Electrochemical properties of AB$_5$ type La$_{0.8}$Ce$_{0.2}$Ni$_4$Co$_{0.5}$Mn$_{0.3}$Al$_{0.2}$ alloy for unified metal hydride fuel cell

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Abstract. Metal hydride materials are widely applied for electrochemical energy storage. AB$_5$ type alloys are the main anode material for Ni-MH batteries. Reversible hydrogen uptake and release provides good opportunities to use metal hydrides for alkaline fuel cell applications. Metal hydrides have good activation performance, high hydrogen sorption/desorption rates, catalytic activity in alkaline solution. Current work presents the first experimental results of AB$_5$ type metal hydride electrodes, measured in a battery mode. The electrochemical properties of the prepared electrodes, such as activation performance, maximum discharge capacity, and high rate dischargeability are investigated in detail.

1. Introduction

Hydrogen is an excellent secondary energy carrier to fit into a global sustainable energy strategy in the next few decades of the 21$^{st}$ century, which withstands the challenges of climate change, depletion of fossil fuels, rising pollution. Hydrogen would play a significant role in medium and long-distance road and rail vehicles; in coastal and international shipping; in air transport; and for longer-term seasonal storage on electricity grids relying on local renewable energy sources and feedstocks [1]. New technologies of electricity/heat production including fuel cells, hydrogen production from renewables and its storage are necessary for the transition to new energy systems based on resource-saving renewable energy technologies. Electro catalytically produced hydrogen is a perspective way to convert and store renewable energy [2]. Hybrid solar/wind/hydrogen based fuel cell power generation systems can effectively convert solar and wind energy into electric energy for remote areas [3].

Metal hydrides are known as good solid-state hydrogen storage materials with high volumetric capacity, high sorption/desorption kinetics and cyclic stability. They are used in stationary hydrogen storage [4-6], hydrogen compression [7-9], thermal energy storage [10-12] as well as electrochemical energy storage [13-16]. Metal hydrides are widely used in Ni-MH batteries, which have a number of advantages for practical applications, such as high specific energy density, resistance to overcharge/overdischarge, fast charge-discharge kinetics, environmental friendliness and safety. A number of studies [17-19] showed practical applicability of metal hydrides as anode material for alkaline fuel cells. Metal hydride based fuel cells can
operate at near ambient conditions and do not require precious catalysts. Their advantage is the possibility to be recharged in two ways: either electrochemically or by hydrogen pressure [19]. Thus, the metal hydride FC is the fuel cell with built-in charge storage, which can operate reversibly as an electrolyzer, and hydrogen is absorbed by the metal hydride alloy, i.e. as unitized regenerative fuel cells.

Metal hydride is formed by reversible interaction of individual metal or multicomponent alloy with hydrogen. Mostly multicomponent intermetallic compounds are used as anode materials. Typically, intermetallic compounds include AB₅ (LaNi₅), AB₂ (ZrMn₂), AB (TiFe) and super-lattice AB₁.₅ (rare earth-Mg-Ni) alloys. For a binary alloy, metal A is a hydride-forming metal, while metal B is a transition or non-transition metal that does not form stable hydride at normal conditions [20].

Despite the great efforts to develop new hydrogen absorbing materials with enhanced working characteristics [16, 21-29] AB₅ type alloys still stay the most popular materials due to their high surface catalytic activity, easy activation and good cycle stability. Partial replacement of constituent metals can significantly improve the electrochemical properties of metal hydride electrodes. Rare earth metals are hydride forming metals and provide hydrogen uptake, Ni is a key element for catalytic activity, Co improves cyclic stability, Mn increases surface activity, Al and Fe provide corrosion resistance [29-31].

We choose La₀.₈Ce₀.₂Ni₄Co₀.₅Mn₀.₃Al₀.₂ alloy as a potential metal hydride electrode and investigate it in terms of crystal structure, hydrogen storage and electrochemical properties in a battery mode.

