Mechanically alloyed Mg$_2$Ni for metal-hydride–air secondary battery

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Abstract

Mechanically alloyed Mg$_2$Ni and a single air (oxygen) electrode are used as the anode and cathode, respectively, in a Mg$_2$Ni-6 M KOH-oxygen rechargeable metal-hydride–air (MH–air) battery. The battery is tested for self-discharge by measuring the open-circuit voltage (OCV) and cycling characteristics. Battery degradation after charge–discharge cycling is characterized by means of X-ray diffraction (XRD) and scanning electron microscopic (SEM) analyses.

1. Introduction

AB$_5$-type hydrogen-storage alloys, such as LaNi$_5$ [1], MmNi$_{3.6}$Co$_{0.7}$Al$_{0.6}$Mn$_{0.1}$ [2,3], La$_{0.8}$Ce$_{0.2}$Ni$_{4.25}$Co$_{0.5}$Sn$_{0.25}$ [4] SrTiO$_3$–LaNi$_{3.76}$Al$_{1.24}$H$_n$ [5], MmNi$_{3.6}$Co$_{0.7}$Mn$_{0.4}$Al$_{0.3}$ [6] and MmNi$_{3.5}$Co$_{0.7}$Mn$_{0.4}$Al$_{0.3}$ [7], have been reported as negative electrode (anode) for metal-hydride–air (MH–air) systems. AB$_5$-type anodes have been successfully used for commercial production of nickel–metal-hydride (Ni–MH) batteries, but the capacity of these alloys and product cost are still unsatisfactory. Another family of hydrogen-storage alloys is the A$_2$B-type, such as Mg$_2$Ni which has been shown to be a potential candidate for use as an anode material in Ni–MH batteries because of its higher hydrogen-storage capability, lower specific weight and lower cost than commercial LaNi$_5$-based alloys [8–10].

Nickel hydroxide Ni(OH)$_2$ is the positive electrode (cathode) material that is widely used in commercial Ni–MH batteries [11–13]. By replacing the heavy Ni(OH)$_2$ material with a lightweight air electrode, however, it is possible to increase the gravimetric energy density and at the same time reduce cost [14]. In this work, polycrystalline Mg$_2$Ni alloy prepared by mechanical alloying is used as the anode, a commercial air electrode as the cathode and 6 M KOH as the electrolyte. The open-circuit voltage (OCV) and charge–discharge characteristics of the battery are investigated and failure is investigated by means of X-ray diffraction (XRD) and scanning electron microscopic (SEM) analyses.

1.1. Metal-hydride–air cell chemistry

In general, the charge–discharge reactions for the Ni–MH rechargeable battery using Ni(OH)$_2$ as the cathode, Mg$_2$Ni as the anode and KOH as the electrolyte solution may be written as [15,16]:

- at the positive electrode:

Ni(OH)$_2$ + OH$^-$ $\xrightarrow{\text{charge discharge}}$ NiOOH + H$_2$O + e$^-$ (1)

- at the negative electrode:

Mg$_2$Ni + 4H$_2$O + 4e$^-$ $\xrightarrow{\text{charge discharge}}$ Mg$_2$NiH$_4$ + 4OH$^-$ (2)

- overall cell reaction:

4Ni(OH)$_2$ + Mg$_2$Ni $\xrightarrow{\text{charge discharge}}$ 4NiOOH + Mg$_2$NiH$_4$ (3)

During the charging process, the Ni(OH)$_2$ at the positive electrode is oxidized to NiOOH, while the alloy M forms MH at the negative electrode. The reactions are reversed during discharging.

The charge–discharge reactions for the MH–air rechargeable battery using an air electrode as the cathode, Mg$_2$Ni as...
the anode and KOH as the electrolyte solution proceed as follows:

- at the positive electrode:

  \[ 4\text{OH}^- \xrightarrow{\text{charge}} \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \]  

- at the negative electrode:

  \[ \text{Mg}_2\text{Ni} + 4\text{H}_2\text{O} + 4e^- \xrightarrow{\text{charge}} \text{Mg}_2\text{NiH}_4 + 4\text{OH}^- \]  

- overall cell reaction:

  \[ \text{Mg}_2\text{Ni} + 2\text{H}_2\text{O} \xrightarrow{\text{charge}} \text{Mg}_2\text{NiH}_4 + \text{O}_2 \]

During the charge process, oxygen gas is produced by water electrolysis on the air electrode and during the discharge process oxygen gas must be supplied to the air electrode [2,3].

