are plotted in Figure 6 and no clear correlation is observed. The correlation between these two HRDs is very clear for  $AB_2$  and  $AB_5$  MH alloys. For example, a linear trend between half-cell and full-cell HRDs can be found in cells made from a series of Zn-doped  $AB_2$ alloys ( $AB_2$ -Zn in Figure 6) from a previous study [21]. In the superlattice MH alloy, only cells made from Sm-based alloys in one annealing study [22] show a linear correlation (Sm-Ann in Figure 6). The lack of correlation between two HRDs for the cells made from substituted superlattice alloys could be attributed to the inconsistent alloy surface, which is highly sensitive to the amount of electrolyte. The interaction/poisoning to the positive



**Figure 5:** Normalized high-rate (2C) capacities vs. the amount of substitutions from cells using Mn, Fe, Co, and Mo substituted superlattice alloys



Figure 7: Discharge voltage profiles for Cell Mo1 at four different temperatures

electrode also affects the full-cell HRD, but this is negligible in the half-cell due to the over-capacity in the positive electrode. Therefore, the half-cell HRD is not an accurate predictor of the high-rate performance of sealed cells made from substitutional superlattice alloys.

Low Temperature: Low-temperature performance for cells at four different temperatures, -10, -20, -30 and -40 °C, were evaluated by charging at RT at a C/5 rate to 105% stateof-charge (SOC), cooling down, then measuring the discharge capacities. Two discharge voltage curves for Cells Mo1 and Mo3 are shown in Figures 7 and 8, respectively. As the temperature decreased, the cell voltage was suppressed and yielded a lower discharge capacity with a fixed cut-off voltage (0.7 V in this case). The discharge capacities obtained at different temperatures are plotted in Figure 9. Mo-addition in the Mm-based superlattice alloy improved the low-temperature performance of the Ni/MH cells, which is also observed in cells with AB<sub>2</sub> [23], AB<sub>5</sub> [24,25], and La-based superlattice [26,27] MH alloys. While Cell Mo3 gave the highest discharge capacity at -10 and -20 °C, Cell Mo5 was the champion at -30 and -40 °C. The effects of Nisubstitution (Mn, Fe, Co, and Mo) on the low-temperature (-10



**Figure 6:** Full-cell HRD (2C capacity over C/5 capacity) vs. halt-cell HRD (100 mA  $g^{-1}$  capacity over 8 mA  $g^{-1}$  capacity) from cells using Mn, Fe, Co, and Mo substituted superlattice alloys



Figure 8: Discharge voltage profiles for Cell Mo3 at four different temperatures



Figure 9: Discharge capacity vs. test temperature for cells using alloys in this study

°C) performance of the cell are plotted in Figure 10, and both 7.0 at% Co and 2.3 at% Mo (Mo3) have the greatest increase in capacity. The ultra-low-temperature (-30 °C) performance of the cells are plotted in Figure 11, and are slightly different from those obtained at -10 °C. At -30 °C, 4.7 at% Co and 4.7 at% Mo (Mo5) show the greatest percentage increase in capacity.

The low-temperature normalized discharge capacity and specific power (HRD) in the Ni/MH batteries made from  $AB_2$  and  $AB_5$  MH alloys are usually highly correlated [28,29]. However, the correlations between the low temperature (both –10 and –30 °C) normalized discharge capacity and the full-cell HRD for the substitutional superlattice alloys are not evident in Figures 12 and 13. For both  $AB_2$  and  $AB_5$  MH alloys, the low-temperature performance is dominated by the surface reactive area and surface catalytic ability, both of which are also the determinants for high-rate reaction. The lack of correlation between the normalized discharge capacity and HRD, as well as the superior low-temperature performance found in superlattice MH alloy, points to a new discharge mechanism at low temperature that requires further investigation.



Figure 11: Normalized -30 °C (C/2) discharge capacities vs. the amount of substitutions for cells using Mn, Fe, Co, and Mo substituted superlattice alloys



Figure 10: Normalized -10 °C (C/2) discharge capacities vs. the amount of substitutions from cells using Mn, Fe, Co, and Mo substituted superlattice alloys

Charge Retention: Charge retention performances were evaluated after 7, 14 and 30 days at RT storage. The initial capacity was obtained by a C/10 rate charge and a C/5 rate discharge to 0.8 V cut-off voltage. The cells were charged at C/10 rate in the beginning and then discharged at C/5 rate to 0.8 V at the end of the storage period. The normalized capacities for Cells Mo1-Mo5 are plotted in Figure 14. As the Mo-content increases, the charge retention of the cell first decreased from Mo1 to Mo4, but increased for Mo5 which is higher than the base case for Mo1. The initial decrease in charge retention is due to the increase of reactive surface area as observed from the larger surface doublelayer capacitance in alloy Mo2 (11th row in Table 1). Further increase in Mo-content boosted the charge retention, because of the formation of an oxide layer on the surface that is similar to Mo-doped AB, MH alloy [23]. The effects of different Nisubstitutions on the 30-day charge retention rate are compared in Figure 15, and the best charge retention performance is achieved by a 4.7 at% Mn substitution (for Ni).



