Surface Modification of MgNi by Perylene

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Amorphous MgNi was modified by ball milling with perylene and its effects on the charge/discharge capacity were examined by using a conventional two-electrode cell. It was found that both the ball milling time and perylene/MgNi ratio had great influence on the discharge capacity and cycle life of MgNi. Three types of effects were identified, depending on ball-milling conditions. One of them was the increase in the discharge capacity at the first cycle, the second type was the deceleration of the degradation of the discharge capacity with charge/discharge cycle, and the last type was the reduction in the charge/discharge capacity. Chemical states of modified surfaces were analyzed by Auger electron spectroscopy (AES) as well as ab-initio calculation. Both AES and ab-initio calculations indicated that carbon atoms can form bonding with both magnesium and nickel atoms, but bonding with magnesium atoms is most preferable. The change in the charge/discharge capacity is attributed to such kind of reactions, and the three distinct effects are ascribed to the presence of different MgNi-perylene composites, formed during the ball milling on the surface, resulting in the retardation or acceleration of Mg(OH)$_2$ formation on the electrode.

(Received May 20, 2002; Accepted July 16, 2002)

Keywords: magnesium, nickel, aromatic compound, surface modification, battery, electrode

1. Introduction

Properties of amorphous MgNi alloys have been extensively studied because of their high potential as anode material of rechargeable Ni/MH batteries. However, owing to the formation of Mg(OH)$_2$ during charge/discharge cycles, the discharge capacity decreases rapidly with the cycles. The cycle life of amorphous MgNi is considerably shorter than other hydrogen storage materials such as AB$_5$ and AB$_2$ type alloys. The present authors have found that the formation of Mg(OH)$_2$ is not necessarily due to charge/discharge cycles, but it is simply formed by chemical reactions with electrolyte solution. In addition, the degradation of charge/discharge properties is attributed to retardation of electron-transfer reactions by Mg(OH)$_2$ resulting in the reduction of hydrogen absorption by the electrode. All hydrogen absorbed could be released from MgNi under conventional discharge conditions. The diffusion of hydrogen in MgNi-powder was not the rate control step for discharge and the diffusion constant of hydrogen in MgNi did not change with the charge-discharge cycles. These results suggest that the properties of MgNi can be improved by surface modification if the formation of Mg(OH)$_2$ can be inhibited.

Iwakura et al. reported that ball milling MgNi with graphite for short time increased the discharge capacity and cycle life of MgNi effectively. This improvement was ascribed to the formation of some compounds by carbon and MgNi, which enhanced the hydrogen absorption ability. The present authors have reported that similar enhancement was observed by vacuum evaporation of carbon.

These results indicate that carbon in various crystal structures have capabilities to improve the electrochemical properties of MgNi. The influence of aromatic compounds and other carbon containing materials, however, has not been studied, although it has been reported that the hydrogen absorption of Mg-graphite composites prepared by mechanical grinding was strongly affected by the presence of benzene, cyclohexane and tetrahydrofuran during grinding. The present authors have started a systematic study on electrochemical characteristics of MgNi modified by aromatic compounds such as benzene (C$_6$H$_6$), phenanthrene (C$_{14}$H$_{10}$), naphtacene (C$_{18}$H$_{12}$), perylene (C$_{20}$H$_{12}$) and corannulene (C$_{20}$H$_8$). These compounds gave qualitatively similar results, while MgNi modified by perylene showed better characteristics than others. Therefore, this paper describes the effects of MgNi modification by perylene on the electrode properties and discusses plausible mechanisms of the effects of surface modification of MgNi on the charge/discharge properties.

2. Experimental

Mg$_2$Ni (below 200 mesh) and Ni (about 3–7 μm) powders were mixed at molar ratio of 1:1. Two grams of the mixture powder were put into a chromium steel vessel of 12 cm$^3$ together with eighteen balls of chromium steel (5.5 mm diameter) in argon atmosphere by using a glove box. A planetary ball mill apparatus (Fritsch P5) was used to grind mechanically the mixture powder at a rotation speed of 350 rpm. After 80 h of ball milling, the MgNi powder was taken out from the vessel and kept in argon.

