

Short Communication

Lithium-magnesium Alloy as an Anode for Lithium-Sulfur Based Batteries

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Lithium-sulphur (Li-S)-based batteries have received much attention due to their overwhelming theoretical energy density (2500 Wh·kg⁻¹). The modification of Li-based anodes is a critical issue relevant to the practical usage of Li-S based batteries, considering the increasing cost of Li metal and the dendritical tendency of anodes. In this study, we demonstrated that a lithium-magnesium (Li-Mg) alloy can also act as the anode of Li-S based batteries and perform comparably to Li. The electrochemical behavior of the Li-Mg alloy could be further improved by the surface nitridation and coating with a layer of molybdenum disulfide. There was no clear dendrite on the surface of the electrode. When the surface was nitrided, the stability of the battery was improved, and when the surface of the Li-Mg anode was coated with molybdenum disulfide by magnetron sputtering, the cycling performance of the electrode was improved, with an increased specific discharge capacity. Thus, this work suggests that the Li-Mg alloy could be a suitable material for replacing lithium as the anode material of Li-S based batteries.

Keywords: Lithium-Magnesium Alloy Electrodes, Surface Modification, Li-S Battery

1. INTRODUCTION

With the rapid development of electric vehicles and portable electronic devices, the demand for energy sources with a high energy density is increasing. Among the high-density energy sources, lithium metal-sulfur (Li-S)-based batteries have attracted widespread attention due to their high capacity and energy density (2500 Wh·kg⁻¹). Lithium is required as the anode material of Li-S based batteries due to its high specific energy (3860 mAh/g), low density (0.59 g/cm³), and lowest electrochemical reduction potential (-3.045 V against a Standard Hydrogen Electrode) [1]. With the increasing use of Li batteries, the cost and limited availability of Li resources are becoming key

concerns among the scientific and industrial communities. The formation of Li dendrites during the electrochemical reaction of pure Li metallic anodes is another major challenge. For example, uneven lithium deposition could cause the uncontrolled development of lithium dendrites [2], and the high chemical reactivity of lithium may lead to the formation of unstable solid electrolyte membranes [3-4]; the extra-large volume expansion could result in an increase in electric impedance [5]. These factors reduce the coulomb efficiency, shorten the battery life, and cause safety issues [6]. Therefore, it is worth investigating materials that could replace metallic Li anodes and their surface modification to ease the usage of Li metal and reduce dendritic Li deposition during the electrochemical cycling processes.

Partially Mg-substituted Li-Mg alloy [7] could not only preserve the merits of pure Li metallic anodes, but also weaken the anode's surface reactivity. Mg ions can also act as transfer ions in the batteries. With the proper substitution of Mg for Li, nearly 90% of the volume fraction of the Li-rich β phase can be achieved, based on the phase diagrams of Li-Mg alloy systems [8], which would aid in providing sufficient exposed surface for the anode reactions. Further, the existence of a Mg-rich phase could strengthen the anode plate and allow it to endure potential volume variations under Li-ion transportation. Therefore, Li-Mg alloy electrodes could exhibit good structural stability for the electrochemical process [9]. Additionally, the ions have a high diffusion rate in Li-Mg alloys at room temperature [9-10]. In this study, we selected a $\text{Li}_{0.8}\text{Mg}_{0.2}$ alloy to determine its electrochemical performance as the anode material of Li-S-based batteries. The surface of the alloy sheet was also modified to improve its performance.

2. EXPERIMENTAL

2.1 Materials preparation

The lithium and the magnesium metals were melted with a weight ratio of 4:1 to create a Li-Mg alloy under an inert atmosphere, which was subsequently rolled into 1 mm-thick sheets. The Li-Mg alloy sheets were cut to serve as the anodes. As the Li-Mg anodes easily oxidize in the air, they were stored in an argon-filled glove box. Surface nitridation was conducted by storing the Li-Mg sheets under nitrogen gas at room temperature for 32 h. Surface coating with molybdenum disulfide (MoS_2) was achieved through RF magnetron sputtering using a MoS_2 target. During sputtering, the background vacuum was below 5.0×10^{-4} Pa, the working pressure was 2.3×10^{-2} Torr, and the sputtering power was 100 W.

