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Decomposition of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ compound upon electrochemical cycling studied by magnetic properties

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Abstract

The effect of iron substitution for cobalt in $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ ($x=0$, 0.35, 0.75) on the evolution of the storage capacity during charge/discharge cycles has been investigated. The partial replacement of Co by Fe improves the cycle lifetime of the alloy. However, the total substitution of Fe for Co leads to a very great loss of capacity and therefore considerable alloy decomposition may occur during cycling, due to the corrosion process. The magnetic properties of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ and their evolution during the electrochemical cycle have been studied in order to characterize quantitatively the alloy decomposition. This study shows that the amount of decomposed alloy increases with the number of cycles and leads to the precipitation of superparamagnetic Ni–Fe bimetallic particles ($d = 1$–10 nm). A correlation is established between the loss of electrochemical capacity, the amounts of decomposed alloy and segregated Ni–Fe particles.

Keywords: Intermetallics; Hydrogen storage materials; Electrode materials; Magnetic measurements

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1. Introduction

Nickel–metal hydride (Ni/MH) batteries using hydrogen storage alloys as negative electrode material have been developed and commercialized recently to replace rechargeable Ni/Cd batteries which are toxic [1]. The AB_5 type hydrogen storage alloy $Mm(Ni, Mn, Co, Al)_5$ is now extensively used in commercial batteries [2,3]. About 10 wt% of Co is necessary to extend the battery lifetime, but this is very expensive: it amounts to almost 40% of the total cost of the alloy. A reduction or elimination of the cobalt in these alloys would considerably lower their cost [4]. The effect of cobalt substitution by other elements has been therefore studied extensively [5,6]. It has been shown that alloys in which cobalt is partially substituted by iron, which is relatively inexpensive, maintain a good cycling stability [7–10]. The lifetime of the electrodes depends on the amount of substitution. This is more apparent in plots of discharge capacity vs. number of cycles. The reduction in the capacity is closely related to the corrosion of the alloy in the aqueous KOH electrolyte [11]. In addition, during the charge and discharge process, the increase and decrease of the volume of the compound due to hydrogen absorption leads to a decrepitation into smaller grains [2,12]. This generates an increase in the surface area, and therefore an increase in the alloy's decomposition rate. The corrosion products were identified by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. These techniques allow one to identify the nature of the segregated elements, but are not quantitative. Magnetization measurement, which is a bulk method, has already been used to determine the size and the amount of segregated superparamagnetic Ni, (Ni–Co) particles in $LaNi_5$ type compounds submitted to hydrogen absorption–desorption either in solid–gas or electrochemical cycles [10,14,15].

The purpose of the present paper is to study the effect of iron substitution on the electrochemical behavior of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ compounds ($x=0$, 0.35, 0.75) and, using magnetic measurements, to characterize quantitatively the alloy decomposition for $x = 0.75$ after

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cycling, in order to get a better understanding of the corrosion process.

2. Experimental techniques

All intermetallic compounds were prepared and characterized as described in Ref. [10]. The electrodes were prepared using the latex technology with the conditions of Refs. [10,16].

A 5 h 30 min charge at C/5 rate (60 mA g^{-1}), 15 min rest and a discharge at C/5 rate (60 mA g^{-1}) down to 0.9 V cut-off voltage, were performed to measure the electrochemical capacity evolution. The magnetization measurements were carried out using a DSM 8 magneto-susceptometer with an applied magnetic field $H \leq 2$ T, and a temperature range between $10 \leq T \leq 850$ K. We used also a Quantum Design SQUID magnetometer with field up to 5.5 T and temperature range between 5 and 300 K. For the magnetic measurements above room temperature the samples were sealed under secondary vacuum in silica tubes in order to avoid oxidation.

