

Electrochemical study of A₂B₇-type hydrogen storage alloy prepared by ball milling

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Abstract. In this study, the hydrogen storage property of the La_{1.5}Mg_{0.5}Ni₇ compound as a negative electrode in Ni-MH batteries was investigated. This compound was elaborated by ball milling in a mechanical grinder for 30 hours at a ball/powder weight ratio of 8:1. The characterization of the powder of the elaborated alloy was examined both by X-ray diffraction and by scanning electron microscope. In this context; the structural property for alloy has two major phases Ni, La₂Ni₇. The powder micrograph shows that the average grain size calculated is approximately 13 μm. The electrochemical characterization of the La_{1.5}Mg_{0.5}Ni₇ electrode was carried out by the galvanostatic charge and discharge polarization in alkaline solution (6M) at ambient temperature. The best discharge capacity is observed in the first cycle (58 mAh g⁻¹). Therefore, the La_{1.5}Mg_{0.5}Ni₇ electrode activation requires only one cycle of charge and discharge. After activation, the discharge capacity gradually decreases during long cycling due to the degradation of the active material of the electrode.

Introduction

Metal hydride/nickel batteries were used due to their high energy density, durability to overcharge/discharge and environmental friendliness [1]. As battery anode materials, the commercialized AB₅ type alloys, however, are subjected to low discharge capacity, restricting the development of MH/Ni. Recently, La–Mg–Ni-based hydrogen storage alloys with AB₃-type or A₂B₇-type superlattice structures have been on focus for their higher discharge capacities than AB₅-type alloys, especially the A₂B₇-type La–Mg–Ni-based alloys of which studies have shown that their cycling stabilities are superior than that of AB₃-type alloys.

The introduction of Mg is important, which can improve hydrogen absorption/desorption pressures and enhance hydrogen storage capacities of the alloys, and the alloys possess superior electrochemical discharge capacities compared to binary La–Ni alloys, making them preferable for using as the electrode materials [2,3]. Therefore, people have focused on studying the effect of amount of Mg on the phase structures and overall properties of those alloys. Deny et al. have investigated the effect of Mg substitution for La on the hydrogenation behavior, thermodynamics and structural properties of Ce₂Ni₇-type La_{1.5}Mg_{0.5}Ni₇ alloy. Results showed that La substitution by Mg had an increase in the reversible hydrogen storage capacity of the alloy [4].

In this paper, the La_{1.5}Mg_{0.5}Ni₇ alloy was prepared by mechanical milling for 30 hours with a ball to powder weight ratio of 8:1. The structural characterization is performed by XRD in order to identify the different existing phases. The electrochemical characterization was performed through the galvano-static polarization in order to test the performance of this compound as active material for the anode of Ni-MH batteries.

Experimental

The $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ alloy was elaborated by mechanical synthesis for 30 hours with a ball to powder weight ratio of 8:1. These alloys are prepared from the elements, commercialized in powders of high purity: La (99% purity, granular particle size); Ni (99.5% purity, particle size $\leq 250 \mu\text{m}$); Mg (97.5% purity, particle size $\leq 45 \mu\text{m}$) in a glove box full of argon. The weights of these elements are adjusted to obtain the desired amount of alloy taking into account stoichiometry. All elements are placed in jars with three stainless steel balls whose volume and diameter are 50 mL and 20 mm respectively. The milling was realized out using a high-energy planetary ball mill with an angular rate of 400 rpm (Retsch PM 400), in an argon atmosphere at room temperature.

The alloys were characterized by X-ray diffraction through the Bruker D8 advance experimental device. The powder morphology of these alloys was analyzed by scanning electron microscopy (SEM, JEOL, SM-5800LV).

All the electrochemical properties were studied at ambient temperature using a beaker closely connected with the Potentiostat-Galvanostat EC-Lab V10.12 system (Bio-Logic).

The measuring cell is composed of three electrodes; M/MH_x negative electrode, Ni(OH)₂/NiOOH positive electrode and Hg/HgO reference electrode [5]. The electrolyte consists of a potash solution with 6 M concentration, which was stirred through the cell by continuous flow of argon. To prepare the negative electrodes, 5% black carbon, 5% polytetrafluoroethylene and 90% powder [6,7] are mixed.

