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Degradation of amorphous MgNi electrode and effect of heat treatment in Ar

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Abstract

The mechanism underlying degradation of an amorphous MgNi electrode was studied. Amorphous MgNi powder was prepared by mechanical alloying, and a charge/discharge cycle test was carried out in 6 M KOH solution. The amount of hydrogen absorbed in the charge process was determined by vacuum hydrogen extraction. The discharge capacity decreased rapidly with progress of the cycle test. The results of the hydrogen extraction indicated that almost all hydrogen absorbed in the charge process was released in the discharge process. X-ray diffraction analyses showed that $Mg(OH)_2$ was formed on the surfaces of MgNi particles after the cycle test. It was deduced that the reduction in the discharge capacity was mainly due to the degradation in absorption capability in the charge process caused by retardation of electron transfer by $Mg(OH)_2$ layer. The cyclic stability of the discharge capacity was improved by heat treatment in Ar at 573 K.

Keywords: Nickel/metal hydride battery; Anode; Magnesium; MgNi; Amorphous; $Mg(OH)_2$

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1. Introduction

It is well known that an anode made of MgNi alloys prepared by ball milling has a larger discharge capacity than conventional AB_5 alloys in the initial stage of charge/discharge cycles [1–19]. The discharge capacity of this type of alloy, however, decreases rapidly with charge/discharge cycles compared with AB_5 alloys [1–19], and extensive studies have been carried out to improve the cyclic stability of the discharge capacity. Iwakura et al. [4,10,16] have reported that improved cyclic stability was obtained by ball milling with graphite. The cyclic stability has been improved also by addition of Al [6,13,18] and Ti [14,17]. Han et al. [17] carried out surface analysis and electrochemical impedance analysis for $Mg_{50}Ni_{50}$ and $Mg_{0.7}Ti_{0.3}Ni_{1.0}$ and reported that Ti retarded the growth of magnesium oxide layer during cycle test and the increase in charge transfer resistance. Cui et al. [15,19] have reported that good cyclic stability was obtained for $Mg_{1.95}Y_{0.05}Ni_{0.92}Al_{0.08}$ ball-milled with fine Ni powder. They also observed that the cyclic stability was strongly dependent on the milling time, and the alloy showing better cyclic stability had lower surface resistance [15,19]. These results indicate that the surface properties of the alloys have a strong influence on the cyclic stability. The role of additive elements, however, has not been fully clarified.

A detailed study of the degradation mechanism for a simple MgNi system is important to clarify the role of additive elements in the improvement. The reduction in the discharge capacity can be caused by retardation of both hydrogen absorption in charge process and desorption in discharge process, and it is necessary to analyze these two effects. This paper describes the degradation of discharge capacity of an amorphous MgNi anode prepared by ball milling and the change in the amount of hydrogen absorbed in charge process with progress of charge/discharge cycles. The mechanism of the degradation is discussed in view of these observations together with results of X-ray diffraction (XRD) analyses.

The present authors have reported in previous papers [20,21] that the surface property of Mg_2Ni was improved by heating in Ar owing to the selective evaporation of Mg resulting in an increase in surface area and in the formation

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of Ni rich phase. Therefore, the cyclic stability of discharge capacity was examined also for an amorphous MgNi powder heated in Ar.

2. Experimental

Amorphous MgNi powder was prepared by mechanical alloying from Mg_2Ni (<200 mesh) and Ni (<7 μm, 99.8% in purity). The mixture of Mg_2Ni and Ni powders (2 g in total) was put into a steel vial (12 cm^3) with 18 steel balls measuring 5.5 mm in diameter under argon atmosphere. The vial was set in a planetary ball mill apparatus (Fritsch P-5), and alloying was carried out at 350 rpm for 80 h. The prepared powder (0.4 g) was compacted into a disk measuring 10 mm in diameter and 1 mm in thickness. The disk was sandwiched between Ni meshes to prepare a sample anode.

A charge/discharge cycle test was carried out at room temperature with a conventional open cell filled with two electrodes and 6 M KOH aqueous solution, where $NiOOH/Ni(OH)_2$ was used as a cathode material. The charge current and time were adjusted to 100 mA/g and 8 h, respectively. After a 5-min rest, the discharge was carried out at 20 mA/g to 1 V in cell voltage. The charge/discharge characteristics were also examined for a sample anode immersed in the KOH solution at room temperature for 100 h prior to the charge/discharge cycle test.

