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Determination of the hydrogen coefficient diffusion D_H in the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ ($0 \leq x \leq 0.75$) electrodes alloys by cyclic voltammetry

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Abstract*— *The hydrogen storage alloys $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ ($0 \leq x \leq 0.75$) were used as negative electrodes in the Ni-MH accumulators. The chronopotentiommetry and the cyclic voltammetry were applied to characterize the electrochemical properties of these alloys. The obtained results showed that the substitution of the cobalt atoms by iron atoms has a good effect on the life cycle of the electrode. The discharge capacity reaches its maximum in $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ (x = 0, 0.15, 0.35, 0.55 and 0.75) are, respectively, equal to 270, 266, 260, 210 and 200 mAh/g after 12 charge-discharge cycles.

The diffusion behaviour of hydrogen in the negative electrodes made from these alloys was characterized by cyclic voltammetry after few activation cycles. The values of the hydrogen coefficient in $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ (x = 0, 0.15, 0.35, 0.55 and 0.75) are, respectively, equal to $5.86\ 10^{-10}$, $1.95\ 10^{-9}$, $3.44\ 10^{-9}$, $2.96\ 10^{-9}$ and $4.98\ 10^{-10}$ $cm^2\ s^{-1}$. However, the values of the charge transfer coefficients are respectively equal to 0.35, 0.6, 0.5, 0.33 and 0.3. These results showed that the substitution of cobalt by iron decreases the reversibility and the kinetic of the electrochemical reaction in these alloys.

***Keywords*— life cycle, discharge capacity, hydrogen diffusion coefficient.**

I. INTRODUCTION

The AB_5-type hydrogen storage alloys have been used as negative electrodes for Nickel-metal hydride (Ni-MH) batteries in order to replace the conventional Ni/Cd accumulators. In fact, the Ni-MH batteries, as compared to the Ni-Cd ones, exhibit a high energy density, a long life cycle, a stronger resistance to over charge-discharge and a good environmental compatibility [1-3]. The $LaNi_5$-based alloy, is the most promising candidate because it can absorb and desorb a large amount of hydrogen in alkaline solution [4]. Neverthless, it exhibits a high equilibrium pressure of 1.7 bar at room temperature and its electrochemical capacity decreases rapidly when increasing the charge discharge cycles. This such latte phenomena was attributed to the oxidation and the formation of the $La(OH)_3$ film at the surface [1]. To decrease the plateau pressure and inhibit the oxidation phenomena, some works have been carried out to replace the lanthanum by mischmetal (a mixture of different rare earth elements such as: Ce, Nd and Pr) and a part of nickel atoms with different transition elements such as Mn, Al and Co [3, 5-8]. Xianxia et al. [9] used the cyclic voltammetry to determine the hydrogen diffusion coefficient in the $MmNi_{3.65}Al_{0.2}Mn_{0.4}Co_{0.75}$ hydride. They [9] found that the value of the hydrogen diffusion coefficient increases with increasing the depth of discharge (DOD). They [9] assume that at low DOD, the hydrogen concentration is higher than that at high DOD. In other words, the number of vacant sites available for hydrogen occupation increases by increasing the DOD leading to an easier diffusion of the hydrogen. Qin Li et al. [10] investigated the hydriding properties of the $MmNi_{5-x}Sn_x$ (x = 0-0.5) aloys by electrochemical measurements and pressure-composition isotherms. They found that the substitution of Ni by Sn leads to an increase of the charge-discharge life cycle and a decrease of the plateau pressure. They [10] attributed this phenomena to the increase of the cell volume unit of the $MmNi_5$ caused by the Sn substitution and the low volume dilatation during hydride formation. Nowadays, the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ alloy is one of the typical compounds used as commercialized electrode materials. Unfortunately, cobalt is an expensive metal and in a typical alloy such as $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$, its price represents almost 50 % of the total cost of the raw material [11]. So, the aim of this work is to examine the effect of the substitution of cobalt with iron on the electrochemical properties of the commercialized $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ compound used as negative electrode in Ni/MH batteries, two alloys were studied namely $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ with $x = 0.55$ and $x = 0.75$. The chronopotentimmetry and then cyclic voltammetry methods are applied to determine the charge transfer coefficient, the hydrogen diffusion coefficient and the electrochemical stability of these two materials. These properties were compared to those published in our previous works [12, 13] for $x = 0$ and $x = 0.35$.

