

Preparation and Electrochemical Characteristics of Mg-Sn Nanoparticles as an Anode Material for Li-ion Batteries

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(Received 02 October 2014, Revised 09 December 2014, Accepted 09 December 2014)

Abstract: Mg-Sn nanoparticles were prepared by an arc-discharge method in a mixture atmosphere of argon and hydrogen gases. Phases, morphologies, and microstructures of the nanoparticles were investigated by means of X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). It was found that the intermetallic compound of Mg_2Sn was generated and coexisted with metallic phases of Mg and Sn within nanoparticles. Based on the model cell, the electrochemical properties were also explored by discharge-charge cycling, cyclic voltammetry, and electrochemical impedance spectroscopy. The initial capacity of the first cycle reached 430 mAh/g. Two visible plateaus at 0.2-0.3 and 0.5-0.75V were observed in the potential profiles, which can be attributed to alloying/de-alloying reactions between Li and Mg_2Sn , respectively.

Key Words : Nanoparticles, Microstructure, Electrochemical properties, Lithium ion batteries

1. Introduction

Lithium ion batteries are currently used as portable power sources in the consumer electronic market. Since the mid 1980's, the reduced size and portable nature of electronic devices such as camcorders, portable telephones and laptop computers has generated enormous demand for high capacity, rechargeable batteries to power these devices. Until now, Li-ion batteries have used $LiCoO_2$ for the positive electrodes and

carbon-based materials for the negative electrodes. The modification to these materials made it possible to roughly double volumetric energy density over the initial product release. In particular, the theoretical limit of the volumetric energy density has almost been reached for the graphite anode material, LiC_6 (372 mAh/g), through the development of highly crystalline graphite materials and the optimization of the electrolyte composition. The only way to meet demand for even more power from equipment manufacturers was to find a new electrode material. In the past 20 years, various lithium alloy-based materials including metal oxides, multiphase alloys and intermetallic compound have been studied extensively as alternatives to the current commercial anode material for

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Li-ion secondary batteries. Among these newly proposed Li alloy materials, Sn-based intermetallic compounds gained much attention due to their numerous advantages, such as high capacity, and favorable voltage plateau. Particularly, many research groups studied the reaction mechanism of Mg_2Sn with Li and some found that that the formation of Li_2MgSn (320 mAh/g) is the main mechanism. However, Roberts et al. reported that the reversible capacity was as high as 400 mAh/g, which is higher than the theoretical capacity. Since there are arguments about Li alloying/dealloying for Mg_2Sn electrode, it will be interesting to explore Mg-Sn system to gain further understanding to Li storage properties.¹⁻³⁾

Apart from reaction mechanism, we also pay attention to the effect by fabricating nanoparticles. Reducing the size of particles often leads to a dramatic change in their physical and chemical properties and it is currently the starting point in most materials investigations. Nanotechnology has been applied to the field of electrochemical energy storage, and these materials with nanostructure possess new properties as compared to conventional bulk materials. Potential advantages, such as higher electrode/electrolyte contact area, short path lengths for electron and Li^+ transport, better accommodation of the strain of anode materials, excellent low-temperature performance, etc, are expected for nanostructured materials. However, some disadvantages along with nanostructures can not be ignored, such as inferior packing of active particles leading to a lower volumetric energy density, occurrence of undesirable electrode reactions due to high surface area, and complex synthesis procedures. Increasingly it is apparent that some very interesting characteristics either result from development of

nanostructured domains within materials during the initial cycles of the cell, or the deliberate construction of such nanostructures. The partial disorder inherent to these materials can have a substantial impact, affecting the kinetics or thermodynamics of the materials in fundamental and beneficial ways. Various methods, such as mechanical alloying (MA), electrostatic spray reductive precipitation (ESRP), can be used to tailor such materials for both negative and positive electrodes. Arc-discharge, as a common method to prepare nanoparticles, has its advantages in fabricating nanostructured materials. The electrochemical performance of electrode materials strongly depends on their structure, morphology and disorder. In this work, Mg-Sn nanoparticles containing compound Mg_2Sn phase were directly prepared in situ by an arc-discharge method. The phases, microstructures, morphologies were investigated by different analytical techniques. Li storage properties were carried out on an Auto Lab Electrochemical System.^{4,5)}