The amount of hydrogen absorbed in the charge process was measured by hydrogen extraction in vacuum at the first, fifth, 14th and 24th cycles. The sample disk was taken out from the cell after the charge process of the designed cycle and installed in a vacuum system. Then the absorbed hydrogen was extracted in vacuum by heating the disk to 673 K. The amount of extracted hydrogen was determined by volumetric method. The absorption amount thus determined was converted to the charge capacity.

The sample powder was analyzed by XRD before the charge/discharge cycle test and after the first, fifth and 24th cycles. In the case of the analysis after the cycle test, the sample disk was taken out from the Ni meshes and pulverized into powder prior to analysis.

The influence of heat treatment in Ar on the cyclic stability was examined as follows. The sample disk was prepared in the above-mentioned procedure and heated in Ar flow at 573 and 648 K for 90 min. The heated disk was sandwiched between Ni meshes and the charge/discharge cycle test was carried out.

3. Results

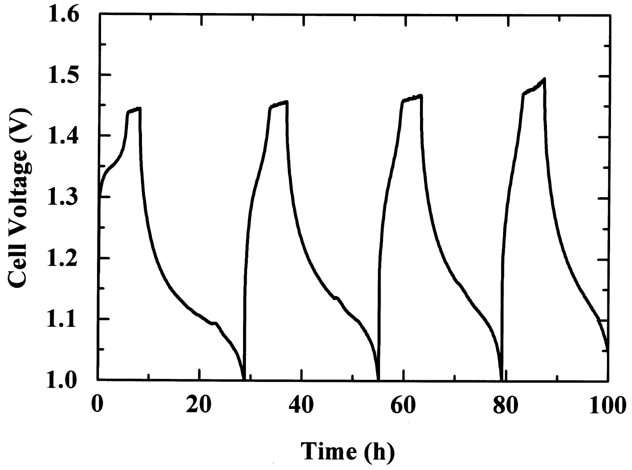

Fig. 1. Changes in charge and discharge curves with cycle number.

Typical examples of charge and discharge curves in the initial stage of the cycle test are shown in Fig. 1. In the charge process of the first cycle, the cell voltage first reached 1.35 V and then increased to 1.43 V at 5 h. Hydrogen gas evolution was marked at the cell voltage above 1.43 V. In the discharge process, it took ca. 20 h to reach to 1 V, i.e. the discharge capacity was ca. 400 mAh/g at the first cycle. The shoulder observed in the charge process at 1.35 V became unclear as the cycle number increased, and the cell voltage rose rapidly to the value above 1.43 V at larger cycle number; the period of time when the cell voltage took the value around 1.35 V was shortened by the progress of the cycle test. In addition, the maximum value of the cell voltage increased with the cycle number. The change in the discharge curves with the cycle number was not as significant as that in the charge curves. The duration of the discharge, however, decreased with increasing cycle number.

Fig. 2 shows the change in the discharge capacity with

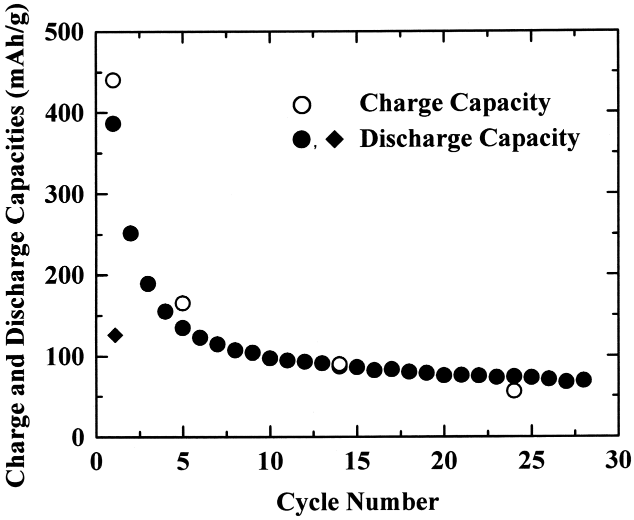

Fig. 2. Comparison between discharge capacity and charge capacity measured by vacuum hydrogen extraction. Solid diamond indicates discharge capacity of sample anode immersed in KOH solution for 100 h before cycle test.

