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Effect of LiOH pretreatment on H_2 absorption kinetics of $LaNi_5$

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Abstract

The effect of a LiOH pretreatment on the H_2 absorption process by $LaNi_5$ was examined using a high-pressure volumetric apparatus. In the course of H_2 absorption and desorption cycles, air was introduced into the reaction bed to oxidize the samples for 5 to 25 min after each desorption. The absorption reaction was significantly disturbed in case without any pretreatment, however, the LiOH pretreated sample reacts with H_2 even after significant oxidation. From the measurement of the pressure dependence on the initial reaction rate and the results of the Auger electron spectroscopy, the effect may be attributed to the accelerated dissociation of H_2 on the oxide surface by the presence of Li in the surface region. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkaline treatment; Hydrogen absorption kinetic; Oxidation; $LaNi_5$; LiOH

1. Introduction

In the activation process of $LaNi_5$, the prior alkaline treatments drastically enhances the initiation of dissociative absorption [1]. In Ni–H batteries, charge–discharge characteristic can be also significantly improved by the pretreatment with alkaline hydroxides [1,2]. The reason for this effect on the initial activating reactions is attributed to the surface modification by the pretreatment with alkaline hydroxide. In this study, $LaNi_5$ with LiOH pretreatment was examined from more practical points of view, i.e. in the course of absorption and desorption cycles, absorption kinetics were investigated after a significant time of oxidation. Also the pressure dependence on the initial reaction rate was measured for estimating the reaction mechanisms.

2. Experimental

$LaNi_5$ samples were prepared by arc melting and subsequent annealing for homogenization. The block sample was pulverized by several H_2 sorption cycles to grain sizes smaller than 60 μm. The powder was placed under dry air for longer than 1 month before use. With this powder three kinds of pretreatments were carried out. One part of the sample powder was placed in 3M LiOH solution for 2 h and dried at room temperature (sample with LiOH). This treatment results in a surface covered by a LiOH layer as a condensed layer after drying. Additionally water rinse was carried out several times for a second part of the powder sample (sample with LiOH+H_2O) using fresh 50 cc distilled water each time for several grams of the sample. For comparison of the LiOH pretreatment with the water treatment, water rinse without prior LiOH treatment was also carried out for a third part of powder sample (sample with H_2O). In the 50 cc distillated water, several grams of the sample powder were put for 5 h without any mechanical treatment and subsequently dried in the air.

After three-fold absorption and desorption cycles using H_2 (99.99999% purity), air was introduced for the first oxidation for 5 min. After oxidation the reaction bed was evacuated by a rotary pump for 10 min, and subsequently the H_2 absorption was recorded for 10 min. In the second and subsequent cycles oxidation step of 5 min and hydrogen step of 10 min with the initial hydrogen pressures of 10, 20 and 40 bar H_2 were performed. The pressure dependence on the initial reaction rate was also measured at each reaction. In case the initial reaction rate is dependent on the applied pressure or root of the applied pressure, molecular H_2 or atomic H is related to the rate determining step, respectively [3].