Figure 12: Normalized -10 °C (C/2) discharge capacities vs. full-cell HRD for cells using Mn, Fe, Co, and Mo substituted superlattice alloys







Figure 15: 30 days charge-retention vs. the amount of substitutions for cells using Mn, Fe, Co, and Mo substituted superlattice alloys

**Cycle Life:** Cycling stability was evaluated using two testing schemes performed at RT: a regular one consisting of a C/2 rate charge and a C/2 rate discharge with a narrower -DV cutoff set at 0.3 mV (C/2-C/2), and an accelerated one with a C rate charge and a C rate discharge with a slightly wider -DV cutoff of 0.5 mV (C-C). The obtained capacity evolutions for C/2-C/2 and C-C cycling schemes are plotted in Figures 16 and 17, respectively, and the results are summarized in the last two rows of Table 2.



Figure 16: Cycle life measured with a C/2-C/2 cycle scheme at room temperature for cells using alloys in this study



Figure 14: Charge retention for cells using alloys in this study

Cycling at a higher rate renders a shorter cycle life [17,19,22,30] due to the heat generated from the internal resistance that leads to a shorter testing time. The capacity degradation of cells using superlattice MH alloys closely resembles cells made with AB<sub>2</sub> alloy [31]. The capacity degradation of AB<sub>5</sub> MH alloy is more gradual due to the loss in the negative electrode capacity from continued oxidation. Also, surface passivation in the AB<sub>2</sub> MH alloy is more abrupt near the end of cycle life, because of venting and electrolyte dry-out originating from a cell capacity imbalance [32]. It is unexpected to see a difference in capacity degradation trends between AB<sub>5</sub> and superlattice alloys, as both contain rare earth elements.



Figure 17: Cycle life measured with a C-C scheme at room temperature for cells using alloys in this study

In both cycling schemes, the cycle life first improved and then deteriorated as the Mo-content in the alloy increased. The best cycle life performances were obtained from Cells Mo4 and Mo3 for C/2-C/2 and C/C schemes, respectively. A study of the failure modes of these cells at the end of their cycle life are reported in the next session.

#### **Failure Analysis**

For the failure analysis, cells in this study can be categorized into three groups based on Mo content: cells with no or low Mo content (Mo1 and Mo2), with intermediate amount of Mo (Mo3

and Mo4), and with the highest Mo content (Mo5). Although failure analysis was performed on all cells after cycling, to avoid redundancy, only cells that went through the C/2-C/2 scheme were selected from one of each group (Mo1, Mo3, and Mo5) to present herein.

Negative Electrode: Cross-section SEM backscattering-electronimages (BEI) of the negative electrodes of Cells Mo1, Mo3 and Mo5 at the end of C/2-C/2 cycling test are shown in Figure 18. Severe pulverization, as reported for La-only superlattice MH alloy [33], was not observed. Even though Cells Mo1 and Mo5 show areas with two substantially different contrasts - the bright areas in the middle of the grains are the unoxidized metal with higher average atomic weights (no oxygen) while the outside gray coatings are the products of oxidation/corrosion - Cell Mo3 only shows one contrast. The chemical compositions of the Mo1, Mo3 and Mo5 alloys at selected positions in the regions analyzed were studied by EDS, and the results are presented in Table 3. Both the main superlattice phase (first spot) and LaMgNi, phase (the second spot) can be identified by their B/A stoichiometries. The gray areas in Cells Mo1 (Mo1-3) and Mo5 (Mo5-4) are confirmed to be oxides based on their high oxygen contents. The average compositions from an area of 200  $\mu m$   $\times$ 200 µm on the SEM were characterized by the EDS analysis, and are summarized in Table 4. The oxygen contents for the C/2-C/2

