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The impedance response of LaY₂Ni₉ negative electrode materials after activation

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ABSTRACT

The electrochemical impedance responses of the LaY₂Ni₉ alloy electrode after activation at different states of charge (SOC), immersion time in 7 M KOH and room temperature was studied. Electrochemical impedance spectrum of the metal hydride electrode obtained was interpreted by an equivalent circuit modelling including the different electrochemical processes taking place on the interface between the MH electrode and the electrolyte. The results indicate that the electrochemical reaction activity of hydride electrode was markedly enhanced with increasing state of charge. The hydrogen diffuses in the bulk of the alloy and this process is not the limiting step for the hydrogen absorption. During a long immersion time a continuous nanocrystalline corrosion scale appears and the modification of passive film towards more organized structure is concluded.

Keywords: A. Intermetallic compounds; D. Electrochemical properties; D. Diffusion

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1. INTRODUCTION

Hydrogen may constitute the main energy vector in the future. There is multiple ways of storing hydrogen. An alternative to the use of gaseous pressure tanks is to store hydrogen in metal hydrides. The new family of ternary intermetallic compounds RM_2Ni_9 (R = rare earth or Ca, M =Mg, Ca, Ti or Y) is studied in this purpose [1-4]. Among the different electrochemical methods used to study metal hydrides, electrochemical impedance spectroscopy (EIS) exhibits some advantages, such as the possibility of analyzing the system at a given state of charge, which is practically not disturbed by the measurement on account of its operation around an equilibrium state and of the small amplitude of the perturbing signal. Also EIS is one of the most employed techniques to study passive layers formation on different metals and alloys [5-6]. In this work, we are interested in studying the electrochemical behavior of AB_3 type alloy, used as a negative electrode in the Ni-MH battery. This appealed to the electrochemical impedance spectroscopy, which allows us to discern the various processes occurring at the electrode | electrolyte surface, such as the charge transfer, the diffusion and others. Many works has studied the spectra with state of discharge [7]. Currently, it is very interesting to study the spectra after activation and at equilibrium potential of the electrode at different states of charge (SOC) and with the immersion time.

2. EXPERIMENTAL PROCEDURES

2.1. Preparation and characterization of the electrodes

The alloy samples were prepared by induction melting of the pure La, Y, and Ni elements in the atomic ratio of 1:2:9 followed by annealing at 750°C for three weeks to ensure good homogeneity.

The electrodes were prepared by so-called “latex” technology [8]. The composite anodic electrodes were made from the intermetallic active material (grain size < 75 μm) mixed with carbon black and PTFE [9] in the weight ratio of 90:5:5. The mixtures were spread out and compressed in sheets 0.25 mm thick on 0.7 x 0.7 cm^2 nickel grids which constitute of the current collector. They were impregnated in 7 M KOH under primary vacuum before any electrochemical test. The samples were observed before and after electrochemical cycling by scanning electron microscopy (SEM).

2.2. Charge–discharge cycling test

The electrochemical measurements were performed by using a Gamry Framework constituted of a Potentiostat–Galvanostat at a room temperature in a conventional three electrode cell. The electrolyte consisted of a 7 M KOH deoxygenated by a continuous flow of argon through the cell. Ni and an $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode were used as a counter and a reference electrode, respectively. The activation of the electrode was realized by galvanostatic charging at C/3 regime then discharging at D/3 regime until the potential reaches the cut-off voltage $E = -0.6$ V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ for many cycles.

2.3. Electrochemical impedance spectroscopy test (EIS)

All EIS measurement was started after activation of the alloy when the equilibrium potential was reached. Pt electrode was used as a counter electrode. A frequency range explored was from 100 kHz to 1 mHz, and the ac perturbing signal was 10 mV peak-to-peak.

3. RESULTS AND DISCUSSION

Fig. 1 A–D shows the EIS of the LaY_2Ni_9 alloy electrode after activation for different states of charge (SOC) and at room temperature. All of these spectra exhibit a small arc of circle in the high-frequency region and a large loop in the low frequency region, which exhibits

marked dependence on the SOC. As a SOC increases, the cord of the high frequency loop decreases.