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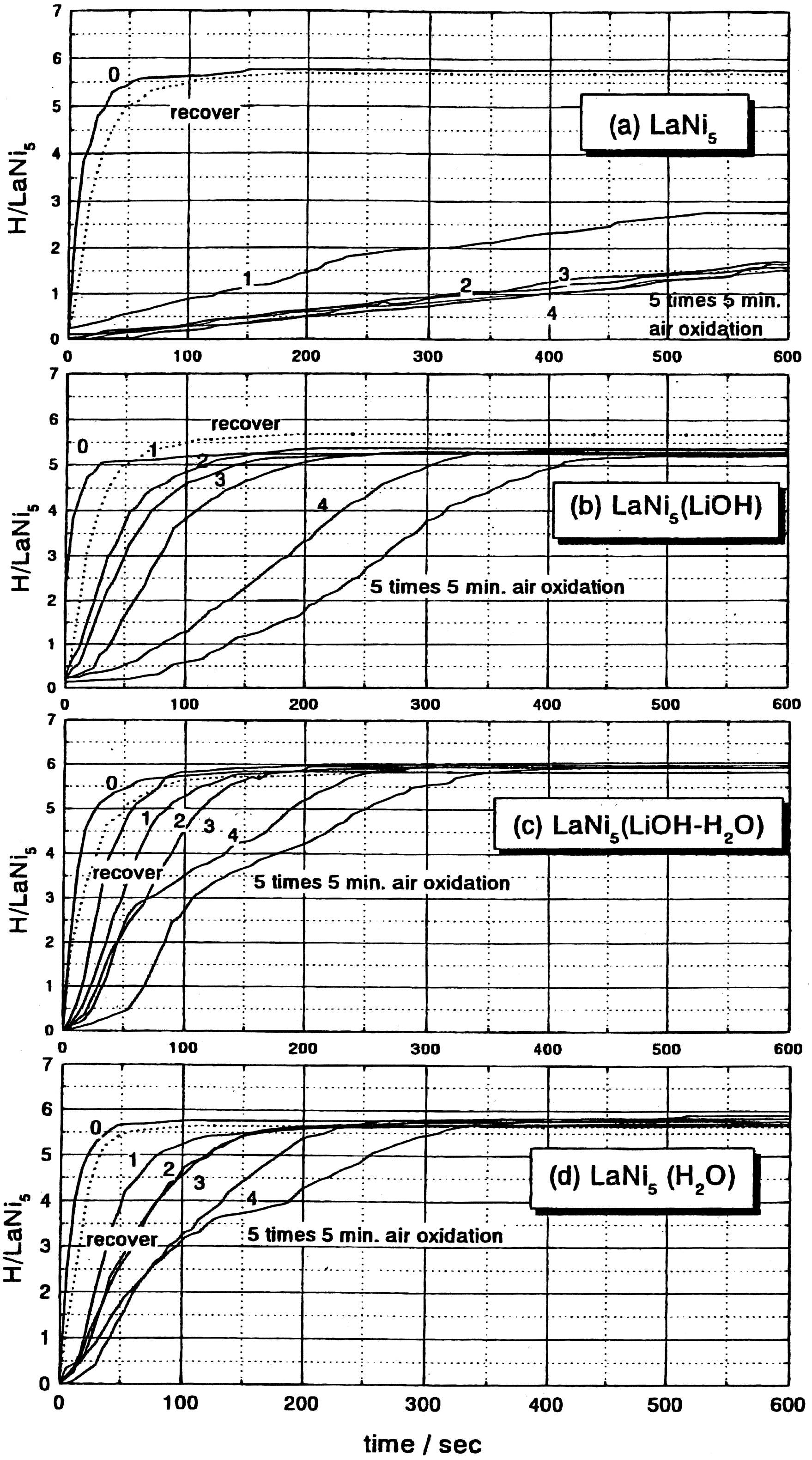

Fig. 1. Hydrogen absorption of $LaNi_5$ with initial pressure of 40 bar H_2 with increasing amount of air oxidation, (a) without, (b) with LiOH, (c) with LiOH+H_2O and (d) with H_2O pretreatment.

Block samples with and without pretreatment were also prepared for depth profiling by Auger electron spectroscopy (AES, PHI-15-155, 3 kV, 10 μA).

3. Results and discussion

3.1. Absorption kinetics with air oxidation

The cyclic H_2 absorption reactions after air oxidation are shown in Fig. 1. With increasing amount of oxidation, the sample is deactivated in case without any pretreatment. The absorption is drastically disturbed by the air oxidation procedure (see Fig. 1a). A significantly oxidized surface seems to stop almost completely the reaction with H_2. On the other hand, the samples with LiOH and also $LiOH+H_2O$ pretreatment react with H_2 even after each significant oxidation (Fig. 1b, c). For comparison, the pretreatment effect of water was also tested. As shown in Fig. 1d, a similar effect to that of the sample $LiOH+H_2O$ was also observed. Reproducibility of the effect of water treatment was confirmed by several experiments. This means that also the water pretreatment prevents the deactivation by the surface oxidation.