2. Experimental details
The AB₅ type La₀.₈Ce₀.₂Ni₄Co₀.₅Mn₀.₃Al₀.₂ intermetallic compound is prepared in an arc furnace under argon atmosphere. The stoichiometric amount of initial metals is remelted three times to achieve high homogeneity of the alloy. After melting, the surface cleaned sample is wrapped in a molybdenum foil and sealed in a stainless-steel tube sample holder with titanium powder under the argon atmosphere. The sample is annealed at 1223 K for 20 hours and quenched into ice water.

XRD pattern of the annealed alloy is obtained from X-ray diffractometry. The measurement conditions are as follows: the step size is 0.02º and the exposition time is 1 s. The 2θ angles scanned are in the range from 15 to 80. Crystal structure and phase composition are performed using Jana2006 and Crystal Impact Match software using JCPDS PDF-2 Data Base.

Hydrogen sorption properties are investigated by the volumetric technique in a Sievert’s type apparatus. Thermodynamic parameters are calculated from Van’t Hoff plot.

In the case of electrochemical studies, metal hydride electrodes are prepared from a powder fraction with particle sizes of 40-60 μm. The electrodes in the form of a tablet with a diameter of 10 mm and a thickness of 1 mm with a total weight of 0.5 g are prepared by cold pressing at a pressure of 25 MPa for 3 minutes. Three electrodes samples named #1, #2 and #3 are manufactured to investigate them in different conditions. The prepared tablets are pressed between the foam nickel plates attached to the current collector.

Electrochemical measurements are carried out in a standard three-electrode cell with a 6M KOH solution as an electrolyte and Hg/HgO reference electrode. A commercial Ni(OH)₂ with a larger capacity is used as the counter electrode. The experiments are carried out on a multichannel potentiostat R-20X8. Activation of the metal hydride electrodes includes 10 charge cycles performed at a current density of 100 mA/g for 4.5 hours and a subsequent discharge at the same current density to a cut-off potential -0.6 V for samples #1 and #3. Sample #2 is discharged at current density 60 mA/g. In addition, sample #3 sandwiched between two steel perforated plates to increase the stability of the working electrode. The relaxation time between the charge and the electrode discharge is 0.5 hours. After activation, hydrogen diffusion rate and the high rate discharge ability performance in the range of discharge current densities of 100 - 1000 mA/g are measured.
3. Results and discussion

3.1. Crystal structure and PCT properties
The crystal structure of La$_{0.8}$Ce$_{0.2}$Ni$_4$Co$_{0.5}$Mn$_{0.3}$Al$_{0.2}$ alloy is well defined as a single-phase and belongs to the hexagonal CaCu$_5$ type. XRD pattern shows a high homogeneity of the obtained sample after annealing (figure 1a). Unit cell parameters are defined as $a = 0.5032$ nm, $c = 0.4035$ nm. PCT isotherms are measured from 295 to 333 K (figure 1b). Equilibrium pressure and hydrogen content at 295 K are 0.032 MPa and 1.1 wt.% H$_2$. Equilibrium pressure is suitable for use as anode material. Thermodynamic parameters obtained from van’t Hoff plot are $\Delta H = 30.1$ kJ/mol and $\Delta S = 88$ J/(mol·K).

![Figure 1. Crystal structure and PCT properties of La$_{0.8}$Ce$_{0.2}$Ni$_4$Co$_{0.5}$Mn$_{0.3}$Al$_{0.2}$ alloy.](image)

3.2. Electrochemical activation performance
Different charge/discharge current densities are applied for the activation of metal hydride electrodes [32-34]. We apply two common ways charge/discharge 100/100 mA/g and 100/60 mA/g currents to evaluate the effect of activation current densities on electrochemical properties of metal hydride alloy. Discharge curves at different discharge current rates are shown in figure 2.

Discharge current density effect is observed for first cycles and equilibrium potential. However, there is no significant influence on the maximum discharge capacity. Lower equilibrium potentials for samples 1 and 3 are related to charge transfer limitations at higher current densities. In addition, equilibrium potential and activation performance of sample 3 are strongly affected by applied perforated plates.
Figure 2. Discharge performance of La$_{0.8}$Ce$_{0.2}$Ni$_{4.5}$Co$_{0.5}$Mn$_{0.3}$Al$_{0.2}$ metal hydride electrode.

