Microvoltammetric Study of Electrochemical Hydrogenation of a Surface-Treated Mg_2Ni Alloy Single Particle

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The effects of surface treatments on the hydrogen storage properties of a Mg_2Ni alloy particle were investigated by the microvoltammetric technique, in which a carbon-filament microelectrode was manipulated to make electrical contact with the particle placed in a KOH aqueous solution. It was found that the hydrogen storage properties of Mg_2Ni at room temperature were improved by the surface treatments with a nickel plating solution. The sodium salts (sodium phosphinate and sodium dihydrogen citrate) contained in the nickel plating solution made the alloy form an amorphous-like state, resulting in an improved hydrogen absorption/desorption capacity at room temperature as high as about 150 mA h g^{-1} from the original value of 17 mA h g^{-1}.

Recently, consumer demand for rechargeable batteries has rapidly increased for portable devices such as cellular phones, lap-top computers, camcorders, and other personal electronic devices.[1] Nickel–metal hydride batteries have attracted much attention for these electronic applications because they have several advantages such as high energy density and environmentally acceptable components as compared with the conventional nickel–cadmium and lead–acid batteries. However, higher performance of nickel–metal hydride batteries is required to meet the demand for new battery markets such as emission-free vehicles.[2]

Mg_2Ni alloy has merits for the improvement of the negative electrode capacity in nickel-metal hydride batteries. Especially, it is theoretically known that Mg_2Ni can absorb up to 3.6 wt% hydrogen to give Mg_2NiH_4, the value being large as compared with 1.4 wt% of $LaNi_5H_6$ and 1.9 wt% of $TiFeH_{1.9}$.[3] However, Mg_2Ni alloy is not readily available at room temperature because the reaction of hydrogenation for Mg_2Ni alloy requires a high temperature of 200—300 °C at even 0.1 MPa.[4,5] Numerous studies have been done to improve kinetic characteristics of Mg_2Ni alloy, while most of them were for the gas phase reaction. A few electrochemical investigations have also been tried with approaches summarized as follows: (i) surface modification with metal coating;[6] (ii) elemental substitutions and composite formation;[7,8] and (iii) mechanical alloying and grinding.[9] Recently, Iwakura et al.[10] greatly improved the electrochemical properties of Mg_2Ni alloy by mechanical grinding, which had a discharge capacity as high as about 1000 mA h g^{-1} at room temperature.

In this study, to improve charge/discharge properties of Mg_2Ni alloys at room temperature, a surface treatment with nickel plating solution containing sodium salts (sodium phosphinate and sodium dihydrogen citrate) as reducing agents was applied, and electrochemical measurements were done by a microelectrode technique focusing on a single alloy particle.[11] A carbon fiber microelectrode was manipulated to make electrical contact with the particle placed in an electrolyte solution, and the electrochemical behavior of active material itself was evaluated without any dilution by a binder and a conductive assistant. The surface-treated Mg_2Ni alloy showed a marked improvement in its charge/discharge capacity at room temperature.

Experimental

Mg_2Ni alloy particles of 1 mm in diameter (JMC Japan) were mechanically pulverized to be 100–250 μm particles. We applied three kinds of surface treatments as listed in Table 1. Treatment with HCl aqueous solution (sample A) was done for all samples as a treatment to remove the surface oxide layers of MgO or $Mg(OH)_2$. This sample A was further treated with Ni-plating solution for 15 min (sample B), or with a sodium salt solution (sample C). The sodium salt solution consisted of just a reducing agent used in the Ni-plating solution. The detailed treatment conditions (solution pH and treatment time) are also contained in Table 1.

The surface morphology of Mg_2Ni alloy particles was studied by SEM (JSM, 5310LL). Specific surface area was measured by the BET method (Shimadzu, ASAP2010). Alloy phase structure was analyzed by X-ray diffractometer (Shimadzu, XD-D1) with Cu $K\alpha$ radiation.