To determine the electrochemical discharge capacity for a given cycle, the negative electrode was charged with current density of -51 mA g^{-1} during 15 hours. Thereafter, this electrode was discharged with the same value of current density and a break potential of -0.6 V compared to the reference electrode.

Results and discussion

Microstructure and morphological analysis

Fig.1 and Fig.2 show, respectively, the X-ray diffraction diagrams (XRD) and their refinement by the Rietveld method of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder.

The XRD spectrum of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder reveals the presence of two main phases Ni (fcc) and La_2Ni_7 (hexagonal) located respectively at 52.08° , 61.34° , 91.63° and 31.31° , 36.81° and 46.57° , 52.08° . Werwiński et al. [10] investigated the influence of La substitution by Mg on the electrochemical and electronic properties of $\text{La}_{2-x}\text{Mg}_x\text{Ni}_7$ alloys ($x = 0.00, 0.25, 0.50, \text{ and } 0.75$) made by mechanical milling for 48 h followed by annealing for 0.5 h at 1123 K. They showed that according to the XRD patterns, the final $\text{La}_{2-x}\text{Mg}_x\text{Ni}_7$ samples did not contain single elemental La and Mg phases. For the sample $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ ($x = 0.5$), according to the X-ray spectrum, shows the phase La_2Ni_7 (89.9 wt.%) with a smaller share of the phase LaNi_5 (8.0 wt.%) and the phase La_2O_3 (3.1 wt.%). Also, Zhang et al. [11] studied the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ compound prepared by induction furnace followed by annealing for different temperatures (1073, 1123 and 1173 K) for 24h, they showed that the compounds exhibited multiphase microstructure, such as Gd_2Co_7 type phase, Ce_2Ni_7 type phase, PuNi_3 type phase, CaCu_5 type phase, and MgCu_4Sn type phase.

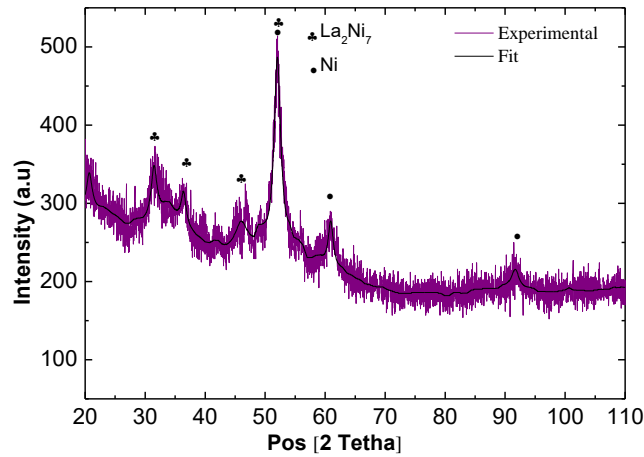


Figure 1. XRD diffractogram of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder elaborated by mechanical alloying during 30 h with a ball/powder weight ratio of 8:1

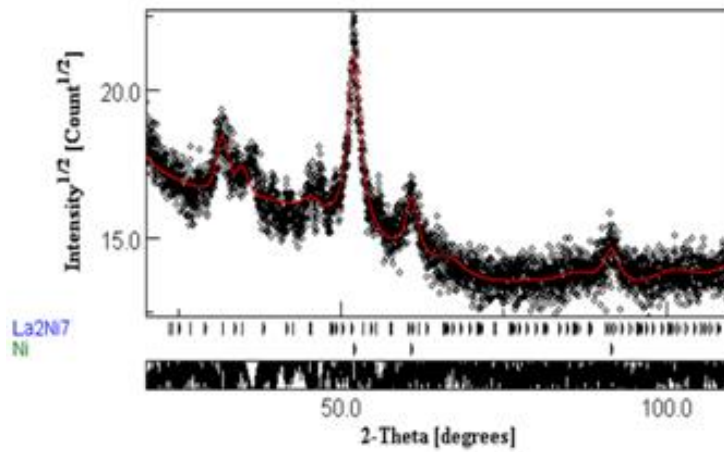


Figure 2. X-ray diffractogram refined by the Rietveld method of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder elaborated by mechanical alloying during 30 h with a ball/powder weight ratio of 8:1

Table 1 group the different crystallographic parameters, such as cell parameters, phase abundance and average crystallite size as well as fit parameters, obtained by Rietveld refinement of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder [12].

