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Electrochemical behavior of amorphous MgNi as negative electrodes in rechargeable Ni–MH batteries

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Abstract

A cyclic voltammogram (CV) of amorphous MgNi clearly showing the hydrogen absorption–emission processes of amorphous MgNi was obtained by using a micropaste electrode technique. The hydrogen absorption was observed as an increase in the cathodic current below −0.9 V vs. Hg/HgO, and the emission as a broad anodic peak at ~−0.9 V. These processes were considerably affected by immersion of the electrode in a KOH solution prior to measurements. The rising part of the cathodic current shifted to the cathodic direction depending on the immersion time. A decrease in the anode peak current and a remarkable shift of the anode peak potential were also observed. Using X-ray diffraction analyses, the deterioration of such electrode properties was attributed to formation of $Mg(OH)_2$ by the alkaline immersion. Potential step measurements gave an apparent diffusion constant (D_{app}) of the hydrogen in the material of $6.8–9.4\times10^{-10}$ cm^2/s, irrespective of the immersion time. These results show that the $Mg(OH)_2$ formed has almost no effect on the diffusion of hydrogen but disturbs electron transfer processes on the electrode surface. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rechargeable hydrogen batteries; Micropaste electrode technique; Amorphous MgNi; $Mg(OH)_2$

1. Introduction

Recently, much interest has been evoked in Ni–MH secondary batteries for their possible applications to portable equipment and transportation media (e.g. hybrid automobiles). Although Ni–MH secondary batteries using $LaNi_5$ alloys have already been marketed, there arises a demand to develop hydrogen secondary batteries having far higher capacity than that of commercially available secondary batteries. Lei et al. have reported that an MgNi alloy prepared by ball-milling can charge–discharge in a secondary battery system at room temperature [1]. This report has opened up new possibilities of Mg-based alloys as electrode materials for next-generation hydrogen secondary batteries [2]. Recently, Kohno and Manda [3] and Nohara et al. [4] have reported that amorphous MgNi prepared by ball-milling of Mg_2Ni and Ni powders exhibits a high discharge capacity (750–1080 mAh/g). However, they also reported that the electrode properties rapidly deteriorate with an increase in charge–discharge cycles [3,4]. Although it has been recently reported that the deterioration is ascribed to $Mg(OH)_2$ formation during charge–discharge cycles [5], it is not clear which reaction process (e.g. electrode reaction or diffusion) was inhibited by the $Mg(OH)_2$ formed. The role of $Mg(OH)_2$ in the capacity deterioration must be elucidated to improve MgNi alloys as a potential electrode material for hydrogen secondary batteries.

Battery performance has conventionally been estimated using charge–discharge test cells with a two-electrode system. However, this conventional method provides us with only summed-up information on the anode and cathode, making is impossible to determine the electrochemical characteristics of the individual electrodes. Recent studies have shown that the electrochemical characteristics of individual electrode materials can be evaluated by using a thin film technique [6,7] or a microelectrode technique [8]. However, these techniques require special equipment and/or knowhow. Recently, we have succeeded in developing a simple electrochemical method called a micropaste electrode technique. This technique can easily evaluate the characteristics of a powdery electrode material, and the characteristics of an intercalation–deintercalation reaction of Li^+ doped in a carbon material were successfully evaluated by using this technique [9].

In this study, the electrochemical behavior of hydrogen absorption–emission from an amorphous MgNi electrode was investigated by using the micropaste electrode technique. The role of $Mg(OH)_2$, which appears to be a cause

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of capacity deterioration, was also examined from the viewpoint of both electrochemical and diffusion kinetics.

2. Experimental

Amorphous MgNi was prepared by ball-milling a mixture of Mg_2Ni (Japan Metals and Chemicals) and Ni powders by using a high-energy ball-mill (Fritsch, pluerisette 5). The powders were first mixed at a ratio of 1:1 (mol%) in a mortar for several minutes, and then the mixture was ball-milled at 350 rpm for 80 h under an Ar atmosphere. The resultant sample powder was confirmed to be amorphous by its characteristic diffraction pattern showing a weak broad peak centered around $2\theta = 40°$. It was mixed with copper powder at the ratio of amorphous MgNi to Cu = 1:2 wt.% and a binder (polytetrafluoroethylene (PTFE), 2–10 wt.%) to form the sample for the micropaste electrode.

