

Charge-Discharge Mechanism of Mg-C powders and Mg-Li Alloy Thin Film Materials

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Abstract

Magnesium-carbon powders and Magnesium-lithium powders were used as the anode materials for lithium ion batteries to investigate the structure and electrochemical behavior in room temperature. The composition of Mg-C powders contained 1:1 and 9:1. The powders and the thermal evaporated films of Mg-10Li were compared with Mg-C systems. In addition, Mg-10Li thermal evaporated film was used as the experimental materials to process the annealing treatment. The results show that Mg-C powders system had the interface effect of a Cu foil to reduce the electrochemical reaction. With increasing the carbon powder content, the charge-discharge characteristics of Mg-C powders was raised. Notably, the Mg-10Li specimen had better cycling properties than that of Mg-50C (1:1). After annealing at 200 °C for 1hr, Mg-10Li alloy film not only increased the capacity, but also improved the charge-discharge cyclability.

Introduction

Adding more active element (lithium) into the magnesium matrix will form the lightest structural materials, magnesium-lithium alloys [1-2]. It is notable that magnesium-lithium alloys possess higher theoretic voltage, theoretic capacities and electrochemical activity relative to other magnesium alloys [3-4]. Many researches [5-7] indicate that the anodes of magnesium-lithium alloys have feasibility for the fuel batteries. Other researches [7-8] indicate that the electrochemical mechanisms of the Mg-Li anode materials have higher capacities.

With the development of nanotechnology, the magnesium alloys whose nanostructures can enhance the performance of magnesium battery. Nowadays the nano or micro magnesium powders getting by ball-milling techniques have applied for magnesium-oxygen batteries [8-10]. (current density: 5mA/cm²; energy density: 565Wh/Kg), but the problems of oxidation still affect the properties of battery powders. Furthermore, the life cycles of fuel battery of AZ magnesium alloys will be improved through the chemical coating of surface [11]. By buffering of the second phases, the magnesium-carbon thin film can also improve the performance of batteries [12-13].

According to our previous studies [14], the electrodes of Mg-Li alloy by vapor deposition had favorable charge-discharge characteristics and higher capacities. Since magnesium alloys apply for air batteries and fuel batteries mostly, the studies focusing on material characteristic for lithium batteries are few. Notably, the electrodes of magnesium matrix possess potential for application. To avoid oxidation and surface problems, we use the mixture of magnesium-carbon powders and the evaporating thin film to study the basic properties of Mg-C and Mg-10Li thin film. The present charge-discharge characteristics lead the Mg-Li alloy to be applied for lithium batteries.

Experimental Procedures

Mg-C powders were prepared from mixture of magnesium powders and carbon powders. The weight ration of these powders were Mg:C=1:1 and Mg:C=9:1, respectively. Mg-C powders were stirred with carbon black (10 wt.%) uniformly and coated on Cu foils. The electrodes were cut for charge-discharge test (the same method with following thin film test). In addition, the Mg-10Li target was made by vacuum melting furnace and then performed the process of evaporating on 10µm Cu foil. The surface of the evaporating specimens were kept as deposited, part of specimens were annealed at 200°C for 1hour under vacuum. Moreover, the thickness of Mg-10Li film was 1.2 µm (named as MgLi film). Every specimen was cut and then the analysis of the charge-discharge characteristic was carried out via the lithium half-cell. In addition, LiPF₆, ethylene carbonate (EC) and diethyl carbonate(DEC)(EC : DEC=1 : 1 vol.) were as the electrolyte.

The surface characteristics and microstructure of both the electrode powders and thin film were observed by SEM and FIB. In addition, the identification of the element was detected using X-Ray, the incident angle was 1°, scanning speed was 2°/min and scanning range was from 20° to 80°. The charge-discharge experiments were performed ten times in fixed current. The magnitude of current was set as 0.1C to theoretic capacity. Termination voltage was 0.01V and 1.5V, respectively. All of data were the average of 3~5 times.

Results and Discussion

The appearances of magnesium powders and carbon powders are shown in Figure 1, the pure magnesium powders present the irregular patterns, belonged to the mechanical refinement powders and the particle size was approximately 150~220 µm (Fig.1 (a)). The average grain size of sphere carbon powders was in 185µm and the structural compactness was higher (Fig.1 (b)).

Figure 2 shows the XRD diffraction of pure magnesium powders and carbon powders. Figure 2 (a) confirms no oxidation of pure magnesium powders and the powders possessed an excellent crystallization. Form the intensity of low angle diffraction, the degree of graphitization for carbon powders was good and no impurity phases in the matrix (Figure 2 (b)).