2. Experimental setup and method

The experimental equipment for production of Mg-Ni nanoparticles was similar to our previous work. In the experimental setup a tungsten rod was used as the cathode. Micron-sized Mg and Sn powders used as the raw materials were weighed pro rata and compressed into a cylindrical block which served as the anode to be evaporated. After the chamber was evacuated, a mixture of hydrogen and argon was introduced as the source of hydrogen plasma and the condensing atmosphere. Arc current and voltage were maintained at 240 A and 30 V, respectively. Before removing the nanoparticles from the chamber, they were experienced a passivation process for stabilization. A series of the compacted master blocks were prepared with different mass

ratios of Mg to Sn (70:30, 50:50, 30:70, 10:90, and 5:95 in wt.%), and the resultant nanoparticles were labeled as sample A - E, respectively.³⁾

The phases in as-prepared nanoparticles were determined by X-ray diffraction (XRD) using a Shimadzu XRD-6000 instrument. The morphology, size and microstructure of the nanoparticles were observed by high-resolution transmission electron microscopy (HRTEM) using a Tecnai220 S-TWIM instrument. Thermogravimetric/Differential thermal analysis (TG/DTA) was conducted on a TGA/SDTA851e instrument in a flow of air at a heating rate of 10 K/min. For the electrochemical performance tests, the Mg-Sn nanoparticles were well mixed with carbon black as a conducting agent and polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidone (NMP) as a binder, with a mass ratio of 75:8:7 to form slurry. The electrodes were prepared by coating the slurry on a Cu foil substrate. After coating, the electrodes were pressed and dried for 4 h at 120 °C in vacuum. The electrodes were cut into disks 14 mm in diameter and about 0.1 mm in thickness as the working electrode. The model cells were constructed by using metallic Li as the counter electrode. The model cells were assembled in an argon-filled glove box, and the electrolyte was 1 M LiPF₆ in EC (ethylenecarbonate)+DMC(dimethylcarbonate)(1:1,v/v). Charge–discharge cyclic performances of the cells were measured at 0–2.0 V with a current density of 60 mA/g. All the electrochemical measurements were carried out on an Auto Lab Electrochemical System.

3. Experimental results and discussion

Fig. 1 illustrates XRD patterns of Mg-Sn nanoparticle samples A-E. Among all samples, the compound Mg₂Sn with cubic lattice (PDFNo. 07-0274) is the main phase, and pure metal phases of Sn and Mg coexist in Sn-, Mg-rich samples. The

passivated layer of MgO emerges in the Mg-rich sample of Mg₂Sn, i.e. cubic and hexagonal lattices, are observed in Mg-Sn nanoparticles. With the increasing of Sn contents, the diffraction peaks of hexagonal Mg₂Sn are more clear in samples. It was reported in the Mg₂Sn alloy prepared by mechanical alloying method that the proportion of hexagonal Mg₂Sn phase increases at the expense of cubic Mg₂Sn as the milling time goes on.