3. Results and discussion

3.1. Electrochemical measurements

Fig. 1 shows the discharge capacity versus the number of cycles of the negative electrodes consisting of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ ($x=0$, 0.35, 0.75) alloys. After a few cycles, a maximum discharge capacity was obtained. The substitution of Fe for Co leads to a small decrease in the maximum capacity from 305 to 260 mAh/g as the iron content increases. The partial replacement of Co by Fe improves the cycle lifetime of the alloy: after 50 cycles only 1.9% of the maximum capacity was lost for $x=0.35$ compared to 14% for $x=0$. However, a total substitution ($x=0.75$) leads to a 66% loss of the discharge capacity after 50 cycles.

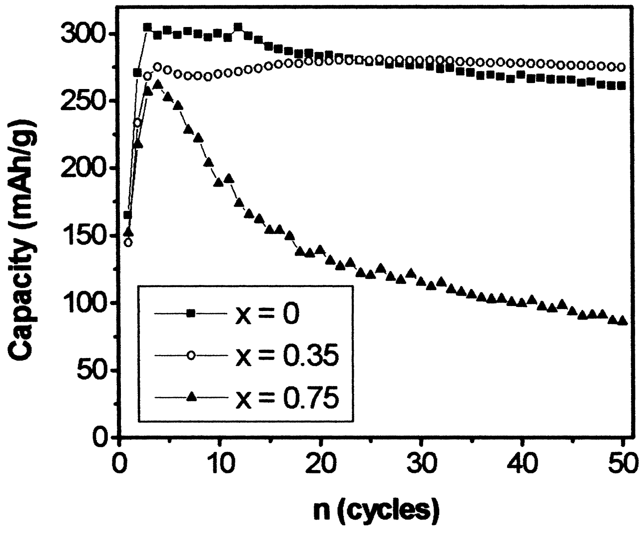

Fig. 1. Discharge capacity versus number of cycles for the compounds $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ ($x=0$, 0.35, 0.75).

3.2. Magnetic measurements

Since the total Fe substitution leads to a very great drop in capacity, a substantial amount of alloy decomposition was suspected upon cycling, due to corrosion process. To quantify this decomposition, magnetic measurements were performed on the starting intermetallic compound and after 10, 20 and 50 cycles for $LaNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$. The intermetallic compound is ferromagnetic with a Curie temperature $Tc=140$ K (Fig. 2a). Upon cycling, the proportion of segregated particles increases at the expense of the intermetallic compound. After 50 cycles and above 140 K, the magnetization of the cycled alloy becomes larger due to the segregated particles' contribution, whereas the jump in the magnetization at Tc decreases, due to the loss of intermetallic compound (Fig. 2a). The amount of alloy remaining (x_a) can be calculated by extrapolating