Detailed procedures to prepare the micropaste electrode have been described elsewhere [8]. In brief, a tungsten metal bar with a diameter of 1 mm was glass-sealed and a cross-section of the sealed bar was polished to a mirror-surface. A concave hole was electrochemically formed by etching tungsten exposed on the polished cross section. The depth of the concave (*d* value) was controlled to be 10–30 μm by changing the etching time. A working electrode was made by packing the prepared sample powder into the concave portion. The sample fixed onto the electrode was extremely scanty in amount, however, its weight could not be measured. Electrochemical measurements were carried out in a 6 M KOH aqueous solution using a three-electrode system with a Pt counter and a Hg/HgO reference electrodes under potential control conditions (EG&G, potentiostat model 263A).

3. Results and discussion

Fig. 1 shows cyclic voltammogram (CV) of the amorphous MgNi measured by using the micropaste technique. The scan rate of the electrode potential was 1 mV/s and the *d* value of the electrode used here was 30 μm. When the potential was scanned from −0.3 V vs. Hg/HgO to the cathodic direction, the cathodic current started to increase at ~ −0.9 V. This increase in the current is attributed to the hydrogen absorption reaction shown in Eq. (1)

$$\text{Emission MgNi} + H_2O + e^- \underset{\text{Emission}}{\overset{\text{Absorption}}{\rightleftarrows}} \text{MgNi–H} + OH^- \tag{1}$$

On the other hand, on reversing potential scan from −1.3 V to the anodic direction, a broad peak was observed at ~ −0.9 V. Since this peak was hardly observed when the potential was reversed from −1.0 V, the observed peak is ascribed to the emission reaction of the hydrogen absorbed in the amorphous MgNi (shown in Eq. (1)). Though the CV (scan rate: 1 mV/s) was measured by using the samples changing the ratio of the binder mixed to 2–10 wt.%, the shape of the CV did not change. In addition, when CV measurement of the amorphous MgNi was also performed at the scan rate 5 mV/s, only potential shift attributed to iR was slightly observed. It should be noted that the cathodic current observed was the sum of the currents consumed in the hydrogen absorption and the hydrogen evolution reactions, because the ratio of integrated value (coulombic charge) of the anodic peak at ~ −0.9 V to that of the cathodic current observed from −0.9 to −1.3 V was ~0.83.

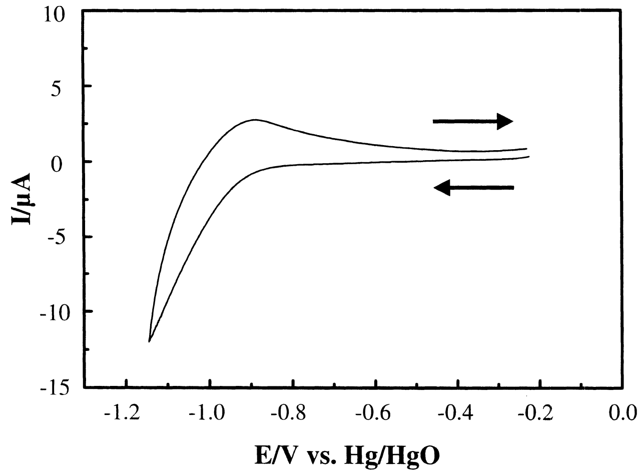

Fig. 1. CV of amorphous MgNi using the micropaste electrode technique.

Recently, the authors have found that simple immersion of the amorphous MgNi in an alkaline solution causes $Mg(OH)_2$ formation on the material surface, resulting in a reduction of discharge capacity [10]. Namely, the decrease in discharge capacity with increasing charge–discharge cycles depends on the duration of alkaline immersion time and is not controlled by electrochemical reactions during charge–discharge cycles. To confirm this evidence more clearly and to understand roles of $Mg(OH)_2$, CV measurements were carried out for the samples immersed in a 6 M KOH solution for 0, 30, 80 and 120 h (Fig. 2). A sample without the immersion gave the same CV as that shown in Fig. 1, indicating that the micropaste technique is a reproducible method. Regarding the immersed samples, the rising part of the cathodic current shifted to the cathodic direction in comparison with that of the sample not immersed. For example, the potentials obtained at −10 μA were −1.11 (0 h), −1.18 (30 h), −1.21 (80 h) and −1.22 V (120 h) vs. Hg/HgO, showing that the potential shift became greater with the immersion time. This indicates that the overvoltage for hydrogen absorption reaction increases with increasing the immersion time. Growth of $Mg(OH)_2$ was confirmed for all of the immersed samples by XRD measurements. However, the quantitative relation-

