

Electrochemical characteristics of Mg–Ni alloys as anode materials for secondary Li batteries

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Received 14 November 1999; received in revised form 5 February 2000; accepted 16 February 2000

Abstract

The electrochemical characteristics of Mg and several Mg–Ni alloys were studied as alternatives to anode materials for secondary Li batteries. Li was alloyed and dealloyed reversibly with Mg at very low voltage region (below 100 mV vs. Li/Li⁺), and the initial capacity obtained was approximately 3070 mA h/g. Alloys of Mg₅₀Ni₅₀, Mg₆₇Ni₃₃ and Mg₇₅Ni₂₅ were prepared by mechanical alloying and characterized using X-ray diffraction (XRD) and Auger electron spectroscopy (AES). Mg₅₀Ni₅₀ and Mg₆₇Ni₃₃ were found amorphous and crystalline, respectively, while Mg₇₅Ni₂₅ was a mixture of Mg and Mg₂Ni phases. Electrochemical tests with these Mg–Ni alloys demonstrated that only Mg₇₅Ni₂₅ reacted significantly with Li at room temperature while Mg₆₇Ni₃₃ reacted with Li at high temperature. Mg₇₅Ni₂₅ showed enhanced cycle performance compared to that of pure Mg. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Mg–Ni alloys; Secondary lithium batteries; Mechanical alloying

1. Introduction

Recently, various Li-based composite materials including metal oxides, multiphase alloys and intermetallic compounds have been studied extensively as alternatives to the current commercial anode material for Li ion battery [1–3]. These materials show much higher capacities than carbonaceous materials and improved cycle performance relative to Li binary alloy systems, such as Li–Sn and Li–Si. These Li binary alloys show poor cyclability due to a large volume change during cycling. Enhancement of cycle performance in these newly proposed Li-alloy-based materials could be accomplished using an ‘inert matrix’ concept and nanocrystallization of active materials.

In our previous study on the reaction mechanism of Mg₂Si with Li [4], it was found that Mg was capable of reversibly alloying/dealloying with Li and also showed very low voltage plateau (below 100 mV vs. Li/Li⁺). In general, Li-alloy-based materials have a voltage penalty of a few hundred millivolts, which reduce the cell voltage and power density. Therefore, the very low voltage plateau of the Mg electrode seems to be very attractive. There have

been, however, few studies on Mg as an anode material for secondary Li batteries [5].

In this study, the electrochemical characteristics of Mg at room temperature were examined. To enhance the capacity retention of Li–Mg alloys, Mg–Ni alloys also were examined. Ni does not react with Li, so it might constitute an inactive matrix for Mg atoms. In addition, extensive studies have been carried out on Mg–Ni alloys for hydrogen storage materials [6–11]. To study the electrochemical behaviors as anode materials for the secondary Li batteries, three different types of Mg–Ni alloys, i.e., amorphous Mg₅₀Ni₅₀, crystalline intermetallic Mg₆₇Ni₃₃ (single Mg₂Ni phase), and Mg₇₅Ni₂₅ (mixture of Mg and Mg₂Ni) were prepared using mechanical alloying technique.

2. Experimental

Mg powders (99.9%; Kojundo Chemical) of –400 mesh size were used as an anode material. Also three different compositions, Mg_{100-x}Ni_x ($x = 25, 33$ and 50) alloys, were prepared by mechanical alloying process. Pure elemental magnesium powder (99.9%, 100 mesh) and nickel powder (99.9%, 325 mesh; Acros Organic) were

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blended for each compositional ratio and milled under Ar atmosphere using vibratory mill with a hardened steel vial of 80 cm³. Milling medium was 3/8 in. hardened steel balls and ball-to-powder ratio was 25. The identification of mechanically alloyed samples was carried out using X-ray diffractometer (MacScience, MXP18A-HF) and the local atomic distribution of each sample was analyzed using Auger electron spectroscopy (AES)/scanning Auger microscopy (SAM) (Perkin Elmer 660 Model). For every measurement, Ar ion sputtering was performed to remove any contaminated surface layer.

