



Annealing effect on phase composition and electrochemical properties of the Co-free La_2MgNi_9 anode for Ni-metal hydride batteries

Wei-Kang Hu^{a,*}, Roman V. Denys^{a,b}, Christopher C. Nwakwuo^c, Thomas Holm^c,
Jan Petter Maehlen^a, Jan Ketil Solberg^c, Volodymyr A. Yartys^{a,c,**}

^a Institute for Energy Technology, Instituttveien 18, P.O. Box 40, NO-2027 Kjeller, Norway

^b Karpenko Physico-Mechanical Institute, NAS of Ukraine, Lviv 79601, Ukraine

^c Department of Materials Science and Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

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ABSTRACT

Present paper focuses on studies of the Co-free La_2MgNi_9 alloys as active materials of negative electrodes in nickel-metal hydride (NiMH) batteries. The effect of annealing treatment on the phase composition, microstructure, hydrogen absorption–desorption and electrochemical properties was investigated. The phase-structural composition, microstructures and morphologies of the phases were analyzed by X-ray diffraction and by scanning electron microscopy. Increase of the annealing temperature to 950 °C leads to a higher abundance of the La_2MgNi_9 and $\text{La}_3\text{MgNi}_{14}$ phases and an elimination of the present at lower temperatures LaNi_{5-x} and LaMgNi_4 intermetallics. The hydrogen absorption–desorption behaviors, the electrochemical performance and electrochemical cycling stability significantly improve after the annealing. For pasted electrodes, the annealed alloys had a discharge capacity of 350–360 mAh g^{-1} compared to 325 mAh g^{-1} for the as-cast sample. The discharge capacity of the annealed samples remained high, almost 50% after 300 cycles with 100% depth of discharge (DOD) in half-cell tests. Pellet electrodes prepared from the annealed alloy and carbonyl nickel powder showed a discharge capacity of 396 mAh g^{-1} . In present work we also report the performance of a small prototype NiMH cell where the annealed alloy was used as the active material in the negative MH electrode and a sintered Ni electrode acted as the positive electrode. After 300 cycles at charge/discharge rates of 0.2 C the cell showed a very good cycling stability with its capacity remaining on the level of 87%.

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1. Introduction

In the next decade rechargeable NiMH batteries have all possibilities to occupy the main segment of the HEV batteries since they offer significant advantages of excellent power densities, fast charge–discharge rates, long service life, very good low-temperature performance as well as good safety features. However, the price of the NiMH battery pack on the international market remains high, 500–600 US\$/kWh. The negative electrode of the NiMH battery comprises of a metal hydride electrode. Current materials used as negative electrodes are AB_5 -type rare earth-based alloys where A is a battery grade mixture of rare earths (La, Ce, Pr, Nd) (it has a higher price than the pure La and Ce metals) and B is a mixture transition metals and aluminum (Ni, Co, Mn, Al) or

AB_3 -type hydrogen storage alloys where A is a rare earth and magnesium mixture (RE, Mg) and B is nickel or nickel together with other transition metals (cobalt, manganese) and aluminum.

Clearly the price of the rare earth metals and cobalt has the most significant impact on the battery cost in total. Due to the recent restrictions on the export from China, since 2011 the prices of rare earths have dramatically increased. To timely and cost effectively address such a challenge for the metal hydride batteries, R&D of new hydride alloys lowering the electrode material cost via replacement of the battery grade rare earth mixture by other metal elements is of primary importance and will affect the market of future renewable energy storage systems and rechargeable batteries.

In the past decade, much work has been invested to develop relatively low cost La–Mg–Ni hydrogen storage alloys for the NiMH battery applications [1–20] instead of more expensive Nd–Mg–Ni anode materials offering benefits of high drain discharge, good performance at subzero temperatures and increased cycle stability [21,22]. However, the alloys from the La–Mg–Ni system close in composition to $(\text{La, Mg})\text{Ni}_3$ have the drawback of forming multi-phase structures (usually containing more than three

* Corresponding author. Tel.: +47 63 80 64 80.

** Corresponding author at: Institute for Energy Technology, Instituttveien 18, P.O. Box 40, NO-2027 Kjeller, Norway. Tel.: +47 63 80 64 53; fax: +47 63 81 29 05.

E-mail addresses: weikang.hu@ife.no (W.-K. Hu), volodymyr.yartys@ife.no, volodymyr.yartys@gmail.com (V.A. Yartys).

phases) and thus suffering from a poor electrochemical cycling stability. Partial substitution of Ni by Co or combination with Mn or Al is reported to improve the cycling stability [21–32]. The metallurgical process used in producing the alloys has a significant effect on the distribution of alloying components, microstructure and electrochemical performance. The electrode additive is also an important parameter contributing to the electrochemical performance of the hydrogen storage alloy. In many reference publications, a rather high quantity of additive materials such as carbonyl Ni powder is used in the metal hydride electrode to improve the discharge capacity. For practical applications, however, usually graphite powder is utilized as an additive material of MH electrode in order to arrive to an affordable cost. The additive content to the electrode composition is also lower, in the range of 5–10 wt.% of graphite, with active material normally occupying more than 90 wt.% in the MH electrode. In present work, we investigate influence of the annealing treatment on the alloy phase composition, microstructures, hydrogen absorption–desorption behaviors and electrochemical performances. The effect of electrode additives such as graphite and carbonyl nickel powder on the discharge capacity of MH electrodes is also studied.