The parameters of fit (R_{wp} and R_p) indicate a good correlation between the theoretical diffractogram and the experimental data for the measured XRD diffractogram. The obtained powder presents two main phases, the first phase is nickel and the second is the La_2Ni_7 .

Fig.3 illustrates the morphological evolution of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder particles during 30 h of milling with a ball to powder weight ratio 8:1.

The SEM observations clearly show that the calculated average grain size of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder is about 13 μm . The average grain size calculated from micrographs is considerably larger than that indicated by XRD.

Table 1. Crystallographic parameters obtained by the Rietveld refinement of $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder elaborated by mechanical alloying during 30 h with a ball/powder weight ratio 8:1.

Alliage	Phases Trouvés	Paramètres de maille (Å)	Abondance de Phase (wt%)	Taille de cristallites (nm)	R_F	Paramètres de fit
$\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$	Ni La_2Ni_7	a= 3.532 a=5.032 et c=24.653	55 45	6.2 11	0.97	$R_{wp} = 6.15$; $R_p = 4.85$

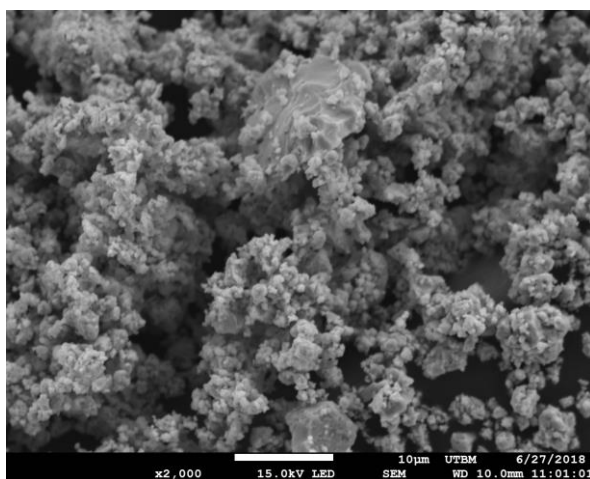


Figure 3. Morphology of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder particles elaborated by mechanical alloying during 30 h with a ball/powder weight ratio of 8:1

Characterization of the electrodes through the galvanostatic polarization

Activation properties of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode

A metallic compound, in electrochemical cycling, is said to be activated if the experimental value of its discharge capacity reaches a maximum value and if the experimental value of its half-discharge potential has become constant. Indeed, some compounds are activated after the first five cycles of charge and discharge; others are activated only after several cycles (from 5 to 25 cycles).

Fig.4 shows the evolution of the discharge curves of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode during the first activation cycles under a current of 0.7 mA

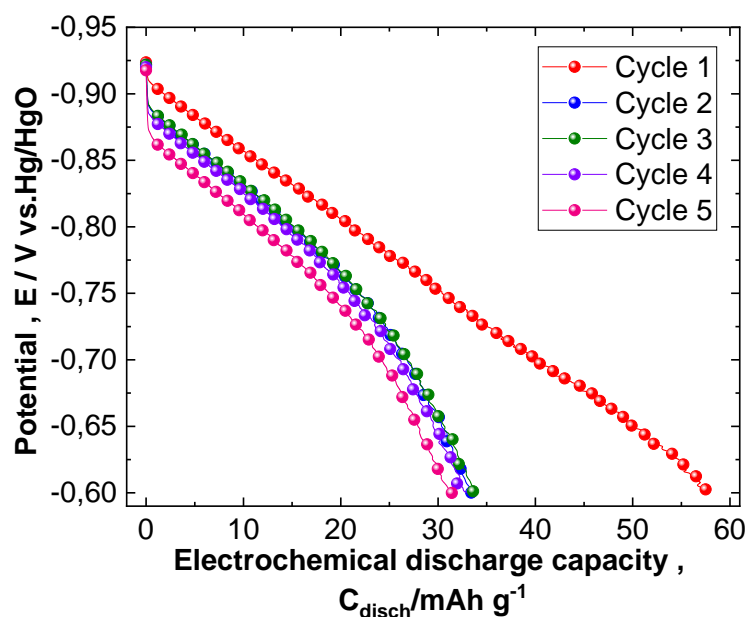


Figure 4. Evolution of the discharge curves of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode during the first activation cycles under a current of 0.7 mA.

