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Electrochemical activity enhancement of a $LaNi_{4.7}Al_{0.3}$ electrode treated with an alkaline solution containing H_2O_2

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Abstract

Enhancement of the electrochemical activity of a $LaNi_{4.7}Al_{0.3}$ electrode was observed subsequent to some charge–discharge cycles in a KOH solution containing hydrogen peroxide. Metallic nickel is enriched at the alloy surface after the treatment, and the concentration of lanthanum decreased during the treatment. The change in the distribution of elements at the alloy surface is expected to lead to a different dispersion state of nickel particles in the region, resulting in improvement of the catalytic activity for the charge-transfer process on the alloy surface.

Keywords: $LaNi_{4.7}Al_{0.3}$; Electrode; Surface treatment; Hydrogen peroxide

1. Introduction

Surface layers enriched with metallic nickel play an important role for the smooth progress of electrochemical hydriding (charging) and dehydriding (discharging) reactions of $LaNi_5$-based alloys. Meli et al. revealed that the composition and thickness of the surface layer formed on a $LaNi_{4.7}Al_{0.3}$ alloy electrode depends on pretreatment [1]. Kuriyama et al. reported that immersion of a $LaNi_{4.7}Al_{0.3}$ electrode in a KOH solution with $Co(OH)_2$ after a few charge–discharge cycles ($Co(OH)_2$–KOH_{aq} treatment) is effective for the formation of a nickel-rich subsurface layer, and results in enhancement of its electrochemical activity [2]. Recently, we observed that a similar treatment with a KOH solution containing H_2O_2 (H_2O_2–KOH_{aq} treatment) also enhances its activity. In this paper, the influence of a treatment of a $LaNi_{4.7}Al_{0.3}$ electrode with a KOH solution containing H_2O_2 on the electrochemical activity and surface states is studied by X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS).

2. Experimental

$LaNi_{4.7}Al_{0.3}$ was purchased from Santoku Metal Industry Co. Ltd. The alloy electrodes for EIS and XPS measurements were prepared using alloy powder from 63 μm to 150 μm in diameter and below 50 μm, respectively. Preparation of electrodes for EIS and XPS, electrochemical cycling, and EIS measurement is described elsewhere [2]. The electrodes were electrochemically cycled in a 6 M KOH solution at 20 °C.

Some of them were treated by immersing them in a 6 M KOH solution containing 1 wt% of hydrogen peroxide for 1 h at room temperature (H_2O_2–KOH_{aq} treatment).

The electrochemical activities of the electrodes were evaluated by the activation enthalpy of the charge-transfer reaction, ΔH^*. The enthalpies were obtained from temperature dependence of charge-transfer resistance, R_{ct}, determined by EIS as follows;

$$\ln\left(\frac{T/R_{ct}}{K/\Omega}\right) = C_0 - \frac{\Delta H^*}{RT}, \qquad (1)$$

where T is temperature, R is the gas constant and C_0 is a constant [2,3].

Depth profiles of the relative concentrations of constituent elements and their chemical states were measured with a Simazu ESCA-750 spectrometer using an X-ray energy of 1253.6 eV (Mg K_α) and equipped with an Ar^+ ion sputtering gun operated at 2 kV.

3. Results and discussion

For $LaNi_{4.7}Al_{0.3}$ electrodes without the H_2O_2–KOH_{aq} treatment and with the H_2O_2–KOH_{aq} treatment before

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electrochemical cycling, the activation enthalpies, ΔH^*, were larger than 42 kJmol^{-1} before the eighth cycle and about 41 kJmol^{-1} upon the twentieth cycle. As shown in Fig. 1, ΔH^*s rapidly decreased to about 37.5~38.5 kJmol^{-1} by the H_2O_2–KOH_{aq} treatment after some charge–discharge cycles. These results indicate that the H_2O_2–KOH_{aq} treatment is effective for the enhancement of the electrochemical activity of surfaces formed by the progress of decrepitation during the electrochemical cycles.

According to XPS spectra of the untreated alloy and the alloy treated after electrochemical cycling, nickel was metallic in the subsurface layer except for the top surface. Most of the lanthanum is oxidized even after sputtering for 70 min. Depth concentration profiles of metal elements as shown in Fig. 2(a) reveal an enrichment of metallic nickel and a decrease of lanthanum oxide in the subsurface region (after 4 to 10 min. sputtering) for the alloy treated after cycling, compared to those for the untreated alloy after the same cycles. Upon 10 min. sputtering the atomic ratio of nickel to lanthanum of the alloy treated after cycling (Ni:La = 3.7) is higher than that of the untreated alloy (Ni:La = 3.1).

Oxygen concentrations at the top surface and in the subsurface region of the alloy treated after cycling are higher by 20% than those for the untreated alloy as shown in Fig. 2(b). After only 1 min. of Ar^+ sputtering, nickel was completely metallic for both samples. On the other hand, lanthanum was mainly oxidized even after 70 min. of sputtering. Thus the higher concentrations of oxygen for the alloy treated upon cycling compared to those for the untreated alloy show that a large amount of lanthanum was oxidized in the subsurface region of the treated alloy during the H_2O_2–KOH_{aq} treatment. Due to the decomposition of hydrogen peroxide, oxygen was evolved during the treatment, leading to an electrode potential of about −0.1 V (vs. Hg/HgO) after the treatment. This suggests that active surfaces of the alloy form as a result of oxidative decomposition of the alloy surface. Precipitation of lanthanum hydroxide crystals at the top surface has been reported in the case of $LaNi_5$-based alloys [1,4,5]. Thus it is speculated that the H_2O_2–KOH_{aq} treatment should accelerate segregation of lanthanum oxide, although the mechanism of nickel enrichment by the H_2O_2–KOH_{aq} treatment is not still clear at the present stage.

