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Effect of alkaline pretreatment on the initial activation of $LaNi_5$ and $LaNi_{2.5}Co_{2.5}$ in the H_2 gas and electrochemical reactions

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Abstract

The effect of the pretreatment by NaOH, LiOH and KOH on the initial activation of $LaNi_5$ in the gas phase and of $LaNi_{2.5}Co_{2.5}$ in electrochemical reactions was investigated. The samples pretreated by alkaline hydrodxides exhibited higher reaction rates than those without pretreatment. The Auger electron spectroscopy (AES) surface analyses confirmed the surface modifications by the alkaline pretreatment. The enhanced initial activations of the alloys may be attributed not only to the Ni enrichment but also to the existence of an alkaline element in surface layers.

Keywords: LiOH; NaOH; KOH; Rare earth; Hydrogen; Kinetics

1. Introduction

During the H uptake in the gas phase or in electrochemical processes, H_2 or H_2O must be dissociatively absorbed or associatively desorbed by the host metal through the surface. Therefore, the interface reactions become one of the most important partial reaction steps. The surface contamination from the contaminants in gas or liquid phases mostly forms a passivated state and controls the whole reaction rates. Previously, we reported the improving effect of the KOH pretreatment on the initial rate of H uptake by $LaNi_{2.5}Co_{2.5}$ in both gas phase and electrochemical reactions [1,2]. The presence of K atoms in the surface oxide layers seems to enhance the dissociation of H_2 and H_2O molecules, resulting in ready initial activation. In this study the effect of alkaline hydroxides, such as of NaOH, LiOH and KOH on the kinetics of the H uptake by $LaNi_5$ or $LaNi_{2.5}Co_{2.5}$ was investigated in the H_2 gas or in the electrochemical reactions, respectively.

2. Experimental

Samples were prepared by arc melting. Subsequent annealing at 1073 K under 10^{-4} Pa was carried out for homogenization. The stoichiometry and crystal structure were confirmed by induction coupled plasma induced photoemission spectroscopy (ICP) and X-ray diffraction analysis (XRD), respectively. All samples were pulverized by 7 N H_2 sorption cycles down to less than 38 μm. The powder sample was oxidized for longer than 30 days under 1 bar in air. The $LaNi_5$ samples for the H_2 gas phase reactions were soaked in 3 M or 6 M alkaline hydroxides for 3 h at room temperature and dried in air. More than 4 M LiOH solution could not be obtained because of limited solubility. In order to reduce the hydroxide layer formed by the alkaline treatments, some of dried samples were subsequently rinsed several times in fresh distilled water at room temperature. The initial activation of the samples was measured using a Sieverts' type apparatus for gas phase reactions. In electrochemical reactions, pellets of $LaNi_{2.5}Co_{2.5}$ powder with Ni powder ($LaNi_{2.5}Co_{2.5}/Ni=0.5$ in weight) pressed with polyethylene powder (5 wt%) were dipped in alkaline hydroxide solutions at 358 K for 3 h. Ni plate and Hg/HgO electrode were used as the counter electrode and reference electrode, respectively, in an open cell. The electrolyte of 6 M KOH was used for all measurements. From the measured current in charging at constant potential of -0.93 V, the concentration of H absorbed by the negative electrodes was calculated. In all electrochemical reactions no bubbles were observed during the charging. For point AES (PHI15-155, 3 kV, 10 μA) analyses, bulk samples were used.

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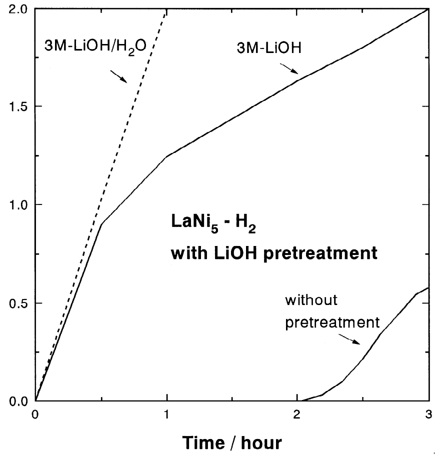

Fig. 1. The initial activation of $LaNi_5$ with and without the LiOH pretreatment in the H_2 gas reaction.

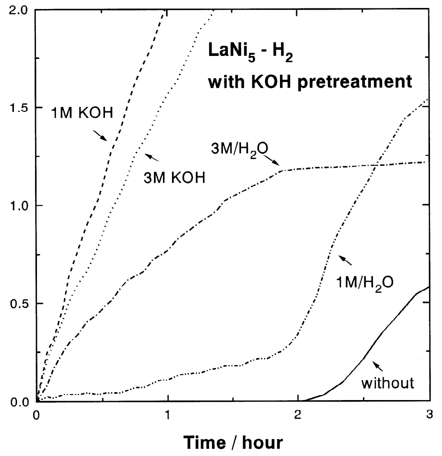

Fig. 3. The initial activation of $LaNi_5$ with and without the KOH pretreatment in the H_2 gas reaction

3. Results and discussion

Figs. 1–3 show the typical initial activations in the H_2 gas phase for the $LaNi_5$ samples with and without alkaline pretreatment, by 3 M LiOH, 3 M, 6 M, 9 M NaOH and 1 M, 3 M KOH, respectively, under an initial pressure of 8 MPa H_2. A large difference between the initial rates of the samples with and without alkaline pretreatment can be observed. The samples with the alkaline pretreatment react with H_2 readily after the H_2 exposure, while the samples without the pretreatment require an incubation time of about 2 h. In spite of a subsequent rinse by distilled water after the alkaline pretreatment, a marked effect by the alkaline pretreatment can still be observed in the rates.