cycled electrodes are higher compared to C-C cycled electrodes due to the former's longer cycle periods and larger cycle numbers. As the Mo-content increases, the oxygen content shows a valley for electrodes with an intermediate amount of Mo (Mo3 and Mo4), indicating a lower degree of oxidation. Oxidation of the alloy also changed the B/A ratio, as more B-site elements (Al and Ni) leached out from the alloy. It can be concluded that while an adequate amount of Mo (2.3-3.4 at%) can retard the oxidation of the alloy by alkaline electrolyte, further increase in Mo-content renders the alloy more vulnerable to the oxidation. The corrosion resistance of the alloy seems to be correlated well with the abundance of the high-Mg LaMgNi<sub>4</sub> phase (Table 1), which is more venerable to oxidation [34]. Similar first increase and then decrease in cycle stability with the increase in the Moamount were also reported before in the La-only superlattice MH alloys [35,36]. Besides, the sudden drops in the capacity curves shown in Figures 16 and 17 indicate that venting with a consequent electrolyte dry-out is the major failure mechanism for cells. Similar sharp capacity drops are commonly observed for cells that employ AB, MH alloys due to poisoning of the positive electrode [31]. However, in the current study, the failure mechanism is via a surface oxide layer forming on the negative electrode that blocks the path for the recombination of oxygen gas generated from the positive electrode during overcharge.



Figure 18: SEM-BEI of negative electrodes from cycled Cells (a) Mo1, (b) Mo3, and (c) Mo5 (scale bar: 25  $\mu$ m)

Location	La	Pr	Nd	Mg	Ni	AI	Со	Мо	0	Mg/A	B/A	Phase
Mo1-1	3.9	8.2	7.9	3.3	67.7	4.3	4.7	0.0	0.0	0.14	3.29	Main
Mo1-2	2.7	8.0	8.3	16.5	61.2	0.6	2.7	0.0	0.0	0.46	1.82	LaMgNi <sub>4</sub>
Mo1-3	1.5	3.3	3.4	0.4	37.0	0.2	2.4	0.0	51.8	0.05	4.60	Oxide
Mo3-1	3.6	8.3	7.9	3.3	67.6	4.4	4.9	0.0	0.0	0.14	3.33	Main
Mo3-2	3.0	8.3	8.3	14.4	62.6	0.4	3.0	0.0	0.0	0.42	1.94	LaMgNi <sub>4</sub>
Mo3-3	0.1	0.0	0.1	0.0	2.7	0.0	0.7	96.4	0.0			Мо
Mo5-1	4.7	8.2	8.0	2.9	65.7	5.5	5.0	0.0	0.0	0.12	3.20	Main
Mo5-2	3.0	8.2	8.3	13.6	62.8	0.8	3.3	0.0	0.0	0.41	2.02	LaMgNi <sub>4</sub>
Mo5-3	0.0	0.1	0.1	0.1	2.1	0.0	0.7	96.9	0.0			Мо
Mo5-4	1.4	3.4	3.3	0.3	36.7	0.2	2.5	0.0	52.2	0.04	4.69	Oxide

 Table 3: Summary of Element Compositions (at%) from EDS Analysis of a few Selected Spots on the SEM-BEI Micrographs of Negative

 Electrodes Made from Alloys Mo1, Mo3, and Mo5 Shown in Figure 18

Table 4: Summary of Element Compositions (at%) from EDS Analysis of a 200  $\mu$ m  $\times$  200  $\mu$ m Area on the Cycled Negative Electrodes

Cell	La	Pr	Nd	Mg	Ni	AI	Co	Мо	0	Mg/A	B/A
Mo1(C)	2.5	5.2	5.3	3.4	45.6	2.1	3.2	0.0	32.7	0.21	3.10
Mo1(C/2)	2.5	5.1	5.1	3.9	40.8	1.0	2.8	0.0	38.8	0.23	2.69
Mo2(C)	2.7	5.5	5.5	3.7	48.4	2.0	3.0	0.5	28.7	0.21	3.10
Mo2(C/2)	2.5	5.2	5.3	3.9	43.2	0.3	2.8	0.2	36.6	0.23	2.75
Mo3(C)	3.1	6.4	6.4	4.4	53.3	2.3	4.1	0.6	19.5	0.22	2.97
Mo3(C/2)	3.0	6.1	6.5	4.1	53.0	1.9	3.6	0.7	21.0	0.21	3.01
Mo4(C)	3.1	6.8	6.7	3.0	52.8	2.7	3.7	1.0	20.2	0.15	3.07
Mo4(C/2)	2.9	6.5	6.5	2.7	50.7	1.9	3.8	0.3	24.7	0.15	3.05
Mo5(C)	3.0	6.1	5.7	4.5	50.4	2.3	3.3	1.0	23.7	0.23	2.95
Mo5(C/2)	2.3	5.0	5.1	3.9	36.7	1.5	2.6	0.4	42.5	0.24	2.53

Note: C and C/2 within the parentheses denote C-C and C/2-C/2 cycling schemes, respectively

This consequently leads to accumulated pressure and eventual venting of the cell.

