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Hydrogenation and Discharge Capacity of a $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ Alloy for Nickel-Metal Hydride Batteries

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Abstract. The preparation of negative electrodes for nickel-metal hydride (Ni-MH) batteries using a $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy in the as-cast state has been carried out. The alloy was mechanically crushed (<44 µm) and a battery was manufactured with this material. The mean discharge capacity achieved using this method was 384 mAh/g. Another two batteries were prepared using a hydrogen powdered $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy at low and high pressures (2-10 bar). It has been shown that hydrogen powdering facilitates the activation of the negative electrode for Ni-MH batteries. This study also included the characterization of the hydrogenated and crushed powders. These materials were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Introduction

Hydrogen storage alloys has been extensively studied due their potential as negative electrode material in Ni-MH batteries. The importance of these alloys at the performance of the Ni-MH batteries is based on the high capacity, high resistance to overcharging and overdischarging, capacity of performing a high rate charge/discharge, and interchangeable with a nickel–cadmium battery. The composition of the hydrogen storage alloy influences directly on the Ni-MH battery characteristics and the La–Mg–Ni system is very promising [1]. Recently, it has been reported that, in the as-cast condition, a $La_{0.7}Mg_{0.3}Al_{0.2}Mn_{0.1}Co_{0.75}Ni_{2.45}$ alloy electrode showed a maximum discharge capacity of ~351 mAh/g with good cycling stability [2]. The aim of this work is to investigate the hydrogenation and the discharge capacity of a $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy as the negative electrode material. Mechanical and hydrogen powering have been employed in this investigation.

Experimental

A commercial $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ cast alloy (5 kg ingot) was studied in this work. The microstructure and chemical analysis of the cast alloy have been reported in a previous paper [3]. The following procedure was adopted for the electrode preparation. Small pieces of the bulk ingot (5 g) were placed in a stainless steel hydrogenation vessel which was evacuated to backing-pump pressure (10^{-2} mbar). The temperature then was raised (500°C) followed by injection of hydrogen (2 bar). Hydrogenation/pulverization at high pressure (10 bar) was spontaneous at room temperature. Manually pressed electrodes (~2x2 cm^2; 1 mm thick) were prepared using 140 mg of the powder (<44 µm) blended with carbon black (67%) and PTFE (33%). Separator and positive electrode ($Ni(OH)_2$) were taken from a commercial battery. At the charge/discharge cycle tests, the charge was conducted using the current 14 mA during 5 hours and discharge at 7mA until voltage reached -0.9 V.

Results and discussion

Cycle life curves of the negative electrodes prepared using the crushed and hydrogenated $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy are shown in Fig.1. The electrode produced with the crushed alloy exhibited a good performance with a mean discharge capacity of 384 mAh/g. Similarly, the electrode prepared using the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy hydrogenated at high pressures exhibited a discharge capacity of 395mAh/g. The negative electrode prepared using a hydrogen powdered alloy at low pressures exhibited an excellent mean discharge capacity (445mAh/g), but a poor performance with increasing cycle number. This can be attributed to the elevated temperature used for low pressure pulverization that causes a modification on the structure of the particles. It has been reported that increasing cycle number, the alloy particles were pulverized due to the cell volume expansion and contraction during the hydrogenation/dehydrogenation process [4]. The powders obtained by hydrogen pulverization (500^{o}C / 2 bar) exhibited a fragile particles. The structure of these materials is shown in Fig. 2. For a comparison the structure of the particles hydrogenated at high pressure is shown in Fig. 3. The hydrogen powdered material at low pressure exhibited a more fragile structure favoring the activation of the negative electrode and a high discharge capacity. On the other hand, the pulverization of the alloy particles during charge/discharge cycling caused a premature loss in the discharge capacity of this electrode. The battery produced with hydrogen powdered material at high pressure shows a better performance and this was attributed to a more ductile powder surface.

