

Supporting Information for

**A start of the renaissance for nickel metal hydride batteries: a hydrogen storage
alloy series with ultra-long cycle life**

Chun Cheng Yang,[‡] Chang Chun Wang,[‡] Miao Miao Li, Q. Jiang^{*}

Key Laboratory of Automobile Materials (Jilin University), Ministry of Education, and School of Materials Science and Engineering, Jilin University, Changchun 130022, China.

** Corresponding author. Tel.: +86-431-85095371; Fax: +86-431-85095876; E-mail: jiangq@jlu.edu.cn (Q. Jiang).*

[†] Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

[‡] These authors contributed equally to this work.

Materials and methods

Fabrication of alloy powders: The LL-series hydrogen storage alloys of $\text{La}_{0.7-x}\text{Ce}_{0.3}\text{Y}_x\text{Ni}_{3.7}\text{Co}_{0.75}\text{Mn}_{0.3}\text{Al}_{0.35}$ ($x = 0, 0.05, 0.10, 0.15$) and $\text{MmNi}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ (c-AB₅) were prepared by ratio-frequency induction melting of rare earth elements La, Ce, Y (99.5%) and other metallic elements Ni, Co, Mn, Al (99.9%) under an atmosphere of high-purity argon. The as-cast ingots were annealed at 1000 °C for 5 hours under an argon atmosphere, followed by mechanical grind to powder. The particle size of the fabricated powder is 50 ± 10 μm as measured by Malvern particle analyzer Mastersizer 2000.

Pressure-composition isotherm measurement: The specimens were activated at 473 K and then the pressure-composition (P-C) isotherms were measured by using a Suzuki Sieverts-type apparatus at 318 K.

Structural characterization: X-ray diffraction (XRD) measurements were carried out on a D/max2500pc diffractometer using Cu K_α radiation. The XRD patterns were analyzed by the Rietveld method using RIETAN2000 software.¹ The morphology of the specimens were characterized with a field-emission scanning electron microscope (FESEM, JSM-6700F, JEOL, 15 keV). X-ray photoelectron spectroscopy (XPS) was carried out at room temperature on an ESCALAB 250 (Thermo Fisher Scientific, UK) X-ray photoelectron spectrometer by using a monochromatic Al-K_α (1486.6 eV) source, and emissions were referenced to the C 1s peak at 284.6 eV. For depth profiling, Ar ionic sputtering was performed with a beam energy of 3 kV, 3 μA for 60s.

Electrode preparation and electrochemical measurement: To investigate the electrochemical properties of LL-series and c-AB₅ alloys, the MH electrodes were prepared by cold pressing the mixture of 0.25 g alloy powder and 1.0 g carbonyl

nickel powder to 15-mm-diameter pellets under a pressure of 8 MPa. Electrochemical measurements were performed by using an Arbin BT-2000 at room temperature in a tri-electrode open cell, consisting of a MH electrode, a sintered Ni(OH)₂/NiOOH counter electrode and a Hg/HgO reference electrode. The electrolyte is 6 M KOH solution. In every cycle of the discharge capacity (C) measurement, the electrodes were charged at 60 mA g⁻¹ for 7.5 hours and then discharged at 60 mA g⁻¹ to a cut-off potential of -0.74V (vs. Hg/HgO). After 4-cycle activation, the maximum discharge capacity C_{\max} was reached. For the measurements of cycle life, the electrodes were charged/discharged at 60 mA g⁻¹ for 4 cycles, and then charged/discharged at 300 mA g⁻¹ until 500 cycles (for LL-series alloys with $x = 0.10$ and 0.15 , until the capacity retention reaches 80%). The capacity retention of $S_{500} = C_{500}/C_m \cdot 100\%$ was used to characterize the cycle stability of MH electrodes, where C_{500} is the discharge capacity at the 500th cycle and C_m is the maximum discharge capacity during cycling at 300 mA g⁻¹. Note that the electrochemical properties of a MH electrode are usually measured in the above tri-electrode system with a Hg/HgO reference electrode. [see Refs.^{24,25,29-40,44,51,53} of the text] The two-electrode system has also been utilized in some reports.²⁻⁵ For example, the discharge curves of a MH electrode were measured in these two systems and the corresponding testing results are similar.⁵ Considering higher stability of the Hg/HgO reference electrode than the sintered Ni(OH)₂/NiOOH counter electrode, the tri-electrode system was chosen in this work, which measures the potential difference between the MH electrode and the reference electrode. For Tafel polarization curves measurement, alloy powders were dispersed on the glassy carbon electrode (GCE) after which Nafion was dropped on the electrode as binder and conductive agent. Then the above electrode was dried in an electronic drying oven. The Tafel polarization curves were measured in a tri-electrode system (GCE as