3.2. Pressure dependence on the initial reaction rate

In Fig. 2, the pressure dependence on the initial reaction rate was plotted. The pressure dependence indicates the rate-determining step according to the following expression,

$$V_0 \propto p^n$$

where V_0, p and n are initial reaction rate, initial pressure and pressure dependence constant, respectively. From the gradient of the curves, such as in Fig. 2, the constant n can be determined. For $n=1$ or 0.5, partial reaction of H_2 dissociation or atomic H diffusion/penetration is the rate determining step, respectively [3]. In Fig. 2, after oxidation the initial reaction rate was reduced in all cases. The sample with LiOH or $LiOH+H_2O$ treatment exhibits almost $n=0.5$ at higher-pressures, while for other conditions n can be determined almost to 1.0. This means the surface without treatment and that with Li exhibit similar initial reaction rate but with different rate determining steps. As a result, after several ten minutes the samples must be differently degraded, which exhibit the different sorption kinetics afterwards.

For the LiOH treated samples at lower pressures, since the reaction was significantly disturbed, only a small initial rate was obtained under the condition in this study. From the dependence measured at 20 and 40 bars, the alkaline pretreatment seems to accelerate the dissociation of H_2 on the sample oxide surface.

3.3. AES depth profiling

Fig. 3 shows depth profiles of the block sample pretreated in the same way as the powder samples. The surface without any pretreatment shows that the surface is covered by a La rich oxide formed by air oxidation. The $LiOH+H_2O$ treated surface was also analyzed. The result shows the surface oxide with a Li element distribution

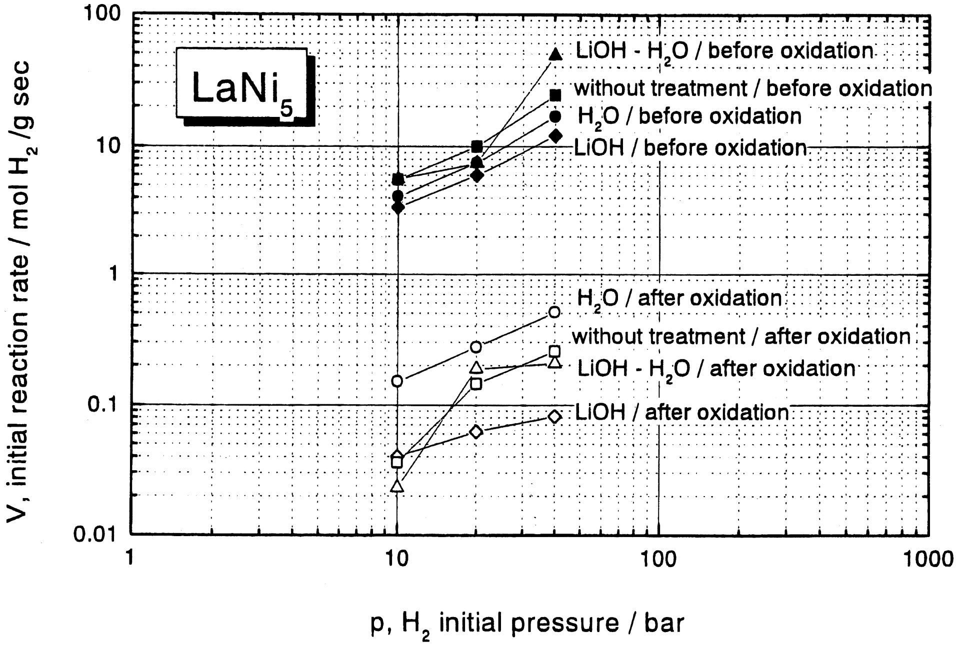

Fig. 2. Pressure dependence of initial reaction rate with and without air oxidation for the sample with different pretreatment.

