

# Material Science and Engineering with Advanced Research

# Effects of Molybdenum to the Hydrogen Storage and Electrochemical Properties of Superlattice Metal Hydride Alloy

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#### Abstract

The structure, gaseous phase, and electrochemical hydrogen storage properties of a series of superlattice metal hydride alloys with nominal compositions Mm<sub>0.83</sub>Mg<sub>0.17</sub>Ni<sub>2.94-x</sub>Al<sub>0.17</sub>Co<sub>0.20</sub>Mo<sub>x</sub>, where Mm is a mixture of La, Pr, and Nd and x = 0.00, 0.05, 0.10, 0.15, and 0.20, prepared by induction melting method were studied. The Mo segregates out of the main phase to form a metallic secondary phase, leading to a larger reactive surface area. The unit cell of the main Nd<sub>2</sub>Ni<sub>7</sub> increases with an increase in Mo-content through changes in both phase composition and abundance. The addition of Mo reduces the abundance of the main Nd<sub>2</sub>Ni<sub>7</sub> phase, and consequently lowers both the gaseous phase storage and electrochemical discharge capacities. However, Mo also promotes the formation of a Nd<sub>5</sub>Co<sub>19</sub> phase, which contributes to a higher surface reactive area at both room temperature and -40°C. A 1.1 at% of Mo partially replacing Ni is recommended for improvement in low-temperature performance without sacrificing the discharge capacities and high-rate dischargeability owing to the improvement in the surface catalytic ability. In addition, the effects of Mo substitutions to the electrochemical properties of the superlattice alloy are also compared to those from other substitutions, such as Mn, Fe, and Co.

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

# Introduction

Nickel/metal hydride (Ni/MH) batteries are widely used in portable consumer electronics, hybrid electric vehicle, and stationary applications [1]. While the conventional active material in the negative electrode of Ni/MH batteries is a rare-earth (RE) based AB<sub>e</sub> metal hydride (MH) alloy, the superlattice MH alloy has become increasingly attractive over the last decade due to its higher energy density, superior high-rate dischargeability (HRD), low self-discharge, improved low-temperature, and hightemperature performances compared to the  $AB_5$  alloy [2–8]. The name of superlattice comes from its unique arrangement of alternative stacking of A2B4 and different numbers of AB5 slabs along the *c*-axis of the crystal [9]. For example, one  $A_2B_4$ plus one AB<sub>5</sub> leads to AB<sub>3</sub> stoichiometry, and one A<sub>2</sub>B<sub>4</sub> plus two AB<sub>5</sub> renders A<sub>2</sub>B<sub>7</sub> stoichiometry. Depending on the inplane orientation of adjacent A<sub>2</sub>B<sub>4</sub> slabs, both hexagonal (C14like) and rhombohedral (C15-like) structures are available [2]. Typically, Mg, an alkaline earth element, is added to the A-site of the superlattice alloy to stabilize the hydride structure, adjust the metal-hydrogen bond strength, and reduce the corrosion nature of the alloy [10]. Research on the superlattice alloy started with ternary alloy (La, Mg)Ni, [11], however, the first commercialized product was made of misch metal (Mm), a combination of La, Nd, and Pr, to extend the cycle life [2]. Ce was abandoned as it promotes the formation of undesirable AB<sub>2</sub> phase in the superlattice alloy [12]. Recently, Sm was also used to substitute the costly Nd and Pr [13]. For the B-site element in the misch-

metal (Mm, mixtures of a few REs) based superlattice alloys, we have conducted a few substitution works, such as Al [14], Mn [15,16], Fe [17,18], and Co [19–21], and reached the following conclusions: Al improves the hydrogen-storage (H-storage) kinetics and enhances the cycle stability; a small amount of Mn (2.3 at%) improves the HRD and charge retention performance; Fe promotes the formation of the desirable Nd<sub>2</sub>Ni<sub>7</sub> phase; and Co provides improved low-temperature performance.