The software ZSimpWin 3.1 was used to develop a circuit model from the spectroscopy data. The modeling process was iterative, using the Chi-square (χ^2) value for the entire model and the percent error values for each circuit component to determine the fit of a given model to the experimental data. The χ^2 value was defined by the following equation:

$$\chi^2 = \sum_{k=1}^{k=n} \left[W'_k \left(Zre_{k,exp} - Zre_{k,calc}(\omega_k, \bar{p}) \right)^2 + W''_k \left(Zim_{k,exp} - Zim_{k,calc}(\omega_k, \bar{p}) \right)^2 \right] \quad (1)$$

Where $Zre_{k,exp}$ ($Zre_{k,calc}$) and $Zim_{k,exp}$ ($Zim_{k,calc}$) are the real and imaginary parts of impedance experimental (calculated), respectively, at the frequency ω_k , W'_k and W''_k are the data statistic weights and n is the number of perturbing a.c. signals used in the fitting calculation. The proposed equivalent circuit used for fitting the EIS of the LaY_2Ni_9 alloy electrode, as shown in Fig. 2 [10]. In this circuit, R_e was assigned to the electrolyte resistance between the reference and working electrodes. R_{tc} is attributed to the charge-transfer resistance of the hydrogen insertion process. The constant phase element ($Q = CPE$), with the associated impedance, $Z_{CPE} = 1/[Y_{CPE}(j\omega)^n]$ [11-13], is introduced because the semicircle is depressed. C_{dl} is the capacitance of the double layer, n_{dl} allowed representing a depressed feature of capacitive loop, CPE_{ad} is modeled as constant-phase element for the frequency depending adsorption capacity of hydrogen on the surface (C_{ad}) and R_{ad} is the resistance for the hydrogen adsorption on the alloy surface. Constant phase element (CPE) is used in this circuit model to take into account the heterogeneity of the electrode surface for reactivity and roughness. The O element is introduced to simulate the diffusion of hydrogen through in the alloy, with the associated tangent hyperbolic impedance,

$$Z_O = \frac{1}{Y_O \sqrt{(j\omega)}} \tanh[B\sqrt{(j\omega)}] \quad (2)$$

Table 1 summarizes the value of parameters determined by the regression calculation. The resistance of the electrolyte was valued to $R_e \approx 0.45 \, \Omega \, \text{cm}^2$. **Fig. 3** shows the variation of the charge-transfer resistance R_{tc} and the exchange current density I_0 as a function of state of charge. The decrease of the charge-transfer resistance is mainly attributed to the improvement of the surface electrocatalytic activity of the MH electrode. The exchange current density I_0 is estimated by the following formula [14] at the equilibrium potential:

$$I_0 = \frac{RT}{nF} \frac{1}{R_{tc}} \quad (3)$$

Where R is the gas constant, n ($=1$) is the number of the exchanged electrons, T is the absolute temperature and F is the faraday constant ($96500 \, \text{C mol}^{-1}$). It can be seen that the I_0 value of the alloy electrode increases with the SOC, this implies that the reactivity of the MH electrode is improved with increasing state of charge. Using micropolarization technique, Tafel polarization technique and EIS, Popovic et al. [15] found that the exchange current density of the AB_5 alloy electrode increases with increasing hydrogen concentration in the alloy electrode and the values of the exchange current determined by AC impedance are in good agreement with values obtained by micropolarization and Tafel polarization. The double layer capacitance values were deduced from the equation [16]:

$$Y_{dl} = C_{dl}^{n_{dl}} (R_s^{-1} + 1/R_{tc})^{1-n_{dl}} \quad (4)$$

The roughness factor, r_f defined as the ratio of the C_{dl} values and the usual value for metal electrodes of $20 \, \mu\text{Fcm}^{-2}$ [17,18]. **Fig. 4** shows the variation of the double layer capacitance C_{dl} and the roughness factor r_f . The value of C_{dl} increases from $0.13 \, \text{mF cm}^{-2}$ at 20% SOC to $0.25 \, \text{mF cm}^{-2}$ at 100% SOC. The surface roughness estimated is between 6.6 and 12.8. An experimental study of Kerner and Pajkossy [19] showed that capacitance dispersion on solid electrodes was due to surface disorder (i.e. heterogeneities on the atomic scale) rather than

roughness (i.e. geometric irregularities much larger than those on the atomic scale). Kim et al. [20] also showed that the contribution of surface heterogeneity can be much higher than the contribution of the surface irregularity to the capacitance dispersion.