The electrochemical apparatus was designed to permit measurements for a single particle, as illustrated in Fig. 1. A carbon fiber (10 μm, diameter) was coated with a thin film of Teflon (Cytop, Aashi Glass) to minimize the background current, and was then cut to give a microdisk electrode. The prepared microelectrode was held with a X–Y–Z micropositioner and was brought into contact with a single particle of the alloy placed in a KOH aqueous solution by handling the positioner under a stereomicroscope. A Pt coil and Hg/HgO were used as the counter and reference electrode, respectively. The size of alloy particles was previously selected

Table 1. Surface Treatment Condition for Mg_2Ni Alloys.

Sample type	Solution	pH	Temperature	Time
A	0.05 M HCl	—	25 °C	3—5 min
B	$NiSO_4$ (30 g dm^{-3}) $NaPH_2O_2$ (10 g dm^{-3}) $NaH_2C_6H_5O_7$ (10 g dm^{-3})	10—12	50—60 °C	15 min
C	$NaPH_2O_2$ (10 g dm^{-3}) $NaH_2C_6H_5O_7$ (10 g dm^{-3})	10—12	50—60 °C	15 min

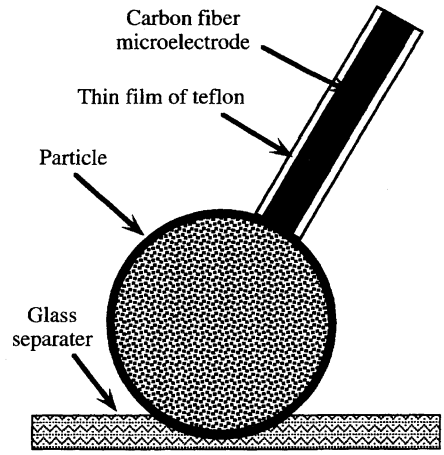

Fig. 1. Schematics of a single particle and microelectrode for microvoltammetry.

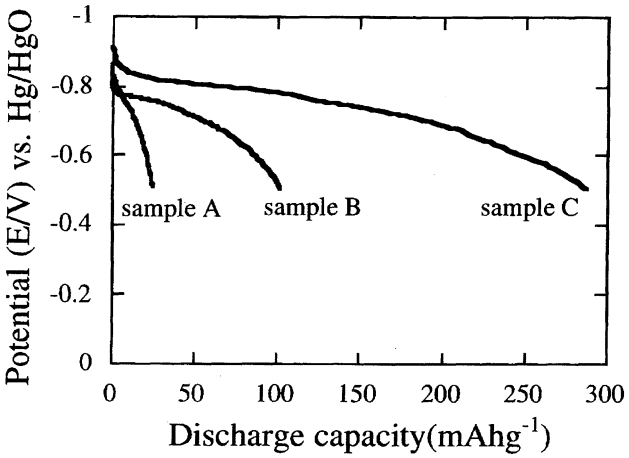

Fig. 2. The effect of surface treatments on the discharge behavior of Mg_2Ni alloy particle in 5 M KOH solution at room temperature.

by using sieves, and the precise dimension of the targeted particle (typically, 150 μm diameter) was reconfirmed by an optical image with a micrometer eyepiece. The weight of a single particle (typically, 10 μg) was measured by a micro-balance (Mettler, MT5) before electrochemical measurements.

Cyclic voltammetry and galvanostatic charge-discharge experiments were done with a potentiostat-galvanostat (Hokuto Denko, HAB-501) coupled with an *x*–*y* recorder (Graphtec model WX1000) and *y*–*t* recorder (Graphtec servocorder SR6211) to record current responses. The charge-discharge current density was set at 100 mA g^{-1} for all samples. All experiments were done at room temperature in a nitrogen atmosphere.

