—Communication—

Mg₂Sn as a New Lithium Storage Intermetallic Compound

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To obtain a new anode material of lithium battery, electrochemical properties were investigated on Mg₂Sn intermetallic compound synthesized by mechanical alloying (MA) method. As a result, we found that the reversible insertion-extraction of a large amount of lithium can electrochemically occur in mechanically alloyed Mg₂Sn. The Mg₂Sn changed its own crystal structure from cubic to orthorhombic with increasing MA time. The compound exhibiting good performances as an anode had a mixture of cubic and orthorhombic phases. The discharge capacity of the Mg₂Sn electrode was still maintained at 250–300 mA h g⁻¹ even after the 20 times charge-discharge cycling. The reaction proceeded without any phase separation and/or decomposition of the compound. Mg₂Sn would be a promising anode material for lithium secondary batteries.

Key Words : Lithium Secondary Battery, Anode Material, Mg₂Sn, Lithium Storage Intermetallic Compound

1 Introduction

Carbon materials, such as graphite and pre-graphitic carbon, are practically used as anode materials in advanced lithium secondary batteries. Although the carbon materials exhibit good electrode performances, they appear to be limited by their charge-discharge capacities. In seeking for materials having larger capacity, several compounds have been proposed.^{1–7)} Among alloy material systems, LiAl is a well known anode material.¹⁾ Li atoms in this type of lithium alloys occupy lattice sites, so that the disintegration is easy to occur during the cycling of lithium insertion-extraction. This is a serious drawback for practical use as an electrode of rechargeable battery.

Some intermetallic compounds, such as Mg₂Ge, appear to be also promising anode materials because the latent capacities of the electrodes consisting of the compounds are much larger than those of carbon materials, especially volumetric energy densities are excellent.^{8–12)} In comparison with LiAl, this type of compounds has a characteristic that the damages during charge-discharge cycling would be avoided, because lithium atoms (or ions) could accommodate at not lattice site but interstitial sites of the lattices.

In the present study, we focused on Sn on behalf of Ge in Mg₂Ge, and synthesized a new anode material, Mg₂Sn, using mechanical alloying. The electrochemical performance of electrode consisting of the compound was investigated.

2 Experimental

Since Mg has a high vapor pressure and stoichiometric Mg-based alloys are difficult to be synthesized by a conventional melting method, mechanical alloying was considered to be a suitable method in this study. A mixture of elemental Mg powder (Goodfellow Cambridge, more than 99.8% pure, particle size *ca.* 50 μ m) and Sn

chip (Wako Pure Chemical Industries, 5N% pure, chip size *ca.* 1 mm) put in a stainless steel vessel (80 ml) together with five balls (ϕ 15). The Mg/Sn ratio was 2.0, and the weight ratio of the balls to sample was about 15:1. The vessel used was sealed with a viton O-ring to keep an argon atmosphere. The milling with the prescribed time interval was done using a high-energy planetary ball mill (Itoh, LP-4/2) at 300 r.p.m. and at room temperature.

To identify the phases and structures of mechanically alloyed samples, X-ray diffraction (Shimadzu, XRD-6000) was carried out using Ni-filtered Cu K α radiation at a 2θ scan of 2 deg min⁻¹. The chemical composition and impurities were determined with ICP emission spectroscope (Shimadzu, ICPS-5000).

Electrochemical performance of an electrode was estimated with a three-electrode cell. The electrode consisted of Mg₂Sn, acetylene black, and poly(vinylidene fluoride) (PVDF) in 75:20:5 in *wt%* on a Cu mesh (1 $\times$ 1 cm²). The acetylene black powder and PVDF were used as a conductive material and a binder, respectively. In the test cell, both counter and reference electrodes were 2 mm thick lithium metal sheets supplied by Mitsui Mining & Smelting. 1 M LiClO₄ dissolved in propylene carbonate (PC) (Mitsubishi Chemical) was used as an electrolyte. The cell performance was evaluated galvanostatically at current densities of 0.1 mA cm⁻² for both charge and discharge at room temperature. Cyclic voltammetric measurements were also carried out in the three-electrode cells.