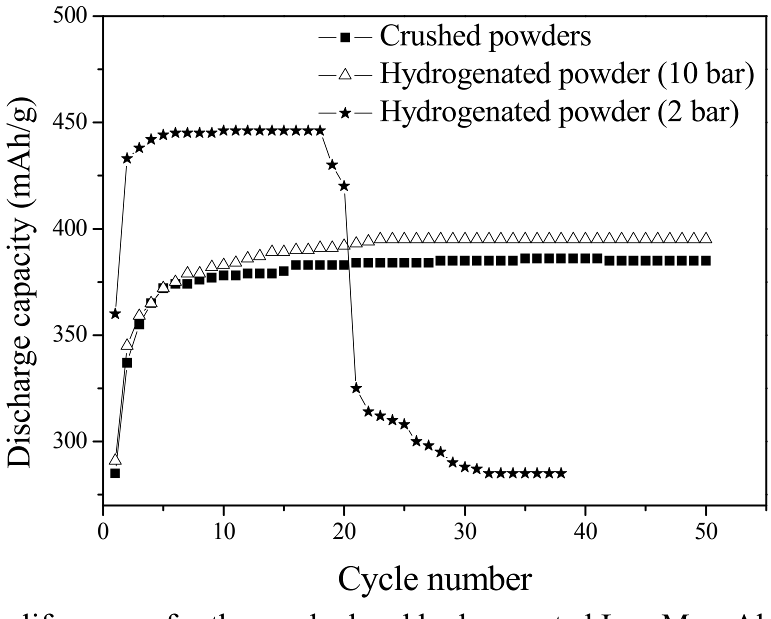

Fig. 1 – Cyclic life curves for the crushed and hydrogenated $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy.

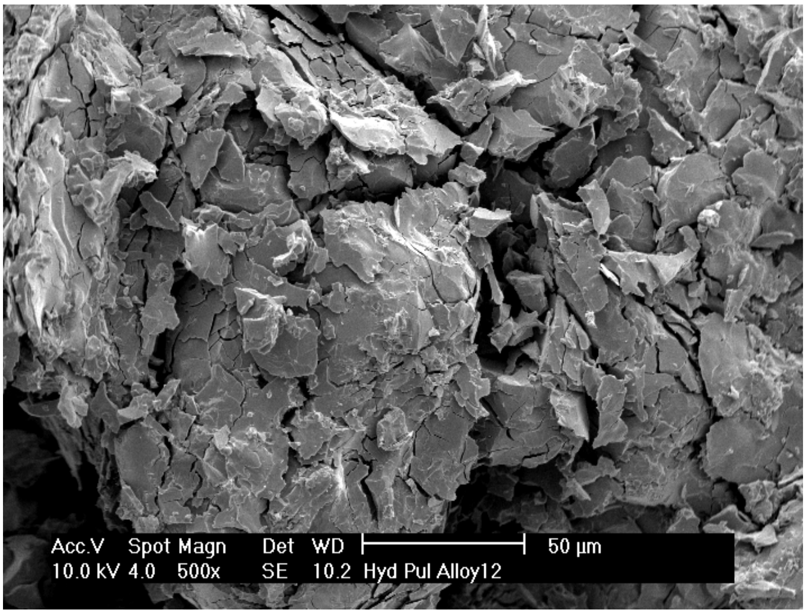

Fig. 2 – SEM micrograph of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy pulverized at 500°C / 2 bar.

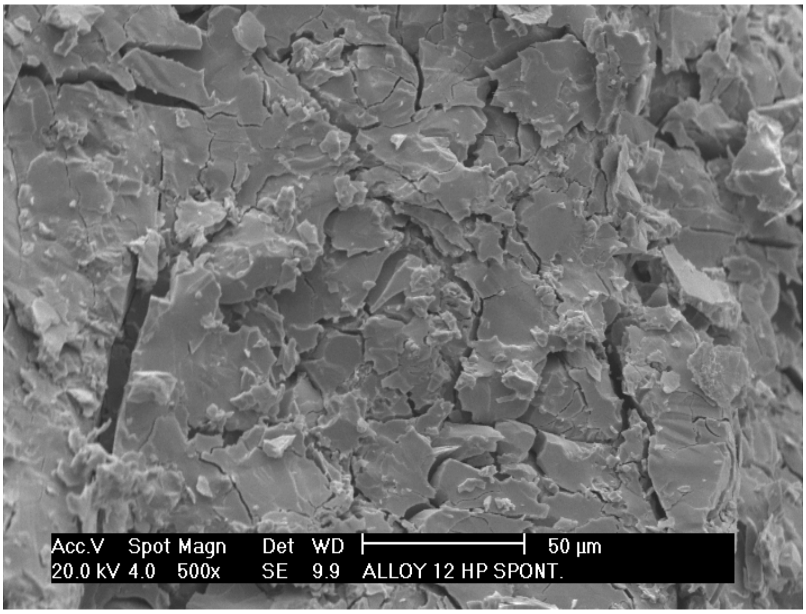

Fig.3 – SEM micrograph of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ hydrogen powdered at 10 bar.

Studies showed that coating the negative electrode of Ni-MH batteries improved the particle of the alloy. Palladium prevents particles size diminishing on charge/discharge cycling [5,6]. Studies on coating the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ hydrogenated powders are underway.
Fig 4 shows the structure of the powder crushed mechanically and used on the preparation of the negative electrodes. A comparison with the images presented previously (Figs. 2 and 3) clearly shows the distinct microstructure of this material. The performance of the electrode prepared using this powder was somewhat inferior to that hydrogenated at high pressure. Moreover, crushing the cast alloy to < 44 µm proved to be very laborious.