Positive Electrode: The cross-section SEM-BEI micrographs of Cells Mo1, Mo3 and Mo5 positive electrodes at the end of C/2-C/2 cycling tests are shown in Figure 19. The occasional small bright spots are the undissolved Co additives. As opposed to what is usually observed for cells made with AB<sub>5</sub> MH alloys [33], the spherical shape of the Ni(OH), particles remained intact. The averaged Co, Zn, and Al-contents on a 200  $\mu m \times 200$ um area determined by the EDS analysis are plotted in Figure 20. Considerable amounts of Al (1 to 5 at%) were found in the cycled positive electrode which were the product of corrosion leaching out of negative electrode. This amount of Al is not sufficiently large to cause the irreversible  $\beta$ -to-g transformation of Ni(OH), (source of positive electrode disintegration) [37]. Positive electrodes cycled using the C/2-C/2 scheme showed higher Al-contamination compared to those using the C-C scheme, due to the former's longer testing periods (longer duration and larger number of testing cycles). The amount of Al found in the positive electrode decreased first and then increased as the Mo-content increases. This trend is consistent with that for degree of oxidation of the negative electrode, as discussed in the previous section. The evolution trends of Co- and Zn-contents in the cycled positive electrode are opposite to that of Al (Figure 20). Severe Al-contamination reduced the Zn and Co atom percentage in the composition of the positive electrode, which could eventually lead to the loss of the Co-conductive network and possibly the formation of a Zn-containing micro-short in the separator [37]. Although Al-contamination is not the main failure mechanism in this study, it can still degrade the cycle stability if oxidation of negative electrode is suppressed by the addition of surfactant binder in the negative electrode paste [38].

**Separator:** Cross-section SEM-BEI micrographs obtained from the separator region of Cells Mo1, Mo3 and Mo5 at the end of C/2-C/2 cycling test are shown in Figure 21, with adjacent negative and positive electrodes located at the top and bottom of the figure, respectively. Significant debris is visible in the separator of these cells, especially Cell Mo3 with the largest number of cycles. Reduction of separator thickness is found for Cell 5 due to excessive loss of electrolyte. Distribution of elements in the separator region was further studied by EDS-mapping, and an example set of elemental mappings from Cell Mo3 is presented



Figure 19: SEM-BEI of positive electrodes from cycled Cells (a) Mo1, (b) Mo3, and (c) Mo5 (scale bar: 25 µm)



Figure 20: Average compositions (in at%) of positive electrodes at the end of C-C and C/2-C/2 cyclings. Zn-contents are magnified six times for easier comparison

in Figure 22. In the separator, only a very small amount of oxide (or hydroxide) can be found. All particles trapped in this region contain mainly Ni and some rare earth elements. This is significantly different from most of the debris containing high Mn and Zn-content observed in other Mn-containing MH alloys [20,30,37,39]. In this study, fine particles broke off from the negative electrode and did not form a micro-short conducting path. Therefore, we conclude that the separator region is not responsible for the fast capacity and cell life degradation in this study.

Failure Modes for Superlattice Alloys: The effects of different Ni-substitution on the cycle life performance are compared in Figure 23. Among these substitutions, 4.7 at% Co benefits the cycle stability by the largest amount. Compared to other substitutional elements, Mo has little influence on the cycle performance of the superlattice MH alloy, similar to the case of Mo in AB<sub>5</sub> MH alloys [24]. In both alloy families, Mo does not participate in the main phase, but rather segregates out to form its own secondary phase. On the contrary, Mo in an AB, MH alloy has a positive contribution to the cycle stability, owing