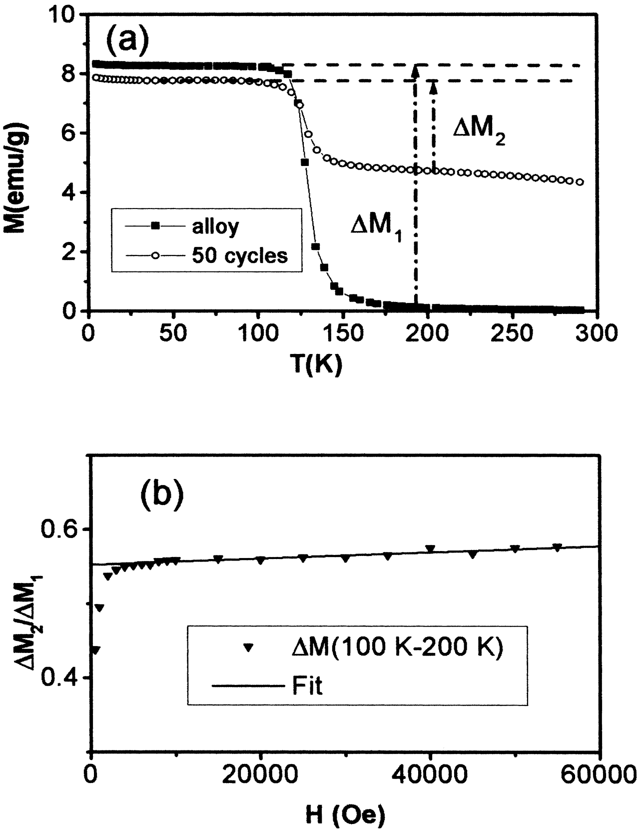

Fig. 2. (a) Magnetization versus temperature for the intermetallic compound $LaNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ before and after 50 cycles with an applied field of 300 Oe. For ΔM_1 and ΔM_2. See text. (b) $\Delta M_1/\Delta M_2$ ratio versus applied field, the amount of remaining alloy is calculated with a linear fit extrapolated to $H=0$.

to $H = 0$ the ratio of the difference of the magnetization curves M(H) before Tc (100 K) and after Tc (200 K) $x_a = \Delta M_2/\Delta M_1$ (Fig. 2b), ΔM_1 and ΔM_2 are respectively the difference of magnetization of intermetallic and cycled alloys between 100 and 200 K. The calculated values for 10, 20, and 50 cycles are reported in Table 1.

The segregated particles are formed by transition metals. In order to check if there is an alloying effect we have compared the Curie temperature of the alloy after 50 cycles to that of Ni and $Ni_{3.55}Fe_{0.75}$ (corresponding to the initial alloy composition) by performing high temperature measurements. As seen in Fig. 3, the Tc of the segregated particles in the cycled alloy (800 K) is closer to that of the $Ni_{3.55}Fe_{0.75}$ alloy (820 K) than to pure Ni (620 K). This result shows that the segregated particles are bimetallic with a small Ni enrichment compared to the starting composition. At 300 K, the saturation magnetization of (Ni,Fe) is 98.4 emu/g.

To determine the quantity and the size of the segregated particles, the magnetization of the bulk alloy was multiplied by x_a and subtracted from that of the cycled alloy for temperatures ranging from 5 to 300 K (Fig. 4). As in Ref. [10], these particles are considered as superparamagnetic and all the curve differences were fitted with a sum of two Langevin functions assuming a double peak particle size distribution. The particle sizes (0.5–10 nm) and the quantity of particles formed as a function on the number of cycles are reported in Table 1.

In order to correlate the weight percent of segregated particles with the atomic percentage of decomposed alloy, one must take into account all the species which are formed during the corrosion process. The alloy decomposition reaction is described below assuming the same type of corrosion layer to that of $MmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75}$, as it was studied by MET [11,13]

$$AB_5 \rightarrow x_a\,AB_5 + (1 - x_a)\,[La(OH)_3 + (Ni_{3.55}Fe_{0.75}) + 0.4\,Mn(OH)_2 - 0.3\,Al]$$

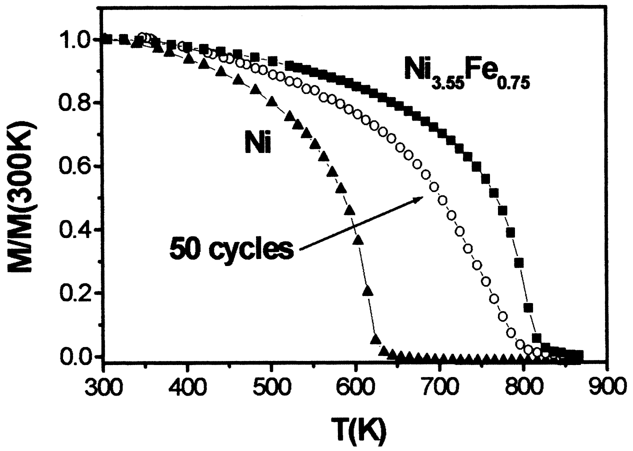

Fig. 3. Normalized magnetization versus temperature for Ni, $Ni_{3.55}Fe_{0.75}$ and $LaNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ after 50 cycles.

