Research Article

Improvement of Charge-Discharge Characteristics of the Mg-Ni Powder Electrodes at 55°C

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Magnesium-nickel (Mg-Ni) powders are used as the anode materials for secondary lithium (Li) ion batteries. Mg-Ni powders with ratios of 1:1 (Mg:Ni) are prepared and their structure and electrochemical behavior at room temperature and 55°C are investigated. The results show that adding Ni powders to Mg powders can reduce the charge-discharge capacities and improve cycling life. In charge-discharge cycle testing at 55°C, the Li ion concentration gradually increased with increasing the duration of electrochemical reactions, indicating that the charge-discharge capacities increase with increment of cycling number. The formation of a solid electrolyte interface (SEI) layer restrains Mg ions from dissolving into the electrolyte and thus improves the charge-discharge capacities at high temperature.

1. Introduction

Magnesium (Mg) was used as a negative electrode in lithium (Li) ion secondary batteries due to its high theoretic capacity [1]. However, pure metal electrodes have a serious problem of volume expansion during cycling that resulted in poor cycling life. Adding poor-activity elements into a pure metal matrix reduces the volume expansion of an electrode. Studies on alloy electrode materials have focused on Sn- [2], Si- [3], and Mg-based alloys [4, 5]. Of the electrodes based on these alloys, Mg-based ones are one of the potential material in Li-ion battery applications. Many studies have indicated that Mg-based alloy electrode, such as Mg-Li, Mg-C, and Mg-Ni alloys, can enhance battery performance via various electrochemical mechanisms [4, 6–8]. Adding Li into Mg can enhance the efficiency of lithiation and delithiation [9] and Mg-C alloys can restrain the growth of the solid electrolyte interface (SEI) layer [4]. In the present study, Mg-Ni powder electrodes were fabricated to suppress the volume change of the electrode and increase oxidation resistance.

Mg-Ni material is a typical active/nonactive alloy system that can effectively suppress the volume expansion and improve battery cycling life. Many researchers have prepared

Mg-Ni alloys using the mechanical grinding method [10, 11]. However, the proportion of Mg to Ni is not easy to control, and Mg-Ni alloys with excessive Ni have reduced charge-discharge capacity [12]. In addition, Mg easily oxidized to form MgO phases during mechanical milling [13]. The formation of MgO phases may degrade the cycling performance of batteries. In this study, Mg powder was directly mixed with Ni powder in a glove box. Because the particle size of Mg powder and that of Ni powder is very different, alloying effect prevents oxidation problems [14].

This method is simple and the composition ratio of elements can be easily controlled. Portable electronic devices generate heat during operation, which affects Li-ion battery performance. Thus, the charge-discharge characteristics of batteries at high temperature are an important issue. However, few studies have investigated the thermal effects on the charge-discharge characteristics of Mg-Ni compound electrodes.

This study synthesizes Mg-Ni powders and investigates the structural and electrochemical characteristics of Mg-Ni alloy electrodes at room temperature and 55°C. The relations of electrical resistance and electrochemical reaction cycles of Mg-Ni electrodes at high temperature are derived. The metal

FIGURE 1: The electrode of pure Mg powder: (a) charge-discharge curve of the first cycle and (b) surface characteristic.

ion content in the electrolyte is determined to understand the influence of heat and clarify the contribution of Ni addition.

2. Experimental Procedures

An insufficient Ni powder concentration does not lead to the generation of a sufficient passivation layer around the Mg powder. An excess of Ni powder might cause more compound phases, resulting in degraded deterioration of charge-discharge capacities [6]. Therefore, magnesium-nickel (Mg-Ni) compound powders were prepared by mixing of Mg (Φ 150~180 μm) and Ni (Φ 2~5 μm) powders in weight ratios of Mg:Ni = 1:1 and then milled with a rotation rate of 600 rpm using a planetary micromill (FRITSCH GmbH, PULVERISETTE 7) to acquire alloying effect. The compound powders are designated according to the weight ratio of Mg to Ni as MN11.

The Mg-Ni compound powders were uniformly stirred with carbon black (15 wt.%) and polyvinylidene fluoride (PVDF, 15 wt.%) and then coated on copper (Cu) foils. And then, the electrodes were dried in an oven at 120°C for 1 hour. The Mg-Ni powder electrodes were cut into disks (13 mm in diameter and about 200 μm in thickness) and Li foil was used as a counter electrode (positive electrode). One M LiPF₆, ethylene carbonate (EC) and, diethyl carbonate (DEC) were used as an electrolyte and the volume ratio of EC to DEC was 1.

This study measured the surface characteristics of powder electrodes using high-resolution scanning electron microscopy (HR-SEM, HITACHI/SU8000). The electrochemical testing was performed with a lithium battery testing (LBT) cell using the battery automatic tester (BAT-750B). The cells were tested at a constant current of 20 mA·g⁻¹. Cyclic voltammetry (CV) was used to investigate the cycling efficacy with electrochemical impedance spectroscopy (EIS,

PARSTAT 2273). The electric potential was limited to the range 0~2 V and the velocity of scanning was 0.05 mV·s⁻¹. In addition, the resistances of powder electrodes after the electrochemical testing were measured using a 4-point probe. Finally, inductively coupled plasma-mass spectrometry (ICP-MS, HEWLETT PACKARD 4500) was used to determine the metal ion content in the electrolyte.