The activation process of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode is fast, it requires only one cycle. Indeed, the value of the maximum capacity is about 58 mAh g^{-1} .

The cycling properties of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode

Fig.5 shows the evolution of the discharge capacity as a function of the number of cycles of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode under a current of 0.7 mA.

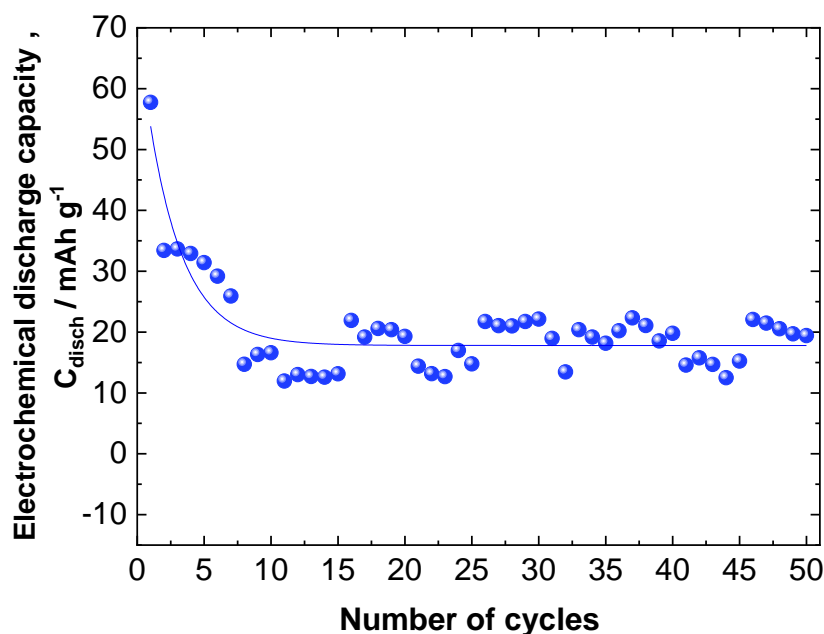


Figure 4. Evolution of the discharge capacity as a function of the number of cycles of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode under a current of 0.7 mA.

After activation, the maximum discharge capacity decreases exponentially with the number of cycles before stabilizing around 16 mAh g^{-1} .

This loss in discharge capacity could be explained by the degradation of the active material, by oxidation and dissolution, thus reducing the interstitial sites available for hydrogen insertion. In fact,

in an electrolytic environment and in contact with potassium, lanthanum as well as magnesium, the constituent elements of the electrode, give hydroxides that are not very soluble and impermeable to hydrogen. Thus, it is possible that during the charging and discharging process, a passivating hydroxide layer is formed on the surface of the electrode grains, preventing the diffusion of hydrogen atoms into the grain volume and blocking the absorption-desorption mechanism. It has been shown that the thickness of this hydroxide layer generally increases with the number of cycles after activation.

The low values of the discharge capacity for the studied compounds during cycling could be explained by the creation of defects within the material during the grinding operation. Indeed, during the process of mechanic-synthesis, the free energy of the material increases considerably and it is stored essentially in the form of disorder. The latter is manifested by the fact that atoms occupy inappropriate sites or that the structure is so distorted that the number of sites available to accommodate hydrogen is reduced.

Conclusion

The elaboration of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ alloy was carried out using a Retsch PM 400 high energy planetary mill during 30 h with a ball to powder weight ratio 8:1.

The structure and electrochemical properties of our alloy have been examined.

The XRD analysis shows that the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ alloy has two major phases (Ni , La_2Ni_7).

The observations by SEM clearly show that the calculated average grain size of the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ powder is about 13 μm .

The $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode is activated during the first cycle. Indeed, the maximum capacity value is about 58 mAh g^{-1} .

After activation, the maximum discharge capacity decreases exponentially with the number of cycles before stabilizing around 16 mAh g^{-1} . It is also observed that the $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ electrode has good charge and discharge stability during electrochemical cycling.

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