For start-stop vehicle applications [22], the low-temperature crank power plays a significant role and has led to a great amount of research on enhancement of crank power for MH alloy at low temperature over the past decade [23,24]. The easiest way to increase the HRD performance in the Ni/MH battery is by elemental substitution [25]. Mo, a second-row transition metal, has been demonstrated to improve the low-temperature performance of AB<sub>5</sub> [26] and AB<sub>2</sub> [27]. The partial substitution of Mo for a La-only superlattice alloy also exhibited excellent lowtemperature performance [28] and improved discharge kinetics [29]. The addition of Mo increased the discharge capacity of a pure body-centered-cubic MH alloy from 61 to 247 mAh g<sup>-1</sup> [30]. Besides, Mo was found to enhance the hydrogen diffusion rate in the bulk of an AB, MH alloy [31]. Therefore, Mo was selected as the substitution element for the study on misch-metal based superlattice alloy, and the results are presented in this paper. Some of the physical properties of Mo are compared with those of Al, Mn, Fe, Co, and Ni in Table 1.

# Methods

MH powder (20 kg per composition) was prepared by Japan Metals & Chemicals Company (Tokyo, Japan) using the induction melting method; the reason for preparing a larger batch compared to standard procedure was to ensure the uniformity of the ingot considering the relatively high melting point of Mo (Table 1). The chemical composition of the MH powder was examined with a Varian Liberty 100 inductively coupled plasma-optical emission spectrometer (ICP-OES, Agilent Technologies, Santa Clara, CA, USA). Microstructure of MH powder was characterized using a Philips X'Pert Pro X-ray diffractometer (XRD, Amsterdam, The Netherlands) and a JEOL-JSM6320F

scanning electron microscope (SEM, Tokyo, Japan) including energy dispersive spectroscopy (EDS). Gaseous phase H-storage was measured at 30, 45, and 60°C after activation using a Suzuki-Shokan multi-channel pressure-concentration-temperature system (PCT, Tokyo, Japan). A half-cell apparatus consists of a negative electrode, prepared by compact MH powder on top of a nickel substrate sheet using a roll mill without using a binder, a pre-activated sintered Ni(OH), counter electrode, and 30% KOH aqueous solution as the electrolyte. The half-cell experiment was performed using a CTE MCL2 Mini cell testing system (Chen Tech Electric MFG. Co., Ltd., New Taipei, Taiwan). A Solartron 1250 Frequency Response Analyzer (Solartron Analytical, Leicester, UK) was used for AC impedance measurements, with a sine wave amplitude of 10 mV and a frequency range of 0.5 mHz to 10 kHz. The magnetic susceptibility of the activated alloys was measured using a Digital Measurement Systems Model 880 vibrating sample magnetometer (MicroSense, Lowell, MA, USA) after immersing the MH powder in 30 wt% KOH solution at 100°C for 4 h.

# **Results and Discussion**

# Alloy selection and preparation

Five alloys (Mo1–Mo5) with the designed composition 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) were prepared using the same procedure previously stated [15,17,19]. The base alloy (Mo1) was selected due to its superior low-temperature performance [20]. The composition of each alloy product was characterized using ICP and compared to the design value- see Table 2. There were small deviations in the Mo content due to the extremely high melting point of Mo (at least 1000°C higher than other elements in the alloy) and negligible solubility of Mo in the superlattice phase. The measured B/A ratio excluding Mo is about 3.3 to 3.4, and a mixture of AB<sub>3</sub> and A<sub>2</sub>B<sub>7</sub> phases is expected.

# Phase composition

The X-ray diffraction patterns of constituent phases of these five alloys are plotted in Figure 1, where all patterns show multiple phases. The phase abundances calculated by the

Element	Al	Mn	Fe	Со	Ni	Мо
Atomic number	13	25	26	27	28	42
Atomic weight	27.0	54.9	55.8	58.9	58.7	96.0
Atomic radius (Å)*	1.43	1.27	1.26	1.25	1.25	1.39
Melting point (°C)	660	1245	1535	1495	1453	2617
Electronegativity	1.61	1.55	1.83	1.88	1.91	2.16
Crystal structure	FCC	BCC	BCC	НСР	FCC	BCC
Heat of hydride formation (kJ mol $H^{-1}$ )	-4	-8	10	15	-3	5

 Table 1: Properties of Selected Elements

Notes: \* A 12-coordinate metallic bond is used here. FCC, BCC, and HCP are abbreviations for face-centered-cubic, body-centered-cubic, and hexagonal-closest-packed, respectively