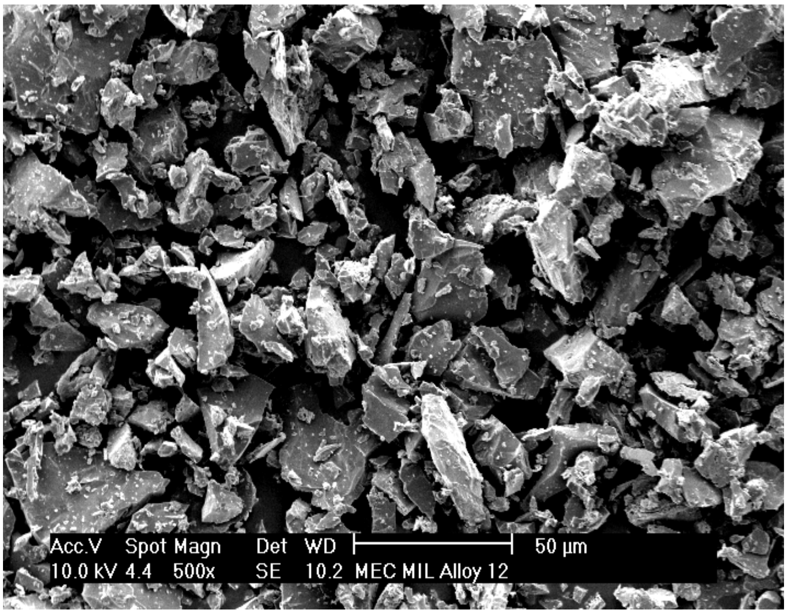

Fig. 4 - SEM micrograph of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ crushed powder used on the preparation of negative electrodes for Ni-MH batteries.

Fig. 5 shows cyclic behavior of the $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy electrodes produced with hydrogen pulverization a low pressure after long time storage at room temperature. Clearly, the oxidation of the powders reduced the discharge capacity. These results are in agreement with the conditions of the Ni-MH batteries operation. MH electrodes are typically designed for use in totally sealed batteries to avoid their oxidation and corrosion. The Ni-MH batteries operate in a strongly oxidizing medium; and their durability (cycle life) strongly depends on oxidation and corrosion resistance of the MH electrode materials [1].

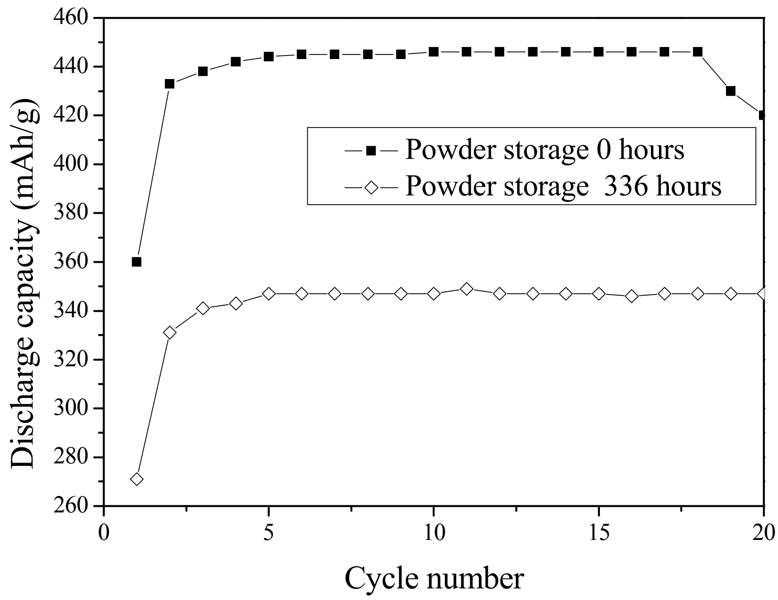

Fig. 5 - Cyclic life curves of $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ powder as function of the storage time.

Conclusions

Negative electrodes produced with a $La_{0.7}Mg_{0.3}Al_{0.3}Mn_{0.4}Co_{0.5}Ni_{3.8}$ alloy hydrogenated at high pressure exhibited an excellent performance and good discharge capacity (395mAh/g). Conversely, electrodes hydrogenated at elevated temperature low pressure showed high discharge capacity (445mAh/g) but poor cycle life. The performance of crushed alloy electrodes was satisfactory although the preparation of fine crushed powders proved to be laborious. As expected, oxidation of the powder on storage at room temperature diminished considerably the performance of the negative electrodes.

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