the cycle number together with that in the charge capacity determined by the vacuum hydrogen extraction. The discharge capacity decreased rapidly with increasing cycle number. The values of the charge capacity were very close to those of the discharge capacity. This suggests that almost all hydrogen absorbed in the charge process was released in the discharge process. Namely, the reduction in the discharge capacity with increasing cycle number is due to the degradation in absorption capability in the charge process and not to the degradation in release capability in the discharge process. In the case of the sample anode immersed beforehand in the KOH solution for 100 h, the discharge capacity was 126 mAh/g at the first cycle as shown in this figure. This value is comparable to the discharge capacity at the sixth cycle of the sample anode tested without prior immersion. The sixth cycle began after an elapse of 96 h from the start of the cycle test, i.e. the alkaline immersion time is close to the period of the prior immersion. This indicates that the duration of alkaline immersion has a strong influence on the charge/discharge characteristics of the alloy.

The results of XRD analyses are shown in Fig. 3. Before the charge/discharge cycle test, a broad peak was observed at 41.5° and sharp peaks appeared at 44.5, 51.8 and 76.5°. The position of the broad peak corresponds to that of amorphous MgNi reported by other researchers [1,3,5–8,10–15,17,22]. The sharp peaks can be assigned to Ni remaining in crystalline state. After the first cycle, no significant change was observed in the XRD pattern. After the fifth cycle, new peaks were observed. These peaks can be assigned to $Mg(OH)_2$ and indicate that $Mg(OH)_2$ was formed on the surface of the powder particles during the cycle test. This observation agrees with that of other researchers [3,14,19]. The XRD pattern after the 24th cycle was similar to that after the fifth cycle.

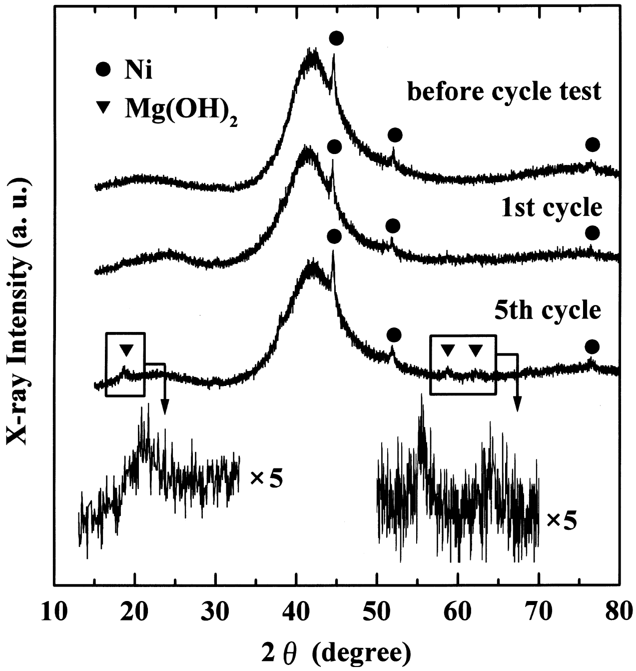

Fig. 3. Results of X-ray diffraction analyses.

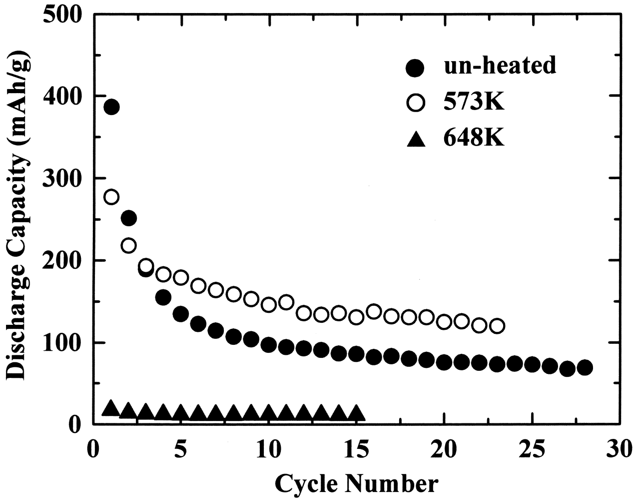

Fig. 4. Influence of heat treatment in Ar on cyclic stability of discharge capacity.

Fig. 4 shows the influence of the heat treatment on the cyclic stability of the discharge capacity. The sample heated at 573 K showed smaller discharge capacity than unheated sample in the initial stage. The discharge capacity of the former, however, decreased slowly compared with that of the latter, and the former showed the larger discharge capacity after four cycles. The sample heated at 648 K showed very small discharge capacity.