II. EXPERIMENTAL DETAILS

The $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ (x = 0, 0.15, 0.35, 0.55 and 0.75) compounds are prepared by UHF induction melting of the pure elements followed by an appropriate annealing to ensure a good homogeneity. The results of the metallographic observations, the electron probe microanalysis (EPMA) and the structural characterization by X-ray diffraction (XRD) of these alloys are listed in table 1. The structural characterization shows that these alloys are indexed in the $CaCu_5$ hexagonal crystalline structure (P6/mmm space group).

Table 1: Lattice parameters and lattice volume of the substituted compounds

Compound	a (Å)	c (Å)	V (Å^3)
$LaNi_5$	5.012	3.984	86.68
$i_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$	5.0343	4.0622	89.1616
$nNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$	5.0422	4.067	89.5438

III. PREPARATION OF THE MH ELECTRODE AND NI/MH CELL

The alloys ingot is ground mechanically and saved to less than 63 µm in glove box under argon atmosphere. The "latex" technology has been used for the electrode preparation [14]. 90% of the alloy powder is mixed with 5% of black carbon (to obtain a good conductivity) and 5% of polytetrafluoroethylen (PTFE). Two pieces of 0.5 cm^2 of this latex are pressed on each side of a nickel grid to prevent the electrode plate from breaking into pieces during the charge-discharge cycling [11]. This set forms the negative electrode of Ni/MH accumulator. The counter electrode was formed by the Ni oxyhydroxide $Ni(OH)_2$, whereas the reference electrode was the Hg/HgO 1 M KOH solution, prepared with deionised water.

IV. ELECTROCHEMICAL MEASUREMENTS

All the electrochemical measurements were performed at room temperature in a conventional three electrode open-air cell using VMP system. The discharge capacity of the electrode was determined by a galvanostatical charging-discharging at C/3 and D/6 regime respectively. Every cycle was carried out by charging fully to –1.3 V and discharging to –0.6 V with respect to Hg/HgO 1 M KOH reference electrode at a temperature of 25°C. After activating the electrode for 30 cycles, the cyclic voltammetry was applied at scan rates of 10, 20, 30, 40 and 50 µv/s between -1.1 and – 0.5 V vs. Hg/HgO.

V. RESULTS AND DISCUSSION

5. 1. Lifetime cycle of the electrode

Figure 1 shows the variation of the discharge capacity of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ and $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ electrodes as function of the number of cycles. The discharge capacity of $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ alloy powder increases to reache 210 mAh/g after 12 cycles and then decreases to 190 mAh/g after a few charge-discharge cycles. However, for the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ compound, the discharge capacity reaches its maximum of 200 after 10 cycles and then decreases to 160 mAh/g after 30 cycles. These results show that the alloy containing the cobalt has a good stability but a bad activity. The capacity decay of the hydrogen storage alloy electrode is mainly due to the pulveverization and oxidation of the active material components to form oxides or hydroxides [15, 18]. In fact the formed oxide or hydroxide layer acts as a barrier to the hydrogen diffusion and leads to the decrease of the number of hydrogen atoms which can be absorbed by the material. Pan et al. [17] and Geng et al. [16] assume that the loss in discharge capacity is due to the deterioration of the negative electrode material with increasing the number of charge-discharge cycles. In fact, during the cycling, the rare earth elements such as La or the transition metal such as Mn segregate to the grain boundaries, where they were subject to corrosion. The corrosion products are disposed on the surface of grain particles as needle-shaped $La(OH)_3$ or as Mn_3O_4. This corrosion phenomenon leads to an increase of the resistance among alloy grains, which in turn decrease the alloy discharge capacity. This decrease may be also attributed to the oxidation of iron on the alloy surface which limit the hydrogen transfer from the surface to the bulk of the alloy and leads consequently to a loss in the amount of hydrogen stored in the material. So, it is easy to conclude that a total substitution of cobalt by iron deteriorates the stability and the lifetime cycle of the electrode made from the considered material.

