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On the cycle life improvement of amorphous MgNi-based alloy for Ni–MH batteries

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Abstract

Amorphous MgNi prepared by mechanical alloying has a high initial discharge capacity (∼ 440 mAh/g) but a low cycle life due to its oxidation and pulverization during cycling. In the present work, a Mg–Ni–Ti–Al quaternary alloy with enhanced cycle life has been elaborated. Al addition creates a synergetic effect with Ti presumably to form a protective layer limiting $Mg(OH)_2$ formation. The $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrode retains 67% of its initial discharge capacity (∼ 400 mAh/g) after 15 cycles compared to 34% for MgNi. The charging conditions have also a great influence on the electrode cycle life as demonstrated by the existence of a charge input threshold under which minor capacity decay occurs. The charge input threshold is higher for $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrode than for MgNi electrode, which may reflect the improvement of the alloy resistance to pulverization. In addition, we pointed out that electrode made from large particles (>150 μm) has a better cycle life. We have then conceived a $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrode with an appropriate particle size having a capacity decay rate as low as that observed for a commercial AB_5 alloy (i.e. ∼ 0.2% per cycle) under controlled charging conditions ($C_{\mathrm{input}} \leq 300$ mAh/g).

Keywords: Nickel-metal hydride batteries; Hydrogen storage alloys; Magnesium-based compounds; Mechanical alloying

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1. Introduction

In the last few years, numerous studies have been conducted in order to improve the cycle life of Mg-based materials. The most encouraging results have been obtained by the partial substitution of magnesium with corrosion resistance elements. Among these substitution elements, titanium appears clearly as a key element for improving the cycle life of Mg-based electrodes. For example, amorphous $Mg_{0.5}Ti_{0.5}Ni$ alloy retains 75% of its initial discharge capacity of 340 mAh/g after 10 cycles in comparison to 39% for MgNi electrode [1]. The cycle life improvement is associated with the formation of TiO_2 onto the alloy surface which limits the formation of $Mg(OH)_2$. However, the global performance of this metal hydride electrode is still far from that required for commercial applications.

In the present study, it will be shown that Mg–Ni–Ti–Al quaternary material with high cycle life can be obtained by conjugating an optimized composition with an appropriate particle size and a strict charge input control.

2. Experimental details

Pure Mg (99.9%, chips), Ni (99.9%, 325 mesh), Ti (99.9%, 325 mesh) and Al (99%, 625 mesh) were used as starting materials. Samples were prepared according to the following stoichiometries: MgNi, $Mg_{0.9}Ti_{0.1}Ni$ and $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$. Ball milling was performed using a Spex 8000 vibratory mill for 10 h. The amorphous structure of the end-products was confirmed by X-ray diffraction analysis (not shown). The as-milled $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ powder was sieved in five fractions: <20 μm, 20–75 μm, 75–106 μm, 106–150 μm and >150 μm.

The charge/discharge cycling tests were performed on an Arbin BT2000 battery tester at room temperature in 6 M

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KOH solution using a three-electrode cell. The working electrode is composed of 100 mg active material mixed with 800 mg of graphite and 20 mg of carbon black. The counter electrode was a nickel wire and the reference electrode was an Hg/HgO electrode. The working electrode was charged at 200 mA/g for 3 h and discharged at 20 mA/g until −0.6 V versus Hg/HgO. The influence of the charge input was studied by varying the charge duration from 60 to 90 min.