Alloy	Source	Mm	Mg	Ni	Al	Со	Мо	B/A
Mo1	Design	19.3	3.9	68.1	4.0	4.7	0.0	3.31
	ICP	19.1	3.6	68.9	3.7	4.6	0.0	3.39
Mo2	Design	19.3	3.9	67.0	4.0	4.7	1.1	3.26
	ICP	18.9	3.9	67.8	3.7	4.6	1.1	3.34
Mo3	Design	19.3	3.9	65.8	4.0	4.7	2.3	3.21
	ICP	18.8	3.6	67.0	3.9	4.7	2.0	3.37
Mo4	Design	19.3	3.9	64.7	4.0	4.7	3.4	3.16
	ICP	18.8	3.3	65.8	4.3	4.6	3.2	3.38
Mo5	Design	19.3	3.9	63.4	4.0	4.7	4.7	3.11
	ICP	19.0	3.4	64.9	4.1	4.7	3.9	3.28

Table 2: Designed Compositions and ICP Results

Notes: All numbers are in at%. B/A is the ratio of B-atom (Ni, Al, and Co) and A-atom (Mm and Mg) as Mo does not enter into the main superlattice phases



Figure 1: XRD patterns using Cu-K<sub>a</sub> as the radiation source

Table 3: Abundances of the Constituent Phases Analyzed by XRD

Phase	Mo1	Mo2	Mo3	Mo4	Mo5
CeNi <sub>3</sub> (H)	-	4.5	6.1	6.8	8.5
NdNi <sub>3</sub> (R)	4.7	5.0	4.2	7.8	-
Nd <sub>2</sub> Ni <sub>7</sub> (H)	72.2	51.6	48.3	44.3	48.0
Nd <sub>5</sub> Co <sub>19</sub> (R)	-	14.2	17.9	15.4	11.1
LaMgNi <sub>4</sub> (H)	23.1	19.7	14.9	12.7	17.6
Мо	-	5.0	8.6	12.9	14.8

Notes: All numbers are in wt%. H an R stand for hexagonal and rhombohedral crystal structures, respectively

Jade 9 software are listed in Table 3. Opposed to cases of Mn, Fe, and Co [15,17,19], Mo segregates out of the superlattice phases in the elemental form. Besides the segregated Mo phase, AB<sub>2</sub> (hexagonal LaMgNi<sub>4</sub>), AB<sub>3</sub> (both hexagonal CeNi<sub>3</sub> and rhombohedral NdNi<sub>3</sub>), A<sub>2</sub>B<sub>7</sub> (only hexagonal Nd<sub>2</sub>Ni<sub>7</sub>), and A<sub>5</sub>B<sub>19</sub> (only rhombohedral Nd<sub>5</sub>Co<sub>19</sub>) phases were identified. The addition of Mo in the composition suppresses the formation of the most desirable Nd<sub>2</sub>Ni<sub>7</sub> phase [13] from 72 to ca. 50 wt% resulting in some electrochemical properties deterioration. The effects of partial substitutions of Mn, Fe, Co, and Mo for the Nd<sub>2</sub>Ni<sub>7</sub> phase abundance are compared in Figure 2.



Figure 2: Nd, Ni, main phase abundance vs. the amounts of substitution

While Mn and Mo reduce  $Nd_2Ni_7$  main phase abundance, Fe and Co increase it by small amounts. Lattice constants of the constituent phases obtained from XRD patterns are listed in Table 4. The lattice constants of the main  $Nd_2Ni_7$  phase show a steady increase as the Mo content increases (the Ni-content decreases) - see Figure 3. The effects of different substitution for  $Nd_2Ni_7$  on unit cell volume are compared in Figure 4 and demonstrated that Mn, Fe, and Mo have similar effectiveness on unit cell volume expansion, while Co keeps the unit cell volume unchanged. Although the curves of unit cell volume expansion changing with the Mn, Fe, and Mo substitution have the similar slope in Figure 4, their mechanisms are different and will be discussed in the next session.



Figure 3:  $\mathrm{Nd_2Ni_7}$  main phase lattice constants vs. the amount of Mo substitution



Figure 4:  $Nd_2Ni_7$  main phase unit cell volume vs. the amounts of substitution

Phase	Lattice constant	Mo1	Mo2	Mo3	Mo4	Mo5
			5.050	5.005	- 0.00	5.004
CeNi <sub>3</sub> (H)	а	-	5.058	5.065	5.062	5.064
	С	-	16.335	16.374	16.387	16.427
NdNi <sub>3</sub> (R)	а	5.023	5.037	5.053	5.033	-
	С	24.819	24.778	24.632	24.769	-
Nd <sub>2</sub> Ni <sub>7</sub> (H)	а	5.024	5.026	5.029	5.030	5.034
	с	24.411	24.426	24.445	24.473	24.493
Nd <sub>5</sub> Co <sub>19</sub> (R)	а	-	5.026	5.039	5.042	5.031
	С	-	48.837	48.855	48.871	48.935
LaMgNi <sub>4</sub>	а	7.092	7.107	7.088	7.096	7.127
Мо	а	-	3.146	3.147	3.145	3.147

