Surface modification of MgNi alloy with graphite by ball-milling for use in nickel-metal hydride batteries

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Both discharge capacity and charge–discharge cycle life of MgNi negative electrodes prepared by mechanical alloying (MA) are greatly improved by surface modification with graphite using a planetary mill.

Magnesium and Mg-based hydrogen storage alloys are expected to be promising energy conversion and storage materials because of hydrogen absorption in large quantities, low mass, rich mineral resources and low material cost. However, very high temperature, > 250 °C in the case of Mg_2Ni, is generally required for reversible absorption and desorption of hydrogen at *ca.* 1 atm.[1,2] Relatively high discharge capacities have recently been reported for MgNi prepared by MA.[3] It has also been reported that Mg_2Ni can be charged and discharged at temperatures as low as *ca.* 70 °C.[4] In both cases, however, their cycle lives were insufficient from the practical viewpoint. In this work, surface modification of MgNi alloy with graphite by ball-milling is investigated for the purpose of improving charge–discharge characteristics, especially with regard to discharge capacity and cycle lifetime of the MgNi alloy.

MgNi was prepared from Mg and Ni mixed powders (total mass of 1 g) by MA under Ar atmosphere for 7 days. The resulting MgNi alloy powder was mixed with graphite powder (Nippon Kokuen, SP-10) in a mass ratio of MgNi to graphite of 5, followed by ball-milling using a planetary mill with an acceleration of *ca.* 100 m s^{-2} for 10 min to prepare the MgNi–graphite composite. Experimental procedures, including the preparation of negative electrodes, and apparatus used were the same as described in our previous papers.[4,5] In charge–discharge cycle tests, each negative electrode was charged for 24 h at 50 mA g^{-1} and discharged to −0.6 V *vs.* Hg–HgO at the same current density. After every charging, the circuit was opened for 10 min. The temperature was kept at 30 °C.

Discharge curves (first cycle) of the MgNi and MgNi–graphite composite electrodes at 30 °C are shown in Fig. 1. In both cases, a plateau of the potential based on the oxidation of absorbed hydrogen was observed at *ca.* −0.8 V *vs.* Hg–HgO. Moreover, the discharge capacity was nearly zero when the electrodes were discharged in the absence of charge, suggesting that the corrosion current was negligibly small under these experimental conditions. It is evident that the discharge capacity is greatly increased by the surface modification of MgNi with graphite. That is, the discharge capacity for the MgNi–graphite composite electrode was *ca.* 510 mA h g^{-1}, *ca.* 1.4 times higher than that of the MgNi electrode (*ca.* 370 mA h g^{-1}).

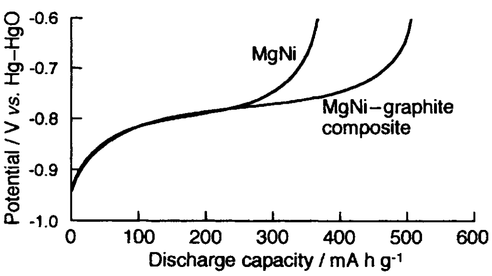

Fig. 1 Discharge curves (first cycle) of MgNi and MgNi–graphite composite electrodes at 30 °C

The discharge capacity as a function of cycle number for the MgNi, MgNi–graphite composite and MgNi–graphite mixture electrodes at 30 °C is shown in Fig. 2. As can be seen, the discharge capacity for the MgNi electrode rapidly decreased with increasing cycle number. In this case, the discharge capacity at the sixth cycle was 0.25 times that at the first cycle, which seems to be caused by oxidation of the alloy surface during charge–discharge cycles.[3,4] On the other hand, in the case of MgNi–graphite composite electrode, the rate of capacity decay was much reduced and the capacity was still *ca.* 300 mA h g^{-1} even for the sixth cycle, *ca.* four times higher than that for the MgNi electrode. Judging from capacity comparison between the MgNi electrode and the MgNi–graphite mixture electrode, the contribution of mixing of graphite with MgNi to the increase in electrode conductivity is not considerable. These results suggest strongly that electrocatalytic activity, hydrogen desorbability and corrosion resistance are largely improved by the surface modification of MgNi with graphite.

Pressure–composition isotherms of hydrogen absorption and desorption in the MgNi powder and MgNi–graphite composite–hydrogen systems at 30 °C are shown in Fig. 3. Since the

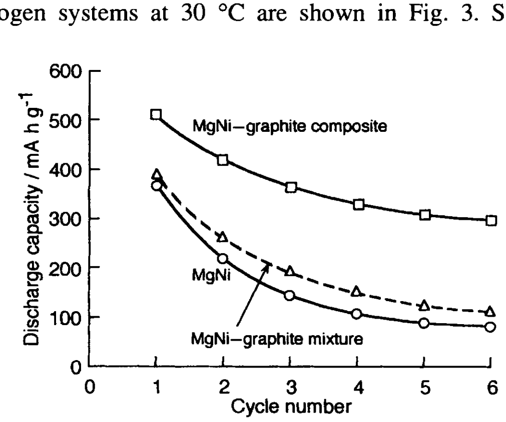

Fig. 2 Discharge capacity as a function of cycle number for MgNi, MgNi–graphite mixture and MgNi–graphite composite electrodes at 30 °C

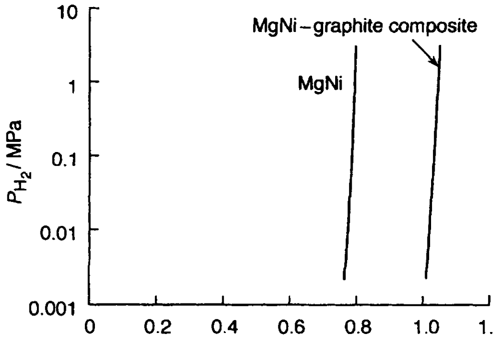

Fig. 3 Pressure–composition isotherms of hydrogen absorption and desorption in MgNi powder– and MgNi–graphite composite–hydrogen systems at 30 °C

equilibrium hydrogen pressure of Mg-based alloys is generally very low (*ca.* 10^{-6} MPa for Mg_2Ni) at 30 °C, the observed pressure–composition isotherms correspond to the formation of metal hydride. The discharge capacities (C_H) evaluated using eqn. (1) from the observed pressure–composition isotherm

$$C_H \text{ (mA h g}^{-1}) = 2 \times 2.68 \times 10^4 \times (\text{H/M})_{0.5}/M \qquad (1)$$

were 497 and 665 mA h g^{-1} for the MgNi powder and MgNi–graphite composite, respectively. Where $(\text{H/M})_{0.5}$ and M represent the atomic ratio of hydrogen to metal at 0.5 MPa and the formula mass of MgNi, respectively. Thus, the calculated discharge capacity for the MgNi–graphite composite is very high, compared with that for the MgNi powder. These data seem to be quite reasonable by reference to Fig. 1.

Furthermore, it is noteworthy that the rates of hydrogen absorption and desorption are very high in the case of the MgNi–graphite composite. Such a remarkable effect for the Mg–graphite composite may be caused by an increase in the number of active sites for hydrogen absorption and desorption with formation of bonds between Mg and graphite. Further work along this line, in addition to study on the corrosion and self-discharge of the MgNi and MgNi–graphite composite electrodes, is now in progress.

In conclusion, one can expect from the presented results that Mg-based alloys should be excellent negative electrode materials of the third generation for nickel–metal hydride batteries.

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