The magnesium powders and carbon powders were mixed with 9:1 and 1:1 (carbon black: 10 wt.% and binder PVDF: 5wt.%) to perform the charge-discharge testing. Figure 3 (a) shows the surface morphology of Mg: C = 9:1 powders coating on the copper foil. The spherical carbon powders were distributed on the matrix and the surface of carbon powders possessed coating characteristics. When the increase in the proportion of carbon

powders, the Mg: C = 1:1 powders had formed. For surface observation of coating layer, many carbon powders were found to have an aggregation (Figure 3 (a)). Regardless of mixing ratio, the magnesium particles could not easily be observed on the coating layers, and the matrix was the fine pore structure. The porosity was closely related with the charge-discharge characteristics.

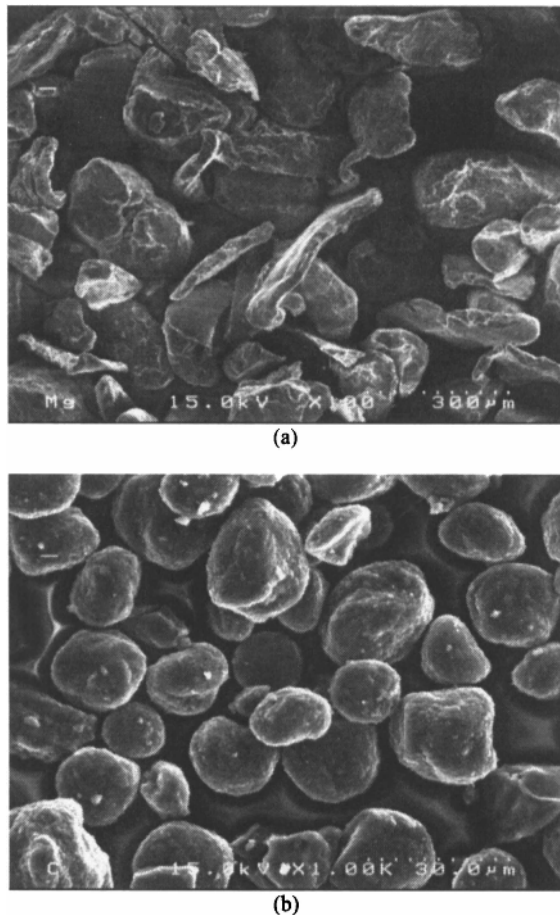


Fig. 1 Appearance of powders: (a) pure Mg powders (b) carbon powders.

Both charge-discharge cycle curves of Mg: C=9:1 electrode and Mg: C=1:1 electrode were shown in Figure 4. It was found that the initial curves of the two electrodes were increased with increasing the number of cycles, and then the trend of curves had stabilized. For Mg: C=9:1 curve (Figure 4 (a)), the charge-discharge cycle curve had two plateau areas could explain the non-stable state of ion reaction [15]. At the end of horizontal area, the ions of electrodes still had higher activation energy to make the charge-discharge capacity upgrade. In Figure 4 (b), increasing the content of carbon powders, Mg: C=1:1 electrode had higher capacity than that of Mg: C=9:1 electrode in the same period of charge-discharge cycle. Notably, Mg: C=1:1 curve has a flat area that confirmed the balance mechanism at lithium ions inserted.

