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Electrochemical characteristics of $LaNi_{4.7}Al_{0.3}$ alloy activated by alkaline solution containing hydrazine

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Abstract

The electrochemical characteristics of $LaNi_{4.7}Al_{0.3}$ alloy treated with an alkaline solution containing hydrazine ($N_2H_4 \cdot H_2O$) have been investigated under various treatment conditions. Hydrazine solution can activate $LaNi_{4.7}Al_{0.3}$ alloy effectively to attain high initial discharge capacity at fast charge and discharge rates and at low polarization. The treated electrode has initial capacity C_0 before charging. In alkaline media the alloy surface disproportionates into $La(OH)_3$ and small clusters of Ni atoms which possess high catalytic activity. The strong reducing agent N_2H_4 is beneficial to maintain the high catalytic activity.

Keywords: Electrochemical characteristics; Hydrazine

1. Introduction

Ni/MH (M, metal) batteries have been developed as alternatives to the Ni/Cd battery. Improvement in the activation characteristics remains one of the important research objectives. In the course of developing a hydrazine fuel cell, a large steady current flow was obtained by anodic polarization in 6 N KOH solution containing hydrazine [1]. Later N_2H_4 was used to enhance the activation rate of $MmNi_5$ and $LaNi_{4.7}Al_{0.3}$ electrodes [2,3]. The aim of this work is to investigate the electrochemical characteristics and surface structure of $LaNi_{4.7}Al_{0.3}$ alloy treated with an alkaline solution containing hydrazine under various treatment conditions.

2. Experimental details

The $LaNi_{4.7}Al_{0.3}$ alloy was ground mechanically to obtain powders of various particle sizes. An amount of 0.216 g was mixed with 5 wt.% polytetrafluoroethylene (PTFE) powder and 25 wt.% Ni powder (Type 255). The mixture of 0.309 g was compressed at ambient temperature to 2.5×10^8 Pa to form a pellet 13 mm in diameter, which was sandwiched between two nickel wire screens.

The electrode was immersed in KOH or NaOH solution containing hydrazine ($N_2H_4 \cdot H_2O$). The treated electrode was placed in the central chamber of a Pyrex cell in which 6 N KOH solution was used as electrolyte. In this experiment hydrazine was not mixed with the KOH electrolyte solution as in Ref. [3]. The quantities of hydrogen absorbed (C_0) were determined by measuring the discharge capacity at 21.6 mA (100 mA g^{-1}). In this work the initial discharge capacity (C_1) means the capacity during the first discharge cycle. The charge–discharge (C–D) cycles were usually conducted under the following conditions: charge at 43.2 mA (200 mA g^{-1}) for 1.5 h, hold for 10 min, then discharge at 43.2 mA until the potential reaches −0.6 V vs. Hg/HgO or the voltage reaches a cut-off value of 0.8 V in the Ni/MH battery.

Surface analyses were carried out by means of X-ray photoemission spectroscopy (XPS) and electron spectroscopy for chemical analysis (ESCA-850M, Shimazu, Japan). The alloy surface was treated with 5 vol.% $N_2H_4 \cdot H_2O$ in 6 N KOH solution for 2 h at 50 °C, then washed with purified water until pH 7 and dried. The base pressure in the spectrometer was 10^{-7} Pa and Mg Kα ($h\nu = 1253.6$ eV) radiation was used at 10 kV and 30 mA. To measure depth profiles, Ar^+ ion bombardment (4×10^{-4} Pa) at 2 kV and 25 mA was used.

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3. Results and discussion

N_2H_4 solution is an excellent reducing agent whose standard electrode potential is −1.15 V. Alkaline solution containing hydrazine can effectively activate $LaNi_{4.7}Al_{0.3}$ alloy. The concentration (vol.%) of $N_2H_4 \cdot H_2O$ in alkaline solution, the temperature and the treatment time were all found to significantly affect the initial activation process of the $LaNi_{4.7}Al_{0.3}$ alloy electrode. The following results are of particular interest.

(1) Under the best treatment conditions the discharge capacity of the $LaNi_{4.7}Al_{0.3}$ alloy during the first cycle (C_1) at high C–D rate reached 271.0 mA h g^{-1} (see Fig. 1). The discharge capacity during the second cycle had already reached the maximum (C_{max}). The ratio of C_1/C_{max} is as high as 95.6% and 96.1% for treated electrodes #1 and #2 respectively, showing good reproducibility. The comparison of the discharge capacities for the treated and untreated $LaNi_{4.7}Al_{0.3}$ alloy is shown in Fig. 2.