The electrodes were prepared by coating the slurries [active material powders (75 wt.%), carbon black (15 wt.%) and polyvinylidene fluoride (PVDF) (10 wt.%) dissolved in *N*-methyl pyrrolidinone (NMP)] on a Cu foil substrate. After coating, the electrodes were pressed and dried for 4 h at 120°C under vacuum. The electrodes were cut into disks (14 mm in diameter and about 0.1 mm in thickness) and the mass of active material was approximately 3 mg. Beaker-type test cells were assembled in an Ar-filled glove box using Celgard 2400 as a separator, 1 M LiPF₆, ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol.%; Merck) as an electrolyte, and Li foil as counter and reference electrodes. All cells were tested at a constant current within a fixed voltage window.

3. Results and discussion

3.1. Synthesis of Mg–Ni alloys by mechanical alloying

Fig. 1 illustrates the X-ray diffraction (XRD) patterns of the mechanically alloyed Mg_{100-x}Ni_x with $x = 50$ and 33. As shown in Fig. 1a, the amorphous phase was formed after 70 h of milling for $x = 50$. Fig. 1b shows that the crystalline phase was produced after 60 h of milling time

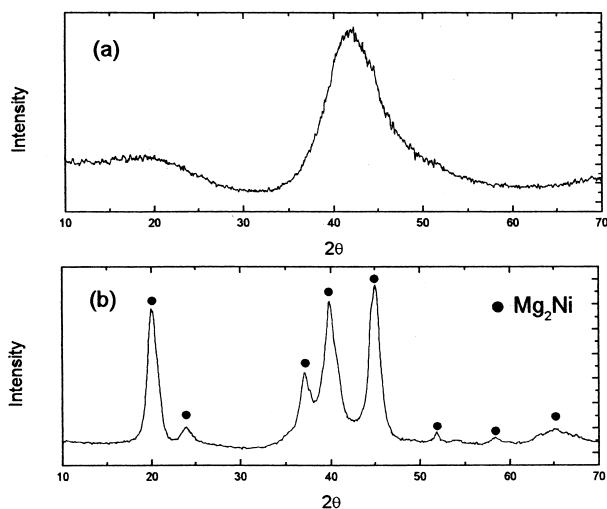


Fig. 1. The XRD patterns of mechanically alloyed Mg_{100-x}Ni_x alloys. (a) Mg₅₀Ni₅₀ for 70 h milling, and (b) Mg₆₇Ni₃₃ for 60 h milling.

for $x = 33$, and the peaks observed in Fig. 1b match well with Bragg peaks of Mg₂Ni. All diffraction peaks are relatively broad, indicating that the crystalline phase is composed of nanosize crystallites, or the lattice is strained during mechanical alloying.

Fig. 2 shows the XRD patterns for mechanically alloyed Mg₇₅Ni₂₅ as a function of milling time. At $t = 40$ h ($t =$ milling time; Fig. 2a), the pattern shows elemental Mg and Ni with no trace of Mg₂Ni, indicating that the produced sample was a mixture of Mg and Ni. However, this sample can be considered as a newly formed mixture through repeated cold-welding and fragmentation process rather than the simple mixture of Mg and Ni powders [6]. At $t = 70$ h (Fig. 2b), intermetallic phase Mg₂Ni was predominantly observed with a trace of metallic Mg. This result agrees well with the work of Liang et al. [7] that the produced powder was a mixture of Mg and Mg₂Ni from their XRD results and lattice parameter analysis, and the supersaturation of Mg in Mg₂Ni might occur to some extent in this powder. Therefore, powders obtained after 70 h of milling time seem to be a homogeneously distributed mixture of Mg and Mg₂Ni. At $t = 100$ h, no further structural changes were observed. In order to confirm the microstructure of Mg₇₅Ni₂₅ alloys, AES analysis was performed with two different Mg₇₅Ni₂₅ alloy samples. In AES analysis, spot analysis (spot size: 10–100 nm) was used to confirm the relative atomic ratio (Mg/Ni) of the selected position in Mg₇₅Ni₂₅ alloys, and the data based on the AES analysis are given in Table 1. While relative atomic ratios of Mg₇₅Ni₂₅ powders milled for 70 h are almost the same at any position, those of Mg₇₅Ni₂₅ powders milled for 40 h show different values at each position. This indicates that Mg-rich region and Ni-rich region are coexisting in Mg₇₅Ni₂₅ alloy particles milled for 40 h. In the case of Mg₇₅Ni₂₅ milled for 70 h, it can be considered that Mg and Mg₂Ni phases are homogeneously distributed.