a working electrode, Ni(OH)₂/NiOOH as a counter electrode, and Hg/HgO as a reference electrode) by scanning the electrode potential at a rate of 1 mVs⁻¹ between -0.4 to 0.1 V (vs. Hg/HgO) using an IVIUM electrochemical analyzer at 298 K.

Alkaline treatment of alloy powders: The alloys powders were immersed in a 15 M KOH solution at 90 °C for 3 days and dried in vacuum after thorough water rinsing. The morphology and structure of the powders were investigated by using a FESEM (JSM-6700F, JEOL, 15 keV) and a transmission electron microscope (TEM, JEM-2100F, JEOL, 200 keV).

Supplementary Figures

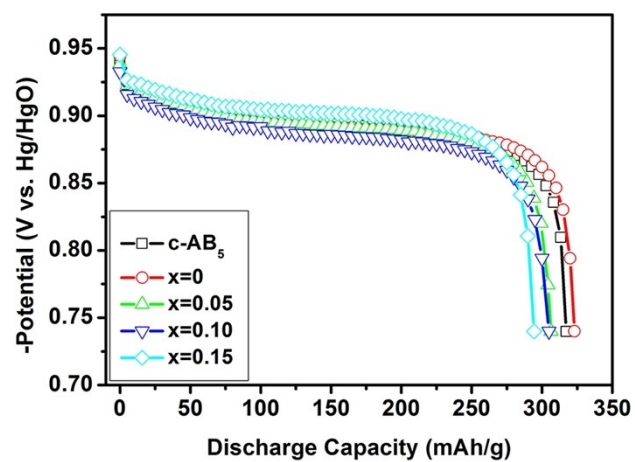


Fig. S1 The discharge capacity curves of c-AB₅ and LL-series alloys at 60 mA/g in half-cell tests at 298 K.

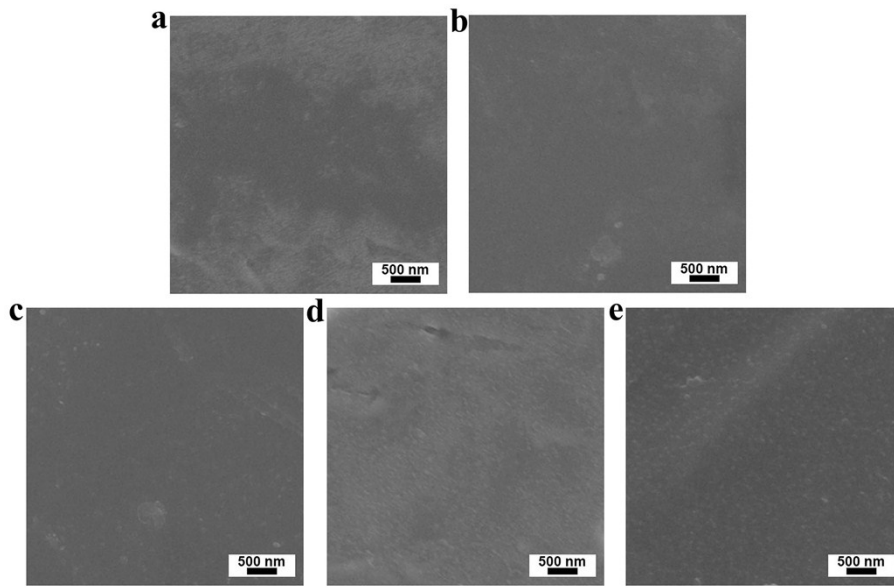


Fig. S2 (a)-(e) are SEM images of surfaces of c-AB₅, and LL-series alloys with $x = 0$, 0.05, 0.10, 0.15, respectively, before cycling.