3. Result and discussion

Fig. 1 presents the cycling discharge capacities for MgNi, $Mg_{0.9}Ti_{0.1}Ni$ and $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrodes. The MgNi electrode displays the higher initial discharge capacity (443 mAh/g) but its capacity decreases rapidly with cycling (capacity decay of 66% after 15 cycles). For $Mg_{0.9}Ti_{0.1}Ni$ electrode, the initial discharge capacity is smaller (415 mAh/g) but its cycle life is higher (capacity decay of 46% after 15 cycles), confirming the positive effect of the partial substitution of Ti for Mg on the electrode cycling dischargeability. Al addition to $Mg_{0.9}NiTi_{0.1}$ induces further cycle life improvement. Indeed, $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ compound losses 33% of its initial discharge capacity of 404 mAh/g after 15 cycles. Its cycle stability is close to the one obtained with $Mg_{0.5}Ti_{0.5}Ni$ electrode [5] but with a gain of 66 mAh/g on the initial discharge capacity. It is assumed that Al addition creates a synergetic effect with Ti presumably to form a more efficient $Al_2O_3 + TiO_2$ protective layer than TiO_2 alone for limiting $Mg(OH)_2$ formation. Chemical surface analyses and corrosion/passivation measurements are required to confirm this issue. A synergetic effect was also observed between Ti and Zr [2,3], Ti and Cr [4,5] and Ti and V [2,5], leading to the formation of a more compact and more protective oxide layer on the electrode surface than by Ti alone. Significant cycle life improvement was also observed with $Mg_{35}Ti_{10}Al_5Ni_{50}$ and $Mg_{35}Ti_{10}Y_5Ni_{50}$ quaternary alloys [6] but their initial discharge capacity (203 and 109 mAh/g, respectively) was much lower than observed in the present study.

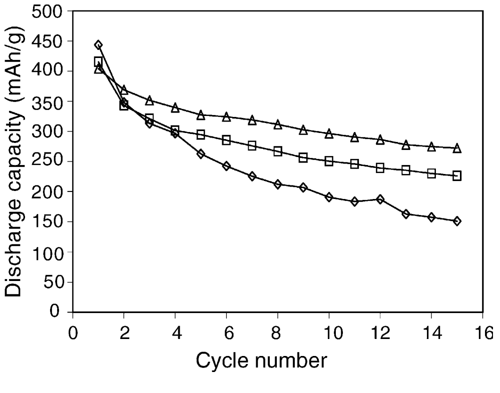

Fig. 1. Cycling discharge capacities of MgNi (◇), $Mg_{0.9}Ti_{0.1}Ni$ (□) and $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ (△) electrodes.

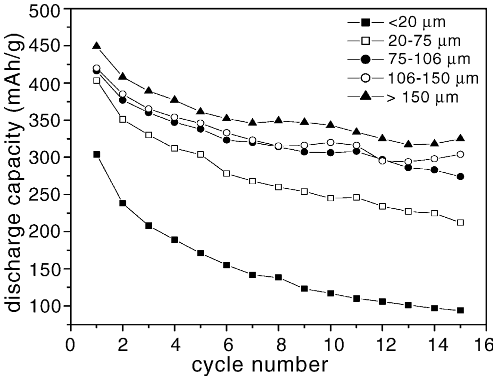

Fig. 2. Cycling discharge capacities of $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrodes with different particle sizes.

The influence of the particle size on the cycling discharge capacities of $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ powder is presented in Fig. 2. It clearly appears that the initial discharge capacity is higher as the particle size increases. The initial discharge capacity of particles larger than 150 µm is 449 mAh/g compared to 420, 416, 403 and 304 mAh/g for 106–150 µm, 75–106 µm, 20–75 µm and <20 µm particle electrodes, respectively. This can be explained by the decrease of the electrode oxidation due to a lower surface area in contact with the electrolyte. Then, because the electrode with the larger particles has a larger fraction of un-oxidized (i.e. active) material, it is not surprising that its initial discharge capacity is higher. Fig. 2 also shows that the electrode cycle life is improved by increasing the particle size. Indeed, the capacity decay after 15 cycles is 28% for >150 µm particles electrode compared to 69% for <20 µm particle electrodes. This confirms that the electrode oxidation is accelerated with decreasing the particle size. It is in accordance with our recent study about the influence of particle size on the electrode performance of MgNi alloy [7].

We have recently shown that the discharge capacity decay of the MgNi electrode upon cycling can be drastically decreased by preventing its pulverization through a limitation of the charge input [8]. In order to evaluate the influence of the alloy composition on the electrode pulverization, we have compared the charge input threshold inducing continuous capacity decay with cycling for MgNi, $Mg_{0.9}Ti_{0.1}Ni$ and $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrodes. For that purpose, charge/discharge cycles were performed by increasing the charge input value from 200 to 300 mAh/g by step of 20 mAh/g. Five consecutive charge/discharge cycles were carried out for each charge input value. The results are presented in Fig. 3. For the three powder compositions, the initial discharge capacity is higher than the charge input. This additional discharge capacity can be associated with the anodic formation of oxides/hydroxides (e.g. Mg(OH), $Ni(OH)_2$, TiO_2, Al_2O_3) at the surface of the powder during the discharge procedure. This additional discharge capacity is not the same for the three compositions, reflecting some differences in their corrosion/passivation behaviour. More