The prepared MgNi powder was mixed with perylene (C$_{20}$H$_{12}$) under argon atmosphere; the content of perylene was 0.2, 1, 2 and 10 mass%. Each MgNi-perylene mixture, 1 g in total mass, was ball-milled under the above-mentioned conditions for 1, 4 and 10 h.

Each of ball-milled MgNi-perylene powder, as well as MgNi powder, was mixed with electrolytic copper powder (2–3 μm) in a mass ratio of 1:3, and 1 g of such mixture was compressed at 590 MPa for 10 min into a disc with 10 mm in diameter in argon. The disc was sandwiched in two nickel meshes and fixed by spot-welding. The charge-discharge curves were measured in 6 M KOH solution controlled at 25°C by water bath. Two-electrode system was used, where the sandwiched sample disc acted as the negative electrode and sintered Ni(OH)$_2$/NiOOH the counter electrode. For each charge-discharge cycle, the sample was charged at 100 mA g$^{-1}$ for 10 h, rested for 5 min, and then discharged at 20 mA g$^{-1}$ to a cut off voltage of 1.0 V.
3. Results and Discussion

Figure 1(a) shows the effects of ball milling time on the discharge capacity at the first cycle for MgNi–0.2 mass% perylene. After ball milling for 1 h, the discharge capacity reached the value of 460 mAh g\(^{-1}\), about 27% higher than that of bare MgNi, 362 mAh g\(^{-1}\). Further ball milling, however, gave smaller discharge capacities as shown in the figure. This implies that there is an optimal ball milling time for MgNi–0.2 mass% perylene to achieve high discharge capacity. For other perylene ratios, similar results were observed. At a given ball milling time, the perylene ratio also affected the discharge capability. The result of 1 h ball milling was shown in Fig. 1(b). There was also an optimal perylene amount, 1 mass%, for MgNi to have high discharge capacity, 497 mAh g\(^{-1}\) in the first cycle.

Such changes in the discharge capacity were attributed to the change in the hydrogen charging process. Figure 2 compares the charge curves of MgNi–0.2 mass% perylene-4 h (indicating ball milling 0.2 mass% perylene with MgNi for 4 h, similar indication is used hereafter) and bare MgNi at the first cycle. For both the bare MgNi and MgNi–0.2 mass% perylene-4 h, the cell voltage began to increase on charging, but the cell voltage for MgNi–0.2 mass% perylene-4 h increased slower than bare one. It was observed that the hydrogen absorption for MgNi takes place at the cell voltage around 1.35 V under the present charging conditions, and the evolution of H\(_2\) gas predominates over hydrogen ingress at higher cell voltage.\(^8\) Accordingly, the modification by perylene is effective to enhance hydrogen acquisition by keeping the lower cell voltage. These observations confirmed that the charge/discharge capacity can be improved by surface modification of amorphous MgNi by aromatic carbon compounds such as perylene, and both the perylene ratio and ball-milling time are crucial for the properties of perylene modified MgNi.

Figure 3 shows changes in the discharge properties with charge/discharge cycles. According to these figures, the effects of modification could be classified into three dis-
distinct types, A, B and C. Type A is the increase in the discharge capacity at the first cycle (Fig. 3(a)). For example, the discharge capacity for MgNi-1 mass%-1 h and MgNi-0.2 mass% perylene-4 h at the first cycle were 497 and 460 mAh g\(^{-1}\), respectively; about 37% and 27% higher than that of bare MgNi (362 mAh g\(^{-1}\)), respectively. But the discharge capacity still decreased with cycles as bare MgNi or even faster. This type of effect appeared, in general, for ball milling with small amount of perylene addition (less than 1 mass%) for short time (shorter than 4 h). Type B is the improvement in the capacity degradation with cycles as seen in Fig. 3(b). Namely, the degradation rate of the discharge capacity was slower than that of bare MgNi, although there appeared no noticeable increase in the capacity at the first cycle. For example, MgNi-1 mass% perylene-4 h and MgNi-2 mass% perylene-10 h showed discharge capacity about 200 mAh g\(^{-1}\) at the 8th cycle, almost twice of that of bare MgNi. This kind of effect was observed for samples of much larger perylene addition (1 and 2 mass%) and longer ball milling than type A.