As shown in figure 3, the samples reach the maximum discharge capacity at the third-fifth cycle. Sample #3 is characterized by later activation, but more stable discharge capacity in the next activation cycles. Samples 1 and 2 show a small reduction of discharge capacity during activation, which is likely because of metal hydride particle decrepitation and precipitation on the bottom of the electrochemical cell. It is well known, that AB$_5$ type alloys are characterized by a significant change (up to 20–25%) of the unit cell volume during hydrogen sorption – desorption. Internal stresses arising from the expansion of particles lead to the gradual destruction of the electrode and the precipitation of metal hydride particles. In this case, sample 3 stabilized by perforated plates shows higher mechanical stability. The highest discharge capacity at the 10th cycle is equal to $C_{\text{max}} = 316.5 \pm 2.5$ mAh/g for all samples. The equilibrium discharge potentials of the electrodes slightly decrease as higher current density and perforated plates are applied (figure 4).

Figure 3. Activation performance of metal hydride electrodes.

Figure 4. Maximum discharge capacity of metal hydride electrodes.

3.3. Hydrogen diffusion properties
The hydrogen absorption/desorption reactions in alkaline aqueous solutions for metal hydrides involve the following steps: charge transfer step, adsorption and absorption of electroactive species, and mass transfer
from the surface to the bulk of metal hydride. In parallel to the hydrogen diffusion reaction, recombination processes described by the Tafel and the Heyrovski reactions are also occurred on the metal hydride surface [37, 38].

The above-mentioned reactions show a complex combination of different processes on the metal hydride electrode during electrochemical reactions. Thus, the estimation of hydrogen diffusion by traditional non-steady state methods is quite difficult. However, diffusion kinetics affect greatly the electrode’s rate capability and accurate determination of diffusion constants are of great interest from both practical point of view and understanding of the mechanisms of insertion processes. In comparison with traditional techniques used to estimate hydrogen diffusion in metal hydride electrodes such as constant potential step methods [32, 33, 39-42], electrochemical impedance spectroscopy [38, 43-45], potentiostatic intermittent titration technique has two major advantages: (i) applying of small potential steps makes it possible to linearize the electrochemical system responses to the potential perturbation and (ii) the potential dependence of the diffusion coefficients of intercalated species can be evaluated continuously in the whole potential domain of interest [46].

Current transients at a low amplitude of 20mV are measured in the potential range from -0.80 V to -0.96 V. Each potential is applied until the constant current is achieved. Experimental curves plotted $I^{1/2}$ vs log t coordinates are time invariant and should provide a horizontal section at short time domains, which corresponds to a typical Cottrellian behavior of diffusion [47]. The horizontal line shows an expected form of $I^{1/2}$ vs log t plot for ideal Cottrellian diffusion (figure 5a).

![Figure 5. Cottrellian time invariant $I^{1/2}$ vs log t plot (a) and linear fitting analysis of $I^{1/2}$ vs $1/t^{1/2}$ plot (b) at $E = 0.92$ V for metal hydride electrode.](image)

It is assumed that the deviation of the $I^{1/2}$ vs log t curves from ideal conditions is because of the action of resistances in the electrochemical system that are not related to diffusion in the solid (for example, charge transfer and surface resistance at the interface), which impede the expected Cottrell behavior at short time domains. However, for small $\Delta E$ used in PITT, the measured current $I(t)$ must "obey" Ohm's law (1):

$$I(t) = \Delta E / [ (R_s + R_{sf} + R_{ct} ) + (DC_{int})^{-1}P D t^{1/2} ]$$

(1)

where $R_s$ – solution resistance, $R_{sf}$ – surface resistance, $R_{ct}$ – charge transfer resistance, $D$ – diffusion coefficient, $C_{int}$ – differential capacity, $l$ – diffusion path length.