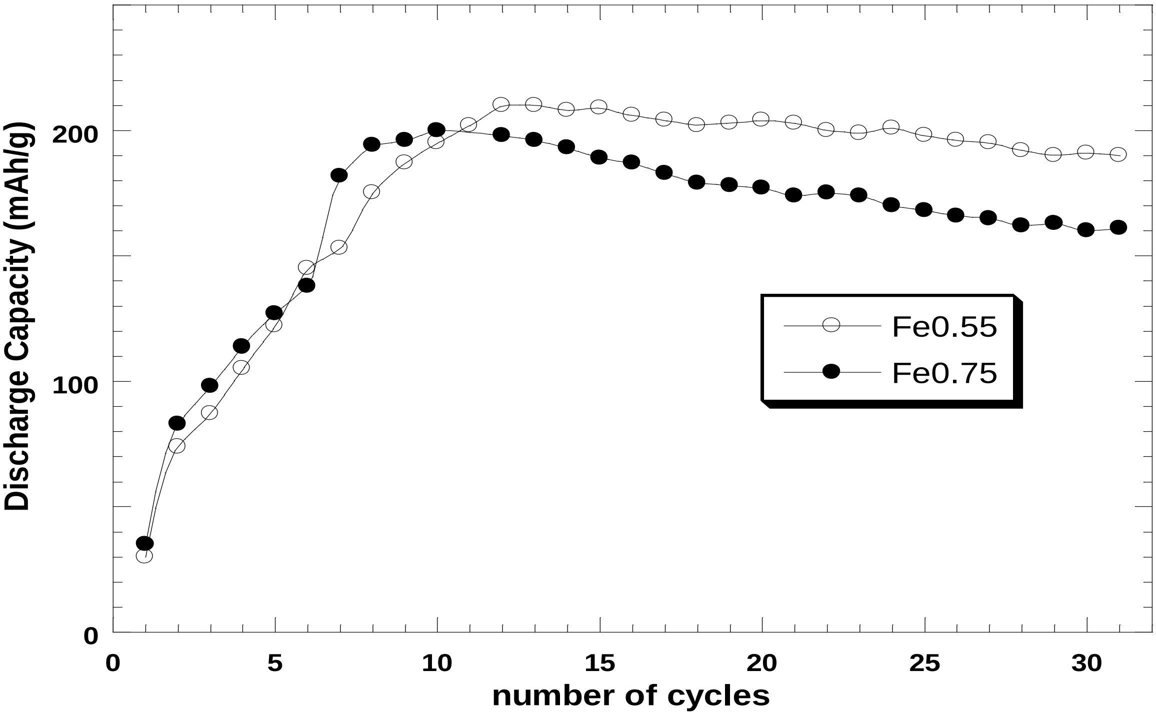

Fig.1: Variation of the electrochemical discharge capacity of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ *(x = 0.55 and 0.75) compounds as a function of the cycle number.*

5. 2. Cyclic voltammetry

Figures 2 and 3 show the cyclic voltammograms of, respectively, the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ and $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ compounds carried out after activation during 30 cycles at scan rates equal to 10, 20, 30, 40 and 50 µv/s. The anodic peak in these voltammograms is attributed to the oxidation of the absorbed hydrogen atoms on the surface. The anodic peak current increases and the potential slightly shifts to the positive direction with increasing the scan rate. Figure 4 shows that the anodic peak potential (E_{ap}) has a linear dependence with log(v). In this case, the anodic peak potential can be given by the Equation 1 as [19, 20]:

$$\frac{dE_{ap}}{d\log(v)} = \frac{2.3\,R\,T}{2\alpha n F} \qquad (1)$$

Where v is the scan rate, R the constant of rare gas, T the temperature of the electrochemical cell, α the charge transfer coefficient, n the number of exchanged electron and F the Faraday constant. Based on this formula, we can determine the value of the charge transfer coefficient α.

Figure 5 shows that the variation of the anodic peak current versus square root of the potential scan rate ($v^{1/2}$) is linear. This behavior indicates that we are in presence of a semi-infinite diffusion and irreversible charge transfer. So, the current of the oxidation anodic peak can be expressed by the Equation 2 as [19, 20]:

$$I_{ap} = 0.496\ \alpha^{1/2}\ (n\ F)^{3/2}\, S\ C_0\ [\frac{vD}{R\,T}]^{1/2}$$

(2)