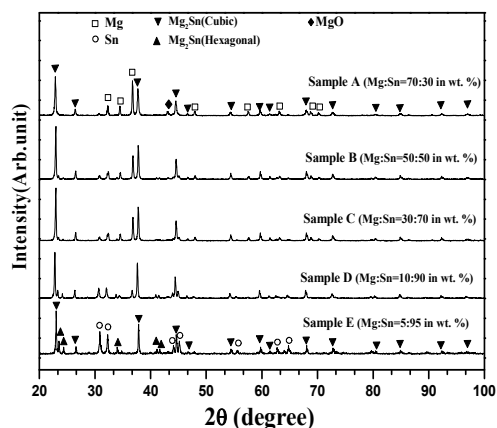


Fig. 1. XRD patterns of Mg-Sn nanoparticles

Pure hexagonal Mg₂Sn phase can be obtained after 65 h of milling, and it irreversibly converted into cubic Mg₂Sn phase as heating at 350 °C in air. It is considered that the difference of the final product was probably due to the various process variables of mechanical alloying, such as mill type, milling speed and so on. In this study, the hexagonal Mg₂Sn phase is expected to form at higher temperature and retain to room temperature by rapid quenching which is of a non-equilibrium condition. In typical sample D which has rich Sn component, the excessive pure Sn phase and the intermetallic compound of Mg₂Sn coexist in nanoparticles. Both of two phases are electrochemically active and favor to Li ions insertion/extraction processes. For the reasons, we selected sample D

as the testing nanoparticle material to further explore its Li storage properties.

TEM image of sample D (a) and its HRTEM (Philips Tecnai G² 20, 200kV) image (b) are given in Fig. 2. The spherical shape of Mg-Sn nanoparticles is similar to many kinds of metal nanoparticles, such as Fe nanoparticles, but has great difference with the characters of pure Mg nanoparticles. It is indicated that Mg-Sn nanoparticles have a relatively wide size distribution, i.e. in the range of 50-400 nm, and homogeneous dispersion without serious aggregation. As shown in Fig. 2(b), HRTEM micrograph of Mg-Sn nanoparticles displays clear lattice images by which the interplanar spacing of Mg₂Sn was calculated as 0.40 nm for (111) plane, which is very close to the observed value (0.39 nm). The largest interplanar spacing of crystal Mg is about 0.28 nm for the (100) plane, which agrees well with the observed value (0.28 nm) of Mg. It can be confirmed that multi-phases coexist in one single particle, i.e. two phases of Mg₂Sn and Mg coexist in one Mg-Sn nanoparticles. Based on XRD profile of Fig. 1, the calculated grain size of Mg₂Sn phase is approximately 47 nm, which implies that several grains in such sizes build a Mg-Sn nanoparticle. Generally, the grain size is smaller than the particle size, which is well proved in the picture of Fig. 2(b).^{6,7)}

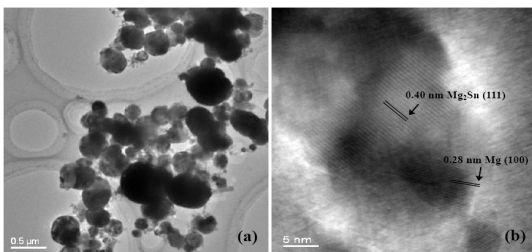


Fig. 2 TEM image of sample D (a) and its HRTEM image (b)

Fig. 3 illustrates potential profiles for the discharge-charge cycles of Mg-Sn/Li cell at a constant current of 60 mA/g. As for discharging, the curves of Mg-Sn/Li cells show a plateau (0.2-0.3 V), while higher potential range (0.5-0.75 V) was obtained for charging. In other words, the dominant voltage plateau shifted from 0.2 to 0.3V for Li-insertion (discharging) and from 0.5 to 0.75 V for Li-extraction (charging). It was also observed that alloying reaction between Li and Mg did not occur during lithiation of Mg. Therefore, it is thought that Mg₂Sn would follow the same reaction mechanism of Mg₂Si and the octahedral site of Mg₂Sn lattice provides Li ion for storage site as well as diffusion path. D. Larcher et al. found that firstly a monophasic insertion of about one Li per formula unit into the FCC Sn framework without extrusion of either Mg or Sn, then a biphasic process leading to the formation of cubic Li₂MgSn accompanied with a progressive expulsion of Mg, and finally the formation of Li-Mg solid solution alloys. H. Sakauchi reported that Li could be inserted into mechanically alloyed Mg-Sn without any structural change and Li in lithiated Mg-Sn should be present in a solid solution. It is also important to note that phase decomposition or segregation did not occur in the lithiated Mg-Sn, whereas phase decomposition or separation reaction could be generally observed by other group. It is reasonable that the plateau in discharge curve could be interpreted as a significant lithium insertion occurred at low potential (0.2-0.3 V), accompanying with the phase transformation from Mg₂Sn to Li₂MgSn. Similarly, the plateau in charge curve could be interpreted as a significant Li extraction occurred at high potential (0.5-0.75 V), with reversible change from Li₂MgSn to Mg₂Sn.

