Journal of Alloys and Compounds 574 (2013) 59–66

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

The effect of the temperature on the electrochemical properties of the hydrogen storage alloy for nickel–metal hydride accumulators

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ARTICLE INFO

Article history:
Received 19 February 2013
Received in revised form 5 April 2013
Accepted 8 April 2013
Available online 17 April 2013

Keywords:
Nickel metal–hydride accumulator
Electrochemical methods
Enthalpy change
Activation energy
Corrosion parameters

ABSTRACT

The electrochemical properties of The $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ alloy as a negative electrode material of a nickel–metal hydride accumulator have been investigated at different temperatures. The Activation of the alloy becomes faster with an increasing temperature. The enthalpy, the entropy and the apparent activation energy of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}H_x$ hydride formation are evaluated. The calculated results show that the enthalpy change, the entropy change and the activation energy are (-29 kJ mol^{-1}), (26.5 JK^{-1} mol^{-1}) and (24.6 kJ mol^{-1}), respectively. The corrosion current density increases with increasing the temperature and the corrosion potential becomes more positive and increases linearly with the temperature. This result is confirmed by the values of corrosion film resistance and the corrosion film capacitance determined through the electrochemical spectroscopy impedance modeling.

1. Introduction

Numerous studies have been performed to develop more efficient AB_5 hydrogen storage alloys, used as negative electrodes in nickel–metal hydride accumulators, in particular mono-and poly-substituted $LaNi_5$ parent compound [1–5]. Several compositions have been studied and the best results in terms of electrochemical performance were obtained with the tri-substituted $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ currently commercialized.

In our previous work [6–10], the electrochemical properties of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ alloy used in commercialized nickel–metal hydride batteries were studied at room temperature. However, the temperature characteristic of the aforementioned alloy has never been researched until now. In this paper, the effect of temperature on the electrochemical properties of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ commercialized alloy were studied, using different electrochemical techniques, such as, the chronopotentiometry, the chronoamperometry, the electrochemical impedance spectroscopy and the potentiodynamic polarization. It was found that the effect of environmental temperature on the electrochemical properties was significantly observed. Different characteristic parameters of the absorption–desorption reaction of hydrogen by the commercialized alloy have been determined, such as the enthalpy change, the entropy change and the activation energy (Fig. 1). The study of the corrosive behavior, of the commercialized electrode, was evaluated at different temperatures.

2. Experimental

The $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ alloy was prepared through induction melting of the pure elements followed by an appropriate annealing to ensure a good homogeneity. The results of the metallographic examination, the electron probe microanalysis device (EPMA – Cameca-Camebax®) and the structure characterization by X-ray diffraction device (XRD – Bruker D8 Advance®) with Cu Kα beam of this alloy is given in Table 1. The structural characterization shows that this alloy is indexed in the CaCu5 hexagonal crystalline structure (*P*6/*mmm* space group). The $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ ingot alloy was grounded mechanically and sieved (to less than 63 μm) in a glove box under an argon atmosphere [11]. The “latex” technology has been used for the electrode preparation [12]. Ninety percent of the alloy powder was mixed with 5% of a black carbon (to obtain a good conductivity) and 5% of polytetrafluoroethylene (PTFE) to give elasticity to the electrode. Two pieces of 0.5 cm^2 of this latex have been pressed on each side of a nickel grid, playing the role of a current collector [13]. This assembly forms the negative electrode of Ni–MH battery. All the electrochemical measurements were performed at different temperatures (13, 23 and 33 °C) in a conventional three electrodes open-air cell coupled directly with a Voltalab40 system (Radiometer Analytical) constituted by a Potentiostat–Galvanostat PGZ301. A nickel mesh and a Hg/HgO electrode have been used as a counter electrode and a reference electrode, respectively. The electrolyte consisted of a KOH (1 M) solution, which was stirred by a continuous flow of argon through the cell. The activation of the electrodes was realized by galvanostatically charging and discharging at a C/3 regime during many cycles.

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http://dx.doi.org/10.1016/j.jallcom.2013.04.046