Where α is the charge transfer coefficient, n the number of the exchanged electron, F the Faraday constant, S the geometric surface of the working electrode (cm^2), C_0 the concentration of the diffusing species ($mol\ cm^{-3}$), D the hydrogen diffusion coefficient ($cm^2\ s^{-1}$) and v the potential scan rate ($V\ s^{-1}$). The concentration of the diffusing species C_0 is determined by Equation 3 as:

$$C_0 = \frac{Q\ M}{m\ F\ V_M} \qquad (3)$$

where M, m, F and V_M are respectively, the molecular mass, the effective mass of material, the Faraday constant and the molecular volume of material. Q is the amount of anodic oxidation hydrogen during the anodic sweep of cyclic voltammetry [21]. It is expressed by Equation 4 as:

$$Q = \int_{t_1}^{t_2} i\,dt = \int_{E_1}^{E_2} \frac{i}{v} dE \quad (4)$$

Where t_1, t_2 and t are times, E_1, E_2 and E are the potentials, i the anodic current and v the potential scan rate. According to Equation 2, the hydrogen diffusion coefficient in this metal hydride electrode can be determined based on the slope of the curve $I_{ap} = f(v^{1/2})$. Based on the slope of Figure 4 and 5, the values of the charge transfer coefficient α and the hydrogen diffusion coefficient D_H are summarized in table 2.

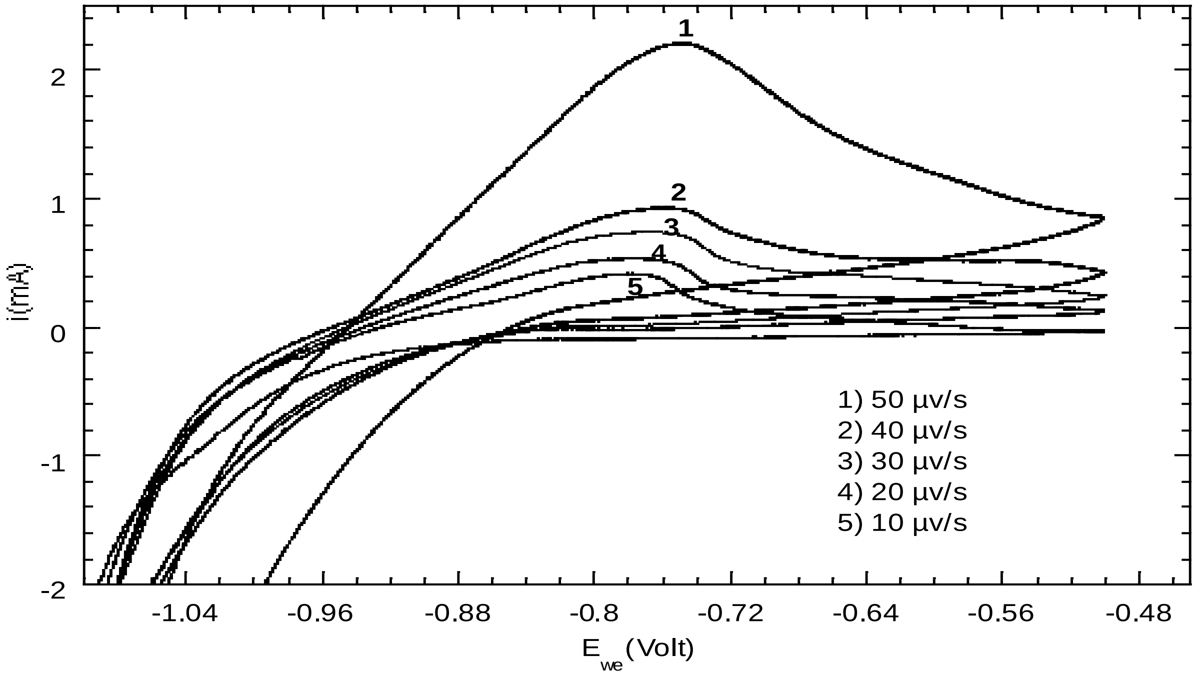

Fig.2: Cyclic voltammograms of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ compound obtained at potential scan rates of 10, 20, 30, 40 and 50 $\mu V\,s^{-1}$.