(2) A treatment temperature higher than ambient, i.e. 50 °C, gives slightly better results for the activation process (see Fig. 3(a)). In concentrated alkaline solution a time of 1–2 h is found suitable for the process (see Fig. 3(b)), but in dilute alkaline solution a longer treatment time gives a more favourable result.

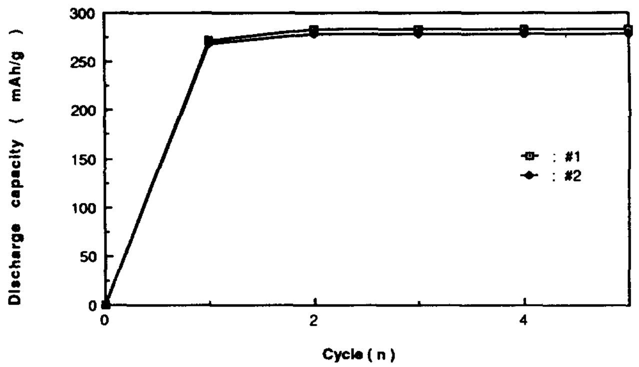

Fig. 1. Discharge capacity vs. cycle curves for N_2H_4-treated $LaNi_{4.7}Al_{0.3}$ alloy (size less than 26 μm; 5 vol.% $N_2H_4 \cdot H_2O$ in 0.1 N NaOH solution, 50 °C, 4 h; charged at 200 mA g^{-1} for 1.5 h, held for 10 min, discharged at 100 mA g^{-1} to 0.8 V at 20 °C).

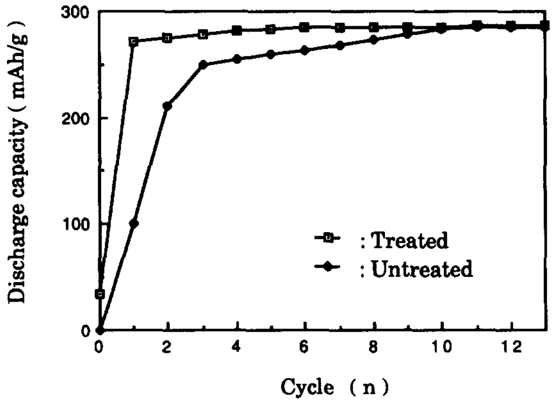

Fig. 2. Comparison of discharge capacity vs. cycle curves for treated and untreated $LaNi_{4.7}Al_{0.3}$ alloy (5 vol.% $N_2H_4 \cdot H_2O$ in 0.3 N KOH solution, 50 °C, 4 h; charged at 200 mA g^{-1} for 1.5 h, held for 10 min, discharged at 100 mA g^{-1} to 0.8 V at 20 °C).