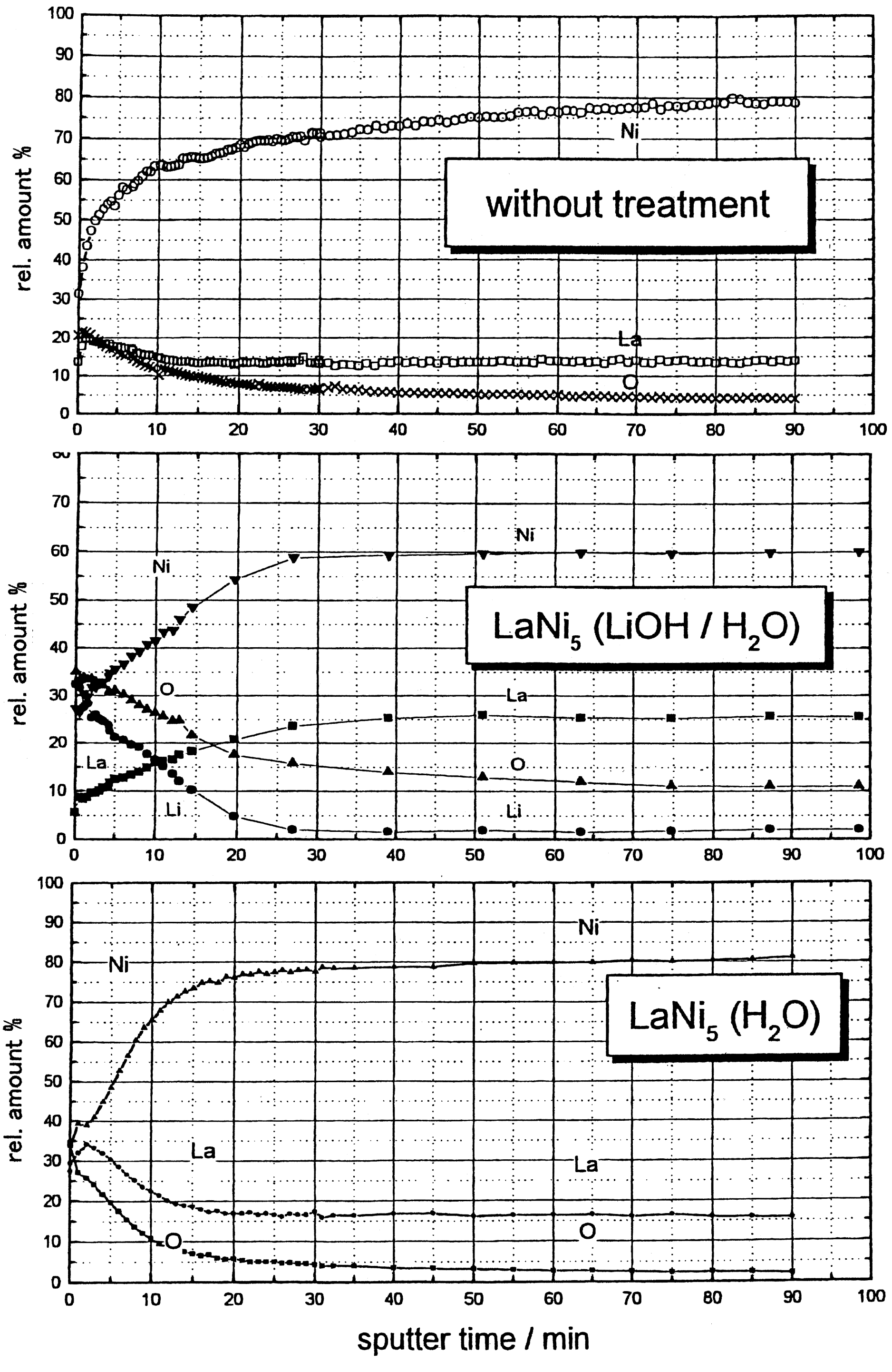

Fig. 3. Elemental depth profiling by AES for block samples, *upper*: without, *middle*: with LiOH+H_2O and *lower*: with H_2O pretreatment.

analogously to the oxygen distribution. A similar alkaline elemental distribution in the surface oxide layer was also observed for the sample pretreated with KOH and NaOH [1,2].