To calculate the effective hydrogen diffusion coefficient, we transform equation (1) to the following form [14, 48]:

$$I(t) = \Delta E / [ (R_s + R_{sf} + R_{ct} ) + (DC_{int})^{-1}P D t^{1/2} ]$$
where $R_\Sigma$, the sum of all non-diffusion resistances, $\Delta Q$ – integral capacity of the electrode at a given potential.

The linear dependence of experimental data on $I t^{1/2}$ vs $1/t^{1/2}$ plot makes it possible to calculate the hydrogen diffusion coefficient for each potential step using equation (2). There is a negligible charge capacity change at low potentials under 0.86 V, which corresponds to less than 1% of the total charge. Highest hydrogen diffusion coefficient values approximately $10^{-10} - 10^{-11}$ cm$^2$/s are obtained at minimum studied state of charge 5-7% and belong to $\alpha$-solid solution formation in metal hydride electrodes. As the state of charge increases hydrogen diffusion coefficients become lower decreasing to $1.2\cdot10^{-13} - 5.5\cdot10^{-14}$ cm$^2$/s (figure 6), because of the saturation of $\beta$-hydride phase. Such behavior of hydrogen diffusion also noted for $\text{AB}_3$ [25, 48] and $\text{AB}_2$ [14] type metal hydride electrodes and assumed to be typical for hydride forming alloys [49]. At the start of measurement, sample 3 shows lower hydrogen diffusion rate because of spatial restrictions caused by perforated plates.

![Figure 6. Hydrogen diffusion coefficient vs state of charge.](image)

4. Conclusions
The hydrogen storage and electrochemical properties of metal hydride materials based on $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_4\text{Co}_{0.5}\text{Mn}_{0.3}\text{Al}_{0.2}$ are studied in terms of crystal structure, hydrogen storage properties, activation performance, maximum discharge capacity and hydrogen diffusion. Hydrogen gravimetric capacity in gas-phase reaction reaches 1.1 wt.% H$_2$, which corresponds to the electrochemical capacity of 316.5 mAh/g. Perforated steel plates provide good mechanical stability of electrode with no significant effect on the hydrogen diffusion and maximum discharge capacity. However, they greatly affect equilibrium potential and may cause side reactions at higher discharge currents. The hydrogen diffusion coefficient is rather low not exceeding $1.2\cdot10^{-13}$ cm$^2$/s in a saturated region. Further improvement of metal hydride composition and its electrochemical properties is necessary for use as anode material.

References
[1] Andrews J and Shabani B 2012 Re-envisioning the role of hydrogen in a sustainable energy economy
[2] Emonts B, et al. 2017 Re-energizing energy supply: Electrolytically-produced hydrogen as a flexible energy storage medium and fuel for road transport. *Journal of Power Sources* **342** pp 320-326 DOI: https://doi.org/10.1016/j.jpowsour.2016.12.073

[3] Fathabadi H 2017 Novel standalone hybrid solar/wind/fuel cell power generation system for remote areas. *Solar Energy* **146** pp 30-43 DOI: https://doi.org/10.1016/j.solener.2017.01.071

[4] Lototskyy M, et al. 2019 Metal hydride hydrogen storage tank for fuel cell utility vehicles. *International Journal of Hydrogen Energy* DOI: https://doi.org/10.1016/j.ijhydene.2019.04.124

[5] Srinivasan S S and Demirocak D E 2017 Metal Hydrides used for Hydrogen Storage, in Nanostructured Materials for Next-Generation Energy Storage and Conversion: Hydrogen Production, Storage, and Utilization ed. Y P Chen, S Bashir and J L Liu Springer Berlin Heidelberg pp 225-255

[6] Kubo K, Kawaharazaki Y and Itoh H 2017 Development of large MH tank system for renewable energy storage. *International Journal of Hydrogen Energy* **42**(35) pp 22475-22479 DOI: https://doi.org/10.1016/j.ijhydene.2017.06.048

