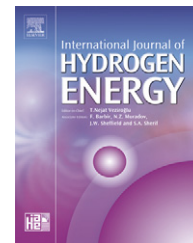


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Magnesium influence in the electrochemical properties of La–Ni base alloy for Ni–MH batteries

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ABSTRACT

The effect of the substitution of La by Mg in the hypo-stoichiometric $\text{La}_{1-x}\text{Mg}_x\text{Ni}_{3.8}\text{Co}_{0.3}\text{Mn}_{0.3}\text{Al}_{0.4}$ ($x = 0.00, 0.05, 0.10, 0.15$ and 0.20) hydride alloys were metallurgically and electrochemically characterized in order to use them as negative electrodes in Ni–MH batteries. The Mg content was added to mother alloys by means of low energy mechanical alloying. The microstructure, composition and crystalline structure of the samples were analyzed by SEM, EDS and X-ray diffraction, respectively, and their electrochemical properties were analyzed by charge/discharge cycling stability and rate capability.

The electrochemical results show that the alloy $\text{LaNi}_{3.8}\text{Co}_{0.3}\text{Mn}_{0.3}\text{Al}_{0.4}$ reaches a maximum discharge capacity of 181.7 mAh/g. $\text{La}_{0.85}\text{Mg}_{0.15}\text{Ni}_{3.8}\text{Co}_{0.3}\text{Mn}_{0.3}\text{Al}_{0.4}$ presents the best behavior in electrochemical cycling stability with a capacity decay of 4.4% after 50 cycles and a capacity reduction rate of 0.117 mAh/g per cycle. The alloy $\text{La}_{0.80}\text{Mg}_{0.20}\text{Ni}_{3.8}\text{Co}_{0.3}\text{Mn}_{0.3}\text{Al}_{0.4}$ obtained the highest discharge capacity at high rate discharge.

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1. Introduction

The predictable depletion of non-renewable energy resources is encouraging numerous research works oriented to find an alternative, clean and sustainable solution. At present, regarding the problem of vehicular transport, we are crossing a transition stage. Some companies are developing hybrid electric vehicles (HEV), whose operation is based on a classic internal combustion engine and an electric one, supported by Ni–MH batteries. The industry still must reduce cost, space and weight in order to commercialize this new technology, thus higher specific energy and power, and long cycle life batteries are required for new products.

In recent years, many investigations in AB_5 type alloys used as negative electrodes of Ni–MH batteries were concerned in

reducing the Co content [1–12]. This element is essential to reduce the alloy degradation produced by electrochemical cycles, because it decreases the oxidation and pulverization of the alloy [7,12,13] and improves the hydrogen diffusivity [14]. However, only 10 wt% of Co content involves between 40% and 50% of raw material total costs [8].

The literature shows many papers related to low Co [2–5]. Hu et al. [2] studied the substitution of Co by Cu, Cr and Si, obtaining a reduction in the discharge capacity but without increasing the degradation among electrochemical cycles. Zuttel et al. [3] and Ayari et al. [4] replaced Co by Fe; and Li et al. [5] studied the rapid quenching effect in alloys with different Co content.

Many researchers [8–12] are analyzing the effect produced by the Co reduction together with the use of a small amount

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of Mg, reporting that La or Mm (mischmetal) replaced by Mg improves the electrochemical performance.

The purpose of this work is to analyze the influence of different quantities of Mg on the electrochemical properties of a La–Ni base alloy used for Ni–MH batteries, added by mechanical alloying.

2. Experimental procedure

The high vapor pressure of Mg and elevated melting point of most of the elements of the alloy, make it difficult to melt them together by usual techniques. Therefore, the mother (base) alloys $\text{La}_{1-x}\text{Ni}_{3.8}\text{Co}_{0.3}\text{Mn}_{0.3}\text{Al}_{0.4}$ ($x = 0, 0.05, 0.1, 0.15$ and 0.2) were obtained by melting the constitutive elements (purity >99.9%) in an induction furnace inside a BN crucible under Ar atmosphere. The samples were re-melted at least twice to ensure their homogeneity. Then the Mg content was incorporated as MgH_2 to each mother alloy by low energy mechanical alloying, using a Uni-Ball-Mill II device (Australian Scientific Instruments). Each base alloy was put into the stainless steel grinding container with its corresponding Mg quantity, under Ar atmosphere. The balls/alloy weight ratio used was 40:1. The milling time was 55 h at room temperature and the rotation velocity 140 rpm.