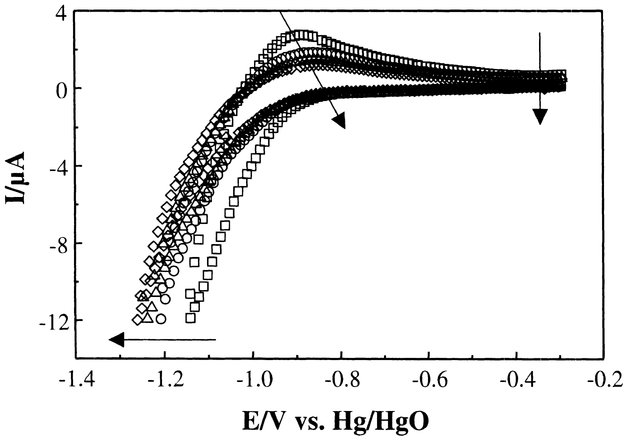

Fig. 2. CVs of MgNi samples immersed in a 6 N KOH solution for various times. Immersion time: 0 h (□), 30 h (○), 80 h (△) and 120 h (◇).

ship between the amount of $Mg(OH)_2$ and the immersion time is not clear at present.

As for the anode peak caused by the hydrogen emission reaction observed at ~ −0.9 V, the peak current decreased with the alkaline immersion from 2.3 (immersion time: 0 h) to 0.6 μA (120 h), and the corresponding coulombic charge also decreased from 0.6 (0 h) to 0.24 mC (120 h). This implies that the amount of hydrogen absorbed by the cathode reaction decreased as the immersion time increased. However, the amounts of coulombic charge consumed in the cathode reaction were almost the same irrespective of the immersion time, indicating that the fraction of the current consumed for hydrogen evolution in the cathodic current increased with the immersion time. Furthermore, the peak potential shifted to the anodic direction with immersion time. This suggests that the rate of electron transfer in the emission reaction is lower in the samples immersed for a long time. These observations indicate that the overvoltages of hydrogen absorption and emission increased by the formation of $Mg(OH)_2$. Namely, $Mg(OH)_2$ plays a role which causes the hydrogen evolution reaction to be greater in the cathodic current.

As to the reduction in the background current observed from −0.3 to −0.4 V, possible causes are a decrease in the effective electrode surface area owing to the segregation of the powdered MgNi and/or a reduction of the static capacitance of the electrode interface resulting from the formation of $Mg(OH)_2$.

The apparent diffusion constant (D_{app}) of the hydrogen in the amorphous MgNi was examined using the potential-step method. The current response of an MgNi sample not immersed in a KOH solution is shown in Fig. 3(a). In this series of measurements, the d value of the electrode was 10 μm and the electrode potential was stepped from −1.1 to −0.3 V vs. Hg/HgO. A large current accompanying a double-layer charging and hydrogen emission was observed in the initial period, and subsequently the current gradually declined to nearly zero. The relational expression of current (I) and D_{app} during the potential step experiment for a thin film electrode is described in Eq. (2) [11]

$$\ln I = \ln(2nFAD_{app}\Delta C/d) - (\pi^2 D_{app} t)/4d^2 \qquad (2)$$

where d is the film thickness (that is, the depth of the concave portion in this experiment), A is the surface area of the electrode and ΔC is the variation of the hydrogen concentration in the film during the potential step. Fig. 3(b) shows the plot of ln I vs. time t, according to Eq. (2). A linear relation between ln I and time t was obtained in the range 430–820 s, and the apparent diffusion coefficient, D_{app}, was estimated from the slope to be 7.68×10^{-10} cm^2/s. This value was almost one or two orders of magnitude smaller than the value of D_{app} of $LaNi_5$ [12,13].