Results and Discussion

1) Chemical Hydrogenation during Surface Treatments. Figure 2 shows the effects of surface treatments on the electrochemical discharge behavior of Mg_2Ni alloy particles at room temperature. These data were obtained after the chemical treatments listed in Table 1 without any additional charging by electrochemical means. The observed electrochemical discharge capacity of samples A, B, and C were 25 mA h g^{-1} ($Mg_2NiH_{0.1}$), 101 mA h g^{-1} ($Mg_2NiH_{0.4}$), and 290 mA h g^{-1} ($Mg_2NiH_{1.2}$), respectively. Particularly, sample C showed about 11 times larger discharge capacity than that of sample A.

The effects of surface treatments on the alloy phase structure were studied by XRD spectroscopy. As shown in Fig. 3, the XRD peaks for Mg_2Ni alloy phase were found to be drastically weakened by surface treatments. This indicates that

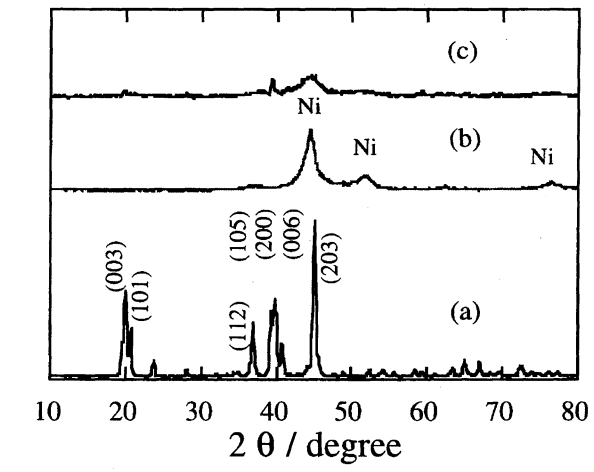

Fig. 3. XRD patterns for Mg_2Ni alloy particles of (a) sample A, (b) sample B, and (c) sample C.

the phase structure of the chemically treated Mg_2Ni alloy was transformed to an amorphous-like state, but the details of the chemistry causing the phase transformation are not clear.

It is well known that there are three types of dimagnesium nickel hydrides; $Mg_2NiH_{0.3}$, Mg_2NiH, and Mg_2NiH_4 denoted as α-, β-, γ-hydride.[12—14] The phase of Mg_2NiH is considered to be an intermediate between $Mg_2NiH_{0.3}$ and Mg_2NiH_4.[15] The theoretical capacities of these compounds are given as 75 mA h g^{-1} for $Mg_2NiH_{0.3}$, 250 mA h g^{-1} for

Mg_2NiH, and 1000 mA h g^{-1} for Mg_2NiH_4.[16] It was also reported that the value of the total hydrogen content in Mg_2Ni alloy is reasonably explained by taking into account the hydrogen contents in the following two regions; the intra-grain region of crystalline Mg_2Ni, and the amorphous Mg_2Ni at the inter-grain amorphous region.[17] The maximum hydrogen contents (Mg_2NiH_4) might correspond to hydrogenation at the inter-grain amorphous region[18] and it is also reported that the amorphous region is first hydrogenated by the solid solution state, expands and so puts the encased grains in metal hydride.[19,20]

Considering together our experimental results with the reported information, the hydrogenation mechanism of Mg_2Ni alloy particles during the surface treatment can be discussed as below. The reducing agent of sodium phosphinate produces a proton and electron at the alloy surface by the catalytic effect of the Ni atoms of the Mg_2Ni alloy, as documented for the electroless nickel plating process.[21] The produced electron is used for production of hydrogen atom in the absence of Ni^{2+} ion in solution. The resulting hydrogen atom inserts into the body of the alloy particle, probably through the amorphous inter-grain with forming of the maximum hydrogen composition, Mg_2NiH_4. However, the total hydrogen content of Mg_2Ni alloy treated by sodium salt solution (sample C) was about 30% ($Mg_2NiH_{1.2}$) of that of Mg_2NiH_4, indicating that the treated Mg_2Ni alloy was not fully amorphous as shown in its XRD pattern, which still have small peaks for Mg_2Ni crystalline phase.