Table 4: Lattice Constants for the Constituent Phases Analyzed by XRD

Notes: All numbers have units of Å. H and R denote hexagonal and rhombohedral structures, respectively

#### Microstructure analysis

The microstructure of the alloys was characterized using SEM back-scattered mode and are presented in Figures 5 and 6 for Mo-free Mo1 and Mo-containing Mo3, respectively. The chemical compositions of marked spots with different contrasts were examined by EDS, and the results are summarized in Table 5. While the AB<sub>2</sub> phase (Mo1-2 and Mo3-3) are represented by a darker region, the main superlattice phases  $(AB_2, A_2B_7, and A_5B_{10})$ are indistinguishable in Figure 5 (Mo1-1). Two main phases with slight difference in contrast can be seen in Figure 6 (Mo3-1 and Mo3-2). Segregated Mo phases with a bright contrast can be easily identified in alloy Mo-3 (Mo3-4). EDS results indicate that the solubility of Mo in the superlattice phases and LaMgNi, phase are negligible. The solubility of Mo is 3-5 at% in C14 phase and 0.2 at% in LaNi, phase as reported previously [26,27]. It is thus suspected that the segregation of Mo in the superlattice phases is due to the immiscible nature between La and Mo [32]. Instead of varying the lattice constants of the main phase directly by replacing the atoms in superlattice phase like Mn, Fe, and Co, Mo modifies them by reduction of Ni (smaller radius) and increase in the Al-content (larger radius). While the reduction of Ni-content with the increase in Mo-content is from the design (Table 2), the increase in the Al-content in the main phase with the increase in Mo-content is due to reduction in the abundance of LaMgNi<sub>4</sub> phase with a very small solubility of Al.



Figure 5: SEM BEI micrographs of alloy Mo1



Figure 6: SEM BEI micrographs of alloy Mo3

#### Gaseous phase characteristics

The gaseous phase H-storage characteristics of the five alloys were investigated by PCT analysis. PCT isotherms measured at 30 and 45°C are plotted in Figures 7–10, and the properties obtained are summarized in Table 6. Both the maximum and reversible capacities measured at both 30 and 45°C decreased as Mo content increased. Even with the enlarged unit cell volume in the main  $Nd_2Ni_7$  phase, the capacities still decreased due to the decrease in the  $Nd_2Ni_7$  phase abundance with the increase in Mo content. The effects of substitution elements on the H-storage capacities are illustrated in Figures 11 and 12. Mn, Fe, Co and Mo substitution has the most negative effect due to the reduction in  $Nd_2Ni_7$  phase abundance (Figure 2). For reversible H-storage capacity,Co and Fe substitution does not make a difference, and Mn and Mo substitution has a negative effect on it.

The PCT plateau pressure, defined as the hydrogen equilibrium pressure in the desorption isotherm corresponding to a 0.75 wt% H-storage capacity, first decreased and then increased with increase in Mo-content at both 30 and 45°C caused by changes in the chemical composition and abundance of the constituent phases. A specific H-storage as the plateau pressure is chosen, because the plateau features in alloys Mo4 and Mo5 are not

Location	La	Pr	Nd	Mg	Ni	AI	Со	Мо	Mg/A	B/A	Phase
Mo1-1	3.7	8.4	8.4	3.3	67.9	3.7	4.6	0.0	0.14	3.20	Main
Mo1-2	2.8	7.8	7.7	15.4	63.3	0.4	2.6	0.0	0.46	1.97	LaMgNi <sub>4</sub>
Mo1-3	28.5	29.6	31.1	0.0	10.2	0.1	0.5	0.0			RE
Mo3-1	4.8	8.5	8.0	2.5	66.4	5.3	4.5	0.0	0.11	3.20	Main-1
Mo3-2	4.2	8.4	8.5	3.4	66.4	4.3	4.8	0.0	0.14	3.08	Main-2
Mo3-3	3.6	8.7	8.2	13.0	63.0	0.7	2.8	0.0	0.39	1.99	LaMgNi <sub>4</sub>
Mo3-4	0.1	0.0	0.2	0.0	1.4	0.0	0.2	98.1			Мо