3.2. Electrochemical behavior of Mg and Mg–Ni alloys

Fig. 3 illustrates the voltage profile of pure Mg electrode for the first cycle at a constant current of 5 mA/g. The first charge (Li alloying) and discharge (Li dealloying) capacities are 3070 mA h/g (Li_{2.78}Mg) and 2150 mA h/g (Li_{1.95}Mg), respectively. The voltage profile of Mg displays a very low voltage plateau: 15 mV (vs. Li/Li⁺) for charge and 50 mV (vs. Li/Li⁺) for discharge and this is a very attractive feature. However, alloying reaction between Li and Mg did not occur at a constant current of more than 10 mA/g, indicating a poor rate capability of pure Mg probably due to a native oxide film or solid electrolyte interface (SEI) formed on the surface of Mg.

Fig. 4 shows the voltage profiles for the first cycle of various Mg–Ni alloy electrodes at room temperature. The voltage profile of Mg₇₅Ni₂₅ after 100 h of milling time is not displayed because the electrochemical behavior of this

material is the same to that of $\text{Mg}_{75}\text{Ni}_{25}$ after 70 h of milling time. The shoulder observed at 0.7–0.8 V (vs. Li/Li^+) in voltage profile is probably due to the electrolyte decomposition reaction commonly observed in Li–graphite system [12]. Li could react only with $\text{Mg}_{75}\text{Ni}_{25}$ alloys and showed a voltage profile similar with that of pure Mg electrode. In the case of amorphous $\text{Mg}_{50}\text{Ni}_{50}$ alloy prepared by mechanical alloying, metallic Ni layer

exists on the top surface of the particle [11], which seems to prevent $\text{Mg}_{50}\text{Ni}_{50}$ from reacting with Li because Ni does not react with Li.

The failure of reaction between Li and Mg_2Ni was contributed by the structural hindrance and kinetic problem. The former had been already suggested by Mao et al. [13]. They reported that SnFe_x did not react with Li in the SnFe_x system because there were no Li diffusion paths