2. Experimental

2.1. Battery components and fabrication

The preparation of Mg$_2$Ni alloy powder by mechanical alloying takes about 20 days and has been described elsewhere [17]. An amount of 1.5 g of Mg$_2$Ni alloy and graphite were mixed in a weight ratio of 5:1 and 10 wt.% polyvinyl alcohol (PVA) was added as a binder to form a slurry. The slurry was smeared on to a circular-shaped nickel current-collector to serve as the anode (active area 50.3 cm$^2$, weight 3.4 g, thickness 0.4 cm). Based on the theoretical specific capacity of Mg$_2$Ni, viz. 250 mAh g$^{-1}$, this cell should have a theoretical capacity of about 110 mAh.

The commercial air electrode consists of two active layers bonded to each side of a nickel mesh. The black material, which is a mixture of catalyst (manganese) on carbon fibers and a Teflon binder is also hydrophobic. The white Teflon layer is porous to air but not to water, and is bonded to the air-side of the electrode (see Fig. 1). The air cathode sheet was cut into a circular shape (active area 50.3 cm$^2$, weight 0.9 g, thickness 0.5 mm).

All battery components were enclosed in a cylindrical plastic casing of dimensions 30 mm (length) and 45 mm (diameter). An electrolyte solution (6 M KOH, volume 35 ml) was poured into the battery casing. The entire battery with electrolyte weighted 66.89 g. A schematic of the design of the Mg$_2$Ni6 M KOHIO$_2$ battery is shown in Fig. 2.

2.2. Battery characterization

A BAS LG-50 galvanostat system was used to perform constant-current charge-discharge characterization and monitoring of the OCV of the cells. For charge-discharge measurement, the battery was charged at 10.0 mA for 1 h and discharged at 0.1 mA. Self-discharge was investigated by measuring the OCV of the battery after charging and stand at open-circuit for 24 h at 25 °C. Since the battery was charged to 10 mAh, it is not fully charged to its theoretical capacity.

2.3. Electrode characterization

After the battery was cycled, the anode and the cathode were dismantled, cleaned and dried in a desiccator. The
crystallographic features of the electrodes before and after cycling were examined by XRD (Philips X’Pert diffractometer and the surface morphology was observed by SEM (Leica 5440).

3. Result

3.1. Cell characterization

The OCV, shown in Fig. 3, dropped from 1.5 (in the first 2 h) to 1.2 V, and then remained steady at 1.2 V for about 14 h. At the end of 24 h, the OCV is between 1.1 and 1.2 V. Compared with Mg$_{1.95}$Y$_{0.05}$Ni$_{0.92}$Al$_{0.08}$|6 M KOH–1 M LiOH|Hg/HgO [15,16], it can be concluded that additives in Mg$_2$Ni-based alloys help to improve the OCV by about 0.2 V.

The charge–discharge characteristics are presented in Fig. 4. The longest discharge was observed for cycle 3 and lasted for 8 h. The battery was subjected to 62 cycles. The average charging voltage was about 1.8 V, the average discharge voltages about 0.9 V, and the voltage drop about 0.9 V. Chartouni et al. [7] working with a MmNi$_{3.5}$Co$_{0.7}$Al$_{0.7}$Mn$_{0.1}$|6 M KOH|La$_0.4$Ca$_0.6$CoO$_3$ battery observed a voltage drop of about 1.1–1.2 V while Gamburzev et al. [4] using a La$_0.8$Ce$_0.2$Ni$_{4.25}$Co$_{0.5}$Sn$_{0.25}$|6 M KOH|Hg/HgO cell measured a voltage drop of about 1.0 V.
3.2. Electrode characterization

The XRD patterns of materials used in the anode before and after 62 cycles are illustrated in Fig. 5. The Mg$_2$Ni peaks decrease with cycling and Mg(OH)$_2$ peaks are formed at positions which agree quite well with the values given in JCPDS (7-239) data and [15,16,18,19] (see Table 1), except for the peak at 32.8°.