The discharge capacity of Mg-Sn nanocomposite anode in the first cycle is 430 mAh/g, but it decreases sharply to 205 mAh/g in the second cycle, and cannot be recovered in the successive cycles. Irreversible capacity (225 mAh/g) is observed in the first cycle, whereas capacity retention has been improved after the third cycle. If the lithium-insertion reaction proceeded based on the formation of Li_2MgSn ($\text{Mg}_2\text{Sn} + 2\text{Li} \leftrightarrow \text{Li}_2\text{MgSn} + \text{Mg}$), the theoretical capacity would be estimated as 320 mAh/g. The higher initial discharge capacity of this Mg-Sn nanocomposite anode can be ascribed to an excess Sn phase in the nanoparticles. The alloying reaction between Li and Mg does not occur at a current more than 10 mA/g, herein Mg phase cannot make remarkable contributions in Li storage even if it was excessively existent. The larger Sn grain inside one particle is also responsible for the large initial capacity loss, because of its greater volume change and internal stress which may result in the destruction and failure of host phases. Generally, the critical problem on Sn-based anode is the severe volume change associated with the pulverization of the active material during the alloying/dealloying reaction with Li ions. Additionally, the large initial capacity loss maybe partly attribute to large specific surface area of nanoparticles, which consume more Li to form the solid electrolyte interface (SEI) layer compared to its corresponding bulk materials. Although the selected Mg-Sn nanocomposite anode in this work has a good initial specific capacity, its performance is not yet fully satisfactory, especially in terms of stability and cycle life. The poor cycle life performance of this electrode is due to the pulverization of larger particles and subsequent loss of the electrical conductivity. Therefore, it is positive that the Mg_2Sn nanoparticles prepared by arc discharge have many attractive features for the anode

material of Li-ion batteries, but much effort should be done in improvement of its electrochemical properties by further tailoring the microstructures of host materials.^{8,9)}

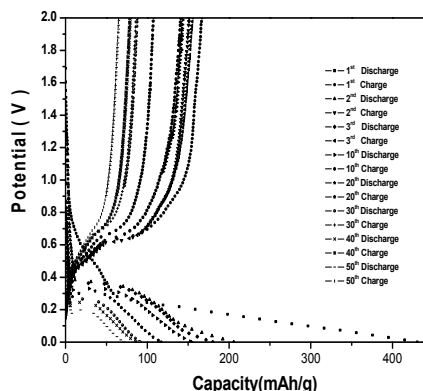


Fig. 3 Potential profiles of Mg-Sn/Li cell cycled in the potential range of 0-2.0 V

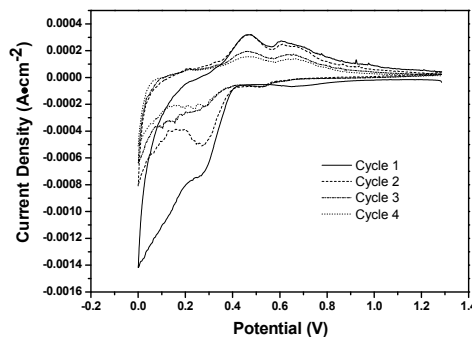


Fig. 4 Cyclic voltammetry curves of Mg-Sn nanocomposite anode. Scan rate: 0.1 mV/s