The diffusion coefficient of hydrogen D_H can be calculated from the Warburg's perfactor A_ω [21].

$$A_\omega = \frac{V_m}{FS\sqrt{2D_H}} \frac{dE}{dx} \quad (5)$$

Where V_m is the molar volume ($324 \text{ cm}^3 \text{ mol}^{-1}$), S is the geometric area (1 cm^2) and dE/dx is the slope of the electrochemical discharge isotherm every at x value at 25°C for LaY_2Ni_9 intermetallic compound. The Warburg's perfactor A_ω , can be estimated from the admittance Y_O , deduced from the fitting of impedance spectra [22].

$$\frac{A_\omega}{\sqrt{\omega}} (1 - j) = \frac{1}{Y_O(j\omega)^{1/2}} = \frac{1}{\sqrt{2}\omega Y_O} (1 - j) \quad (6)$$

$$A_\omega = \frac{1}{\sqrt{2}Y_O} \quad (7)$$

Combining (eq. 5) with (eq. 7), we can obtain [23]:

$$D_H = \left[\frac{V_m Y_O}{FS} \frac{dE}{dx} \right]^2 \quad (8)$$

The hydrogen diffusion coefficient D_H , is $7.21 \cdot 10^{-12}$, $2.28 \cdot 10^{-10}$ and $1.8 \cdot 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively for 50%, 70% and 100% of SOC. A similar value was found by the potential-step method [24,25] and EIS method at 50% of DOD [26]. The value of the diffusion penetration

δ , deduced from the parameter B by the following equation: $\delta = B \sqrt{D_H}$, is estimated to be

around $\delta \sim 39 \text{ }\mu\text{m}$ and $4.6 \text{ }\mu\text{m}$. These values are lower compared with 0.25 mm , thick of the

sheets. Relying on the scanning electron microscopy observation (Fig. 5) we can deduce that the hydrogen diffuses in the bulk of the alloy and this process is not the limiting step for the hydrogen absorption.

The adsorption capacitance of hydrogen on the surface C_{ad} , deduced from the equation $C_{ad} = (Y_{ad}R_{ad})^{1/n_{ad}}/R_{ad}$, and the resistance for the hydrogen adsorption R_{ad} are shown in

Fig. 6. It can be seen that the R_{ad} values remains essentially constant between 0% and 70% of SOC thereafter decrease sharply up to 100% of SOC. The variation in the values of the C_{ad} could be attributed to surface heterogeneity, due to the variations in the microstructure of the alloy when transforming from solid solution phase (α phase).

Fig. 7A–B shows the impedance diagrams of a LaY_2Ni_9 electrode immersed in 7 M KOH at open circuit condition, during 3 and 4 days in quiescent solution with 100% SOC. The impedance spectra's are formed by two capacitive loops at the high frequency range and the low frequency range. This last shows an asymmetrical form. This can be attributed to a diffusion impedance process with a finite thickness of diffusion layer. An equivalent electric circuit illustrated in Fig. 8 with three time constants has been tried to reproduce these results. In this circuit, each element is attributed, in agreement with the values obtained of the parameter regression calculation. R_e is the electrolyte resistance, R_t the charge transfer resistance, R_F the faradaic resistance associated likely to the oxidation–reduction process in the passive layer, C_d is the double layer capacitance, C_F is the faradaic capacitance, α_d and α_F are the coefficients allowing representing the depressed shape in the Nyquist diagram and Z_{diff} is the diffusion impedance [27]:

$$Z_{diff} = R_D \frac{\tanh \sqrt{j\omega\tau_D}}{\sqrt{j\omega\tau_D}} \quad (9)$$

With

$$\tau_D = \frac{\delta_D^2}{D_H} \quad (10)$$

Where R_D is the diffusion resistance, τ_D the diffusion time constant and δ_D the thickness of the diffusion layer. Based on the equivalence between (eq. 2) and (eq. 9), R_D and τ_D are determinate by: $R_D = B/Y_O$ and $\tau_D = B^2$.

The impedance spectra are then analysed with the software ZSimpWin 3.1. The calculation results are presented in [Table 2](#).

In all cases, the high frequency limit of the measured impedances is close to $0.5 \Omega \text{ cm}^2$. This resistance corresponds well to that due to the finite conductivity of the medium, that is, the electrolyte resistance. The values of α_d and α_F are located between 0.8 and 0.9, the values frequently reported on a solid electrode, and reveal heterogeneity of the electrode surface. The C_d values are between 170 and 200 μFcm^2 , these values suggest that the reason of this capacitance could reasonably be attributed to the double layer with the passive film. It can be noticed that the capacitance decreases from 3 to 4 days, which corresponds to the modification of passive film towards more organized structure. The faradic resistance R_F increases with the immersion time. As this resistance is to be associated with the stability of the passive film, it can be concluded that the passive film is more stable. The value of C_F is compatible with the hypothesis on the origin of this loop attributed to an oxidation–reduction process involving corrosion products. F. Maurel et al. [\[28,29\]](#) have shown that during exposure of alloy to a KOH aqueous electrolyte, a continuous nanocrystalline corrosion scale and well-defined (hollow or solid) as corrosion products. F. Maurel et al. [\[30\]](#) also studied the effect of yttrium on the corrosion for nickel–metal hydride batteries. The R_d increases for 4 days of immersion; however, τ_D is slightly affected.