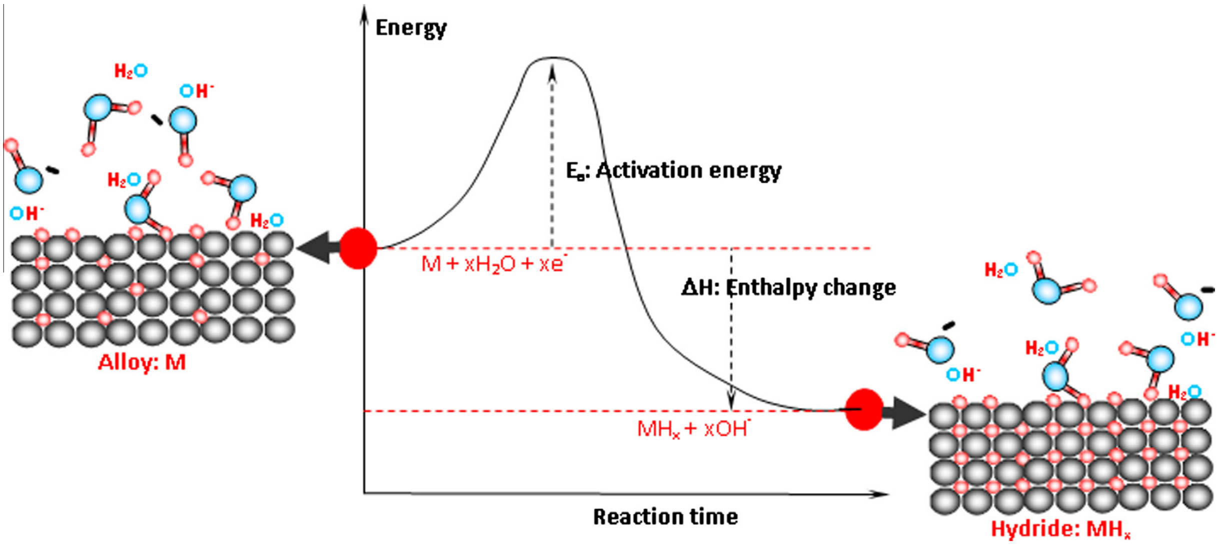

Fig. 1. The parameters characterizing the hydruration reaction, such as the enthalpy change and the activation energy, of the intermetallic alloy.

Table 1
Annealing treatment conditions and characterization results of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ alloy.

Compound	Annealing treatment condition	EPMA analysis	XRD analysis (cell parameters and volume)		
			a (Å)	*c* (Å)	*V* (Å^3)
$LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$	12 days, 1000 °C	$La_{1.00}Ni_{3.52}Mn_{0.38}Al_{0.27}Co_{0.73}$	5.069	4.044	89.987

- The electrochemical isotherms were conducted in galvano-static mode after activation at different temperatures, through the method of discharge under a very low regime, charging at C/30 regime up to 50% over charge to ensure the complete charging of the hydride electrode, then discharging at D/30 regime until the potential reaches the cut-off voltage $E = -600$ mV vs. Hg/HgO, to provide a quasi-equilibrium state during the electrochemical measurements.
- The constant potential discharge (CPD) was applied after activation at different temperatures using a chronoamperometry method.
- The potentiodynamic polarization tests were carried out at a scan rate of 1 mVs^{-1}, between (−600 mV) and (−1200 mV) vs. Hg/HgO, to estimate the current density and the potential corrosion of the electrodes in KOH solution at different temperature.
- Impedance measurements were realized after activation at different temperatures. The electrode was charged to a state of charge (SOC) of 10% at C/10 rate. After that, a rest of 5 h was applied for the open-circuit to get a stabilized potential (variation of 1 mVh^{-1}). The electrochemical impedance spectrum of the electrode was measured with ac perturbation of ±5 mV as amplitude and 1 mHz to 50 kHz frequency range.

3. Results and discussion

3.1. Electrochemical cycling of the alloy

Figs. 2 and 3 represent, respectively, the curves of discharge at C/3 rate and the variation of the ration of, $\frac{C_n}{C_{max}} \times 100$, during the first cycles of activation of $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ electrode, at the temperatures of 13, 23 and 33 °C. Wherein C_n is the capacity at the nth cycle and C_{max} is the maximum capacity at a given temperature.

At the temperature of 13 °C, the activation is very slow and the capacity does not present significant values. Indeed, after 12 cycles of activation, the capacity reaches only 14 mAh g^{-1} representing 72% of its maximum value (Figs. 2a and 3).

At the temperature of 23 °C (Figs. 2b and 3), we note that at the first cycle, the capacity is 3 mAh g^{-1}, representing 2% of the maximum capacity, the half discharge potential is (−625 mV) and the curve does not present a clear landing. At the seventh cycle the capacity is 58 mAh g^{-1} (39%) and the half discharge potential is (−689 mV). These curves evolve at the end of the twelfth cycle reaching only 84% (125 mAh g^{-1}) of the maximum capacity (150 mAh g^{-1}) and the half-discharge potential becomes constant with the appearance of an equilibrium plateau.

The same observations are announced for the temperature of 33 °C. However, although the capacity value obtained after 12 cycles is the same as that of 23 °C, the evolution of discharge curves for the temperature 33 °C is faster (Figs. 2c and 3).

The environmental temperature had a great influence on the initial activation rate of the alloy (Figs. 2 and 3). The higher the temperature is the higher the activation rate becomes.

Fig. 4 illustrates the variation of the capacity versus the number of cycles of the $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$ electrode at C/3 rate and at different temperatures.

At the temperature of 13 °C, the electrochemical discharge capacity remains constant independently of cycling and its maximum value does not exceed 20 mAh g^{-1}.

At the temperature of 23 °C, the electrochemical discharge capacity undergoes a progressive increase during cycling with a good held cycling.

At the temperature of 33 °C, the electrochemical discharge capacity increases rapidly to a maximum value of about 147 mAh g^{-1}, then undergoes a significant decrease. The loss in capacity is of 20% after 30 cycles.

The increased temperature promotes the subsequent growth of the active surface of the electrode and consequently the improvement of the kinetic properties of absorption and desorption of hydrogen. On the other hand, it accelerates the oxidation through the formation of an oxide film on the surface of the electrode, thereby degrading the kinetic properties and reduces the active surface. Thus, it is reasonable to consider the compromise of the double effect of the increasing temperature.

The relations between the discharge capacity and the environmental temperature at C/3 and C/30 discharge rates are shown in Fig. 5. The capacity at C/30 discharge rate increased with an