Fig. 4 represents the cyclic voltammetry performances at 0.1 mV/s scan rate for Mg-Sn nanocomposite anode. The peaks in the cyclic voltammetry curves correspond to the plateaus showed in Fig. 3. With respect to the Mg_2Sn electrode, one cathodic peak at 0.3 V can be observed, while two anodic peaks can be observed at the potentials of 0.46 and 0.61 V, respectively. All the reversible cathodic and

anodic peaks correspond to Li insertion/extraction with the active materials, respectively. The cathodic peak corresponds to inserting of Li into Mg_2Sn forming Li_2MgSn phase. It was reported that the anode peaks at 0.46 and 0.61 V were attributed to the delithiation of Li_2MgSn phase. As for the cyclic voltammetry performances of Sn-based anode materials, similar results were also reported by other groups.

After the first discharge, the derivative curves become similar for subsequent cycles and Sn-containing materials obey a similar mechanism during Li insertion/extraction with Sn, so it is speculated that the reversible peaks exhibit similar mechanisms for Li insertion/extraction in this work. Besides the reversible peaks, an irreversible peak appears in the first cycle at 0.55-1.0 V and is in good agreement with the potential plateaus observed in Fig. 3, which is most probably related to SEI formation.

Nyquist plots of the Mg-Sn nanocomposite anode before cycling and after four cycles are shown in Fig. 5, and the insert is also given to clarify the characteristics at high-frequency. Before cycling, it could be found that the patterns include two parts: one is a no well-defined semicircle at high-frequency, and the other is a straight line in low frequency range. This simple shape of impedance diagram has no information of SEI film formation. After four cycles, the well-defined semicircle turns into a depressed semicircle, which can be characteristic of two partially overlapped semicircles. Meanwhile, a straight line in the low frequency range is observed. According to the previous reports, the high-frequency semicircle represents the Li-ions migration through the solid SEI layer, the middle-frequency semicircle is related to the electron transfer through the electrode-electrolyte interface, and the sloping straight line at

low frequency corresponding to Warburg impedance, which reflects the Li-ions solid-state diffusion in the bulk materials. The results of electrochemical impedance measurements can further confirm the existence of SEI film on the surface of Mg-Sn nanocomposite anode.

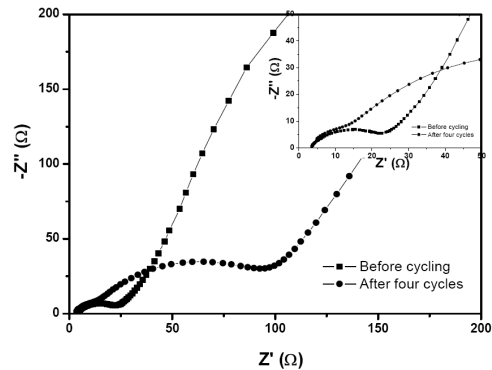


Fig. 5 Nyquist plots of Mg-Sn nanocomposite anode before cycling and after four cycles. The inset shows the enlarged one at high-frequency

5. Conclusions

The Mg-Sn nanoparticles prepared by arc discharge method have the phases of cubic Mg_2Sn , hexagonal Mg_2Sn , Mg and Sn inside one nanoparticle. The initial discharge capacity of Mg-Sn nanocomposite anode is 430 mAh/g. Capacity loss is observed after first cycle which can be attributed to the formation of SEI layer and the presence of pure Sn phase. A reversible cathodic peak emerges at 0.3V, while two anodic peaks appear at 0.46 and 0.61 V, respectively. These reversible reactions correspond to the formation/deformation of Li_2MgSn and become main mechanism of Li storage in Mg-Sn nanoparticles. Measurement of electrochemical impedance further confirms the existence of SEI film on the surface of Mg-Sn nanocomposite anode.

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