2) Electrochemical Charge/Discharge Properties. Figure 4 shows cyclic voltammograms at scan rate of 3 mV s^{-1} for the sample particles of A, B, and C type in 1 M KOH aqueous solution (1 M = 1 mol dm^{-3}). The anodic current peak of hydrogen oxidation was observed at around −0.78 V vs. Hg/HgO for all samples, indicating the possible charge/discharge by electrochemical means. The sample C particle was found to have a higher oxidation charge than that of the sample A and B, suggesting that the electrochemical hydrogen absorption/desorption was also improved by surface treatments. The change in crystal structure recognized in XRD spectra (Fig. 3) would be one of the origins of the high electrochemical activity of sample C. In addition, a nickel-rich surface layer may be formed by our reductive treatment. It has been point out that nickel has the ability to catalyze the electrochemical hydrogen absorption and desorption.[10,22–26]

Figure 5 shows the charge and discharge behavior of Mg_2Ni alloy particles measured in 5 M KOH aqueous solution at a constant current density of 100 mA g^{-1}. The electrochemical hydrogen charging process for Mg_2Ni alloy in alkaline solution is initiated by the particle–electrolyte interface reaction,

$$H_2O + Mg_2Ni + e^- \Leftrightarrow Mg_2NiH_{ad} + OH^- \quad (1)$$

followed by diffusion of the adsorbed hydrogen into the bulk of alloy. During the 80 min of charging, a potential plateau is observed at around −1.0 V, corresponding to a hydrogen

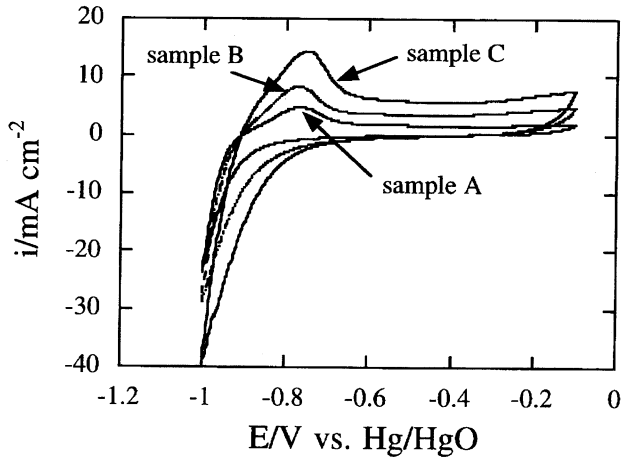

Fig. 4. Cyclic voltammograms for the treated Mg_2Ni alloy particles at 3 mV s^{-1} (1st cycle) in 1 M KOH solution at room temperature.