[7] Tarasov B P, et al. 2018 Cycling stability of RNi5 (R = La, La+Ce) hydrides during the operation of metal hydride hydrogen compressor. *International Journal of Hydrogen Energy* **43**(9) pp 4415-4427 DOI: https://doi.org/10.1016/j.ijhydene.2018.01.086

[8] Yartys V A, et al. 2016 Metal hydride hydrogen compression: recent advances and future prospects. *Applied Physics A* **122**(4) p 415 DOI: 10.1007/s00339-016-9863-7

[9] Lototskyy M V, et al. 2014 Metal hydride hydrogen compressors: A review. *International Journal of Hydrogen Energy* **39**(11) p 5818-5851 DOI: http://dx.doi.org/10.1016/j.ijhydene.2014.01.158

[10] Manickam K, et al. 2019 Future perspectives of thermal energy storage with metal hydrides. *International Journal of Hydrogen Energy* **44**(15) pp 7738-7745 DOI: https://doi.org/10.1016/j.ijhydene.2018.12.011

[11] Feng P, et al. 2019 Techno-economic analysis of screening metal hydride pairs for a 910 MWth thermal energy storage system. *Applied Energy* **242** pp 148-156 DOI: https://doi.org/10.1016/j.apenergy.2019.03.046

[12] Nyamisi S N, Lototskyy M, and Tolj I 2018 Selection of metal hydrides-based thermal energy storage: Energy storage efficiency and density targets. *International Journal of Hydrogen Energy* **43**(50) pp 22568-22583 DOI: https://doi.org/10.1016/j.ijhydene.2018.10.100

[13] Wijayanti I D, et al. 2020 Hydrides of Laves type Ti–Zr alloys with enhanced H storage capacity as advanced metal hydride battery anodes. *Journal of Alloys and Compounds* **828** pp 154354 DOI: https://doi.org/10.1016/j.jallcom.2020.154354

[14] Volodin A A, et al. 2019 Study of hydrogen storage and electrochemical properties of AB2-type Ti0.15Zr0.85La0.03Ni1.2Mn0.7V0.12Fe0.12 alloy. *Journal of Alloys and Compounds* **793** pp 564-575 DOI: https://doi.org/10.1016/j.jallcom.2019.03.134

[15] Zhang L, et al. 2018 A new AB4-type single-phase superlattice compound for electrochemical hydrogen storage. *Journal of Power Sources* **401** pp 102-110 DOI: https://doi.org/10.1016/j.jpowsour.2018.08.080

[16] Ouyang L, et al. 2017 Progress of hydrogen storage alloys for Ni-MH rechargeable power batteries in electric vehicles: A review. *Materials Chemistry and Physics* **200** (Supplement C) pp 164-178 DOI: https://doi.org/10.1016/j.matchemphys.2017.07.002

[17] Hu W-K and Noréus D 2009 Metal hydrides as bi-functional catalysts for hydrogen generation and oxidation in reversible MH-air fuel cells. *Electrochemistry Communications* **11**(11) pp 2212-2215 DOI: https://doi.org/10.1016/j.elecom.2009.09.033
[18] Chartouni D, et al. 2002 Metal hydride fuel cell with intrinsic capacity *International Journal of Hydrogen Energy* **27**(9) pp 945-952 DOI: http://doi.org/10.1016/S0360-3199(01)00186-0

[19] Folonari C, et al. 1980 Metal hydride fuel cells: A feasibility study and perspectives for vehicular applications *Journal of the Less Common Metals* **74**(2) pp 371-378 DOI: https://doi.org/10.1016/0022-5088(80)90175-7

[20] Hirscher M, et al. 2020 Materials for hydrogen-based energy storage – past, recent progress and future outlook *Journal of Alloys and Compounds* **827** pp 153548 DOI: https://doi.org/10.1016/j.jallcom.2019.153548

[21] Liu Y, et al. 2011 Rare earth–Mg–Ni-based hydrogen storage alloys as negative electrode materials for Ni/MH batteries *Journal of Alloys and Compounds* **509**(3) pp 675-686 DOI: https://doi.org/10.1016/j.jallcom.2010.08.157