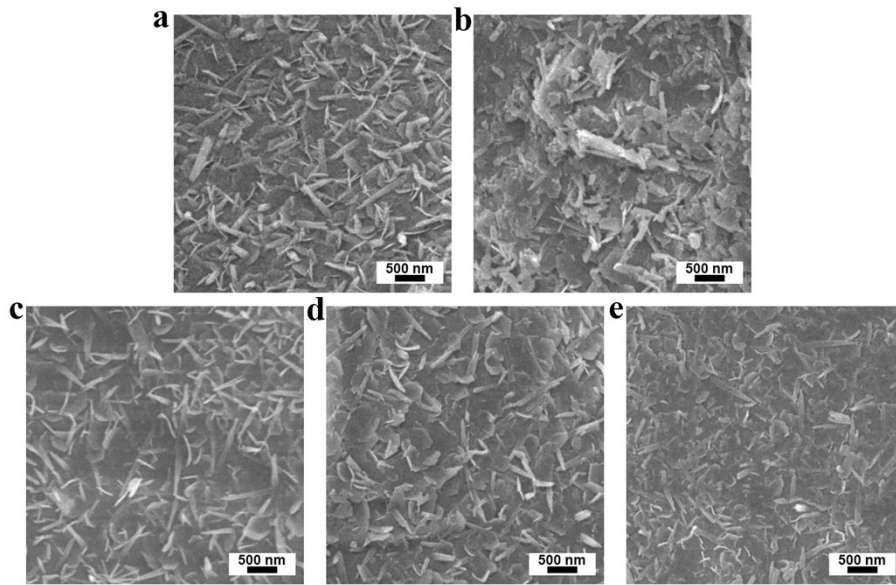


Fig. S3 (a)-(e) are SEM images of surfaces of c-AB₅, and LL-series alloys with $x = 0$, 0.05, 0.10, 0.15, respectively, after KOH treatment.

Supplementary Tables

Table S1 The electronegativity (χ) of 17 rare earth elements where the data are from Ref.⁴⁹ of the text except those of Pm, Eu, Tb and Yb.⁶

Elements	χ	Elements	χ	Elements	χ
La	1.10	Eu	1.20 ⁶	Tm	1.25
Ce	1.12	Gd	1.20	Yb	1.1 ⁶
Pr	1.13	Tb	1.10 ⁶	Lu	1.0
Nd	1.14	Dy	1.22	Y	1.22
Pm	1.13 ⁶	Ho	1.23	Sc	1.36
Sm	1.17	Er	1.24		

Table S2 Structural parameters of c-AB₅ and LL-series alloys before cycling, which are refined by the X-ray Rietveld analysis.

Alloys	Phase	Space Group	Lattice Parameters			
			$a(\text{\AA})$	$c(\text{\AA})$	c/a	$V(\text{\AA}^3)$
$x = 0$	CaCu ₅ -type	$P6/mmm$	5.0217(1)	4.0508(7)	0.8067	88.467(2)
$x = 0.05$	CaCu ₅ -type	$P6/mmm$	5.0138(0)	4.0547(8)	0.8087	88.274(6)
$x = 0.10$	CaCu ₅ -type	$P6/mmm$	5.0066(0)	4.0491(6)	0.8087	87.898(4)
$x = 0.15$	CaCu ₅ -type	$P6/mmm$	5.0018(8)	4.0485(3)	0.8094	87.719(1)
c-AB ₅	CaCu ₅ -type	$P6/mmm$	4.9943(2)	4.0517(5)	0.8113	87.523(9)

Notes and references

- 1 F. Izumi and T. Ikeda, *Mater. Sci. Forum*, 2000, **321**, 198-205.
- 2 W. Du, L. Zhang, Y. Li, Y. Zhao, S. Yang, B. Liu and S. Han, *J. Electrochem. Soc.*, 2016, **163**, A1474-A1483.
- 3 R. Tang and Y. Liu, *Int. J. Hydrogen Energy*, 2002, **27**, 1057-1062.
- 4 X. Zhao, Q. Li, K. Chou, H. Liu and G. Lin, *J. Alloys Compd.*, 2009, **473**, 428-432.
- 5 R. Tang, L. Liu, Y. Liu and G. Yu, *Int. J. Hydrogen Energy*, 2003, **28**, 815-819.
- 6 <https://en.wikipedia.org/wiki/Electronegativity> (accessed 16.08.18)