4. Discussion

The degradation rate of the MgNi alloy in the charge/discharge cycle test was comparable to that induced by the alkaline immersion under open circuit potential as shown in Fig. 2. This observation suggests that the degradation is mainly caused by modification of the particle surface through the chemical reaction of the sample powder with the KOH solution. Namely, the formation of $Mg(OH)_2$ on the surface of MgNi is one of the dominant mechanisms underlying the degradation. In order to understand the detailed mechanism of the degradation, cyclic voltammograms (CVs) of the amorphous MgNi powder were examined by a micro-paste method [23], in which the sample powder was immersed in the KOH solution for various periods of time prior to the measurements. The diffusion coefficient of hydrogen in the sample was also determined by a potential step method [23]. The immersion caused the shift of the rising part of the reduction current and the oxidation peak in the CVs, and the shift increased with the immersion period. On the other hand, the diffusion coefficient was not significantly dependent on the duration of the immersion. From these results, it can be deduced that the $Mg(OH)_2$ layer retards the electron transfer at the surface of MgNi powder. This is consistent with the observations of Cui et al. [15] and Han et al. [17] that the alloy having lower charge transfer resistance showed better cyclic stability.

Under the present charging conditions, the cell voltage has to increase to keep the charging current constant when the electron transfer is retarded by the formation of $Mg(OH)_2$. This increase in the cell voltage corresponds to the shift from the value around 1.35 V to that above 1.43 V shown in Fig. 1. The reduction in the charge capacity shown in Fig. 2 has strong correlation with the change in the charge curve with the cycle number, i.e. the amount of absorbed hydrogen decreased as the shoulder at 1.35 V became smaller. Furthermore, hydrogen gas was evolved at the cell voltage higher than 1.43 V as mentioned above. These results strongly indicate that hydrogen ingress into the sample takes place at the cell voltage around 1.35 V. At higher cell voltage, the evolution of hydrogen gas predominates over the hydrogen ingress, and hence hydrogen can be scarcely absorbed by the sample. It can be concluded that the degradation of amorphous MgNi electrode was mainly caused by the retardation of electron transfer in the charge process by the $Mg(OH)_2$ layer formed on the particle surface through the chemical reaction between the alloy and the KOH solution.

The improvement of the cyclic stability by heating in Ar at 573 K can be explained as follows. In the previous paper, the surface of an Mg_2Ni sheet was examined with a scanning electron microscope and an energy dispersive X-ray spectrometer after heating in Ar at 823 K for 90 min [21]. Many small pores were formed owing to the selective evaporation of Mg [21]. Results of XRD analyses showed that $MgNi_2$ appeared by heating. A certain amount of Mg should evaporate from the amorphous MgNi during the heat treatment at 573 K for 90 min. The increase in specific surface area brought about by the evaporation could lead to the decrease in the areal current density and in the overvoltage during the charge process. It is also supposed that the growth of $Mg(OH)_2$ is suppressed by the enrichment of Ni at the surface. The cyclic stability could be improved by these two effects. The reduction in the charge capacity in the initial stage can be ascribed to crystallization. Orimo et al. [22] have examined the crystallization of amorphous MgNi heated at 5 K/min and reported that Mg_2Ni appeared at 596 K and $MgNi_2$ at 676 K. It is appropriate to consider that the present amorphous MgNi crystallized in part during the heat treatment at 573 K and the crystallized parts made a very small contribution to the charge and discharge. The crystallization may be completed by heating at 648 K for 90 min, and this could be the reason why the significant decrease in the discharge capacity was observed after the heat treatment at this temperature. The optimization of heat treatment conditions is necessary to obtain better charge/discharge properties.

5. Conclusions

Degradation mechanism was studied for an amorphous MgNi anode. Discharge capacity decreased rapidly with progress of charge/discharge cycle test, in which the degradation rate was comparable to that induced by immersion in KOH solution under open circuit potential. The charge capacity measured by vacuum hydrogen extraction indicated that almost all hydrogen absorbed in the charge process was released in the discharge process. Results of XRD analyses showed that $Mg(OH)_2$ was formed on the anode particles. It was deduced that the reduction in the discharge capacity is mainly due to the degradation in the absorption capability in the charge process caused by the retardation of electron transfer by the $Mg(OH)_2$ layer on the particle surfaces. The cyclic stability of the discharge capacity was improved by heating in Ar at 573 K. This improvement was ascribed to the change in the specific surface area and the surface composition brought about by selective evaporation of Mg.

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