2. Experimental

2.1. Preparation of La_2MgNi_9 alloy and structural characterization

The precursor La_2MgNi_9 alloy was prepared by intermediate frequency induction melting under argon atmosphere from the starting element metals with a purity of not less than 99.5%. After induction melting, the melt was poured into a water-cooled copper mold. As-cast alloy ingots of about 3 kg per batch were obtained. The alloy ingot was crushed and collected in a stainless steel cylindrical cell. The operation was done in an argon-filled glove box. Subsequently the cylindrical cell was inserted into a furnace and the material was annealed at 800, 900 and 950 °C for, respectively, 12, 6 and 6 h. At higher annealing temperatures of 900–950 °C, the required for the completion of the homogenization annealing time was limited to just 6 h. The annealing was two times longer at the lowest annealing temperature of 800 °C. The annealed alloys were then further ground into the powders with a particle size of 40–60 μm and used in the electrochemical measurements and phase-structural analysis. X-ray diffraction (XRD) with $\text{Cu K}\alpha_1$ radiation was used to identify the phase structure and composition of the alloys. The XRD data were collected using diffractometer Bruker D8 DISCOVER with a Ge-monochromator and a LYNX-Eye detector. The morphology and phase composition of the alloys were analyzed using a Zeiss Supra 55 VP scanning electron microscope (SEM) with a field emission gun (FEG) and equipped with a Bruker EDX detector. The samples were embedded in polyfast resin with carbon filler and prepared by grinding in successive steps, and polishing, until a mirror-like surface was obtained. Images were captured in the backscattered electron (BSE) mode in order to enhance phase contrast. ZAF corrections were also applied to the EDX spectroscopy data, for precise chemical analysis of the samples.

2.2. Preparation of MH electrodes and electrochemical measurements

Pasted MH electrodes were prepared in the following steps: (a) mixing of the alloy powder (40–60 μm particles) with fine graphite powder in a weight ratio of 10:1 and then adding 3% PTFE solution as binder to make a paste; (b) the mixture was then pasted on a Ni foam substrate with a size of 30 mm \times 30 mm \times 1.5 mm with

a nickel strip welded on in advance; (c) after drying, it was cold pressed with an extra Ni foam forming a sandwich structure.

Pellet MH electrodes were prepared by mixing MH alloy powder having a particle size of 40–60 μm with carbonyl Ni powder with a specific surface area of $\sim 0.7 \text{ m}^2/\text{g}$. The weight ratio of MH alloy to carbonyl nickel powder was chosen as 1:4. The pellet electrode was made by cold-pressing of the powder mixture into a pellet under a pressure of 12 MPa with a diameter of 10 mm and then sandwiched between two Ni foams.

Electrochemical properties were tested in a three-electrode system with a 9N KOH solution electrolyte at room temperature. A sintered $\text{Ni}(\text{OH})_2$ electrode with a larger than the MH electrode capacity and a Hg/HgO (9N KOH) electrode were used as the counter-electrode and reference electrode, respectively. The MH electrode was first activated at a 0.1C rate for three charge–discharge cycles. Then, the rate capability and cycling stability were evaluated galvanostatically. The end potential of the discharge was set at -0.74 V vs. the Hg/HgO electrode.

In addition, a small prismatic NiMH prototype cell composed of a sintered $\text{Ni}(\text{OH})_2$ electrode, an annealed La_2MgNi_9 alloy MH electrode, separator and 9N KOH electrolyte was made for the evaluation of the performance. The cell capacity is limited by the capacity of the positive electrode. The small prismatic NiMH cell was activated first at 0.1 C rate for 2 cycles. The discharge voltage of the cell was controlled by the electrochemical test station; the measurements were terminated at 1.0V.

3. Results and discussion

3.1. Influence of annealing temperature on the phase composition, micro-structure and PCT diagrams of H_2 absorption–desorption

3.1.1. Phase composition of the alloy

Fig. 1a presents the X-ray diffraction patterns of as-cast and annealed alloys at different annealing temperatures. The as-cast alloy was found to be rather inhomogeneous containing five intermetallic phases: La_2MgNi_9 (PuNi₃ type) as the most abundant phase, rhombohedral $\text{La}_3\text{MgNi}_{14}$ (Gd_2Co_7 type), two modifications of $\text{La}_4\text{MgNi}_{19}$ (rhombohedral {3R} $\text{Ce}_5\text{Co}_{19}$ type and hexagonal {2H} $\text{Pr}_5\text{Co}_{19}$ type), LaMgNi_4 (MgCu_4Sn type) and LaNi_{5-x} (CaCu_5 type). The latter compound is the only one which does not dissolve Mg and is a formed as enriched by lanthanum $\text{LaNi}_{\sim 4.9}$ alloy.

Fig. 1b gives the XRD profiles of Rietveld refinements of the La_2MgNi_9 alloy annealed at 950 °C. Table 1 summarizes the results of the Rietveld refinements of XRD data for the as-cast and annealed alloys. Chemical composition of the as-cast alloy estimated from the phase fractions of the formed constituents equals to $\text{La}_{16.7}\text{Mg}_{6.7}\text{Ni}_{76.6}$ and, despite a rather small loss of the alloy's weight, $\sim 0.6\%$, noticeably deviates from the target composition $\text{La}_{16.7}\text{Mg}_{8.3}\text{Ni}_{75}$. Such a deviation is caused by evaporative loss of Mg during the melting. No further loss of Mg occurred during the annealing treatment, as it was confirmed by the samples weight control after the annealing, in agreement with unchanged average composition, as is presented in Table 1.

The evolution of phase composition of the alloy resulting from the annealing treatment at 800–950 °C is shown in Table 1 and Fig. 2. It can be seen that fractions of LaNi_{5-x} and LaMgNi_4 gradually decrease before disappearing with increase of the annealing temperatures. At the same time, abundances of La_2MgNi_9 and $\text{La}_3\text{MgNi}_{14}$ phases correspondingly increase reaching maxima at 950 °C.

The values of lattice parameters of the constituent phases prepared at different conditions vary within narrow ranges and well agree with the literature data [32–36].

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