In the case of larger amounts of perylene addition, e.g. 10 mass%, both the discharge capacity and cycle life were reduced as seen in Fig. 3(c). This kind of negative effect was classified as type C. In this case, it was observed that a longer ball milling time resulted in the lower discharge capacity and shorter lifetime. Type C effect was also observed in some extent for a long ball milling time and a small amount of perylene addition.

According to our previous studies, it was concluded that 1) the discharge capacity of amorphous MgNi is determined by the amount of hydrogen absorbed during charge process, and almost all hydrogen absorbed can be released in discharge process under the present discharge conditions, 2) the formation of Mg(OH)\(_2\) on the surface of MgNi retards the electron transfer and consequently decreases the hydrogen absorption by MgNi, and 3) carbon evaporated onto MgNi surface suppresses the retardation of electron transfer and consequently improve the cycle life. On account of these observations, the changes in the electrode properties presently observed by modification with perylene are ascribed to the improvement and/or debasement of the hydrogen absorption and/or the Mg(OH)\(_2\) formation.

Figure 4 shows X-ray diffraction patterns of bare and perylene-modified MgNi powders. The broad peak around 41.5° was assigned to amorphous MgNi and sharp peaks at 44.5, 51.8 and 76.5° were due to Ni remaining in a crystalline state. No significant difference was observed between the diffraction patterns of bare MgNi and of perylene-modified powders. This observation suggests that the bulk of the powder did not change markedly by ball-milling with perylene. Namely, the changes in electrochemical properties observed are ascribed to the modification of surface states.

Changes in the diffraction patterns with immersion in 6 M KOH solution for 120 h are also shown in Fig. 5. Very strong Mg(OH)\(_2\) peaks can be seen for MgNi-10 mass% perylene-10 h specimen showing type C effect; the intensities of Mg(OH)\(_2\) peaks are significantly larger than those for bare MgNi. This observation indicates that a larger amount of Mg(OH)\(_2\) was formed during the immersion for MgNi-10 mass% perylene-10 h specimen than for bare one. The specimen ball-milled with 1 mass% perylene for 1 h (type A) also showed higher intensities of Mg(OH)\(_2\) peaks than bare MgNi. On the other hand, MgNi-1 mass% perylene-4 h specimen, which showed type B effect, gave the Mg(OH)\(_2\) peaks significantly weaker intensities in comparison with those showing type A and C effects; the comparison with the bare specimen was difficult because the intensities of Mg(OH)\(_2\) peaks were so small for these specimens. It is, however, clear that the rate of degradation in discharge capacity increased with the increasing extent of Mg(OH)\(_2\) formation for the specimens ball-milled with perylene.

In order to examine changes in the surface states of specimens with perylene-modification, Auger electron spec-

![Fig. 4 XRD patterns by Cu K\(_\alpha\) radiation for (a) bare MgNi and (b) MgNi-10 mass% perylene-10 h.](image)