A similar enhancement in the initial rate could also be observed in the electrochemical reactions. Fig. 4 shows the change in the H concentration for $LaNi_{2.5}Co_{2.5}$ in 3 M, 6 M KOH, 3 M, 6 M NaOH and 3 M LiOH at 298 K as a function of the reaction time. The $LaNi_{2.5}Co_{2.5}$ sample treated by 6 M KOH exhibits the highest reaction rate at the first charge. Such a higher rate can be obtained only after several reaction cycles for the samples without pretreatment. The 3 M NaOH treated sample shows the lowest rate. From the results for the KOH and NaOH pretreatments, the concentration seems to be important for the effect of pretreatment.

Concerning the kind of alkaline hydroxides, among the 3 M alkaline pretreated samples, LiOH pretreatment yields the highest reaction rate up to about 100 min, however, with a lower H absorbtion after 350 min. The KOH pretreatment yielded no reduction in the capacity. The charging capacity (H/M) of the first cycle in 6 M KOH (as electrolyte) was reduced by the 3 M NaOH and 3 M LiOH pretreatments at a constant charging potential of −0.93 V.

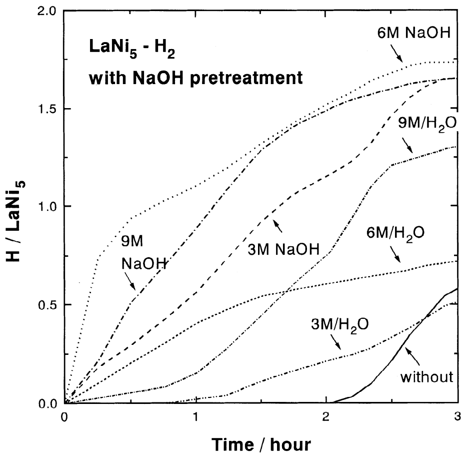

Fig. 2. The initial activation of $LaNi_5$ with and without the NaOH pretreatment in the H_2 gas reaction.

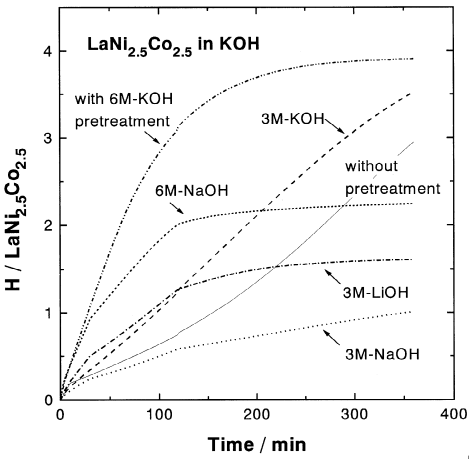

Fig. 4. Initial H absorption in electrochemical process by $LaNi_{2.5}Co_{2.5}$ pretreated with and without alkaline hydroxides.

This reduction seems to be related to the kind of electrolyte used. This reduction by the LiOH and NaOH pretreatments was observed only in the initial activation. With increasing number of the cycles, the charging capacity was increased up to $[H]/[LaNi_{2.5}Co_{2.5}]=4$. This means that the reduced capacity in the initial activation was not caused by the dissolution of the alloy elements. The reduction in the charging capacity seems to be related rather to interactions between K and Li or Na atoms on the electrode surface.

In the course of pretreatment, the sample surfaces were modified by the hydroxide solutions, by dissolution of La, Ni and Co. These elements were also clearly recognized in the test solution observed by ICP analyses. Figs. 5 and 6 show the AES surface depth profiling for the samples with and without 6 M NaOH and 3 M LiOH pretreatments obtained with Ar^+ sputtering (3 kV). After the NaOH pretreatment, Na and O atoms are enriched in the surface (Fig. 5b). The NaOH recrystallized surface layers must be removed by rinsing in water. However, the enriched Na can still be seen in the surface region (Fig. 5c). In addition, the Na concentration decreases with the O concentration from the surface to the inside. This means that Na atoms are present in the surface oxide layers. Similar results were also obtained for the sample treated by LiOH (see Fig. 6a). A similar depth profiling was also observed on $LaNi_{2.5}Co_{2.5}$ [2]. As shown in Figs. 5d and 6b the relative amounts of La and Ni for the sample with NaOH/LiOH and water rinse pretreatments was calculated from the peak height in the AES analyses. Other samples treated by KOH exhibit similar profiles. The La atoms are enriched in the surface because of the segregation by oxidation. Additionally, the further outer side of the surface is relatively enriched by Ni. This result of the Ni enrichment in the surface region agrees with results of the X-ray photoelectron spectroscopy (XPS) analyses by Kuriyama et al. [3] and Meli et al. [4]. The metallic Ni enrichment on the subsurface caused by oxidation may create the active site for the interface reaction.