The thickness of the anode was observed to expand from 0.4 to about 1.0 cm after cycling. This is probably due to the PVA binder in the anode material which had absorbed water from the electrolyte. Electron micrographs of Mg$_2$Ni–graphite–PVA anode before and after cycling at different magnifications are presented in the Fig. 6a and b, and c and d, respectively. The anode is quite smooth and flat before cycling, but after cycling some portions of the surface become thicker (see Fig. 6d). The thickening of the anode material justifies the above observation of anode expansion.

In order to study the effect of cycling on the air electrode, the fibrous carbon was separated from the nickel mesh. XRD patterns of the Ni mesh, fibrous carbon and air electrode were obtained before cycling. After cycling, the air electrode was again subjected to XRD. The XRD patterns are shown in Fig. 7. The peaks detected at 44.6, 52 and 77° are assigned to

<table>
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<th>2θ (°)</th>
<th>JCPDS (7-239) data</th>
<th>Present work</th>
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<td>18.6</td>
<td>32.8 38.0 50.9 58.6 62.1 68.3 68.8 72.0</td>
<td>19.3 38.7 51.5 59.3 62.9 69.2 68.9 72.2</td>
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Table 1

XRD pattern for cycled Mg$_2$Ni–graphite–PVA compared with Mg(OH)$_2$ from JCPDS (7-239) data

Fig. 5. XRD pattern on anode electrode (graphite additive, PVA binder, Mg$_2$Ni active material, Mg$_2$Ni–graphite–PVA) before and after cycling.

Fig. 6. Scanning electron micrographs of Mg$_2$Ni–graphite–PVA anode: (a and b) before, and (c and d) after cycling at different magnifications.
nickel mesh, whereas the 18.5° peak is attributed to the fibrous carbon material. The intensities of these peaks reduce significantly after cycling. The XRD pattern of the air cathode after 62 cycles also shows the presence of phases at 30.5, 32.6, 38.9, 39.4, 52.0 and 67.7°. Electron micrographs of the air electrode are given in Fig. 8a and b which shows the catalyst covering the surface of the electrolyte side. In Fig. 8c and d it can be seen that the catalyst at the surface has peeled off after cycling.

4. Discussion

The self-dehydriding of the Mg2Ni anode during storage probably decreases with increasing storage time following the reduction in the OCV, as shown in Fig. 3. The voltage decreases rapidly during the initial stage of storage in the first 2 h, but slowly thereafter. Luo and co-workers [15,16] reported that the self-dehydriding of a Mg2Ni-based anode is mainly responsible for a high self-discharge rate. The high self-discharge rate from ~1.5 to 1.2 V of a Mg2Ni6 M KOH/O2 cell is almost the same at that for Mg1.95Y0.05– Ni0.92Al0.08|6 M KOH–1 M LiOH/Hg/HgO [15,16]. Mg2Ni-based cells exhibit much higher self-discharge rates than other Ni-MH batteries with AB5-type anodes [20,21]. The plateau time of the charge–discharge characteristics increases during the first three cycles. This suggests that activation of the alloy surface occurs during initial cycling [18].

The XRD data show that failure of the battery is due to oxidation of the active material Mg2Ni to form Mg(OH)2. The Mg2Ni alloy is easily oxidized, especially when it comes into contact with the highly corrosive electrolyte. Rapid degradation during the charge–discharge process hampers a continuous reaction with hydrogen and results in a decay in capacity [10,19,22–24]. The formation of Mg(OH)2 may be represented by the following reaction [23]:

\[
\text{Mg}_2\text{Ni} + 4\text{OH}^- = 2\text{Mg(OH)}_2 + \text{Ni} + 4e^- \quad (7)
\]

It has been reported [25,26] that the discharge capacity and cycle-life of the Mg2Ni–graphite anode are much better than
5. Conclusions

The failure of a battery using mechanically alloyed Mg$_2$Ni can be attributed to anode degradation to Mg(OH)$_2$ and air electrode damage upon cycling. Battery failure can also be due to thickening of the anode which might exert excess stress on the anode-current-collector interface. The voltage drop on discharge is rapid compared with other systems using air electrodes and mixed rare-earth metal anodes. The capacity is low because the battery is not fully charged.

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References