[22] Takasaki T, et al. 2013 Cobalt-free nickel–metal hydride battery for industrial applications *Journal of Alloys and Compounds* **580** pp S378-S381 DOI: https://doi.org/10.1016/j.jallcom.2013.01.092

[23] Young K-H, Chang S, and Lin X 2017 C14 Laves Phase Metal Hydride Alloys for Ni/MH Batteries *Applications Batteries* **3**(3) pp 27

[24] Yan H, et al. 2017 Investigations on AB3-, A2B7- and A5B19-type LaYNi system hydrogen storage alloys *International Journal of Hydrogen Energy* **42**(4) pp 2257-2264 DOI: https://doi.org/10.1016/j.ijhydene.2016.09.049

[25] Volodin A A, et al. 2016 Phase-structural transformations in a metal hydride battery anode La1.5Nd0.5MgNi9 alloy and its electrochemical performance *International Journal of Hydrogen Energy* **41**(23) pp 9954-9967 DOI: https://doi.org/10.1016/j.ijhydene.2016.01.089

[26] Verbovity's'kyi Y V and Zavalii I Y 2016 New Metal-Hydride Electrode Materials Based On R1–xMg xNi3–4 Alloys for Chemical Current Sources *Materials Science* **51**(4) pp 443-456 DOI: 10.1007/s11003-016-9861-0

[27] Denys R V, Yartys V A, and Webb C J 2012 Hydrogen in La2MgNi9D13: the role of magnesium *Inorg. Chem.* **51**(7) pp 4231-8 DOI: 10.1021/ic202705u

[28] Zhang Y-h, et al. 2012 Electrochemical performances of the as-melt La0.75–xMg0.25Ni3.2Co0.2Al0.1 (M = Pr, Zr; x = 0, 0.2) alloys applied to Ni/metal hydride (MH) battery *International Journal of Hydrogen Energy* **37**(19) pp 14590-14597 DOI: https://doi.org/10.1016/j.ijhydene.2012.07.020

[29] Liu Y, et al. 2011 Advanced hydrogen storage alloys for Ni/MH rechargeable batteries *Journal of Materials Chemistry* **21**(13) pp 4743-4755 DOI: 10.1039/C0JM01921F

[30] Zhao X and Ma L 2009 Recent progress in hydrogen storage alloys for nickel/metal hydride secondary batteries *International Journal of Hydrogen Energy* **34**(11) pp 4788-4796 DOI: https://doi.org/10.1016/j.ijhydene.2009.03.023

[31] Feng F, Geng M, and Northwood D O 2001 Electrochemical behaviour of intermetallic-based metal hydrides used in Ni/metal hydride (MH) batteries: a review *International Journal of Hydrogen Energy* **26**(7) pp 725-734 DOI: https://doi.org/10.1016/S0360-3199(00)00127-0

[32] Zhang W, et al. 2009 Study on kinetics and electrochemical properties of low-Co AB5-type alloys for high-power Ni/MH battery *Electrochimica Acta* **54**(4) pp 1383-1387 DOI: https://doi.org/10.1016/j.electacta.2008.09.019

[33] Giza K 2013 Electrochemical studies of LaNi4.3Co0.4Al0.3 hydrogen storage alloy *Intermetallics* **34** (Supplement C) pp 128-131 DOI: https://doi.org/10.1016/j.intermet.2012.11.014

[34] Yao Q R, et al. 2014 Electrochemical properties of the LaNi4.5Co0.25Al0.25 hydrogen storage alloy in wide temperature range *Journal of Alloys and Compounds* **606** (Supplement C) pp 81-85 DOI: https://doi.org/10.1016/j.jallcom.2014.04.026

[35] Tilha M, et al. 2014 Kinetic and thermodynamic studies of hydrogen storage alloys as negative
electrode materials for Ni/MH batteries: a review Journal of Solid State Electrochemistry 18(3) pp 577-593 DOI: 10.1007/s10008-013-2300-3

