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# A strategy for designing new $AB_{4.5}$-type hydrogen storage alloys with high capacity and long cycling life

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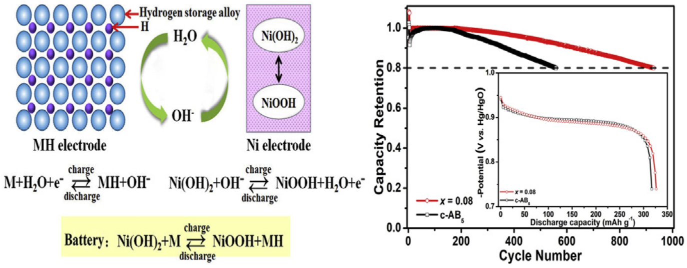
## HIGHLIGHTS

- A novel $AB_{4.5}$-type hydrogen storage alloy is designed for Ni-MH batteries.
- The alloy shows a high capacity of 326.7 mAh $g^{-1}$ and a long life of 928 cycles.
- The superior performances are caused by accurate Mg-substitution for Ni.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

In order to compete with Li-ion batteries, the discharge capacity and cycling life of nickel metal hydride batteries need to be further improved. However, this is rather difficult due to poor performances of the negative electrode materials—hydrogen storage alloys. In this work, a new strategy is proposed for designing hydrogen storage alloys with high capacity and long cycling life through theoretical analysis and density functional theory simulation, which points out that it is crucial to substitute Ni atoms inside the alloy with Mg by the precise control of stoichiometric ratio and Mg content. The candidate alloy $La_{0.62}Mg_{0.08}Ce_{0.2}Y_{0.1}Ni_{3.25}Co_{0.75}Mn_{0.2}Al_{0.3}$ [corresponding to (LaCeYMg) $(NiCoMnAl)_{4.5}$] exhibits a high capacity of 326.7 mAh $g^{-1}$ and a capacity retention of 80% after a long cycling life of 928 cycles, showing great potential for applications in nickel metal hydride batteries. The design strategy also provides new insights into the development of new-type high-performance hydrogen storage alloys.

## 1. Introduction

Energy storage devices and related materials have been extensively studied in order to meet the world's challenges of energy crisis and environmental pollution [1–8]. Nickel metal hydride (Ni-MH) batteries have key technology advantages for applications in new-energy vehicles, power tools, modern military devices *etc.* [9–12]. However, in order to compete with Li-ion batteries, their discharge capacity and cycling life need to be further improved, which are limited by the poor performances of their negative electrode materials — hydrogen storage alloys (HSAs) [13–15]. Recently, a long-life series (LL-series) HSAs were developed by substituting La with high-electronegativity Y to enhance alloys' corrosion resistance, where one of them, the $La_{0.55}Ce_{0.3}Y_{0.15}Ni_{3.7}Co_{0.75}Mn_{0.3}Al_{0.35}$ alloy shows a cycling life of 1407 cycles, the highest datum among reported results [16].

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**Table 1**
Summary of performances of HSAs for Ni-MH batteries. The performance of the commercial Li-ion battery is also listed for a comparison.