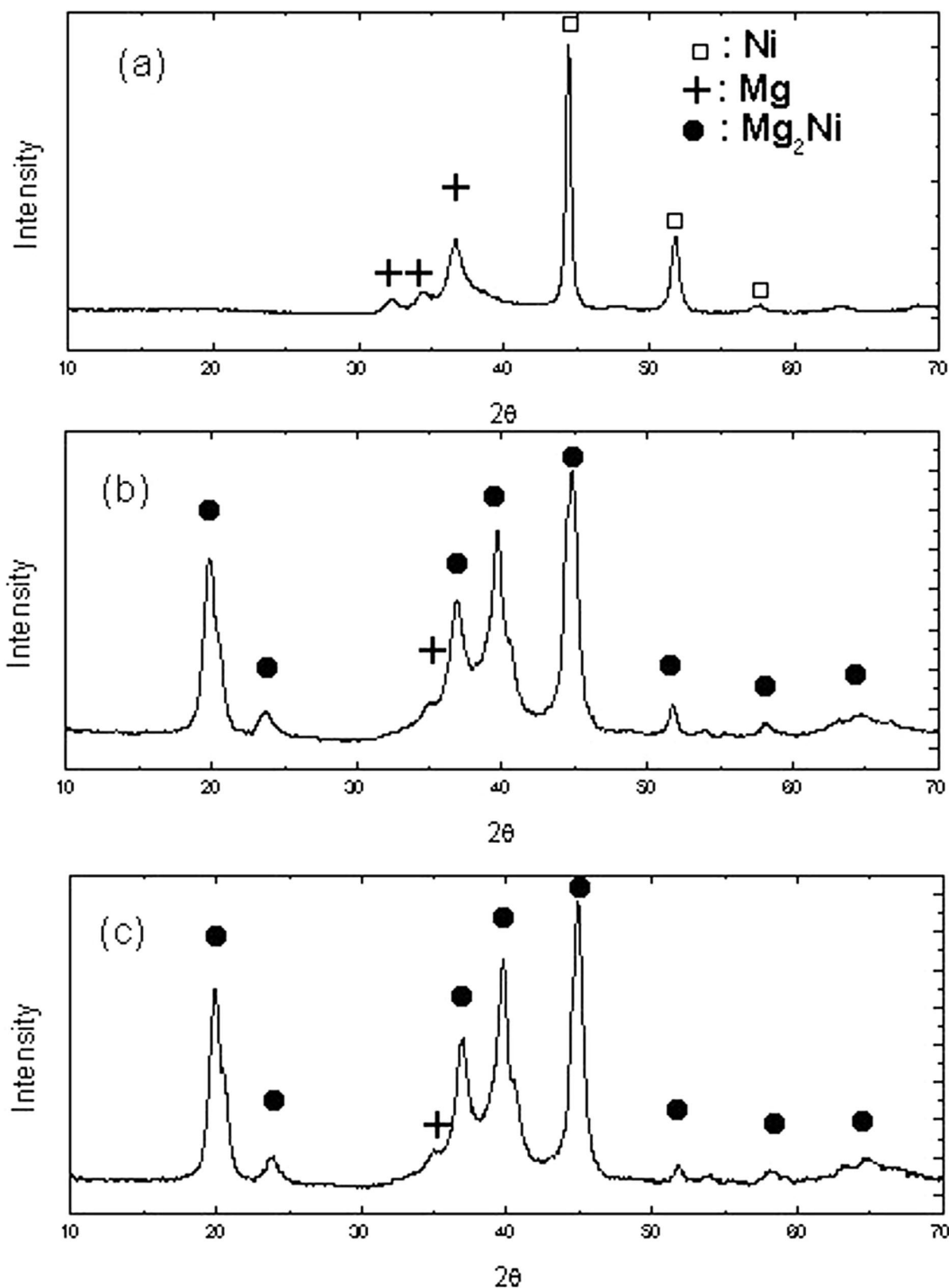


Fig. 2. The XRD patterns of mechanically alloyed $\text{Mg}_{75}\text{Ni}_{25}$ with respect to various milling times. (a) $t = 40$ h, (b) $t = 70$ h, and (c) $t = 100$ h.

Table 1

The relative atomic ratio (Mg/Ni) of $Mg_{75}Ni_{25}$ alloy particle for different milling times

Milling time (h)	Mg/Ni ratio for the different spot positions on the same particle
40	1.29, 4.06, 2.80, 2.13, 3.17
70	3.06, 3.06, 3.15, 3.08, 3.87

among the Sn atoms in the lattice of SnFe. The latter was commonly observed in the Mg-based hydrogen storage alloys where an appreciable amount of hydrogen absorbing/releasing occurred only at elevated temperature [9].