[36] Borzenko V I, et al. 2019 Hydrogen sorption properties of metal hydride beds: Effect of internal stresses caused by reactor geometry International Journal of Hydrogen Energy 44(12) pp 6086-6092 DOI: https://doi.org/10.1016/j.ijhydene.2019.01.052

[37] Castro B E and Milocco R H 2007 State estimation in Volmer–Heyrovsky reactions coupled with sorption processes: Application to the hydrogen reaction Journal of Electroanalytical Chemistry 604(1) pp 1-8 DOI: https://doi.org/10.1016/j.jelechem.2007.01.002

[38] Zhang B, et al. 2018 Investigations on kinetics properties of hydrogen adsorbing/desorbing reactions for metal hydride electrodes International Journal of Hydrogen Energy 43(49) pp 22427-22437 DOI: https://doi.org/10.1016/j.ijhydene.2018.10.037

[39] Lin J, et al. 2014 High temperature performance of La0.6Ce0.4Ni3.45Co0.75Mn0.7Al0.1 hydrogen storage alloy for nickel/metal hydride batteries International Journal of Hydrogen Energy 39(25) pp 13231-13239 DOI: https://doi.org/10.1016/j.ijhydene.2014.06.112

[40] Liu B, et al. 2012 Microstructures and electrochemical properties of LaNi3.55Co0.2xMn0.35Al0.15Cu0.75(V0.81Fe0.19)x hydrogen storage alloys International Journal of Electrochemical Science 7 pp 11966-11977

[41] Zhou W, et al. 2017 Improvement in low-temperature and instantaneous high-rate output performance of Al-free AB5-type hydrogen storage alloy for negative electrode in Ni/MH battery: Effect of thermodynamic and kinetic regulation via partial Mn substituting Journal of Power Sources 343 (Supplement C) pp 11-21 DOI: https://doi.org/10.1016/j.jpowsour.2017.01.023

[42] Zhou W, et al. 2017 Low-temperature and instantaneous high-rate output performance of AB5-type hydrogen storage alloy with duplex surface hot-alkali treatment Journal of Alloys and Compounds 692 (Supplement C) pp 364-374 DOI: https://doi.org/10.1016/j.jallcom.2016.08.292

[43] Li X, et al. 2012 Electrochemical hydrogen absorbing properties of graphite/AB5 alloy composite electrode Journal of Alloys and Compounds 510(1) pp 114-118 DOI: https://doi.org/10.1016/j.jallcom.2011.09.001

[44] Hunmana R M, et al. 2012 Electrochemical behavior of metal hydride electrode with different particle size International Journal of Hydrogen Energy 37(19) pp 14966-14971 DOI: https://doi.org/10.1016/j.ijhydene.2011.12.093

[45] Tliha M, et al. 2010 Kinetic behaviour of low-Co AB5-type metal hydride electrodes Materials Science and Engineering: B 175(1) pp 60-64 DOI: https://doi.org/10.1016/j.mseb.2010.07.003

[46] Montella C 2006 Apparent diffusion coefficient of intercalated species measured with PITT: A simple formulation Electrochimica Acta 51(15) pp 3102-3111 DOI: https://doi.org/10.1016/j.electacta.2005.08.046

[47] Aurbach D, Levi M D, and Levi E 2008 A review on the solid-state ionics of electrochemical intercalation processes: How to interpret properly their electrochemical response Solid State Ionics 179(21) pp 742-751 DOI: https://doi.org/10.1016/j.ssi.2007.12.070

[48] Volodin A A, et al. 2015 Hydrogen diffusion in La1.5Nd0.5MgNi9 alloy electrodes of the Ni/MH battery Journal of Alloys and Compounds 645 (Supplement 1) pp S288-S291 DOI: https://doi.org/10.1016/j.jallcom.2014.12.201

[49] Young K, et al. 2016 Transmission electron microscope studies in the surface oxide on the La-containing AB2 metal hydride alloy Journal of Alloys and Compounds 672 pp 356-365 DOI: https://doi.org/10.1016/j.jallcom.2016.02.182