4. CONCLUSION

The effect on the SOC of AB₃ alloys, as well as the long time immersion in KOH in quiescent solution with 100% SOC, has been studied by EIS. EIS measurements indicate that the kinetic properties of the alloy improved with increasing state of charge, mainly due to a fast hydrogen transfer in the bulk of the alloy and the higher electrocatalytic activity of the surface. The transformation of α to β phase is probably a limiting step in the mechanisms of hydrogenation of metal hydride electrode. The value of the exchange current density I_0 increases with the SOC, indicating a good kinetics of the reaction of hydriding/dehydriding in the LaY₂Ni₉ alloy. The penetration depth of hydrogen by diffusion process is estimated to be around 39 μm and 4.6 μm . The hydrogen diffusion towards the alloy matrix is not the limiting factor for the hydrogen absorption. During a long time immersion in KOH a corrosion layer appears and the modification of passive film towards more organized structure.

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Table 1: The fitting parameters of the equivalent circuit Fig.2 for EIS spectra of the LaY₂Ni₉ electrode, after activation and at different SOC.

SOC(%)	$R_e, \Omega \text{ cm}^2$	CPE_{dl}		$R_{tc}, \Omega \text{ cm}^2$	$I_0, \text{mA g}^{-1}$	$\chi^2 \times 10^{-3}$
		$Y_{dl}, \text{mF s}^{n-1} \text{ cm}^{-2}$	n_{dl}			
20	0.402	0.48	0.87	68.63	07.65	5.96
50	0.434	0.90	0.84	53.22	09.90	5.95
70	0.443	1.00	0.84	27.87	18.90	4.76
100	0.461	1.03	0.85	18.91	27.80	4.28

SOC(%)	CPE_{ad}		$R_{ad}, \Omega \text{ cm}^2$	O			$\chi^2 \times 10^{-3}$
	$Y_{ad}, \text{F s}^{n-1} \text{ cm}^{-2}$	n_{ad}			$Y_O, \text{F s}^{n-1} \text{ cm}^{-2}$	$B, \text{s}^{0.5}$	
20	0.09	0.95	4892.0	-		11.75	5.96
50	0.11	0.96	0307.3	0.08		14.69	5.95
70	0.10	0.91	0122.7	0.45		14.00	4.76
100	0.06	0.79	0001.9	0.04		03.43	4.28

Table 2: The fitting parameters of the equivalent circuit Fig.8 for EIS spectra of the LaY₂Ni₉ electrode, after activation at 100% SOC.

Days	$R_e (\Omega \text{ cm}^2)$	$R_t (\Omega \text{ cm}^2)$	$C_d (\mu \text{F cm}^{-2})$	$R_F (\text{k}\Omega \text{ cm}^2)$	$C_F (\text{F cm}^{-2})$	$R_d (\Omega \text{ cm}^2)$	$T_d (\text{s})$	$\chi^2 \times 10^{-4}$
3	0.521	3.881	200	0.4	0.15	26	0.025	1.93
4	0.516	4.747	170	1.75	0.15	30	0.022	2.15

FIGURE CAPTIONS

Figure 1: Electrochemical impedance spectra at different SOC and at open circuit condition (A) 20%SOC, (B) 50%SOC, (C) 70%SOC, (D) 100%SOC.

Figure 2: The electrical equivalent circuit model to represent experimental impedance spectra of LaY_2Ni_9 electrode with SOC.

Figure 3: Charge-transfer resistance and the exchange current density of the LaY_2Ni_9 alloy as a function of the state of charge.

Figure 4: Double layer capacitance and roughness factor of the LaY_2Ni_9 alloy as a function of the state of charge.

Figure 5: SEM picture of the LaY_2Ni_9 alloy (a-b) before, (c-d) after cycling in KOH.

Figure 6: Adsorption capacitance of hydrogen on the surface and resistance for the hydrogen adsorption as a function of the state of charge.

Figure 7: The impedance diagrams of a LaY_2Ni_9 electrode immersed in 7 M KOH at 100% SOC.

Figure 8: The electrical equivalent circuit model to represent experimental impedance spectra of LaY_2Ni_9 electrode with immersion time.

(A)

(B)

(C)

(D)

Figure 1

Figure 2

Figure 3

Figure 4

(A)

(B)

(C)

(D)

Figure 5

Figure 6

(A)

(B)

Figure 7

Figure 8