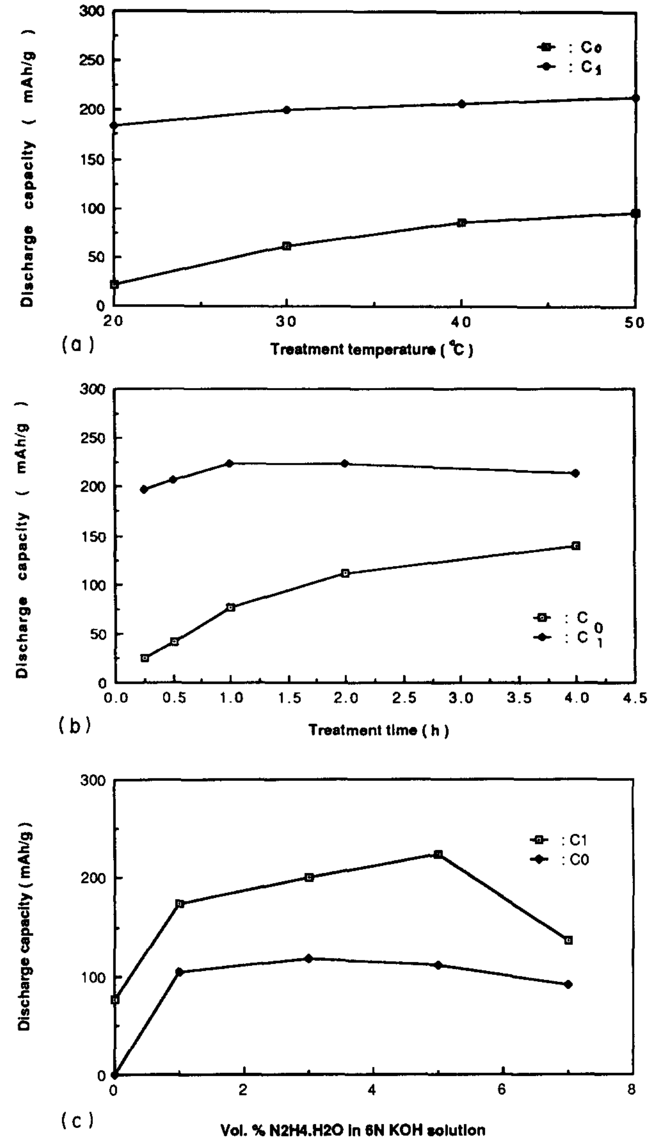

Fig. 3. Discharge capacities C_0 and C_1 of $LaNi_{4.7}Al_{0.3}$ alloy treated (a) at various temperatures (5 vol.% $N_2H_4 \cdot H_2O$ in 6 N KOH solution, 1 h), (b) for various treatment times (5 vol.% $N_2H_4 \cdot H_2O$ in 6 N KOH solution, 50 °C) and (c) with various hydrazine concentrations (30 °C, 1 h) (size (a), (b) less than 112 μm, (c) less than 75 μm; discharged at 100 mA g^{-1} to −0.6 V vs. Hg/HgO for C_0; charged at 200 mA g^{-1} for 1.5 h, held for 10 min, discharged at 200 mA g^{-1} to −0.6 V vs. Hg/HgO for C_1).

(3) A much higher concentration of N_2H_4 solution cannot accelerate the activation process. The $LaNi_{4.7}Al_{0.3}$ alloy activated by 6 N KOH solution containing hydrazine exhibits higher C_0 and C_1 than the alloy activated by 6N KOH solution (see Fig. 3(c)).

(4) During the N_2H_4 treatment process the $LaNi_{4.7}Al_{0.3}$ alloy absorbs hydrogen in considerable amount, C_0, but there is no functional relationship between C_0 and C_1.

(5) Typical charge and discharge curves of $LaNi_{4.7}Al_{0.3}$ electrodes at several treatment temperatures are shown in Fig. 4. The polarization of the treated alloy electrodes is decreased by about 60 mV.

(6) A schematic representation of an alloy particle of an $LaNi_{4.7}Al_{0.3}$ alloy electrode activated by an alkaline solution containing hydrazine is shown in Fig. 5. In this solution N_2H_4 can be decomposed into gaseous N_2 and atomic hydrogen H_{ad} chemically adsorbed at the electrode surface. H_{ad} penetrates the surface layer and diffuses into the interstitial sites of the alloy lattice to form a metal hydride. H_{ad} turns into absorbed hydrogen H_{abs}. Otherwise it can combine to form molecular H_2 as bubbles generated in the solution.

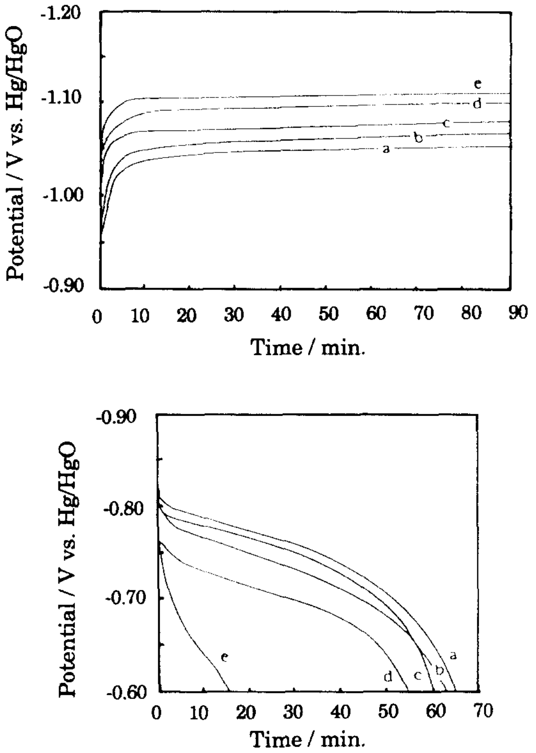

Fig. 4. Charge (top) and discharge (bottom) curves for treated and untreated $LaNi_{4.7}Al_{0.3}$ alloy during the first cycle at 200 mA g^{-1} (5 vol.% $N_2H_4 \cdot H_2O$ in 6 N KOH solution, 1 h): a, 50 °C; b, 40 °C; c, 30 °C; d, 20 °C; e, untreated, charged at 200 mA g^{-1} for 1.5 h, held for 10 min, discharged at 200 mA g^{-1} to -0.6 V vs. Hg/HgO.