Table 5: Summary of EDS Results in at% from a few Selected Spots in the SEM-BEI Micrographs of Alloys Mo1 and Mo3 Shown in Figures 5 and 6





**Figure 7:** PCT Isotherms of alloys Mo1, Mo2, and Mo3 measured at 30°C. A and D denote absorption and desorption, respectively



Figure 8: PCT Isotherms of alloys Mo4 and Mo5 measured at 30°C. A and D denote absorption and desorption, respectively



**Figure 9:** PCT Isotherms of alloys Mo1, Mo2, and Mo3 measured at 45°C. A and D denote absorption and desorption, respectively

Figure 10: PCT Isotherms of alloys Mo4 and Mo5 measured at 45°C. A and D denote absorption and desorption, respectively

Table 6: Summary of G	Gaseous Phase H-storage Properties
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Gaseous Phase Properties	Unit	Mo1	Mo2	Mo3	Mo4	Mo5
Capacity at 2 MPa and 30°C	wt%	1.36	1.35	1.29	1.26	1.17
Reversible capacity at 30°C	wt%	1.29	1.00	1.01	0.94	0.81
Desorption pressure at 30°C	MPa	0.010	0.005	0.006	0.004	0.009
Slope factor at 30°C	%	80	56	58	46	52
Hysteresis at 30°C		0.29	0.31	0.20	0.35	0.44
Capacity at 2 MPa and 45°C	wt%	1.30	1.19	1.14	1.09	0.98
Reversible capacity at 45°C	wt%	1.27	1.03	1.03	0.89	0.86
Desorption pressure at 45°C	МРа	0.020	0.012	0.018	0.020	0.048
Slope factor at 45°C	%	84	77	76	77	70
Hysteresis at 45°C		0.41	0.44	0.30	0.29	0.33
$-\Delta H_{h}$	kJ·mol H₂ <sup>−1</sup>	37.0	46.8	48.9	48.8	48.2
$-\Delta S$	J·mol H <sub>-</sub> <sup>-1</sup> ·K <sup>-1</sup>	103	129	138	135	139





Figure 11: Gaseous phase maximum hydrogen-storage capacity at 30°C and 2 MPa vs. amounts of substitution

distinctive. Compared to other substitutional elements, Mo has a relatively large influence in the PCT plateau pressure- see Figure 13.

The slope factor, defined as the ratio of the storage capacity measured in the desorption isotherm between 0.005 and 0.2 MPa to the reversible capacity, is an indicator for the uniformity of the chemical composition [33]. The Mo-substituted alloys (Mo2–Mo5) have slope factors smaller than that in the Mo-free Mo1, which implies a less uniform composition and is in accordance with the decrease in the abundance of Nd<sub>2</sub>Ni<sub>7</sub> main phase (Table 3).

The PCT hysteresis is defined as ln  $(P_A/P_D)$ , where  $P_A$  and  $P_D$  are the plateau pressures at 0.75 wt% storage amount from absorption and desorption isotherms, respectively. It is an indicator of the elastic energy required to deform the lattice boundary between the metal ( $\alpha$ ) phase and the hydride ( $\beta$ ) phase, and has been correlated to the pulverization rate of the alloy particle during

Figure 12: Gaseous phase reversible hydrogen-storage capacity at  $30^{\circ}$ C and 0.001 MPa vs. amounts of substitution

absorption-desorption cycling [34]. An alloy with a smaller PCT hysteresis decrepitates slower. In this study, both 30 and 45°C PCT hystereses decrease and then increase with an increase in Mo content, which suggests that a small amount of Mo partially replaced by Ni in the superlattice alloy may improve the cycle stability by preventing severe pulverization. Effects of substitution on PCT hysteresis are plotted in Figure 14 and Mn and Co have greater impacts on PCT hysteresis compared to Mo and Fe.