Figure 21: SEM-BEI of separator areas from cycled Cells (a) Mo1, (b) Mo3, and (c) Mo5 (scale bar: 50  $\mu m)$ 

to the incorporation of Mo in the AB, phase that improves corrosion resistance to KOH electrolyte [23]. Mo, as a top protective layer, also improves the cycle stability of a La<sub>2</sub>MgNi<sub>7</sub> superlattice alloys [40]. The failure modes of a few representative superlattice MH alloys used in the cell are listed in Table 5. As the cycle life is a weak-link property (i.e., the weakest factor dominates the performance), the combination of multiple wellbalanced failure modes is more desirable. For example, cells with superlattice alloys having only Al and an intermediate amount of Co showed good cycle life performance with multiple failure modes and are considered well balanced among different failure mechanisms. In other cells with inferior cycle performance, results from the failure analysis can be used to identify the area that needs the most improvement. For example, methods to reduce the metal hydride alloy oxidation rate, such as addition of surfactant in the negative electrode paste [38], addition of Y in either positive electrode or negative electrode [41], and surface fluoride treatment [42-45], should be considered to extend the life performance of this series of superlattice alloys.

## Conclusion

In summary, among the four misch-metal based superlattice metal hydride alloys with partial replacement of Ni by Mo, Mn, Fe and Co, respectively, we found that although the Al-only alloy showed the longest cycle life, 4.7 at% Mo increased the high-rate dischargeability and -10 °C low-temperature performance, 4.7 at% Co rendered the best -30 °C low-temperature performance, and 4.7 at% Mn increased charge retention. Instead of applying a single composition for most battery applications, as in the case of AB<sub>e</sub> alloy, the composition of the superlattice alloys should be tailored based on the specific application requirement. As for the failure analysis, venting of the gas/mixture from the pressure build-up in the cell is the major failure mechanism; the accumulated pressure in the cell is caused by a dense oxide surface layer formed on MH alloy blocking the path for recombination of oxygen gas during overcharge. A modest amount of Mo (2.3 - 3.5 at%) can slow down the oxidation of MH alloy; however, further reduction in oxidation rate by other means is still possible.





Figure 23: Room temperature C/2-C/2 cycle life vs. the amount of substitutions from cells using Mn, Fe, Co, and Mo substituted superlattice alloys

Alloy	A-site	Al	Со	Fe	Mn	Мо	Failure Mode	Reference
F1	La, Pr, Nd	4.0	0	0	0	0	ED/MO/MP	17
F3	La, Pr, Nd	4.0	0	0	4.7	0	ED/MO/MP	17
F5	La, Pr, Nd	4.0	0	0	9.3	0	MP/MO	17
C2	La, Pr, Nd	4.0	2.3	0	0	0	MP/PS	19
С3	La, Pr, Nd	4.0	4.7	0	0	0	ED/MP/PS	19
C5	La, Pr, Nd	4.0	9.3	0	0	0	MO/ED	19
Fe2	La, Pr, Nd	3.9	4.6	1.2	0	0	MP	18
Fe5	La, Pr, Nd	3.9	4.6	4.6	0	0	MO	18
Mo3	La, Pr, Nd	4.0	4.7	0	0	2.3	ED/MO	This work
Mo5	La, Pr, Nd	4.0	4.7	0	0	4.7	ED/MO	This work
В	La, Pr, Nd	0	13.6	0	0	0	MP	8
Ce0.4	La, Ce, Nd	4.4	0	0	0	0	MP	34
В	La	2.3	9.3	0	0	0	MP	46
В	La	0	11.6	0	0	0	MP/MO	33,47

Table 5: Summary of Major Failure Modes of the Ni/MH Cells using a Few Selected Superlattice MH Alloys

Note: The first column lists the name of the alloy in the cited reference. Columns 3–7 are the atomic percentages of non-Ni B-site atoms. ED, MP, MO, and PS denote electrolyte dry-out, MH alloy pulverization, MH alloy oxidation, and positive electrode swelling, respectively

#### References

- Teraoka H. Development of low self-discharge nickel-metal hydride battery – [Accessed on 2017 Oct 2]. Available from: http://www. scribd.com/doc/9704685/Teraoka-Article-En
- Teraoka H. Development of Ni-MH ESS with Lifetime and Performance Estimation Technology. Presented in the 34<sup>th</sup> International Battery Seminar & Exhibit; 2017 Mar 20–23; Fort Lauderdale, Florida, USA.
- Teraoka H. Ni-MH Stationary Energy Storage: Extreme Temperature & Long Life Developments. Presented in the 33<sup>th</sup> International Battery Seminar & Exhibit; 2016 Mar 21–24; Fort Lauderdale, Florida, USA.
- Teraoka H. Development of Highly Durable and Long Life Ni-MH Batteries for Energy Storage Systems. Presented in the 32<sup>th</sup> International Battery Seminar & Exhibit; 2015 Mar 9–12; Fort Lauderdale, Florida, USA.