Fig. 5 shows the voltage profiles for the first cycle of $Mg_{50}Ni_{50}$ and Mg_2Ni electrodes at elevated temperature, i.e., 60°C. Amorphous $Mg_{50}Ni_{50}$ electrode does not react with Li even at 60°C, while the voltage profile of Mg_2Ni indicates that Mg_2Ni reacted with Li at 60°C. Li reacts with Mg_2Ni reversibly at higher temperature, but shows very poor kinetics of lithiation and delithiation at lower temperature. $Mg_{75}Ni_{25}$ alloy electrode milled for 70 h, a mixture of Mg and Mg_2Ni (Fig. 4d), shows a smaller first cycle charge–discharge capacity than that of less milled one ($t = 40$ h; Fig. 4c), which is a mixture of Mg and Ni. The reason is that the amount of active phase (Mg) in $Mg_{75}Ni_{25}$ alloy decreases with the increase of milling time and Mg_2Ni is almost inactive at room temperature as mentioned previously.

Fig. 6 compares the cycle performances of Mg and $Mg_{75}Ni_{25}$. While pure Mg shows very poor cyclability, $Mg_{75}Ni_{25}$ shows slight enhancement of the cycle performance. The drastic capacity decrease of Mg electrode is probably owed to the large volume change associated with cracking and crumbling of the active material, which is the characteristic of the Li–binary alloy anode. These results strongly indicate that the inert phase in the $Mg_{75}Ni_{25}$ alloys, which is Ni in the mixture of Mg and Ni, or Mg_2Ni

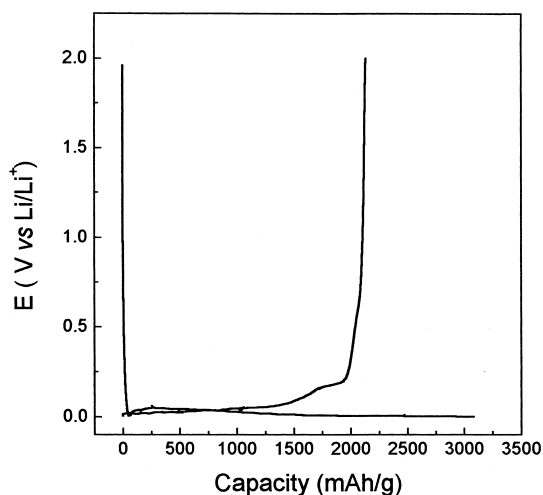


Fig. 3. The voltage profile of Mg electrode at a constant current of 5 mA/g.