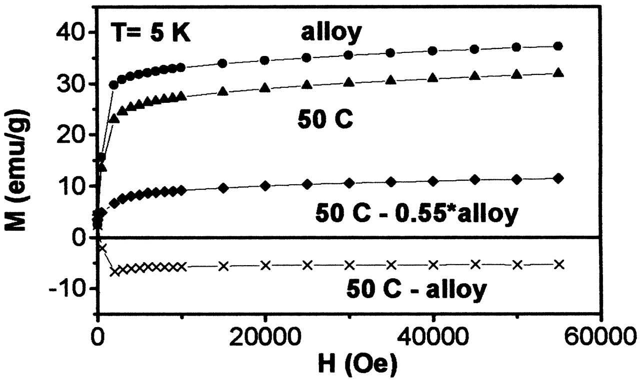

Fig. 4. Magnetization versus applied field at 5 K for $LaNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ before (alloy) and after 50 cycles (50C); magnetization curve differences between cycled (50C) and uncycled (alloy) samples: (50C-alloy) and (50C–0.55*alloy) showing that only the remaining alloy contribution ($*x_a = 0.55$) should be subtracted to obtain the contribution of the superparamagnetic particles.

After a corrosion treatment, solid needles of $Mm(OH)_3$ were distributed over a continuous corrosion layer composed of a solid solution of (Ni,Co), (Ni,Co)O and $Mm(OH)_3$. A few grains of $Mn(OH)_2$ were found to be randomly scattered over the electrode surface. The Al was found to be entirely dissolved in the electrolyte and trapped in the positive electrode. From this reaction, and knowing x_a, the percentage of Ni–Fe (wt%) can be calculated, and is given in Table 1. This quantity of metallic Ni–Fe is larger than that calculated from the magnetization curve refinement (Table 1). This result indicates that the remaining Ni and Fe atoms probably form oxide or hydroxide compounds, which contribute weakly to the magnetization curves. It was found in [11] that some of the Ni–Co particles are oxidized and also a

Table 1
Fitted and calculated parameters of the magnetization curves for cycled $LaNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ between 5 and 300 K

Number of cycles	C_n/C_{max} (%)	x_a (wt%)	x_a (at%)	% Type 1 particles		% Type 2 particles		wt% Total fitted	wt% Total calculated
					d1 (nm)	(wt%)	d2 (nm)		
10	91	88	90	0.8 (0.1)	8.4 (0.4)	1 (0.1)	1.1 (0.3)	1.8	6.1
20	79	84	86	2 (0.1)	9.7 (0.7)	5 (0.1)	1 (0.1)	7	8.3
50	44	55	58.5	7.8 (0.1)	8 (0.3)	3.3 (0.1)	1 (0.1)	11	24

C_n/C_{max} = the ratio of the capacity after n cycles over the maximal capacity, x_a = % of initial alloy, type 1 particles = largest (at 300 K), type 2 particles = smallest (at 5 K).

few CoO(OH) grains were observed on the electrode surface. A similar kind of product can be expected when replacing Co with Fe. Since the loss of the discharge capacity decreases more than the amount of AB_5 alloy as the number of cycles increases, other contributions must be responsible for this decrease. As the amount of oxide is large it can also prevent electrical contact between the grains, which might explain the large decrease in the capacity.

4. Conclusion

The electrochemical study of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ ($x=0$, 0.35, 0.75) has shown that the total substitution of Fe for Co leads to drastic decrease in the electrode lifetime, whereas the partial substitution has a positive effect. Magnetization measurements have been used to characterize the corrosion effect for $x=0.75$. The proportions of decomposed alloy and of the segregated superparamagnetic Ni–Fe particles have been calculated by appropriate data analysis. The balance of the reaction indicates that the Ni–Fe particles are partially oxidized. The drastic loss of capacity for $x=0.75$ is therefore due to the decrease in the amount of alloy and to the loss of electrical contact between the grains due to the large amount of isolating oxide in the corrosion layer.

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