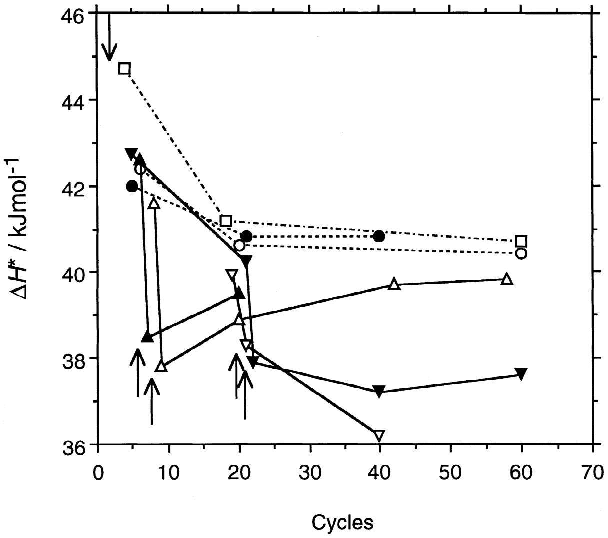

Fig. 1. Plots of the activation enthalpy, ΔH^*, versus the cycle number. The points at which the H_2O_2–KOH_{aq} treatments were carried out are indicated by arrows.

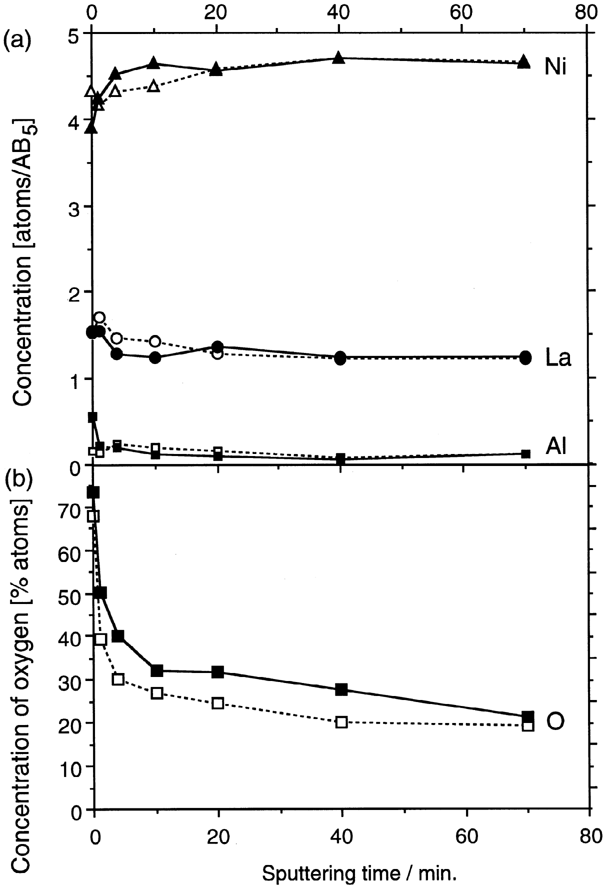

Fig. 2. Depth concentration profiles of elements for the $LaNi_{4.7}Al_{0.3}$ alloy particles of the untreated electrode after 5 cycles, and of the electrode after 5 cycles followed by the treatment. (a) lanthanum, nickel, and aluminum and (b) oxygen.

According to Fig. 1 and Fig. 2(a), the steep decrease in activation enthalpy after the H_2O_2–KOH_{aq} treatment at the fourth cycle nearly coincides with the enrichment of metallic nickel and the decrease of lanthanum concentration. This result suggests that a nickel enrichment contributes to improve the electrochemical activity of the alloy surface. Since lanthanum existed as oxide in the subsurface region, the nickel-rich layer is regarded as a nickel catalyst supported on lanthanum oxide. Thus an increase in concentration of metallic nickel is expected to lead to a different dispersion state of nickel particles in the region, resulting in improvement of the catalytic activity for charge-transfer reaction on the alloy surface.

4. Conclusion

The electrochemical activity of a $LaNi_{4.7}Al_{0.3}$ electrode was enhanced by the H_2O_2–KOH_{aq} treatment only upon electrochemical charge–discharge cycles. Simultaneously, the concentration of metallic nickel was increased and that of lanthanum decreased in the subsurface region of the alloy treated with the H_2O_2–KOH_{aq} solution. Therefore the H_2O_2–KOH_{aq} treatment is a surface treatment which enriches metallic nickel in the subsurface region of hydrogen storage alloys. The change in elemental distribution is expected to lead to different dispersion states of nickel particles in the region, resulting in an improvement of the catalytic activity for charge-transfer reaction on the alloy surface.

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