Changes in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were calculated based on Van't Hoff equation- see Eqn. (1) using the desorption pressures (*P*) at 0.75 wt% H-storage measured at different temperatures:

$$\Delta G = \Delta H - T \Delta S = R T \ln P, \tag{1}$$

where T and R are the absolute temperature and ideal gas constant, respectively. Both values are listed in the last two rows of Table 6. Apparently, the metal-hydrogen bonds in the Mo-



**Figure 13:** Hydrogen equilibrium pressure at 0.75 wt% hydrogenstorage and 30°C in the desorption isotherm vs. amounts of substitution

containing alloys are stronger (greater magnitude of negative  $\Delta H$ ) than that in the Mo-free Mo1. The possible explanations are the partial replacement of Nd<sub>2</sub>Ni<sub>7</sub> phase by Nd<sub>5</sub>Co<sub>19</sub> phase (Table 3), expansion of the unit cell volume of Nd<sub>2</sub>Ni<sub>7</sub> phase (Figure 3), and re-distribution in the chemical composition of superlattice phases. Partial substitution of Mo for Ni reduces  $\Delta S$  to be closer to the ideal value ( $\Delta S$  of free hydrogen gas, -135 J mol H<sub>2</sub><sup>-1</sup> K<sup>-1</sup> [35]). The hydrides of the Mo-containing alloys are more ordered than that of the Mo-free alloy.

#### **Electrochemical measurement**

**Capacity and HRD:** In the room temperature (RT) half-cell testing, the electrode was charged with a 100 mA  $g^{-1}$  current for 4 h and then discharged with the same current until a cutoff voltage of 0.9 V was reached. Two consecutive pulls at 50 and



Figure 15: Full discharge capacities obtained with a discharge current of 8 m A  $g^{\rm -1}$ 



Figure 14: Hysteresis between PCT absorption and desorption isotherms at 0.75 wt% hydrogen-storage and 30°C vs. amounts of substitution

8 mA  $g^{-1}$  were conducted after a 5 min. rest. The sum of three discharge capacities was used as the full discharge capacity. The full discharge capacities from the first 13 cycles are plotted in Figure 15. All alloys show excellent activation behavior and reach the maximum capacity in the first or second cycle. The highest maximum capacities of all alloys in this study are listed in the first row of Table 7, which show a decreasing trend with an increase in Mo content, consistent with the trend in gaseous phase H-storage capacities (Figure 11). Effects of various substitutions on the full discharge capacity are illustrated in Figure 16. The capacity is improved only when the substitution amount of Co is above 2.3, but deteriorated in all the others cases.

HRD, defined as the ratio of capacity obtained at 100 mA  $g^{-1}$  and the full discharge capacity, is a measurement of the initial



Figure 16: Electrochemical discharge capacity measured with a discharge current of 8 mA  $g^{-1}$  vs. amounts of substitution

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Electrochemical and Magnetics Properties	Unit	Mo1	Mo2	Mo3	Mo4	Mo5
Full discharge capacity	mAh g <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, $I_0$	mA g <sup>-1</sup>	24.7	24.5	24.5	24.0	24.1
Charge-transfer resistance at RT	Ω <b>/g</b>	0.100	0.085	0.101	0.095	0.122
Double-layer capacitance at RT	F g <sup>-1</sup>	0.40	0.50	0.33	0.41	0.39
RC product at RT	s	0.04	0.04	0.03	0.04	0.05
Charge-transfer resistance at –40°C	Ω <b>/g</b>	3.1	1.6	4.3	4.3	4.5
Double-layer capacitance at –40°C	F g <sup>-1</sup>	0.59	0.77	0.61	0.61	0.63
RC product at -40°C	s	1.9	1.3	2.6	2.6	2.8
Total saturated magnetic susceptibility, Ms	emu g <sup>-1</sup>	0.84	0.93	0.81	0.81	0.84
Applied field where M.S. = $\frac{1}{2}$ Ms, H <sub>1/2</sub>	kOe	0.12	0.11	0.14	0.13	0.14

Table 7: Summary of Electrochemical Half-cell Properties and Magnetic Measurement Results

particle pulverization and the ease in forming a catalytic surface. The HRD of all the alloys stabilize in about 4 cycles (see Figure 17), and are compared at the 3<sup>rd</sup> cycle in the second row in Table 7. A small amount of Mo-substitution at the expense of Ni does not sacrifice HRD; however, larger amounts (Mo4 and Mo5) have a negative impact on HRD. As seen from the plot in Figure 18, only 2.2% Fe and 7 % Co substitution improves HRD to some degree while the other substitutions deteriorate it.