![Fig. 5 XRD patterns by Cu K\(_\alpha\) radiation for some tested powders after immersion in 6 M KOH solution for 120 h: (a) MgNi, (b) MgNi-10 mass% perylene-10 h (Type C), (c) MgNi-1 mass%-4 h (Type B) and (d) MgNi-1 mass% perylene-1 h (Type A).](image)
Hence, it can be concluded that evaporated carbon reacted toposcopy was applied for a Mg$_2$Ni plate covered with a carbon evaporated film, because a plate type specimen is more suitable for accurate surface analysis than powder. The surface state of this specimen is not exactly the same as that of amorphous MgNi modified by perylene. Nevertheless, this specimen can be considered as a model to understand the changes in surface states, because the influences of carbon evaporation observed in the previous study were similar to present type A and B effects. Figure 6 shows the typical Auger electron spectra of bare and carbon evaporated Mg$_2$Ni specimens. In addition to Mg and Ni, carbon and oxygen were detected from both specimens. It should be emphasized that the carbon evaporation resulted in the increase in the peak intensity of carbon as well as Mg-peak. The detailed spectra of Mg KLL transition are shown in Fig. 7. The peak took the maximum at 1182.5 eV in the case of the bare specimen. According to the literature, metallic Mg shows a peak in a range from 1183.0 to 1186.5 eV and it is shifted by oxidation to the lower energy side about $-5.9$ to $-6.2$ eV. Hence, the broad peak observed at 1182.5 eV can be ascribed to coexisting metallic and oxidized Mg. The carbon evaporation resulted in the shift of this peak to higher energy side as shown in this figure. On the other hand, no significant change was observed in Ni-peak by carbon evaporation as seen in Ni MVV transitions shown in Fig. 8 as differential spectra. The peaks appearing around 64 eV for both the bare and carbon evaporated samples indicate that Ni was present mainly in a metallic state. Hence, it can be concluded that evaporated carbon reacted selectively with Mg. By use of X-ray photoelectron spectroscopy, Iwakura et al. have observed similar phenomena that the Mg 2s peak is caused to shift toward the lower energy side by ball-milling of MgNi with graphite. Both of these XPS and AES observations suggest that a part of magnesium existed on the surface had been oxidized and it was reduced partially by forming Mg–C bonds. Consequently the electron density around a magnesium atom increased, resulting in the shifts of AES and XPS peaks as mentioned above. Similar changes in the surface state can be expected for perylene-modified MgNi. Therefore, it is plausible that the selective reaction between carbon and Mg takes place during ball milling of MgNi with perylene.

To examine mechanisms underlying the change in electrochemical properties by the surface modification, the electron redistribution caused by interactions between MgNi and perylene was calculated for a model cluster by means of Gaussian-98. In this calculation, amorphous MgNi is assumed to consist of Mg$_2$Ni$_2$ tetrahedral cluster units as suggested by Orimo et al. The calculations were carried out for combinations with perylene and benzene by keeping the Mg$_2$Ni$_2$ tetrahedral structure, because the modification by these compounds gave similar charge/discharge curves and capacity degradations with cycles as mentioned in Section 1. Since the model calculations also gave a similar trend, the results are shown for Mg$_2$Ni$_2$-benzene clusters for simplicity. Three different combinations were assumed between carbon atoms of benzene (or perylene) and a Mg$_2$Ni$_2$ cluster as shown in Fig. 9, which shows isosurfaces of electron densities and partial atomic charges obtained by Gaussian-98 calculation. The calculation showed that a compound by two Mg–C bonds (denoted as Mg$_2$–B, Fig. 9(b)) is most stable, and the order of compound stability was Mg$_2$–B > NiMg–B (Fig. 9(c)) > Ni$_2$–B (Fig. 9(d)). The same order of stability was obtained for perylene compounds, suggesting that compounds like the Mg$_2$-perylene type is most likely formed by ball-milling of MgNi with perylene.

As for the Mg$_2$-perylene compound like Fig. 9(b), Mg–C bonding is accompanied by partial charge separation, by which Mg atoms are charged much more positively and Ni more negatively than bare Mg$_2$Ni$_2$ (Fig. 9(a)). On forming the Mg–C bond, nickel atoms on the surface are kept free from carbon and then are expected to play a role as active sites for electrochemical reaction. This implies that hydrogen ab-

![Fig. 6 Auger electron spectra of bare and carbon deposited Mg$_2$Ni specimens.](image1)

![Fig. 7 Detailed Auger electron spectra of Mg KLL transition for bare and carbon deposited Mg$_2$Ni specimens.](image2)