3. Results and Discussions

3.1. Charge-Discharge Characteristics of the Mg-Ni Electrodes at Room Temperature. Figure 1(a) shows the voltage profile for the first cycle of a pure Mg powder electrode at room temperature. The charge-discharge curve has a plateau at a voltage of 1.0~0.75 V, which is associated with the formation of the SEI layer [6]. The initial discharge capacity of the Mg powder electrode (151 mAh·g⁻¹) was much lower than that of Mg film electrode (2644 mAh·g⁻¹) in our previous experiment, which is due to the surface oxidation and looseness of the Mg powder electrode. The surface characteristics of Mg powder electrode before charging and discharging is shown in Figure 1(b). Some cracks appear on the surface of the electrode, which allowed the Li ions to react with the Cu foil, resulting in degraded charge-discharge capacities. Although the Mg film electrode has good charge-discharge characteristics, the electrochemical reaction might be an explosion hazard due to its activity [1]. Adding Ni powder to Mg powder can promote structural compactness, which may improve the charge-discharge characteristics of a battery. Therefore, the Ni powder was mixed with Mg powder to form a compound phase around Mg powder to avoid intense electrochemical reaction.

Figure 2(a) shows the initial charge-discharge profiles of the MN11 powder electrodes at room temperature. Compared to the initial discharge capacity of the pure Mg powder

FIGURE 2: MN11 compound powders at room temperature: (a) charge-discharge curves of the first cycle and (b) charge-discharge capacities as a function of cycle number.

electrode, that of MN11 powder electrodes was low, indicating that Mg activity was restrained by Ni [15]. Previous studies [6, 16] have indicated that the Mg_2Ni and MgNi_2 alloy phases generated in the Mg-Ni alloy system can restrain volume expansion and thus improve the cycling life of a battery. There is a voltage plateau at 0.2~0.5 V, indicating that the Li ions became embedded in the positive electrode (Li foil). The potential voltage of 0.5~1.25 V was associated with some Li ions moving out from the electrode matrix. The charge-discharge capacities as a function of cycle number for the MN11 powder electrode at the room temperature are shown in Figure 2(b). In addition to having higher initial discharge capacity, MN11 electrode had stable charge-discharge characteristics in the subsequent electrochemical reactions. This result may attribute to the formation of the SEI layer in the initial charge-discharge reaction [17]. Generally, the charge-discharge characteristics of battery could gradually deteriorate with cycling [18]. However, the proposed MN11 electrode still maintained stable charge-discharge capacities due to alloying effect reduced oxidation problem.

3.2. High-Temperature Cycling Performance. In general, the cycle life of a battery operated in a high-temperature environment deteriorates quickly. In order to understand the effects of heat treatment on the cycling performance of batteries, the charge-discharge characteristics at 55°C were tested. The initial discharge curve of the MN11 electrode at 55°C has two plateaus, at voltages of 0.9 and 0.2 V, respectively (Figure 3(a)). The plateau at 0.9 V only appears in the initial discharge curve, indicating that the SEI layer formed [17]. The voltage plateau at 0.2~0 V appears in every discharge curve and is attributed to the potential of lithiation and delithiation [8]. In a high temperature environment, the voltage plateau at 0.2~0 V was longer compared to that of the Mg-Ni electrode at room temperature. This result is due to more Li ions becoming embedded into the electrode matrix

at 55°C due to the high temperature increasing the kinetic energy and chemical activity. Figure 3(b) clearly shows that the cycling capacities of the battery increased with increasing cycle number. This reveals that the Li foil (positive electrode) could more easily react with the electrolyte to liberate more Li ions in the cell at 55°C. Also, the heat affected the diffusion rate of Li ions in the cell. Although a high temperature environment enhances capacity, the cycling performance of the battery deteriorates more quickly. Nevertheless, the Mg-Ni powder electrode had good high temperature cycling characteristics. In fact, some Li ions did not participate in the reaction at room temperature. At 55°C, the heat enhanced the kinetic energy and chemical activity, promoting more Li ions to participate in the reaction and caused the diffusion rate of Li ions to increase with increasing the duration of electrochemical reactions.

To investigate the thermal effect on the electrochemical reaction, the cyclic voltammetry (CV) of the MN11 electrode at 55°C is presented in Figure 4. There is a peak at 0.25 V in the charge curve, indicating that a large number of Li ions inserted into the MN11 electrode. After the first cycle, the irreversible reaction is associated with the formation of the SEI layer [19]. With increasing the cycle number, the peak at 0.25 V gradually increased, indicating that cycle performance improved, which is consistent with Figure 3(b). In addition, the potential voltage shifted, which is related to the variation of the internal resistance of the powder electrode [20].