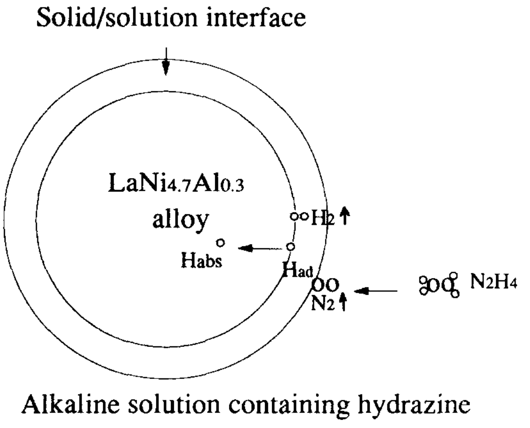

Fig. 5. Schematic representation of an alloy particle of an $LaNi_{4.7}Al_{0.3}$ alloy electrode activated by an alkaline solution containing hydrazine.

(7) $LaNi_{4.7}Al_{0.3}$ alloy acts as a catalytic reactant in this reaction to break N–H bonds as illustrated in the following equations:

$$N_2H_4 \xrightarrow{LaNi_{4.7}Al_{0.3}} N_2\uparrow + 4H_{ad} \begin{cases} \rightarrow H_{abs} \\ \rightarrow 2H_2\uparrow \end{cases} \qquad (1)$$

$$H_{ad} \longrightarrow H_{abs} \qquad (2)$$

The spectra for the La $3d_{5/2}$, Ni $2p_{1/2}$ and Al 2p levels of the treated and untreated samples are shown in Fig. 6 as a function of sputtering time. The La $3d_{5/2}$ core level spectrum is observed to split into two species with a separation energy of 4.0 eV (see Fig. 6, top). From the separation energy and binding energy the La bonding on the surface is recognized to be La_2O_3 with $La(OH)_3$. Metallic La ($E_b = 836$ eV) remains in the sublayer, where a limited amount of La_2O_3 coexists with it. It is observed that Ni exists in the metallic state in the sublayer judging from its binding energy ($E_b = 870$ eV). Al exists in the form of Al_2O_3 ($E_b = 73.7$ eV) in accordance with the Al 2p peak. After argon ion sputtering, metallic Al ($E_b = 72.0$ eV) appears. After the treatment the La $3d_{5/2}$, Ni $2p_{1/2}$ and Al 2p core levels were again determined (see Fig. 6, bottom). From the separation energy and binding energy the La bonding on the surface is recognized to be $La(OH)_3$. There is no La_2O_3 on the surface as there was with the untreated sample. It is observed that Ni exists as $Ni(OH)_2$ in the top layer, but after argon ion sputtering for only 1 min, metallic Ni appears, which is similar to the untreated case. On the treated surface no Al and Al_2O_3 exist, which contrasts with the untreated case. According to the ESCA results, in alkaline solution the alloy surface disproportionates into $La(OH)_3$ and small clusters of Ni atoms which possess high catalytic activity. Because the standard electrode potential of the reaction

$$Ni(OH)_2 + 2e^- = Ni + 2OH^- \qquad (3)$$

is -0.69 V, the strong reducing agent N_2H_4 can keep the small clusters of Ni atoms active to some degree. Therefore the N_2H_4-treated alloy electrode gives high initial capacity and low polarization at fast C–D rates. Free $La(OH)_3$ and the absence of Al_2O_3 are of benefit to the catalysis by small clusters of Ni atoms.