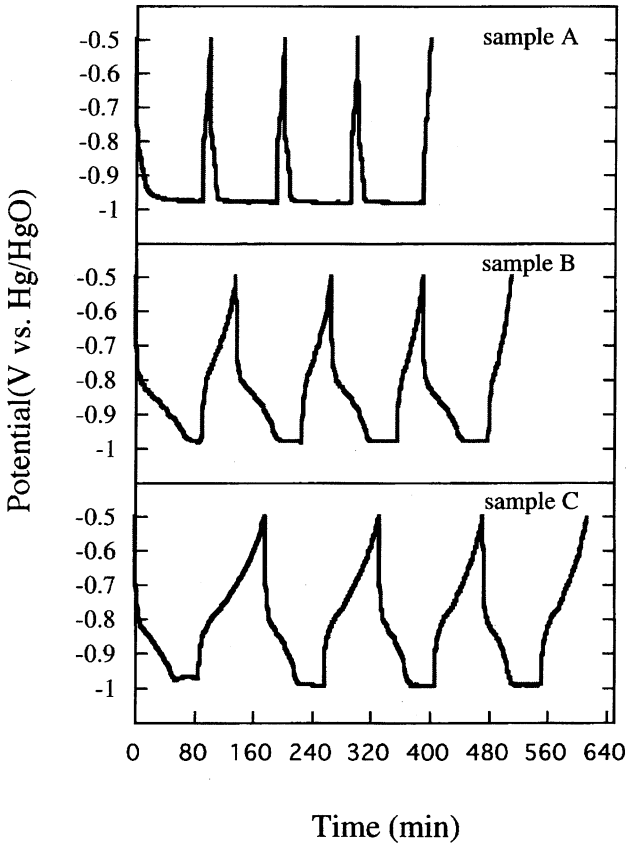

Fig. 5. Charge and discharge behavior of the surface-treated Mg_2Ni alloy particles for a successive cycles in 5 M KOH solution at room temperature.

evolution called overcharging. The discharge capacities of 1st cycle obtained with the cut-off voltage of −0.5 V were 17 mA h g^{-1} for sample A, 77 mA h g^{-1} for sample B, and 150 mA h g^{-1} for sample C. The surface porosity should be changed by surface treatment and contributes to the capacity improvement. However, the BET surface area for sample C was just 1.3 times larger than that of the sample A particle, indicating thus that the marked effect of surface treatment on

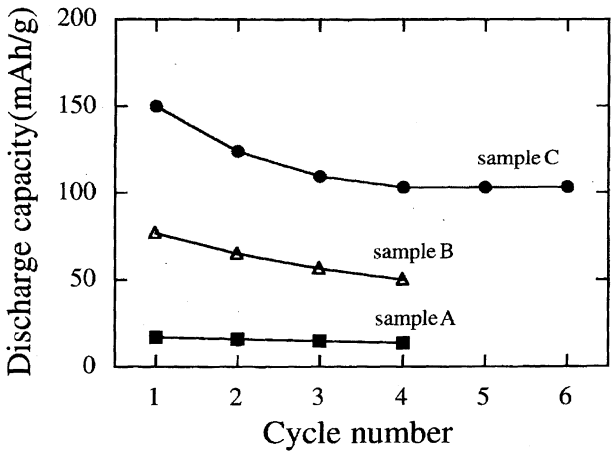

Fig. 6. Discharge capacity of the surface-treated Mg_2Ni alloy particles as a function of cycle number in 5 M KOH solution.

discharge capacity can be ascribed chiefly to the structural change of alloy crystal and/or the formation of a nickel-rich surface layer.

Figure 6 shows the change of discharge capacity with the cycle number of electrochemical charge/discharge shown in Fig. 5. For the first few cycles, the capacity decay of the sample C particle proceeds more rapidly than the case of the A and B sample particles. However, the discharge capacity of C type sample reached a stable value of 103 mA h g^{-1} during 4 cycle, which is more than 7 times of the capacity of sample A. The chemically induced hydrogen (about 290 mA h g^{-1} in Fig. 2) for the sample C particle was decreased to about 150 mA h g^{-1} (at the 1st cycle) for the electrochemical charge–discharge method. The chemical and electrochemical hydrogen charging are essentially different processes, and the difference in temperature would emphasize the deviation. The chemical charging (surface treatment) was done at a temperature of 50—60 °C, while all of the electrochemical experiments were done at room temperature. A higher temperature increases the equilibrium hydrogen pressure,[19] resulting in smoother hydrogen absorption. Iwakura et al.[27] reported that the electrochemical discharge capacity of Mg_2Ni alloy was increased by elevating the temperature.

Conclusion

The effects of surface treatments on the hydrogen storage properties of Mg_2Ni alloy were evaluated by single-particle measurement achieved by the use of a microelectrode. This technique gives information about the alloy itself without any dilution with additives such as organic binder. While the nickel-plating improved the charge/discharge capacity of Mg_2Ni alloy to some extent, the reducing agent in the plating solution was found to dramatically increase the capacity at room temperature.

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