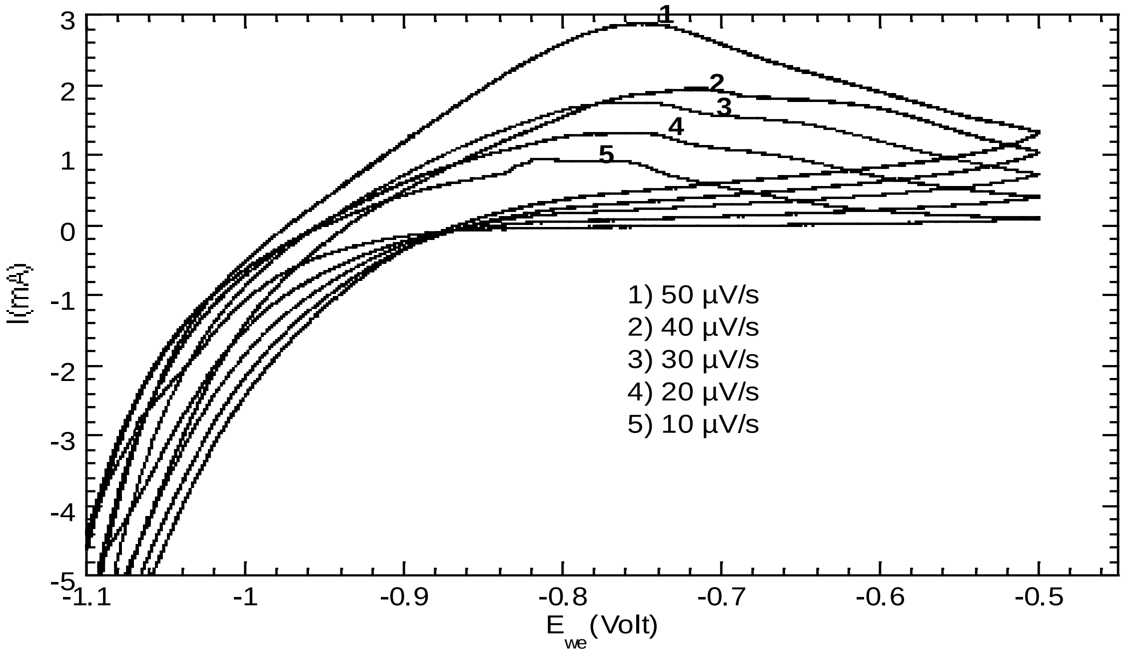

Fig.3: Cyclic voltammograms of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ compound obtained at potential scan rates of 10, 20, 30, 40 and 50 $\mu V\,s^{-1}$.

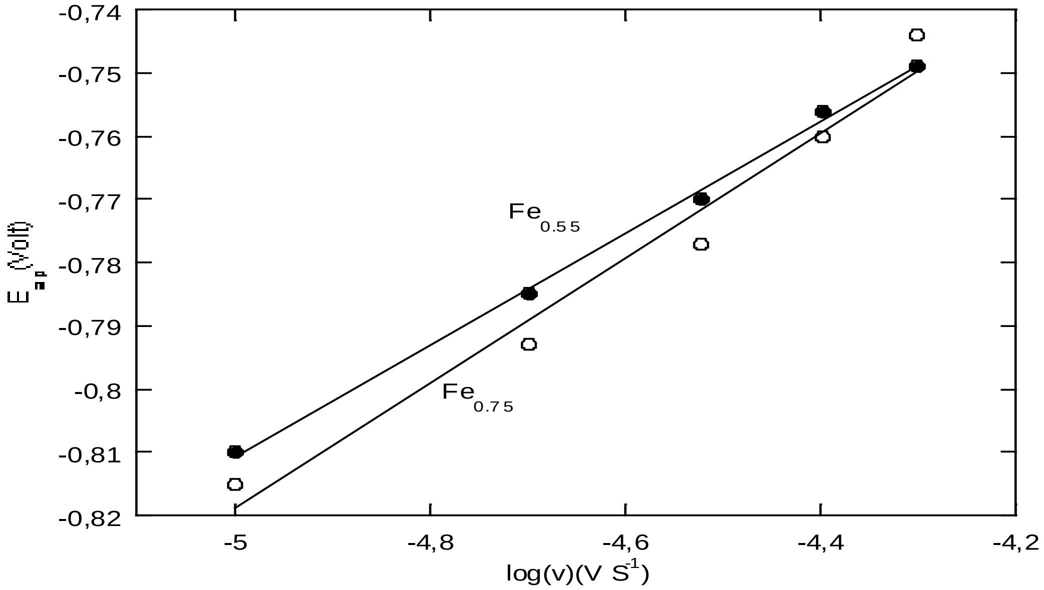

Fig.4: Variation of the anodic peak potential of cyclic voltammograms of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ and $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ electrodes as a function of log(v).