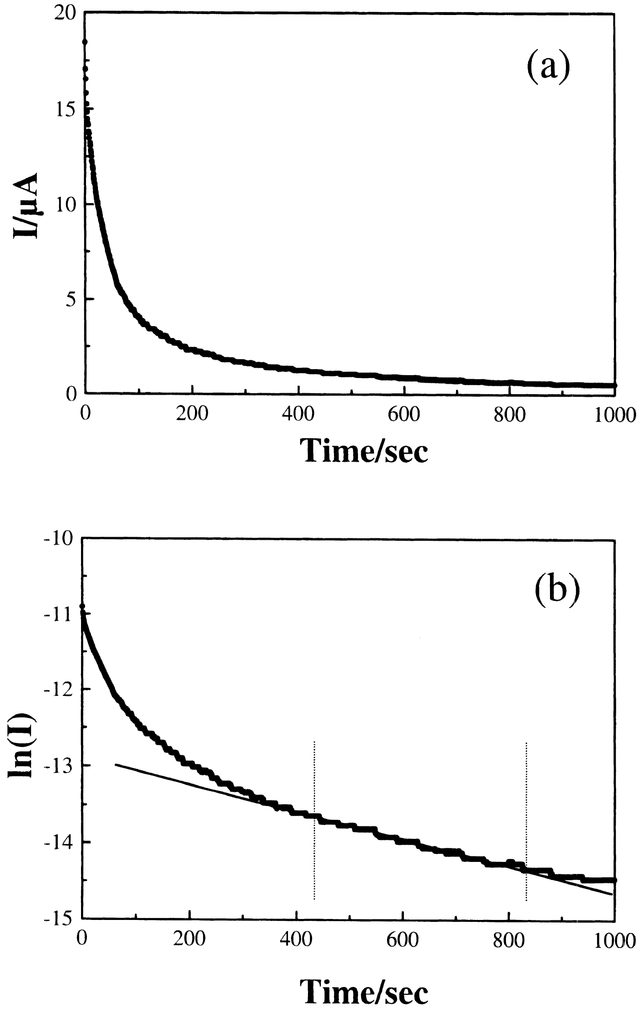

Fig. 3. (a) Current response of the micropaste electrode using the potential step method. (b) Relationship between ln I and measurement time (t).

Fig. 4 shows the values of D_{app} evaluated similarly for the samples immersed for 0, 30, 80, 120 and 200 h. Except for the sample immersed for 200 h, measurements were repeated 2 or 3 times and the values obtained have been

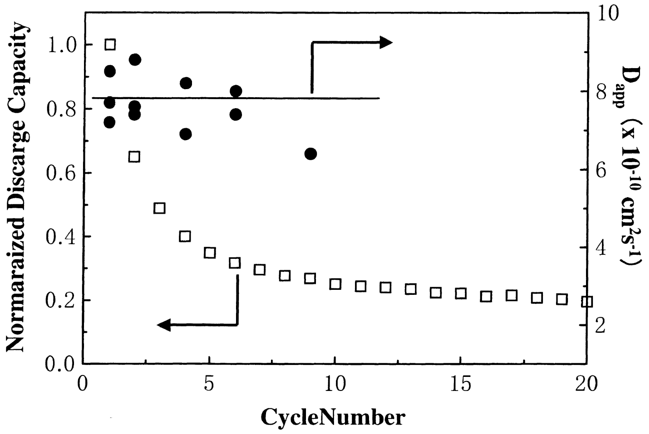

Fig. 4. Relationship between the normalized discharge capacity (□) and the apparent diffusion constant of hydrogen (●).

plotted in this figure. The immersion times of the samples have corresponded to cycle numbers of the charge–discharge test (e.g. the charge–discharge test of five cycles was taken for ~120 h in our experiment) and the discharge capacities of the individual cycles were normalized to the discharge capacity (430 mAh/g) at the 1st cycle. The charge–discharge cycle test was carried out by using a conventional two-electrode cell. The details will appear in a separate paper [10]. Fig. 4 shows that the discharge capacity was drastically decreased from 1 to 0.4 until 5th cycle, followed by gradual further decreased. This phenomenon is almost in agreement with the capacity deterioration behavior previously reported [3,4,10]. On the other hand, the D_{app} values determined here were 6.8–9.4$\times 10^{-10}$cm^2/s, being almost constant irrespective of the alkaline immersion time. These results clearly indicate that $Mg(OH)_2$ formed does not disturb the diffusion process of hydrogen.

4. Conclusions

The electrochemical behavior of hydrogen absorption–emission over amorphous MgNi was investigated using the micropaste electrode method. The cause of the capacity deterioration of MgNi was also examined for MgNi samples immersed in a KOH solution by the CV and potential-step methods. The results clearly showed that the $Mg(OH)_2$ formed on the electrode surface does not affect the diffusion process but affects the electron transfer process. In other words, the capacity deterioration is caused by the hydrogen generation reaction on the electrode interface becoming more predominant than the absorption reaction. Improvement of the capacity deterioration of amorphous MgNi by modification of the electrochemical catalyst (e.g. Mg, Ni) [14,15] seems to coincide with the results obtained in the present study.

Problems in the micropaste electrode technique were also clarified in the present research. In the case of amorphous MgNi, disconnection of the sample from the concave portion of the electrode occasionally occurs owing to hydrogen evolution reaction. From now on, further improvement in the stability of the micropaste electrode is intended for detailed investigation of the electrochemical characteristics of other candidate alloys for hydrogen batteries.

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