- Website page. [Accessed on 2017 Dec 19]. Available from: http:// news.panasonic.com/global/press/data/2014/02/en140213-3/ en140213-3.html
- Takasaki T, Nishimura K, Saito M, Fukunaga H, Iwaki T, Sakai T. Cobalt-free nickel-metal hydride battery for industrial applications. J. Alloys Compd. 2013; 580(Suppl 1):S378–S381. doi: https://doi. org/10.1016/j.jallcom.2013.01.092.
- Zelinsky MA, Koch JM, Young K. Performance comparison of rechargeable batteries for stationary applications (Ni/MH vs. Ni-Cd and VRLA). Batteries. 2018; 4(1):1. doi:10.3390/batteries4010001.
- Koch JM, Young K, Nei J, Hu C, Reichman B. Performance comparison between AB<sub>5</sub> and superlattice metal hydride alloys in sealed cells. Batteries. 2017; 3(4):35. doi:10.3390/batteries3040035.
- Meng T, Young K, Hu C, Reichman B. Effects of alkaline pre-etching to metal hydride alloys. Batteries. 2017; 3(4):30. doi:10.3390/ batteries3040030.

- Yasuoka S, Magari Y, Murata T, Tanaka T, Ishida J, Nakamura H, et al. Development of high-capacity nickel-metal hydride batteries using superlattice hydrogen-absorbing alloys. J. Power Sources. 2006; 156(2):662–666. doi: https://doi.org/10.1016/j. jpowsour.2005.05.054.
- Kai T, Ishida J, Yasuoka S, Takeno K. The effect of nickel-metal hydride battery's characteristics with structure of the alloy. Proceedings of the 54<sup>th</sup> Battery Symposium in Japan; 2013. p. 210.
- Yasuoka S, Ishida J, Kai T, Kajiwara T, Doi S, Yamazaki T, et al. Function of aluminum in crystal structure of rare earth-Mg-Ni hydrogen-absorbing alloy and deterioration mechanism of Nd<sub>0.9</sub>Mg<sub>0.1</sub>Ni<sub>3.4</sub> and Nd<sub>0.9</sub>Mg<sub>0.1</sub>Ni<sub>3.3</sub>Al<sub>0.2</sub> alloys. Int. J. Hydrogen Energy. 2017; 42(16):11574–11583. doi: https://doi.org/10.1016/j. ijhydene.2017.02.150.
- Young K, Wong DF, Wang L, Nei J, Ouchi T, Yasuoka S. Mn in mischmetal based superlattice metal hydride alloy—Part 1 Structural, hydrogen storage and electrochemical properties. J. Power Sources. 2015; 277:426–432. doi: https://doi.org/10.1016/j. jpowsour.2014.10.093.
- Young K, Ouchi T, Nei J, Yasuoka S. Fe-substitution for Ni in misch metal-based superlattice hydrogen absorbing alloys – Part 1. Structural, hydrogen storage, and electrochemical properties. Batteries. 2016; 2:34.
- Wang L, Young K, Meng T, Ouchi T, Yasuoka, S. Partial substitution of cobalt for nickel in mixed rare earth metal based superlattice hydrogen absorbing alloy – Part 1 structural, hydrogen storage and electrochemical properties. J. Alloys Compd. 2016; 660:407– 415. doi: https://doi.org/10.1016/j.jallcom.2015.11.134.
- Young K, Lin X, Jiang C, Yasuoka S. Effects of molybdenum to the hydrogen storage and electrochemical properties of superlattice metal hydride alloy. Mater. Sci. Eng. Adv. Res. 2018; 2(2):13–26. doi: https://doi.org/10.24218/msear.2018.25.
- Young K, Wong DF, Wang L, Nei J, Ouchi T, Yasuoka S. Mn in misch-metal based superlattice metal hydride alloy – Part 2 Ni/MH battery performance and failure mechanism. J. Power Sources. 2015; 277:433–442. doi: https://doi.org/10.1016/j. jpowsour.2014.10.092.
- Meng T, Young K, Nei J, Koch JM, Yasuoka S. Fe-substitution for Ni in misch metal-based superlattice hydrogen absorbing alloys – Part 2. Ni/MH battery performance and failure mechanisms. Batteries. 2017; 3(3):28. doi:10.3390/batteries3030028.
- Wang L, Young K, Meng T, English N, Yasuoka S. Partial substitution of cobalt for nickel in mixed rare earth metal based superlattice hydrogen absorbing alloy – Part 2 battery performance and failure mechanism. J. Alloys Compd. 2016; 664:417–427. doi: https://doi. org/10.1016/j.jallcom.2016.01.007.
- 20. Young K, Yasuoka S. Capacity degradation mechanisms in nickel/ metal hydride batteries. Batteries. 2016; 2(1):3. doi:10.3390/ batteries2010003.
- Young K, Ouchi T, Lin X, Reichman B. Effects of Zn-addition to C14 metal hydride alloys and comparisons to Si, Fe, Cu, Y and Moadditives. J. Alloys Compd. 2016; 655:50–59. doi: https://doi. org/10.1016/j.jallcom.2015.09.157.
- Young K, Ouchi T, Nei J, Koch JM, Lien Y. Comparison among constituent phases in superlattice metal hydride alloys for battery applications. Batteries. 2017; 3(4):34. doi:10.3390/ batteries3040034.