4. Conclusions

(1) N_2H_4 treatment improves the surface properties of hydrogen storage materials. It results in high initial discharge capacity and low polarization at fast charge

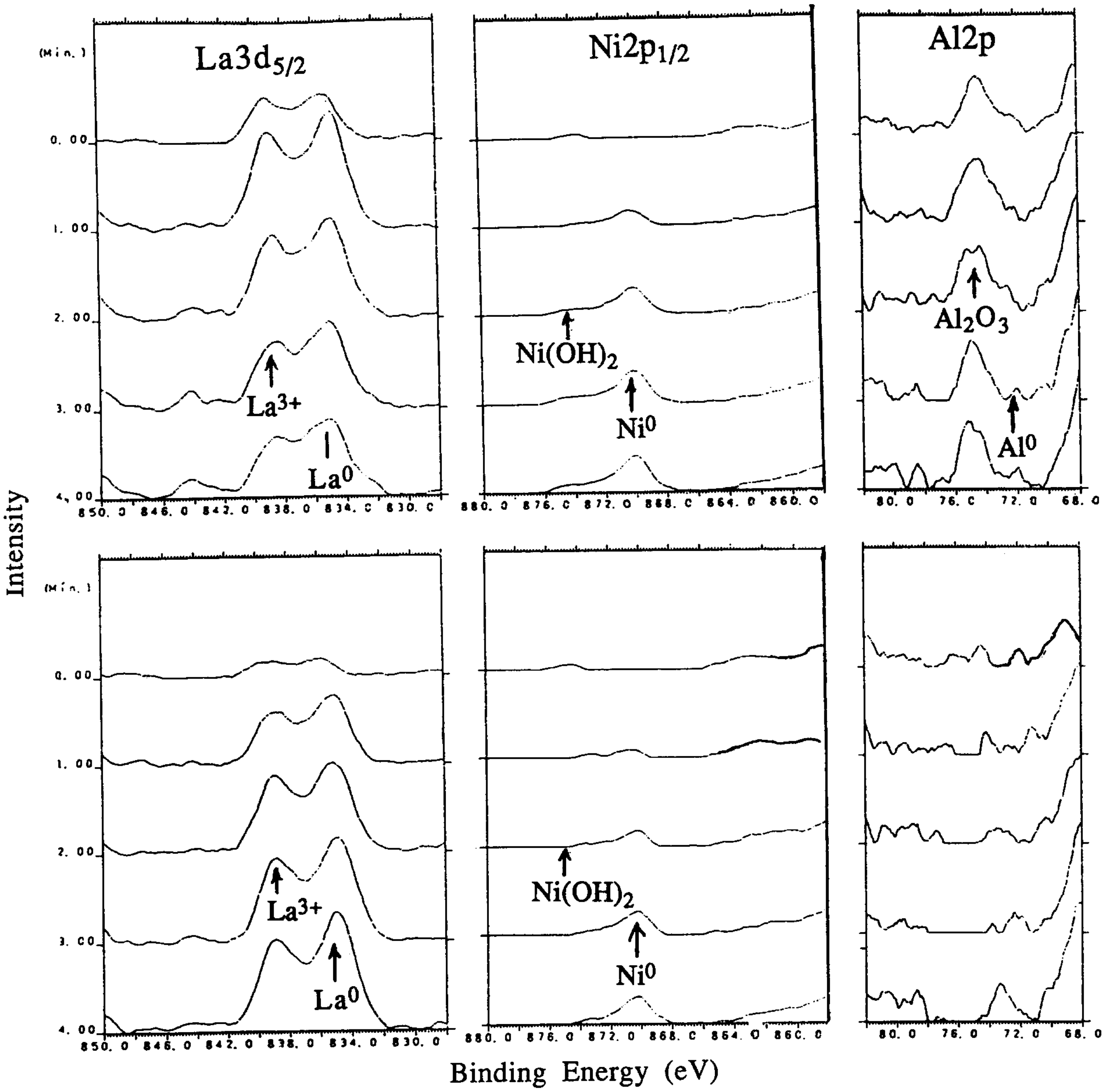

Fig. 6. Measured XP spectra of the La $3d_{5/2}$, Ni $2p_{1/2}$ and Al 2p levels for N_2H_4-treated (bottom) and untreated (top) $LaNi_{4.7}Al_{0.3}$ alloy.

and discharge rates. Traditional gas–solid and electrochemical charge–discharge activation methods have not reached such levels.

(2) The method employed in this work to activate $LaNi_{4.7}Al_{0.3}$ alloy has a much wider relevance and does not need to be restricted to this alloy. The method is applicable to AB_5, AB, A_2B, AB_2 and almost all hydrogen storage materials.

(3) The proposed method is advantageous because of its simple procedure and estimated low cost.

Acknowledgments

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