2.2 Morphology characterizations and electrochemical tests

LIR 2032 coin-type cells were assembled in an argon-filled glove box ($\text{H}_2\text{O} < 0.5$ ppm, $\text{O}_2 < 0.5$ ppm, MBRAUN LABSTAR) to assess the electrochemical performance using a 1-M bis (trifluoromethanesulfonyl) imide lithium (LiTFSI) electrolyte, 1 wt% LiNO_3 in a mixed 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) solvent with a volume ratio of 1:1, and a polypropylene

microporous film separator (Celgard 2300). The cathode was composed of a carbon-sulfur composite material. The galvanostatic charge/discharge tests were conducted on a LAND test system (BTS-5V 20mA) with a potential range of 1.6-2.8 V (VS. Li/Li⁺ electrode). Following the electrochemical test, the working electrode was removed from the cells using a battery removal machine and quickly transferred into the glove box for later scanning electron microscope observation (Germany MERLIN Compact Scanning Electron Microscope). As the Li-Mg alloy electrode is highly oxidizable, the assembled battery was disassembled and transferred to an argon-filled glove box to prevent air pollution.

3. RESULTS AND DISCUSSION

Figure 1 presents the initial charge/discharge capacity curves and the cycling performance of the Li-Mg and pure Li anodes with the same sulfur cathode and a current rate of 0.2 C. According to the initial charge/discharge curves of the pure Li and Li-Mg alloy anodes (Fig. 1a), both cells exhibit clear polysulfide formation plateaus at approximately 2.1 V and reductions at approximately 2.3 V. Therefore, the doping of magnesium had no adverse effect on the redox reaction of sulfur cathodes. The initial discharge capacity of the pure Li anode (851 mAh/g) was higher than that of the Li-Mg anode (790 mAh/g). Although there was a minor decrease in the capacity, the battery with the Li-Mg anode still exhibited a higher capacity than the reported lithium aluminum alloy [18] and good cycling stability, similar to the latest reported Li-Mg alloy electrode [19]. According to the cycling performance in Fig. 1b, the coulomb efficiency of the cell with the Li-Mg anode (average of 82%) was better than that of the pure Li anode (approximately 73%). The discharge capacity of the cell with pure Li rapidly degraded from 851 to approximately 450 mAh/g after 13 cycles. In contrast, the cell with the Li-Mg anode exhibited a better cycling behavior and higher remaining capacity of 560 mAh/g, although its initial discharge specific capacity was lower.

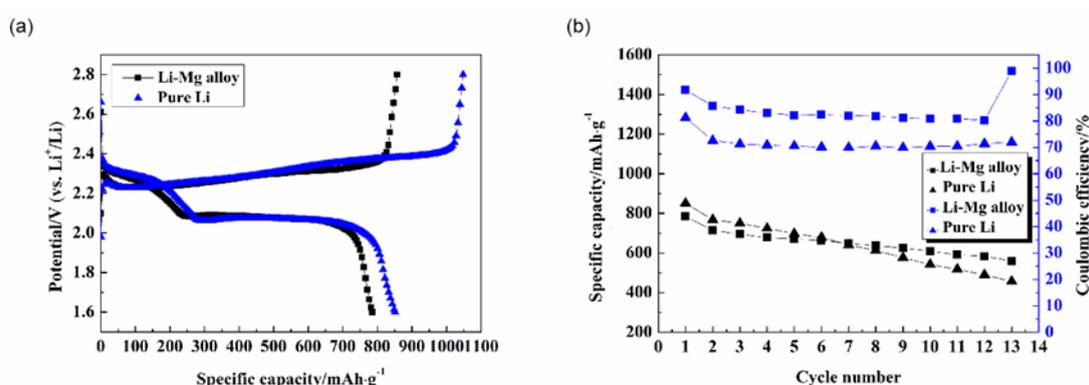


Figure 1. Electrochemical performance of the Li-S based batteries with pure Li and Li-Mg alloy electrodes (Mg % = 20 wt%) at 0.2 C: (a) initial charge/discharge specific capacity curves; (b) cycling performance curves.

As shown above, the performance of the cell with the Li-Mg anode was comparative to that of the cell with the pure Li anode. Figure 2 exhibits the surface of the Li-Mg sheet after 100 cycles at 0.2

C. In comparison to the reference pure Li anode [11], there were no dendrites and surface corrosion on the surface of the Li-Mg alloy electrode after 100 cycles at 0.2 C. This is also consistent with the high stability of the Li-S battery with the Li-Mg alloy anode at 0.2 C. Thus, it can be deduced that the Li-Mg alloy could be a good candidate as an anode for the batteries that require Li metallic sheets.

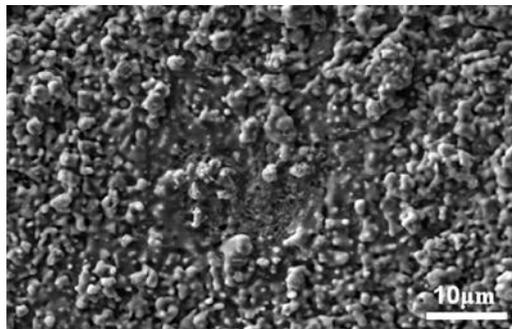


Figure 2. Surface morphology of Li-Mg alloy electrode after 100 cycles at 0.2 C.