- Young K, Ouchi T, Huang B, Reichman B, Fetcenko MA. Effect of molybdenum content on structural, gaseous storage, and electrochemical properties of C14-predomoinant AB<sub>2</sub> metal hydride alloys. J. Power Sources. 2011; 196(20):8815–8821. doi: https://doi.org/10.1016/j.jpowsour.2011.06.010.
- Young K, Ouchi T, Reichman B, Koch J, Fetcenko MA. Effects of Mo additive on the structure and electrochemical properties of low-temperature AB<sub>s</sub> metal hydride alloys. J. Alloys Compd. 2011; 509(9):3995–4001. doi: https://doi.org/10.1016/j. jallcom.2010.12.205.
- Erika T, Sebastian C, Fernando Z, Verónica D. Temperature performance of AB<sub>5</sub> hydrogen storage alloy for Ni-MH batteries. Int. J. Hydrogen Energy. 2016; 14(43):19684–19690. doi: https:// doi.org/10.1016/j.ijhydene.2016.04.015.
- Zhang X, Sun D, Yin W, Chai Y, Zhao M. Crystallographic and electrochemical characteristics of La<sub>0.7</sub>Mg<sub>0.3</sub>Ni<sub>3.5-x</sub>(Al<sub>0.5</sub>Mo<sub>0.5</sub>)<sub>x</sub> (x=0-0.8) hydrogen storage alloys. J. Power Sources. 2006; 154(1):290–297. doi: https://doi.org/10.1016/j.jpowsour.2005.03.217.
- Yuan J, Li W, Wu Y. Hydrogen storage and low-temperature electrochemical performances of A<sub>2</sub>B<sub>7</sub> type La-Mg-Ni-Co-Al-Mo alloy. Prog. Nat. Sci.: Mat. Int. 2017; 27(2):169–176. doi: https://doi.org/10.1016/j.pnsc.2017.03.010.
- Young K, Ouchi T, Fetcenko MA. Roles of Ni, Cr, Mn, Sn, Co, and Al in C14 Laves phase alloys for NiMH battery application. J. Alloys Compd. 2009; 476(1-2):774–781. doi: https://doi.org/10.1016/j. jallcom.2008.09.146.
- Young K, Ouchi T, Banik A, Koch J, Fetcenko MA, Bendersky LA, et al. Gas atomization of Cu-modified AB<sub>5</sub> metal hydride alloys. J. Alloys Compd. 2011; 509(14):4896–4904. doi: https://doi. org/10.1016/j.jallcom.2011.01.204.
- Young K, Koch JM, Wan C, Denys RV, Yartys VA. Cell performance comparison between C14- and C15-predominated AB<sub>2</sub> metal hydride alloys. Batteries. 2017; 3:29.
- Young K, Chang S, Lin X. C14 laves phase metal hydride alloys for Ni/ MH batteries applications. Batteries. 2017; 3(3):27. doi:10.3390/ batteries3030027.
- Young K, Wu A, Qiu Z, Tan J, Mays W. Effects of H<sub>2</sub>O<sub>2</sub> addition to the cell balance and self-discharge of Ni/MH batteries with AB<sub>5</sub> and A<sub>2</sub>B<sub>7</sub> alloys. Int. J. Hydrogen Energy. 2012; 37(12):9882–9891. doi: https://doi.org/10.1016/j.ijhydene.2012.03.117.
- Zhou X, Young K, West J, Regalado J, Cherisol K. Degradation mechanisms of high-energy bipolar nickel metal hydride battery with AB<sub>5</sub> and A<sub>2</sub>B<sub>7</sub> alloys. J. Alloys Compd. 2013; 580(Suppl 1):S373– S377. doi: https://doi.org/10.1016/j.jallcom.2013.03.014.
- Yasuoka S, Ishida J, Kishida K, Inui H. Effects of cerium on the hydrogen absorption-desorption properties of rare earth-Mg-Ni hydrogen-absorbing alloys. J. Power Sources. 2017; 346:56–62. doi: https://doi.org/10.1016/j.jpowsour.2017.02.008.
- 35. Li W, Zhang B, Yuan J, Yan Y, Wu Y. Effect of Mo content on the microstructures and electrochemical performances of La<sub>0.75</sub>Mg<sub>0.25</sub>Ni<sub>3.2-x</sub>Co<sub>0.2</sub>Al<sub>0.1</sub>Mo<sub>x</sub> (x = 0, 0.10, 0.15, 0.20) hydrogen storage alloys. J. Alloys. Compd. 2017; 692:817–824. doi: https:// doi.org/10.1016/j.jallcom.2016.09.113.
- Zhang H, Fu L, Zheng X, Li X. Effects of molybdenum substitution on the electrochemical properties of La<sub>2</sub>MgNi<sub>8-x</sub>CoMo<sub>x</sub> alloys. Mat. Let. 2018; 222:33-36. doi: https://doi.org/10.1016/j. matlet.2018.03.132.