The surface of the sample with only H_2O pretreatment shows a different behavior. On the La rich oxide layer, a small Ni peak was found. In the course of H_2O treatment La may be significantly oxidized and also removed from the surface. The rest Ni forms a thin concentrated layer in subsurface. According to the thermodynamic data [4], oxidized Ni can be easily reduced by H_2 with higher pressure at room temperature. Molecule H_2 may be

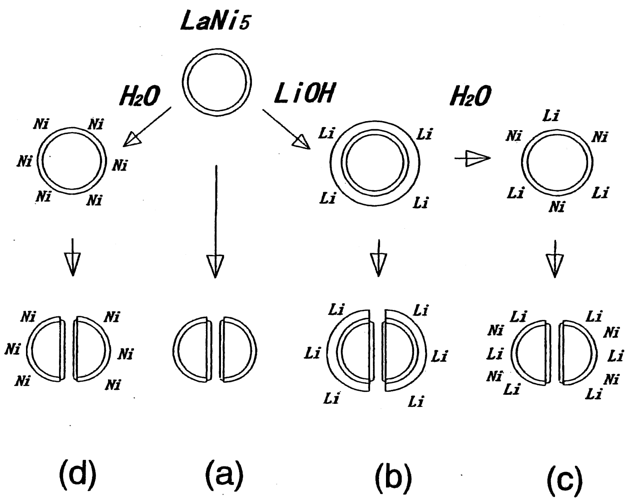

Fig. 4. Suggested reaction mechanisms of the samples with and without pretreatment.

therefore easily dissociated at the concentrated Ni layer, which enables the faster reaction even after the significant oxidation.

3.4. Suggested reaction model

In Fig. 4, the suggested reaction model is presented schematically. The original $LaNi_5$ powder particle is covered with the La rich oxide. After each pretreatment, different layer as analyzed by AES covers the particle surfaces. Through the activation, the pulverization occurs and clean surface is generated by the hydrogenation. However, subsequent oxidation by air the generated clean surface must be deactivated (see Fig. 1a). As shown in Fig. 1b, c, LiOH pretreated surfaces exhibited the activity for the H_2 absorption. This means, the original surface with Li element must be still activated even after significant oxidation.

In this study the importance is that LiOH layer covers the surface pretreated by LiOH (without H_2O) as condensed layer after drying. Dissociative reaction occurs also on this surface. The small degradation of the reaction rate by the oxidation shown in Fig. 1b, c, may be, therefore, attributed also to the decrease the ratio of original surface area to bulk volume yielded by the degradation at the hydrogenation if the result of pulverization is considered.

The effect of alkaline element on a transition metal as a reaction promoter is also reported [5], where the work function of the surface is changed by the alkaline element.

Similar reaction mechanism can be also explained for the surface with Ni rich layer prepared by the H_2O treatment. Metallic Ni, which is yielded by the reduction of NiO by H_2 even after the significant oxidation, can accelerate the dissociation of H_2 [6,7]. In this case, the rate determining step seems to be still dissociation of H_2. This means that the H diffusion is rather faster (Fig. 2).

4. Conclusion

In this paper the effect of LiOH and also the water pretreatment on the H_2 absorption by $LaNi_5$ was demonstrated with several significant oxidation during the sorption cycles. The existence of Li in the surface oxide layer accelerates the H_2 dissociation on the surface. Therefore, under significantly oxidizing condition the powder sample of $LaNi_5$ can more easily react with H_2. Similar effect was also observed for the sample with H_2O pretreatment. The surface was characterized by the enriched Ni layer, which accelerates the H_2 absorption.

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