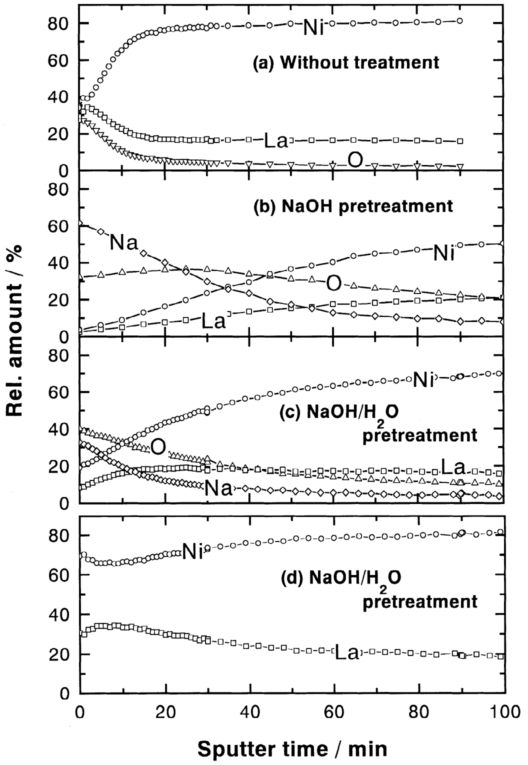

Fig. 5. AES depth profiling of bulk $LaNi_5$; (a) without NaOH (b) with NaOH (c) with NaOH and H_2O treatments and (d) relative amount of La and Ni obtained from the peak height for the sample with NaOH and H_2O pretreatment. (3 kV Ar^+, with a sputtering rate of about 1.5 nm min^{-1}.)

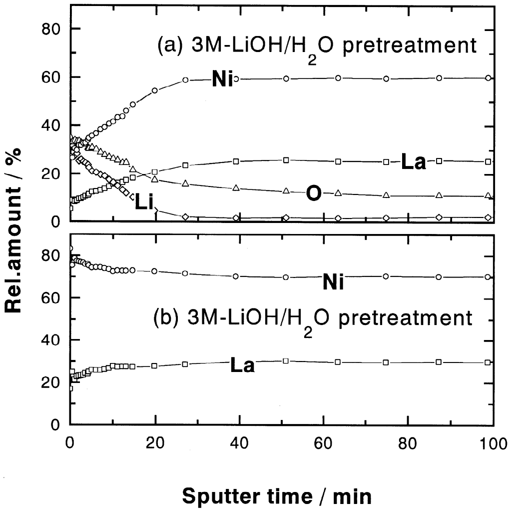

Fig. 6. AES depth profiling of bulk $LaNi_5$; (a) with LiOH and H_2O treatments and (b) relative amount of La and Ni obtained from the peak height for the sample with LiOH and H_2O pretreatment. (3 kV Ar^+, with a sputtering rate of about 1.5 nm min^{-1}.)

However, in addition to this subsurface structure, the presence of alkaline elements may play an important role in the interface reactions. From the results of the initial activation, the alkaline pretreated surface seems to have already active sites. The surface layer of alkaline hydroxides is thick enough to cover the enriched Ni clusters. The effect of alkaline is also reported for other metals. Notoya [5] reported the effect of alkaline element on the H_2O electrochemical dissociative reaction. Additionally, the alkaline atoms on the Fe surface are known to reduce the activation energy for NH_3 chemisorption, so that the dissociation of NH_3 becomes easier [6]. The alkaline atoms seem to modify the electronic structure of the surface, resulting in the acceleration of the dissociation of H_2 or H_2O.

4. Conclusion

The presence of alkaline elements on the surfaces of $LaNi_5$ and $LaNi_{2.5}Co_{2.5}$ seems to be important for the dissociation of H_2 and H_2O. By pretreatment with alkaline hydroxides, the surface becomes modified and subsequent H_2 absorption reaction in the H_2 gas phase starts in spite of the fact that the surface is covered by a layer of hydroxide. A similar effect was also observed in electrochemical reactions. At a constant charging potential of −0.93 V, the accelerated rate could be measured even at the first cycle while the storage capacity of the H absorption was reduced, but gradually increased with charging cycles. The easy initial activation of the samples covered even by thick oxide layers may be attributed not only to the Ni enrichment in the subsurface layer but also to the presence of alkaline element in the surface oxide, in which an electron transfer from the surface to the H_2 and H_2O molecules can easily occur.

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