- Shinyama K, Magari Y, Kumagae K, Nakamura H, Nohma T, Takee M, et al. Deterioration mechanism of nickel metal-hydride batteries for hybrid electric vehicles. J. Power Sources. 2005; 141(1):193– 197. doi: https://doi.org/10.1016/j.jpowsour.2004.09.010.
- Ouchi T, Young K, Moghe D. Reviews on the Japanese Patent Applications regarding nickel/metal hydride batteries. Batteries. 2016; 2(3):21. doi:10.3390/batteries2030021.
- Zhu WH, Zhu Y, Tatarchuk BJ. Self-discharge characteristics and performance degradation of Ni-MH batteries for storage applications. Int. J. Hydrogen Energy. 2014; 39(34):19789–19798. doi: https://doi.org/10.1016/j.ijhydene.2014.09.113.
- Zhang H, Zheng X, Wang T, Li X. Molybdenum nano-film induced discharged for La<sub>2</sub>MgNi<sub>9</sub> hydrogen storage alloy. Mat. Design. 2017; 114:599–602. doi: https://doi.org/10.1016/j. matdes.2016.11.102.
- 41. Arnaud O, Le Guenne L, Audry C, Bernard P. Effect of yttria content on corrosion of  $AB_s$ -type alloys for nickel-metal hydride batteries. J. Electrochem. Soc. 2005; 152:A611–A616.
- 42. Li C. Hydrogen storage alloy and fluorinated hydrating alloy batteries. Chin. J. Power Sources. 1995; 19:34–37.

- Sakashita M, Li Z.P, Suda S. Fluorination mechanism and its effects on the electrochemical properties of metal hydrides. J. Alloys Compd. 1997; 253–254:500–505. doi: https://doi.org/10.1016/ S0925-8388(96)03047-2.
- 44. Sun Y, Iwata K, Chiba S, Matsuyama Y, Suda, S. Studies on the properties and characteristics of the fluorinated AB<sub>5</sub> hydrogenabsorbing electrode alloys. J. Alloys Compd. 1997; 253–254:520– 524. doi: https://doi.org/10.1016/S0925-8388(96)03055-1.
- Sun Y, Suda S. Studies on the fluorination method for improving surface properties and characteristics of AB<sub>5</sub>-types of hydrides.
   J. Alloys Compd. 2002; 330–332:627–631. doi: https://doi. org/10.1016/S0925-8388(01)01668-1.
- 46. Young K, Ouchi T, Wang L, Wong DF. The effects of Al substitution on the phase abundance, structure and electrochemical performance of  $La_{0.7}Mg_{0.3}Ni_{2.8}Co_{0.5-x}Al_x$  (x = 0, 0.1, 0.2) alloys. J. Power Sources. 2015 ;279:172–179. doi: https://doi.org/10.1016/j. jpowsour.2015.01.022.
- Liu Y, Pan H, Gao M, Lei Y, Wang Q. XRD study on the electrochemical hydriding/dehydriding behavior of the La-Mg-Ni-Co-type hydrogen storage alloys. J. Alloys Compd. 2005; 403(1-2):296–304. doi: https://doi.org/10.1016/j.jallcom.2005.04.195.