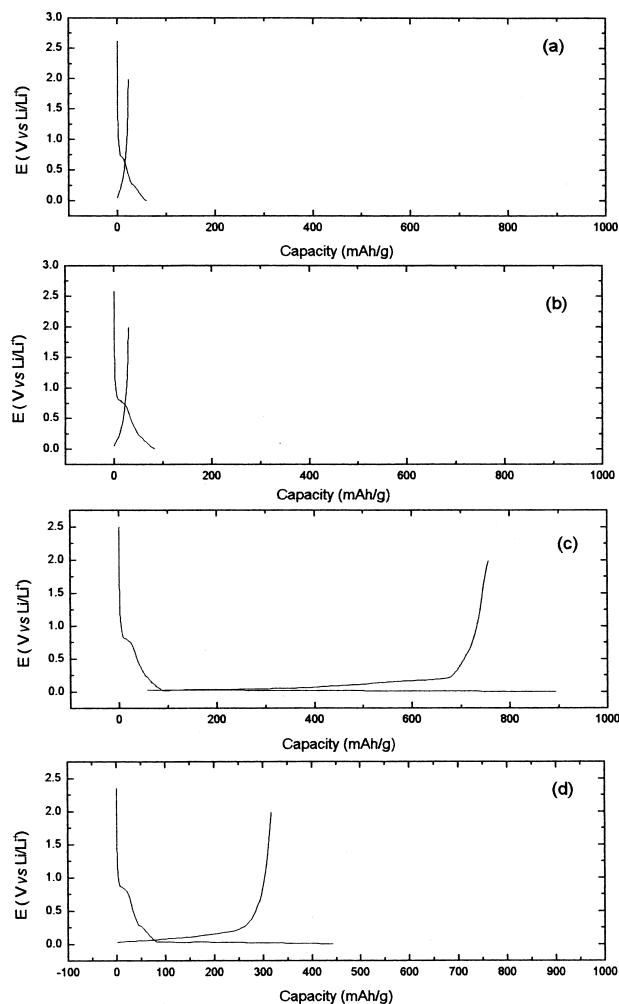


Fig. 4. The voltage profiles of various Mg–Ni alloy electrodes at a constant current of 10 mA/g. (a) $Mg_{50}Ni_{50}$, (b) $Mg_{67}Ni_{33}$, (c) $Mg_{75}Ni_{25}$ (40 h), and (d) $Mg_{75}Ni_{25}$ (70 h).

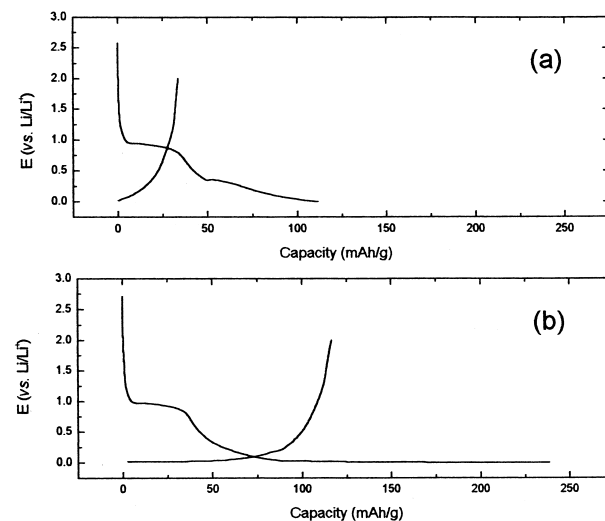


Fig. 5. The voltage profiles of $Mg_{50}Ni_{50}$ and Mg_2Ni electrodes at 60°C. (a) $Mg_{50}Ni_{50}$ (constant current of 10 mA/g), (b) Mg_2Ni (constant current of 30 mA/g).

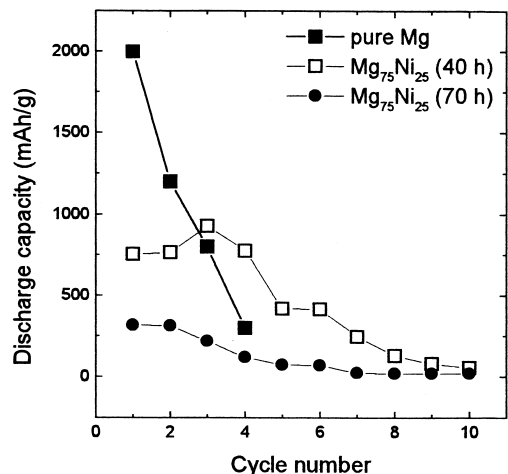


Fig. 6. Cycle performances of Mg and Mg₇₅Ni₂₅ electrodes.

in the mixture of Mg and Mg₂Ni, plays a role in holding the electrode material together upon cycling.

4. Conclusions

It was found that Li was alloying and dealloying reversibly with Mg at very low voltage region: 15 mV (vs. Li/Li⁺) during charging and 50 mV (vs. Li/Li⁺) during discharging. The initial capacity obtained was approximately 3070 mA h/g. XRD and AES analyses showed that amorphous Mg₅₀Ni₅₀ and crystalline Mg₂Ni were

obtained by mechanical alloying, and Mg₇₅Ni₂₅ was composed of Mg (active)/Mg₂Ni (inactive) phase. Electrochemical tests with these materials revealed that Mg₇₅Ni₂₅ alloys reacted with appreciable amount of Li at room temperature, and Mg₆₇Ni₃₃ reacted with Li only at higher temperature. In addition, Mg₇₅Ni₂₅ alloy showed enhanced cycle performance compared with that of pure Mg.

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