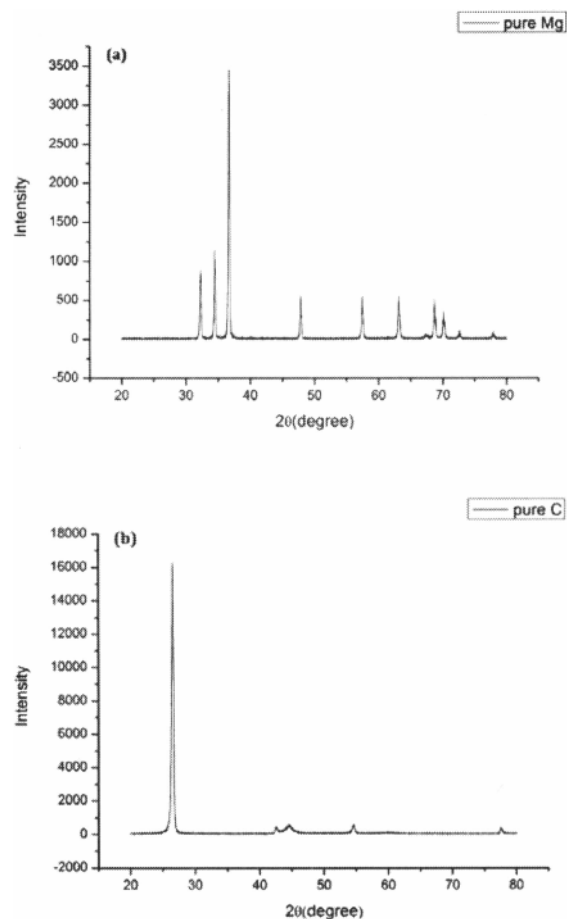
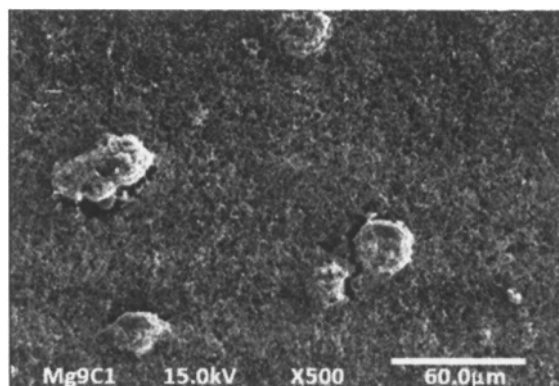
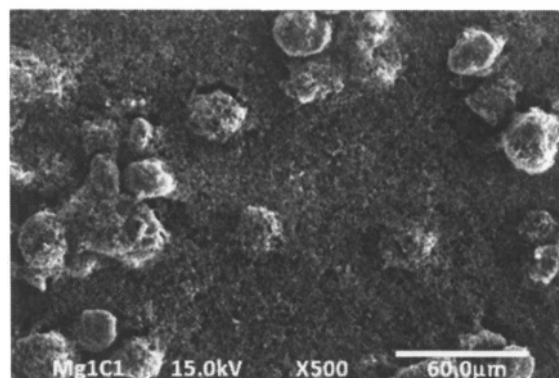


Fig. 2 XRD of powders: (a) pure Mg powders (b) carbon powders.

Compared with related literature of metal based [16], we found that the initial charge-discharge capacity of Mg-based electrodes increased, result from the magnesium ions and lithium-ions induced the activation gradually. In other words, the initial reaction duration, the lithium ion cannot reach the inside lattice of magnesium electrodes. Through the coating cracks in the interface between the carbon sphere and the matrix, the Li ions had contacted the copper foil easily to have lower initial capacitance. Increasing the reaction time, the depth of lithium ions into the magnesium based matrix increased to improve the charge-discharge capacity. This is why the charge-discharge cycle curve of the system increased with increasing the number of cycles. Due to lithium ions insert at magnesium matrix step by step, we can confirm that the phase structure of magnesium matrix had a closely related with the insertion lithium ions. Base on this fact, Mg-10Li alloy powder electrode was prepared in order to compare with related electrical data.



(a)



(b)

Fig. 3 Surface characteristics of Mg-C mixed powders: (a) Mg:C =9:1 powders (b) Mg:C =1:1 powders.

Fig. 5(a) shows the appearance of Mg-10Li alloy powders, the particle size distribution was from 40µm to 300µm. Fig. 5(b) shows the surface characteristics of Mg-10Li alloy powders coated on Cu foils, it displayed a great decreasing of crack amount between Mg-10Li alloy powders and Cu foil. Notably, Mg-10Li alloy powders doesn't present a good charge-discharge property (was lower than 100mAh/g), it indicated that the matrix of Mg-10Li powders belonged to eutectic-like hcp structure [6], it was easy to form lithium oxide and hindered the insertion of lithium ions in the pulverization process, resulted in affecting the electrochemical characteristics of Mg-10Li powder electrode.

To avoid oxidation and keep the eutectic-like structure of Mg-10Li matrix, the thin film electrode of Mg-10Li using thermal evaporation was studied. Fig. 6(a) shows the surface characteristics of evaporating Mg-10Li alloy film, it was found that there was rolling textures at the surface of thin film. After annealing at 200°C in vacuum, the roughness of Mg-10Li thin film was improved and a small amount of Li-rich phase precipitated (Fig. 6(b): dark zone). In addition, the cross-section using FIB was observed (Fig. 7), the thickness of Mg-10Li thin film was about 1.2 µm and the interface of Mg-10Li/Cu was not continuous (had interface cracks) after heat treatment.