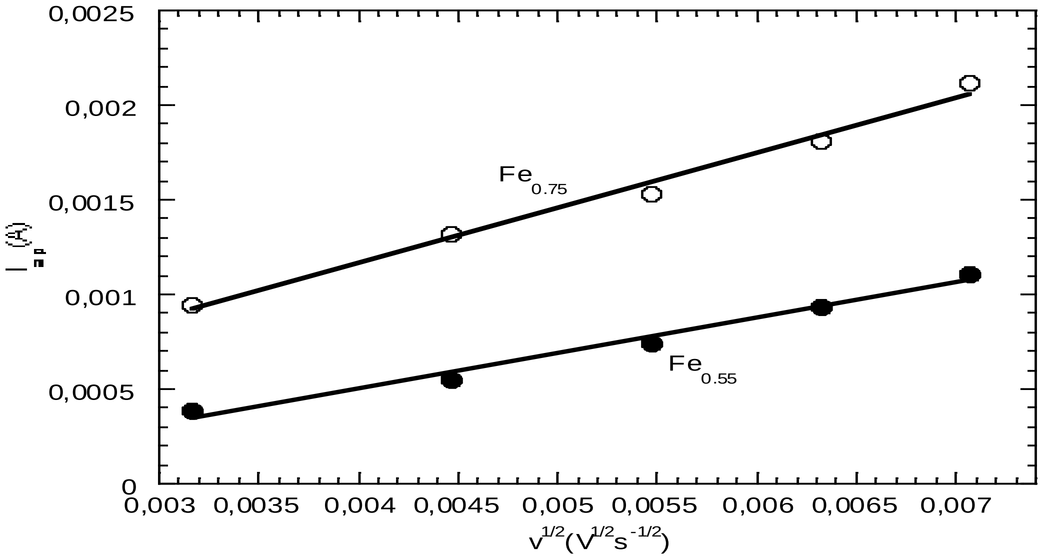

Fig.5: Variation of the anodic peak current of the cyclic voltammograms of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ and $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ electrodes as a function of the square root of potential scan rate.

Table 2: The maximum discharge capacity C_{max}, the charge transfer α and the hydrogen diffusion coefficient D_H for the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75-x}Fe_x$ (x = 0, 0.35, 0.55 and 0.75) compounds.

Compound	Maximum discharge Capacity (mAh/g)	Charge transfer coefficient α	Hydrogen diffusion coefficient D_H ($cm^2\,s^{-1}$)
$MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ [12]	270	0.35	$5.86\ 10^{-10}$
$MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.6}Fe_{0.15}$	266	0.6	$1.95\ 10^{-9}$
$MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35}$ [13]	260	0.5	$3.44\ 10^{-9}$
$MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$	210	0.33	$2.96\ 10^{-9}$
$MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$	200	0.3	$4.98\ 10^{-10}$

Based on table 2, it can be seen that the maximum discharge capacity decreases when the iron content increases. The probable reason for this decrease is the reduction of the number of the available sites of hydrogen when the cobalt is substituted by iron. On the other hand, the addition of the iron facilitates the oxidation of the surface of the alloy by the combination with oxygen to form an oxide film which in turn inhibits the hydrogen diffusion and leads to a loss in the discharge capacity. The obtained values of the charge transfer coefficient α and the hydrogen diffusion coefficient D_H indicate good electrochemical kinetics and an acceptable reversibility of the reaction.

VI. CONCLUSION

The electrochemical properties of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ and $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ compounds have been investigated by two electrochemical methods which are the chronopotentiometry and the cyclic voltammerty. The following conclusions can be drawn:

- The discharge capacity for the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ reaches a maximum value of 210 mAh g^{-1} after 12 cycles and then decreases to about 190 mAh g^{-1} after 30 cycles. However, for the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ compound, the discharge capacity reaches its maximum of 200 mAh g^{-1} after 10 cycles and then decreases to 160 mAh g^{-1} after 30 cycles.
- The values of the charge transfer coefficient of the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ and the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ compounds are, respectively, equal to 0.33 and 0.3. This indicates a good reversibility of the electrochemical reaction for these alloys which means a good absorption-desorption kinetics in the case of solids.
- The values of the hydrogen diffusion coefficient D_H for the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.2}Fe_{0.55}$ and the $MmNi_{3.55}Mn_{0.4}Al_{0.3}Fe_{0.75}$ compounds are, respectively, equal to $2.96\ 10^{-9}$ and $4.98\ 10^{-10}$ $cm^2\ s^{-1}$.

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