| Material | Capacity performance | Cycling performance | Reference |
|---|---|---|---|
| $La_{0.62}Mg_{0.08}Ce_{0.2}Y_{0.1}Ni_{3.25}Co_{0.75}Mn_{0.2}Al_{0.3}$ (Ni-MH battery) | 326.7 mAh $g^{-1}$ at 60 mA $g^{-1}$ (0.2 C) | 80% after 928 cycles at 300 mA $g^{-1}$ (1 C) | This work |
| $LaNi_2Co_3Al_{0.1}$ (Ni-MH battery) | 289 mAh $g^{-1}$ at 40 mA $g^{-1}$ (0.125 C) | 93% after 500 cycles at 400 mA $g^{-1}$ (1.25 C) | [23] |
| $La_{0.55}Ce_{0.3}Y_{0.15}Ni_{3.7}Co_{0.75}Mn_{0.3}Al_{0.35}$ (Ni-MH battery) | 294.3 mAh $g^{-1}$ at 60 mA $g^{-1}$ (0.2 C) | 98.9% after 500 cycles at 300 mA $g^{-1}$ (1 C) | [16] |
| $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ (Ni-MH battery) | 317.3 mAh $g^{-1}$ at 60 mA $g^{-1}$ (0.2 C) | 83.2% after 500 cycles at 300 mA $g^{-1}$ (1 C) | [16] |
| $La_{1.5}Mg_{0.5}Ni_7$ (Ni-MH battery) | 391.2 mAh $g^{-1}$ at 100 mA $g^{-1}$ (0.25 C) | 82% after 150 cycles at 400 mA $g^{-1}$ (1 C) | [17] |
| $La_{0.95}Sm_{0.66}Mg_{0.40}Ni_{6.25}Al_{0.42}Co_{0.32}$ (Ni-MH battery) | 368 mAh $g^{-1}$ at 70 mA $g^{-1}$ (0.2 C) | 80% after 239 cycles at 400 mA $g^{-1}$ (1 C) | [18] |
| $La_{0.78}Mg_{0.22}Ni_{3.73}$ (Ni-MH battery) | 372 mAh $g^{-1}$ at 60 mA $g^{-1}$ (0.15 C) | 85.3% after 100 cycles at 400 mA $g^{-1}$ (1 C) | [19] |
| $LaY_2Ni_{9.7}Mn_{0.5}Al_{0.3}$ (Ni-MH battery) | 385.7 mAh $g^{-1}$ at 70 mA $g^{-1}$ (0.2 C) | 76.6% after 300 cycles at 70 mA $g^{-1}$ (0.2 C) | [20] |
| $La_2MgNi_9$ (Ni-MH battery) | 397.5 mAh $g^{-1}$ at 100 mA $g^{-1}$ (0.25 C) | 60.6% after 100 cycles at 100 mA $g^{-1}$ (0.25 C) | [21] |
| $LaCaMgNi_9$ (Ni-MH battery) | 356 mAh $g^{-1}$ at 60 mA $g^{-1}$ (0.2 C) | 79% after 100 cycles at 150 mA $g^{-1}$ (0.5 C) | [22] |
| Commercial Li-ion battery (cathode: $LiCoO_2$; anode: graphitized carbon) | 1005 mAh at 1C | 74.5% after 286 cycles at 1 C | [24] |

**Table 2**
Weight percentages (wt%) of raw materials for the alloy powders fabrication of $La_{0.7\text{-}x}Mg_xCe_{0.2}Y_{0.1}Ni_{3.25}Co_{0.75}Mn_{0.2}Al_{0.3}$ ($x$ = 0.04, 0.08 and 0.12) and c-$AB_5$ alloys.

| Samples | La | Ce | Y | Mg | Mm | Ni | Co | Mn | Al |
|---|---|---|---|---|---|---|---|---|---|
| $x$ = 0.04 | 24.16 | 7.36 | 2.30 | 0.35 | | 49.43 | 11.45 | 2.85 | 2.10 |
| $x$ = 0.08 | 22.99 | 7.45 | 2.33 | 0.61 | | 50.03 | 11.59 | 2.88 | 2.12 |
| $x$ = 0.12 | 21.78 | 7.53 | 2.36 | 0.92 | | 50.61 | 11.73 | 2.92 | 2.15 |
| c-$AB_5$ | | | | | 33.38 | 49.20 | 10.36 | 5.16 | 1.90 |