The nomenclature used for the obtained alloys is Mg_x , where x denotes the Mg quantity, e.g. $\text{Mg}_{0.05}$ is the denomination used for the alloy $\text{La}_{0.95}\text{Mg}_{0.05}\text{Ni}_{3.8}\text{Co}_{0.3}\text{Mn}_{0.3}\text{Al}_{0.4}$.

The crystalline structures of the resulting alloys were examined using X-ray diffraction (Philips PW3710 equipment). The morphology and elemental microanalysis of the electrodes before hydriding were studied by scanning electronic microscopy (SEM) and electrons dispersion spectroscopy (EDS) (Philips 515 and 500 equipments, respectively).

For the electrochemical characterization, 100 mg of milled alloy were mixed with the same quantity of Teflonized Carbon (TC: Vulcan XC-72 + 33 wt% PTFE) and compressed up to 3000 kg/cm^2 . TC acts as a mechanical support and is electrical conductor. The mixture, together with a Ni central mesh connected to a Ni wire as current collector, was placed inside a cylindrical die before compression to conform a negative electrode of metal hydride. The dimensions of the disk-shape negative electrodes obtained are 11 mm in diameter and 1 mm in thickness. A Ni mesh connected to a Ni wire was used as counter-electrode and Hg/HgO was used as reference electrode (+0.098 V vs. NHE).

For electrochemical measurements, the electrodes were submerged in a cell with a KOH 8M solution at 23°C used as electrolyte. Each hydride electrode was submitted to 50 electrochemical charge/discharge cycles. The charge current used for all the experiments was $I_c = -100 \text{ mAh/g}$ during 4 h for activation cycles. After activation the time was adjusted to supply a charge of 125% of the nominal capacity. The discharge cut-off voltage was fixed at -600 mV . The discharge current drained for both activation and cyclic stability measurements was 50 mA/g . For rate capability studies the discharge current regimes varied from $C/10$ to $5C$.

3. Results and discussion

3.1. Crystallographic characterization

Fig. 1 shows the X-ray diffraction of the alloys before hydriding, in which a direct correspondence with the hexagonal CaCu_5 type structure and the spatial group $P6/mmm$ can be seen.

The diffraction patterns obtained confirm that alloys are homogeneous due to the appearance of peaks corresponding

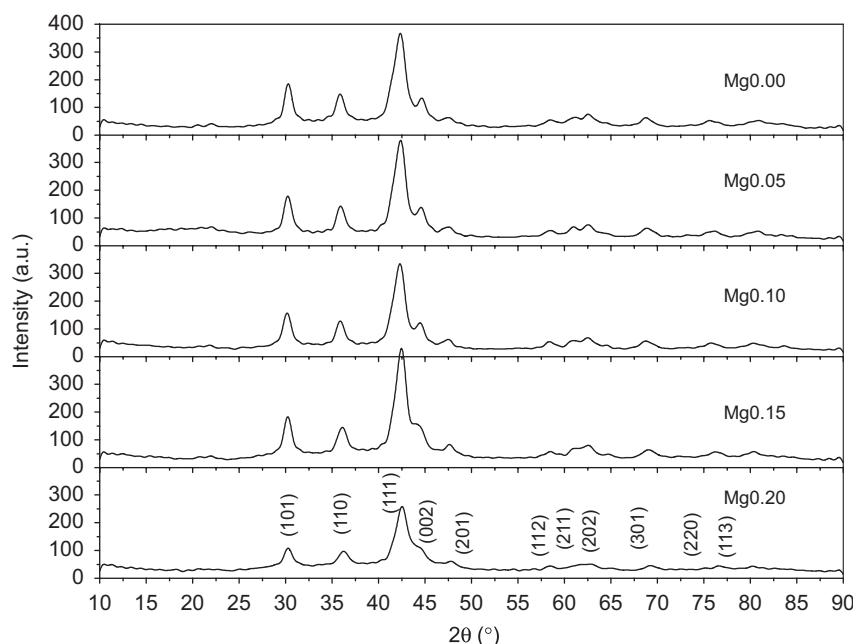


Fig. 1 – XRD of alloys before hydriding.

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