![Fig. 8 Detailed Auger electron spectra of Ni MVV transition for bare and carbon evaporated Mg$_2$Ni specimens.](image3)
Fig. 9 Calculation results for three different combinations between carbon atoms of benzene and a Mg2Ni2 cluster by Gaussian-98. The isosurfaces of electron densities and partial atomic charges are indicated. (a) Mg2Ni2 cluster, Mg atom (red) with positive charge and Ni (green) with negative charge, (b) carbon atoms combine with Mg atoms, Mg2-B, (c) carbon atoms combine with Mg atom and Ni atom, NiMg-B, and (d) carbon atoms combine with Ni atoms, Ni2-B. These results were graphed by MOLEKEL 4.2.23)

sorption by the MgNi-electrode can be improved. In addition, the formation of Mg(OH)2 is expected to be retarded in this case, because Mg atoms bound to C will be blocked from the attack by OH− ions or H2O molecules in the electrolyte solution. However, the complete retardation of Mg(OH)2 formation cannot be expected because of the large positive charge and low electron density of Mg atoms. As for Ni2-perylene compound as Fig. 9(d), there appeared no appreciable change in atomic charges from the bare MgNi. In this case, however, no improvement in electrochemical properties can be expected, because magnesium is not active for the reaction. In addition, Mg atoms can be oxidized easily to form Mg(OH)2, resulting in the poor discharge capacity and cycle life. As for MgNi-perylene like Fig. 9(c), it will be active in some extent but less than Mg2-perylene.

Although the mechanism underlying the reaction between MgNi and perylene during ball milling has not been fully understood, the type A and B effects can be most likely ascribed to the formation of Mg2-perylene composite. This is because the formation of free Ni atoms on the surface and retardation of Mg(OH)2 formation by Mg–C bonding, although the distinction between these positive effects is open to further studies. Similar mechanism can be expected for the improvement in the discharge capacity and cycle life observed in the previous study by carbon evaporation.14) Conversely, type C effect can be attributed to the formation of Ni2-perylene composite, where non-active Mg atoms are left on the surface, leading to the Mg oxidation to form Mg(OH)2.

It should be also mentioned here that Gaussian 98 calculations resulted in rupture of the MgNi tetrahedron and formation of Mg–C and Ni–C compounds in the case of no restriction of keeping the tetrahedral structure. This suggests that rigorous ball milling of MgNi with perylene and/or other carbon compounds causes destruction of the tetrahedral functional structure of MgNi, leading to the loss of electrochemical and hydrogen absorbing properties. This appears to be one of the reasons of type C effect, the reduction of discharge capacity and cycle life by excessive ball milling with carbon compounds.

Concerning AES as well as XPS analyses, a Mg AES peak
should shift toward lower kinetic energy side and the Mg XPS peak to higher side if bare MgNi surface is modified by carbon compounds as perylene and graphite, because the atomic charge of Mg becomes much positive by the modification. The present AES spectra and XPS observations by Iwakura et al.,13) however, indicate that a part of Mg on the surface was covered by adsorbed oxygen or oxides. Accordingly, the atomic charge of Mg on the as-prepared MgNi surface is far more positive than that of the carbon modified surface. As a result, it is expected that the Mg AES peak shifts to the higher energy side and the Mg XPS peak moves toward the lower energy side by carbon modification of oxidized surfaces, in accordance with the observations.

4. Conclusions

Amorphous MgNi powder was ball-milled with perylene and the effects on electrochemical properties were investigated. It was found that both the ball milling time and perylene/MgNi ratio had great influence on the discharge capacity and cycle life of MgNi. Three types of effects were observed: increase in discharge capacity (type A), improvement in the resistance to degradation (type B), and significant reduction in both of the discharge capability and resistance to degradation (type C). These effects were ascribed to the modification of the alloy surface through interactions between constituent elements and carbon in perylene. Ab-inito calculation by Gaussian-98 suggested that the effect of the surface modification is strongly dependent on the combination of carbon and constituent elements of the alloy. The improvements of types A and B are ascribed to the formation of free metallic Ni on the surface and the retardation of Mg(OH)2 growth owing to Mg-carbon bonding.

Acknowledgements

This work has been supported in part by a Grant-in-Aid for Scientific Research on Priority Areas A of “New Proton Function” of the Ministry of Education, Science, Sports and Culture of Japan. Thanks are offered to Japan Metals and Chemicals Co. for the gift of Mg2Ni powder and Matsushita Electric Industrial Co. for positive electrode material. The authors would like to express their sincere thanks to Dr. K. Fujii of Institute of Nuclear Safety System for the help in Auger analyses.

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