Surface modifications are widely accepted to aid in improving the electrochemical performance of pure Li metallic anodes [12-16]. Here, we attempted to test whether the surface modifications are also useful for enhancing the properties of the current Li-Mg anode in the cells with a sulfur cathode. Figure 3 shows the initial specific charge/discharge capacity curves of the initial Li-Mg alloy anode and the Li-Mg alloy anodes modified by surface nitridation and surface coating with a molybdenum disulfide layer and the same sulfur cathodes with a current rate of 0.2 C. All cells exhibited two similar voltage plateaus in the discharge profiles at approximately 2.3 and 2.1 V and a long plateau during the charging process, corresponding to the reduction of elemental sulfur to lithium sulfide (Li_2S_n , $4 \leq n \leq 8$) and further reduction to polysulfide ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$), and the conversion of lithium sulfide to elemental sulfur and lithium, respectively [17].

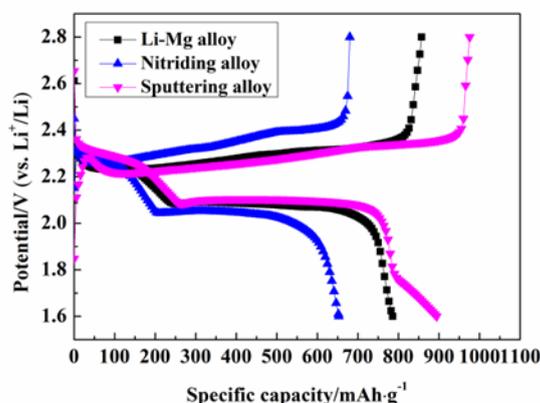


Figure 3. The initial charge/discharge specific capacity curves of Li-S-based batteries with different Li-Mg alloy electrodes at 0.2 C.

The voltage plateaus suggest that the surface nitridation and coating with molybdenum disulfide layer had no adverse effect on the oxidation-reduction process of the sulfur cathode or the original Li-Mg alloy electrode. The discharge voltage plateau of the cell with the sputtered alloy anode is longer and more stable than that of the original alloy anode, while that of the cell with the nitrided alloy anode had little effect. This suggests that the surface coating with the molybdenum disulfide layer is beneficial for the deposition/stripping of lithium ions during operation, and exhibited a similar protecting role, as reported in the lithium metal anode [20].

The cycling performance of the Li-S batteries with the initial and modified Li-Mg-alloy anodes at 0.2 C are compared in figure 4. When the Li-Mg alloy anode was modified by surface nitridation, the initial specific capacity of the cell was 653 mAh/g and decreased to 468 mAh/g after 14 cycles, with an improved coulomb efficiency. When the Li-Mg alloy anode was modified by surface coating with the molybdenum disulfide layer, the cell exhibited a higher specific capacity of 894 mAh/g after 14 cycles and relatively good stability, which might be related to the improvement of the surface morphology of the Li-Mg alloy electrodes (Fig. 2). Therefore, the above results indicate that surface modification can be implemented to enhance the electrochemical performance of the Li-Mg-alloy anodes for Li-S based batteries, to a certain extent.

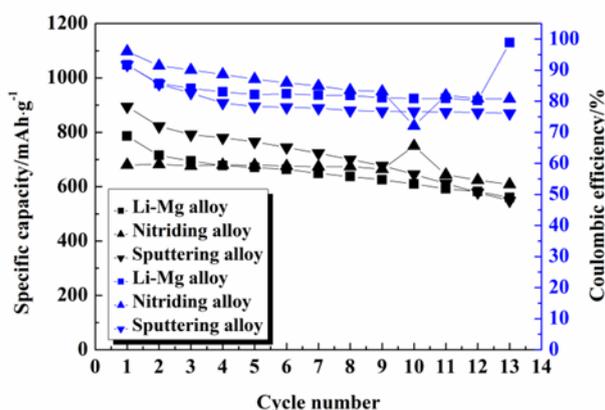


Figure 4. Cyclic performance of the Li-S batteries with different Li-Mg-alloy electrodes at 0.2 C.

4. CONCLUSIONS

In this study, the Li-Mg alloy was demonstrated to be applicable as anode materials for Li-S-based batteries. The cells with the Li-Mg-alloy anodes could not only slow the formation of dendrites, but also exhibited better cyclic stability than the pure Li anode in the current Li-S-based batteries. In addition, surface modification methods can be used to improve the electrochemical performance of Li-Mg-alloy electrodes. When the Li-Mg alloys were modified by coating with a molybdenum disulfide layer, the electrochemical performance of the cells with the Li-Mg alloy anodes was improved, to a certain extent.

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