After 5 charge-discharge cycles, the surface characteristics of the MN11 electrode at room temperature (MN11-RT) and 55°C (MN11-HT) were recorded to clarify the growth behavior of the SEI layer (Figure 5). The surface morphology of the MN11-RT powder electrode shows many cracks (Figure 5(a)). The continuous lithiation and delithiation reactions caused a volume expansion of the electrode, resulting in the fracture of the SEI layer [21]. For the MN11-HT electrode, the electrode surface has a dense SEI layer

FIGURE 3: (a) Initial charge-discharge curves and (b) charge-discharge capacities as function of cycle number for MN11 compound electrode at 55°C.

FIGURE 4: Cyclic voltammograms of MN11 electrode with 55°C measured for 5 cycles at scan rate of 0.05 mV s⁻¹.

and fewer cracks (Figure 5(b)). The growth rate of the SEI layer was faster in the high temperature environment [22]; the electrode surface was covered with thicker SEI layer. As a result, the thicker SEI layer was more able to resist the volume expansion of the electrode.

In addition, the SEI structure might decompose during the electrochemical reaction at high temperature, as its thickness did not continuously increase. This explains the improved charge-discharge characteristics of the Mg-Ni electrode at high temperature. The cracks may affect the resistance of the electrode. Therefore, the resistivity of MN11-RT

TABLE 1: The resistance value of the Mg-Ni electrode at room temperature (RT) and 55°C (HT) after different charge-discharge cycling.

Sample	Resistivity ($\Omega \cdot \text{cm}$)		
	1st cycle	3rd cycle	5th cycle
MN11-RT	4.0×10^4	5.6×10^3	7.8×10^3
MN11-HT	2.1×10^4	2.2×10^3	1.7×10^3

TABLE 2: The dissolution of metal ions concentration in an electrolyte for MN11 and pure Mg electrode.

Sample	Ion concentration ($\mu\text{g} \cdot \text{mL}^{-1}$)	
	Mg	Ni
MN11	2.760	0.469
Mg	5.709	N/A

and MN11-HT electrodes at various charge-discharge cycles were measured (Table 1). The resistance of the MN11-RT electrode decreased from the first to the third cycles and then increased. The main reason was that the intense volume expansion of the electrode increased the number of cracks. In contrast, the resistance of the MN11-HT electrode continuously decreased with increasing charge-discharge cycle. This result might be associated with the thicker SEI layer restraining the volume expansion, which is consistent with the CV results (Figure 5(b)).

In order to clarify the thermal effects on ion liberation behavior, the electrolyte was examined using ICP-MS (Table 2). The electrolyte of the MN11-HT electrode had fewer Mg ions ($2.760 \mu\text{g} \cdot \text{mL}^{-1}$) compared to the electrolyte of the Mg electrode ($5.709 \mu\text{g} \cdot \text{mL}^{-1}$). This result indicates that adding Ni powder can reduce the liberation of Mg ions.

FIGURE 5: The surface characteristics of the solid electrolyte interface layer of MN11 electrode with (a) room temperature and (b) 55°C after 5 charge-discharge cycles.

FIGURE 6: Schematic illustrations of pure Mg and the Mg-Ni electrode with the duration of the charge-discharge reactions.

In addition, the Mg-Li compound phases formed at high temperature, enhancing electrode's ability to resist fracture [23].

Schematic illustration of pure Mg and the Mg-Ni electrode with charge-discharge duration is shown in Figure 6. For the pure Mg electrode at the room temperature, the SEI layer was thinner and the volume expansion of the electrode was more obvious, resulting in serious cracks after the charge-discharge. In addition, Mg easily oxidized to form MgO phases, which decreased the activity of Mg. The MgO phases prevented Li ions to react with Mg and thus degraded the charge-discharge efficiencies. Mg-Ni compound phases could restrain the activity of Mg and the volume expansion of electrode during the charge-discharge processes. Notably, a fewer MgO phases allowed Li ions to react with Mg more easily. At 55°C, the heat increased the kinetic energy and chemical activity, making the Li ion concentration increase with increasing charge-discharge cycles. In addition, the growth rate of the SEI layer was faster, which reduced the crack density. The high temperature also caused the decomposition of the SEI layer, which prevented the SEI layer from increasing without bound. The Mg-Ni electrode at 55°C has good charge-discharge capacities, making it suitable for Li-ion battery operation at high temperature.

4. Conclusion

Ni powders mixed with Mg powders were found to effectively suppress the activity of Mg and the volume expansion of the electrode due to the formation of a passivation layer and the existence of Mg-Ni (Mg_2Ni and MgNi_2) alloy phases. Adding Ni powder reduced Mg dissolution without significantly degrading. At high temperature of 55°C, the charge-discharge capacities and cycling performance of the Mg-Ni alloy electrode were enhanced. The main reason was that the high temperature increased the kinetic energy and chemical activity, making the Li ion concentration increase with electrochemical reaction time. Additionally, the electrode at high temperature formed a thicker SEI layer, which resisted the volume expansion of the electrode. The decomposition of the SEI structure at high temperature caused the cycle life of the battery. The Mg-Ni alloy electrode is thus suitable for application in Li-ion batteries operated at high temperature.

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