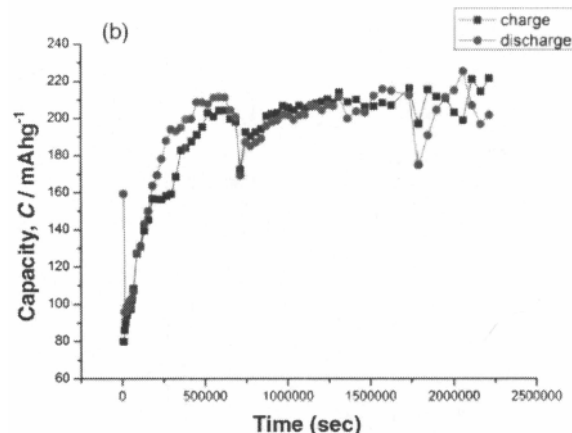
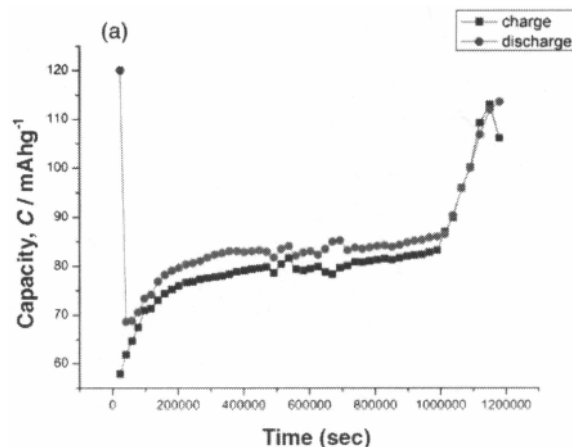
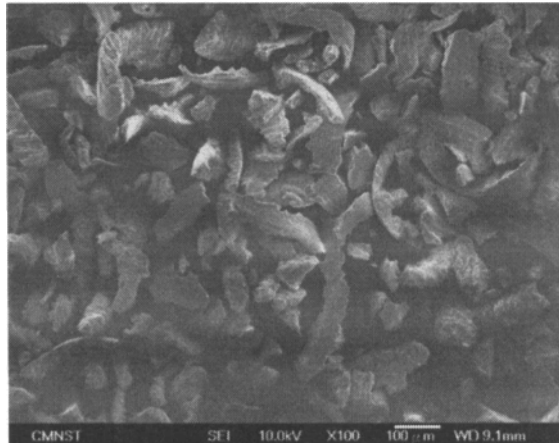


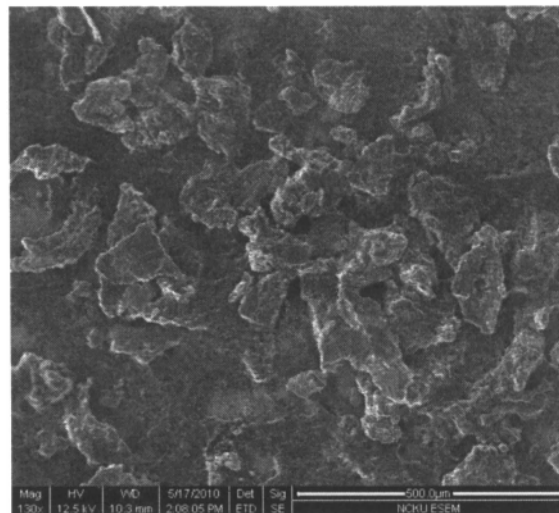
Fig. 4 Cycle performance of Mg-C mixed powders at 0.1 C-rate: (a) Mg:C =9:1 powders (b) Mg:C =1:1 powders.

Previous references [15] showed the interface characteristics (thin film /Cu foil) of electrodes using mechanical polishing were intact but it was not true. It was confirmed that there were not complete metallurgy bonding at interface between Mg-10Li thin film and Cu foil, and the interface existed some cracks (Fig. 7). Compared with the other thin films [17], the matrix of the evaporating Mg-10Li thin film was uniform and had no voids. According to electrodes references [18-19], the annealing would increase the uniformity of thin film, so the charge-discharge experiment of annealed Mg-10Li thin film was performed at room temperature.

Figure 8 shows the curve of charge-discharge capacity for annealed Mg-10Li alloy film, which takes the first cycle as the basic value (380 mAh/g). The result illustrated that Mg-10Li alloy film had the highest capacity at the first cycle and rapidly decreased with increasing of the cycle number. After 10 cycles, the discharge capacity of the electrodes still maintained about 70%. The decline mechanism had a relation with the phase change of electrode matrix.