**Diffusion constant and surface exchange current:** The contributions from bulk hydrogen transport and surface electrochemical reaction to the HRD were studied by measuring hydrogen diffusion constant (D) and surface reaction current ( $I_o$ ), and the results are summarized in the third and fourth rows in Table 7. Details of the testing methods are available from our earlier work [19,36]. The D values in the Mo-containing alloys

are higher than that in the Mo-free Mo1 alloy. The increase in D of the Mo-contacting alloys is not attributed to the segregated Mo phase, because thehydrogenation for Mo is endothermic (Table 1). It may originate from the decrease in the abundance of the main Nd<sub>2</sub>Ni<sub>7</sub> phase, and consequently a higher level of synergetic effects from other phases. The effects of various substitutions to D are plotted in Figure 19. Only 2.3 and 7.0% Co substitution increases the D value out of four elemental substitutions.

The  $I_{o}$  values of all alloys are similar and the addition of Mo unexpectedly does not change the kinetics of the surface reaction, since a higher surface area would be expected because Mo oxide has an extremely high solubility in alkaline solution [37]. The stability of Mo oxide in alkaline solution can compared by the relatively large equilibrium constants of the leached out product from Mo [38]:





Figure 17: High-rate dischargeability (HRD) measured in the first 13 cycles

Figure 18: High-rate dischargeability (HRD) vs. amounts of substitution



Figure 19: Room temperature hydrogen diffusion constant in the bulk (D) of alloy vs. amounts of substitution

- $MoO_{3} + H_{2}O = HMoO_{4}^{-} + H^{+}, log(HMoO_{4}^{-}) = -3.7 + pH$  (2)
- $MnO + H_{2}O = HMnO_{2}^{-} + H^{+}, \log (HMnO_{2}^{-}) = -16.57 + pH$ (3)

FeO + H<sub>2</sub>O = HFeO<sub>2</sub><sup>-</sup>+ H<sup>+</sup>, log (HFeO<sub>2</sub><sup>-</sup>) = 
$$-18.30 + pH$$
 (4)

$$CoO + H_2O = HCoO_2^- + H^+, log (HCoO_2^-) = -16.67 + pH$$
 (5)

The benefits of Mo substitution in MH alloy must be countered by the reduction in the abundance of main  $Nd_2Ni_7$  phase. The effects of partial substitutions of Mn, Fe, Co and Mo for MH alloy on  $I_0$  are plotted in Figure 20. Only Co substitution makes a positive contribution to the surface electrochemical reaction kinetics. Neither *D* (bulk) or  $I_0$  (surface) can explain the lower HRDs of alloys Mo4 and Mo5. AC impedance measurements in the following section will further explain the cause of the HRD behavior. AC impedance: AC impedance were measured at both RT and  $-40^{\circ}$ C and both the charge-transfer resistance (*R*) and doublelayer capacitance (*C*) obtained from the Cole-Cole plots are listed in Table 7. There are two main determining factors for *R* value: one is the surface reactive area, which is proportional to *C*, and the other is the surface catalytic ability, which can be quantified by *RC* product (also listed in Table 7.). The trends of *R* and *C* vs. Mo content measured at RT are very similar to those measured at  $-40^{\circ}$ C. Only alloy Mo2 shows lower *R* values from both increased surface area (larger *C*) and improved surface catalytic ability (lower *RC*). Even though the lower *R* in Mo2 may be attributed to the synergetic effect with the secondary phases [39], the initial increase in the reactive surface area in Mo2 might come from the sudden increase in the abundance of Nd<sub>5</sub>Co<sub>19</sub> phase, which



Figure 20: Room temperature surface exchange current  $({\rm I_{o}})$  vs. amounts of substitution

was previously correlated to the higher reactive surface area [13]. Further increase in Mo at the expense of highly catalytic Ni [25] and decrease in the  $Nd_2Ni_7$  phase abundance increased the *R*. The effects of Mn, Fe, Co and Mo substitutions on *R*, *C*, and *RC* at -40°C are shown in Figures 21, 22, and 23, respectively. Only 1.1% Mo and 4.7% Co substitution is beneficial to the low-temperature performance (lowering *R*). In the reactive surface area (*C*), all substitutions except Mo contribute to the increase in *C*. In the Mo-containing alloys, only Mo2 shows a larger reactive area from the contribution of  $Nd_5Co_{19}$  phases. In the comparison of surface catalytic ability (*RC*), alloys with 1.1% Mo and 4.7 and 7% Co show the best results (lowest *RC*).