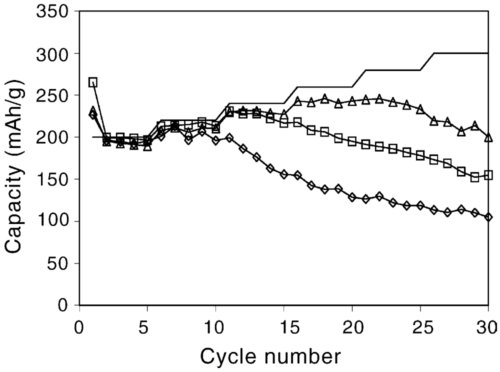

Fig. 3. Cycling discharge capacities with charge input increasing from 200 to 300 mAh/g (solid line) for MgNi (◇), $Mg_{0.9}NiTi_{0.1}$ (□) and $Mg_{0.9}NiTi_{0.1}Al_{0.05}$ (△) electrodes.

interestingly, the discharge capacity decay does not appear at the same charge input value. For MgNi electrode, the discharge capacity decreases rapidly once the charge input value is higher than 220 mAh/g. For $Mg_{0.9}Ti_{0.1}Ni$ electrode, the capacity degradation is observed for a charge input higher than 240 mAh/g and for $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrode, the charge input threshold is 260 mAh/g. From the initial discharge capacity (C_1 in Fig. 1) and the charge input threshold inducing continuous capacity degradation ($C_{\text{threshold}}$ in Fig. 3) for each electrode, their maximum state of charge before pulverization (corresponding in first approximation to the $C_{\text{threshold}}/C_1$ ratio) can be estimated at 50, 58 and 64% for MgNi, $Mg_{0.9}Ti_{0.1}Ni$ and $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrodes, respectively. These results may reflect a decrease of the volume expansion and/or an improvement of the mechanical properties for $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ alloy and, in less extent, for $Mg_{0.9}Ti_{0.1}Ni$ alloy compared to MgNi material.

Finally, we have compared the cycling dischargeability of our optimized Mg-based electrode (i.e. $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ with particles size larger than 150 μm) with a commercial AB_5 material (i.e. $MmNi_{3.6}Co_{0.8}Al_{0.35}Mn_{0.25}$ from Treibacher). The experiment was performed with a charge input of 300 mAh/g. Results are shown in Fig. 4. From the second cycle, the two electrodes display a similar capacity decay rate (ca. 0.2% per cycle). Moreover, $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$ electrode maintains its discharge capacity ∼ 10% higher than for the commercial $LaNi_5$-based material. Additional improvement is expected through an optimization of the cell construction.

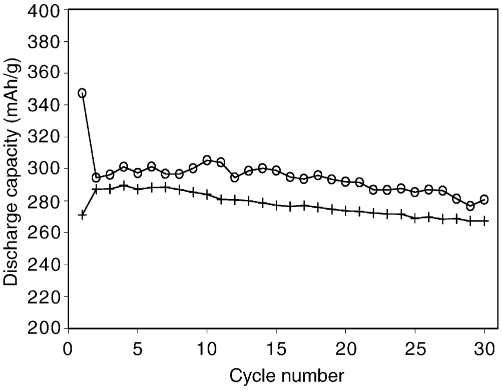

Fig. 4. Cycling discharges capacities of $Mg_{0.9}NiTi_{0.1}Al_{0.05}$ alloy with particles larger than 150 μm (○) and commercial $LaNi_5$-based material (+). Charge input = 300 mAh/g.

4. Conclusion

It was shown that Mg-based hydrogen storage alloy with a remarkable cycle life can be obtained by combining an optimized composition (i.e. $Mg_{0.9}Ti_{0.1}NiAl_{0.05}$) with an appropriate particle size (i.e. particles size >150 μm) and a strict charge input control (i.e. $C_{\text{input}} \leq 300$ mAh/g).

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