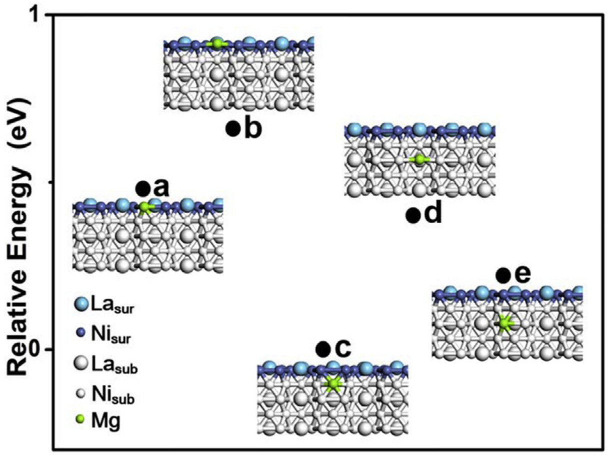

**Fig. 1.** DFT calculation results of system energies of $AB_5$-type HSAs with different structural configurations. Here, the energy of the most stable configuration is set to 0 eV to facilitate comparison. (a) and (b) are crystal structures of a Ni or La atom in $LaNi_5$ substituted by a Mg atom on the outmost surface, respectively. (c)–(e) are crystal structures of a Ni atom with 3g, a La atom or a Ni atom with 2c in $LaNi_5$ substituted by a Mg atom on the subsurface, respectively. $La_{sur}$ and $Ni_{sur}$ represent La and Ni atoms on the outermost surface, respectively; and $La_{sub}$ and $Ni_{sub}$ represent La and Ni atoms on the subsurface, respectively.

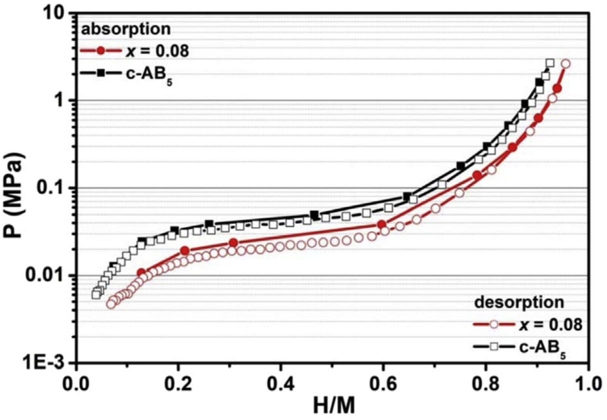

**Fig. 2.** The P-C isotherms of $La_{0.62}Mg_{0.08}Ce_{0.2}Y_{0.1}Ni_{3.25}Co_{0.75}Mn_{0.2}Al_{0.3}$ ($x$ = 0.08) and $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ (c-$AB_5$) alloys at 318 K.

However, its discharge capacity is only 294.3 mAh $g^{-1}$, which is about 7% lower than that of the commercial $AB_5$-type HSA $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ (c-$AB_5$ alloy with a capacity of 317.3 mAh $g^{-1}$) [16]. Meanwhile, great efforts have been devoted to enhancing the discharge capacity of HSAs [17–21]. It has been demonstrated that $AB_3$-type HSAs with superlattice structure have high theoretical capacity [21,22]. For example, the $La_2MgNi_9$ alloy shows a discharge capacity of 397.5 mAh $g^{-1}$, but its cycling life is less than 100 cycles, far from the requirement for practical application in Ni-MH batteries [21]. Thus, a series of $A_2B_7$- and $A_5B_{19}$-type superlattice HSAs were developed, such as $La_{0.95}Sm_{0.66}Mg_{0.40}Ni_{6.25}Al_{0.42}Co_{0.32}$, $La_{0.78}Mg_{0.22}Ni_{3.73}$, $LaY_2Ni_{9.7}Mn_{0.5}Al_{0.3}$, *etc.* [18–20]. Their maximum discharge capacity could reach 385.7 mAh $g^{-1}$, but the cycling life is less than 300 cycles yet [20]. Table 1 summarizes the performances of different HSAs [16–23] for Ni-MH batteries (the performance of commercial Li-ion battery [24] is also listed for a comparison). It can be seen that the existing HSAs don't have both higher capacity and longer cycling life than c-$AB_5$ alloy. Therefore, how to develop high-capacity and long-life HSAs has become a big challenge facing Ni-MH batteries.

In this work, a novel strategy has been proposed for designing HSAs with high capacity and long cycling life by considering the structural properties, electronegativity and surface atomic coordination states. The rationality of this strategy was verified with the density functional theory (DFT) simulations and experiment results. Following this strategy, a new $AB_{4.5}$-type HSA has been designed and fabricated by employing Mg-substitution and sub-stoichiometry, which exhibits a high capacity of 326.7 mAh $g^{-1}$ and a long cycle life of 928 cycles.