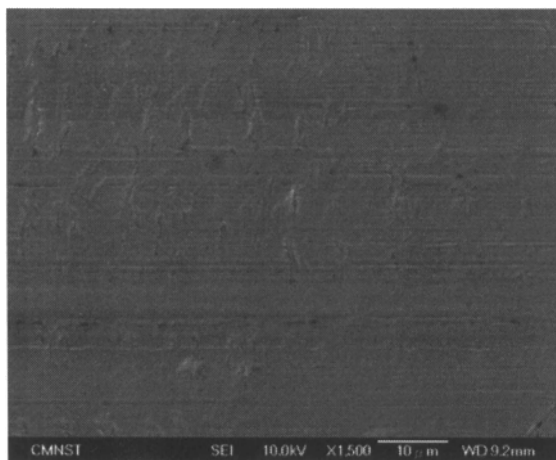


(a)

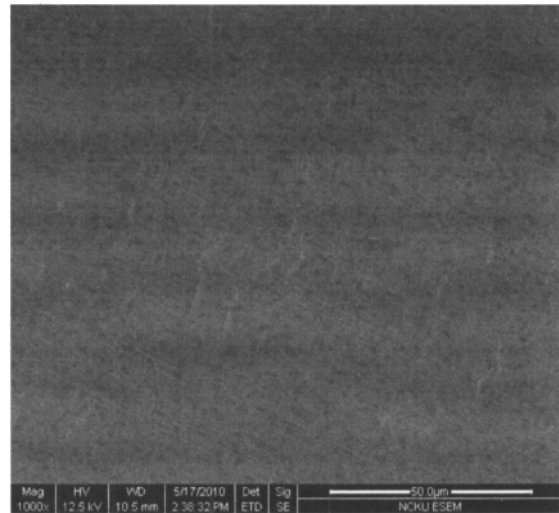


(b)

Fig. 5 SEM photograph of alloy powders: (a) MgLi powders (b) MgLi powders coated on the Cu foil.



(a)



(b)

Fig. 6 SEM photograph of thermal coated films: (a) MgLi alloy film (b) annealed MgLi alloy film.

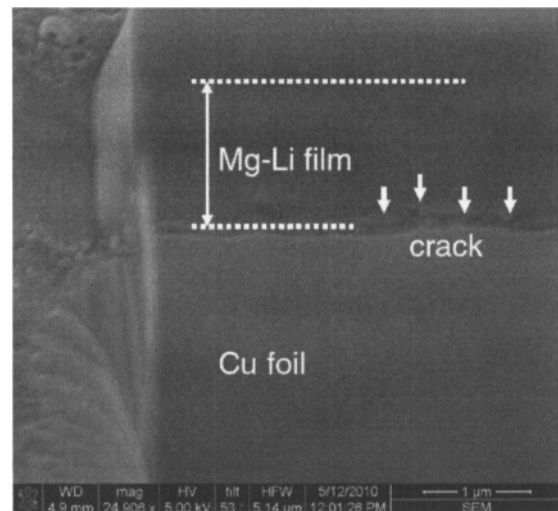


Fig. 7 Cross-section observations of annealed MgLi alloy films using FIB.

In fact, during the thermal evaporation and annealing process, Li-rich phases were observed in the matrix of Mg-10Li film, this phase (Li-rich) had higher activity and was not easy to form passivation layers. But it had dissolution effect for electrolyte and then hindered the insertion of ions. The magnesium matrix with solid solution of Li atom contributed to relieve the dissolution effect and electrochemical balance, so it could reduce the slope of charge-discharge curve. Therefore, the evaporating Mg-10Li thin film actually possesses the feasibility for the application of lithium ion batteries.

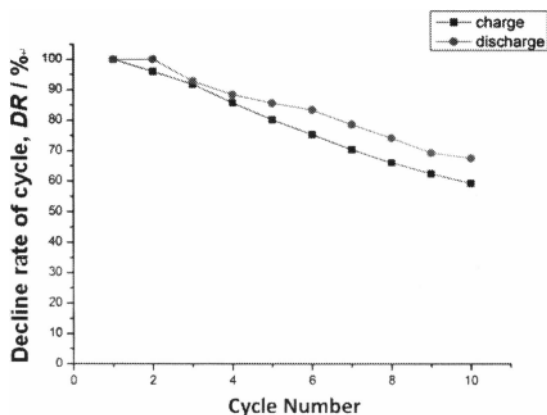


Fig. 8 Decline rate of charge-discharge capacities as a function of cycle number for annealed Mg-10Li alloy film. (Taking the first cycle as the base value)

Conclusion

Both magnesium-carbon (Mg-C) powders and the evaporating Mg-10Li thin film possessed the feasibility for the application of lithium ion batteries. To avoid the oxidation and the generation of coating cracks, increasing the carbon content raised the charge-discharge characteristic of magnesium-carbon powder electrode. In evaporating Mg-10Li thin films, the heat treatment stabilized phase structure to improve the charge-discharge cycle life.

Acknowledgements

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