The effects of adding Mo to different alloys on *R*, *C*, and *RC* at  $-40^{\circ}$ C are compared in Figures 24–26. The data for AB<sub>5</sub> and AB<sub>2</sub> are from our previous reports [26,27]. Both A<sub>2</sub>B<sub>7</sub> and AB<sub>5</sub> MH alloys show similar low *R* values at  $-40^{\circ}$ C, and alloy Mo2 exhibits



Figure 21: Surface charge-transfer resistance (R) measured at -40°C vs. amounts of substitution



Figure 23: Surface catalytic ability (RC product) at  $-40^{\circ}$ C vs. amounts of substitution

the lowest R value. Although the R values of  $AB_2$  shrink due to the addition of Mo, they are still significantly higher than those from  $A_2B_7$  and  $AB_5$  alloys. For the reactive area (C),  $AB_5$  shows the largest value and shares the same trend (first increase and then decrease) with the addition of Mo. The reactive area in these alloys are in the order of  $AB_5 > A_2B_7 > AB_2$ , exactly the same as the order of B/A stoichiometric ratio. By comparing the RC products,  $A_{2}B_{7}$  alloys have the best surface catalytic ability (the lowest *RC*) and AB, alloys have the worst. While both A, B, and AB, MH alloys show excellent low-temperature performance, the former is due to the relatively large reactive area and the latter is from the superior surface catalytic ability. Future research on improving the low-temperature performance of MH alloys should focus on increasing the surface catalytic ability of AB<sub>5</sub> and increasing the surface reactive area of  $A_2B_7$  MH alloys. The addition of Mo happens to address the corresponding direction in each alloy.









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1.4

1.2

1.0

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10

8

Δ

amounts of Mo for  $A_2B_7$ ,  $AB_2$ , and  $AB_5$  MH alloys

#### Magnetic susceptibility measurement

Since the difference of saturated magnetic susceptibility  $(M_s)$  between MH alloy and metallic Ni is as high as 7 orders of magnitude[40],  $M_s$  has been used to quantify the total volume of metallic Ni inclusions imbedded in the surface oxide after activation [41,42]. These nano-scale Ni particle catalysts are crucial for the surface electrochemical reaction. From the magnetization curve, the applied magnetic field corresponding to half of  $M_s$  ( $H_{1/2}$ ) can be associated with the magnetic domain size (Ni cluster size) [41]. Both values are reported in the last two rows in Table 7. Alloy Mo2 shows the highest amount of catalytic Ni, and is consistent with the lowest *RC* product

O−Mn

Fe



**Figure 28:** Applied magnetic field strength corresponding to half of saturated magnetic susceptibility  $(H_{1/2})$  vs. amounts of substitution



measured from the AC impedance. This improvement is the synergic effects of the new surface generated from the Mo phase and an increased abundance of the beneficial Nd<sub>5</sub>Co<sub>19</sub> phase. The effects of substitutions on the amount of catalytic Ni ( $M_s$ ) are compared in Figure 27, indicating that only a small amount of Mo (1.1 at%) can increase the  $M_s$  out of four elements at different substitution levels. The size of Ni clusters changing withvarious amount of substitutions are plotted in Figure 28. Even though Mn substitution reduces the size of metallic Ni on the surface (larger  $H_{1/2}$ ), Fe substitution increases (smaller  $H_{1/2}$ ) it. A smaller size of metallic Ni on the surface is preferable, as it leads to a larger surface area of the catalytic Ni cluster.







A2B7

▲ AB2

# Conclusion

Different from other transition metals (Mn, Fe, Co), the partial substitution of Mo replacing Ni in the misch-metal based superlattice metal hydride alloy segregates to form an electrochemically inert secondary phase. Addition of Mo promotes the formation of CeNi3 and Nd5Co19 phases at the expense of the main Nd<sub>2</sub>Ni<sub>7</sub> phase. The lattice constants of the Nd<sub>2</sub>Ni<sub>2</sub> phase increase proportionally with the increasing Mo content, due to the reduction in Ni and the increase in Al in Nd<sub>2</sub>Ni<sub>7</sub> phase. The enlarged unit cell of the main Nd<sub>2</sub>Ni<sub>7</sub> phase did not increase the hydrogen storage capacity, due to the decrease in its abundance concurrently with an increase in Mo content. Both the discharge capacity and high-rate dischargeability decreased when Mo content is relatively higher at the expense of Ni. Although the diffusion constants of the Mo-containing alloys are higher than that of the Mo-free alloy, no obvious improvement in the half-cell high-rate dischargeability was observed. Weighing all aspects for the electrochemical requirement, an addition of 1.1 at% Mo is recommended for low-temperature applications of a nickel/metal hydride battery.

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