3 Results and Discussion

Figure 1 shows XRD patterns of the mechanically alloyed products using elemental Mg and Sn as starting materials. The cubic Mg₂Sn phase was obtained by MA for only 3 hours which were much shorter than the case

Fig. 1 Changes in XRD patterns of Mg_2Sn with mechanical alloying (MA) time.

of Mg_2Ge previously reported.⁹⁻¹¹) Interestingly, when the MA treatment was proceeded for a longer time, the diffraction peaks belonged to the orthorhombic Mg_2Sn phase appeared in the XRD pattern. Furthermore, the cubic phase disappeared, and single orthorhombic phase was obtained after 7.5 h MA treatment. It is noteworthy that such a phase transformation was never seen for Mg_2Ge and Mg_2Si .¹¹)

ICP analysis showed that the compositions of the 5 h and 140 h MA samples were $\text{Mg}_{2.0}\text{SnFe}_{0.037}\text{Cr}_{0.000}\text{Ni}_{0.001}$ and $\text{Mg}_{2.0}\text{SnFe}_{0.086}\text{Cr}_{0.017}\text{Ni}_{0.005}$, respectively. Although both samples were a little contaminated, the concentrations of impurities were very low even in the 140 h MA sample and the ratio of Mg to Sn was 2.0 as desired. Consequently, MA was found to be the most favorable preparation method in the present study.

Figure 2 illustrates charge-discharge (Li insertion-extraction) curves of the Mg_2Sn electrode with the mixed phase. The first charge (Li-insertion) capacity of the electrode was *ca.* 960 mA h g^{-1} , suggesting Mg_2Sn has a large latent power as an anode material. On the other hand, the electrode exhibited the first discharge (Li-extraction) capacity of *ca.* 350 mA h g^{-1} . The value was comparable to the theoretical one of graphite electrode. A large irreversible capacity was observed at the first cycling, which would be due to partial stabilization of lithium in the Mg_2Sn lattice. An idea to improve the low discharge efficiency is to define the upper and lower potential range for the charge/discharge cycle as was observed in the Cu_6Sn_5 electrode.¹³) However, considering the labilization of lithium in the compound, there should be another idea. If some elements are partially substituted for Mg or Sn in the compound, or the crystallinity of the compound is changed, the lithium in the compound would be labilized. Consequently, the compound would be able to vary its electrode performance. These

Fig. 2 Charge-discharge curves for the Mg_2Sn electrode with a mixed phase.

factors should be clarified in future together with the fact that the acetylene black included in the electrode as a conductive material will also have some charge/discharge capacity.

Here, to study the states of lithiated Mg_2Sn , XRD was carried out on the samples having various Li-insertion steps. As shown in Fig. 3, no decomposition of the compound was observed and no new phase, such as Li-Sn alloys, appeared at any indicated potentials. The fact suggests a possibility that the lithiated Mg_2Sn forms a lithium solid solution. The discharge efficiency of the Mg_2Sn electrode was relatively low, as shown in Fig. 2, but no structural change of the compound was observed. This would be due to that lithium atoms in the lithiated Mg_2Sn are present in a solid solution. Recently, Kepler *et*

Fig. 3 XRD patterns of Mg_2Sn at various lithiated steps. Each datum was obtained at 1st charge-discharge cycle.

al. discovered a unique intermetallic insertion electrode consisting of Cu_6Sn_5 .¹³⁾ In this compound, the structural change occurs due to lithiation. The Li-insertion mechanism for Mg_2Sn appears to be different from that of Cu_6Sn_5 . To confirm whether Li-Sn alloys form or not, we carried out the cyclic voltammetry on the Mg_2Sn electrode. The voltammogram obtained at the first cycle is shown in Fig. 4. No remarkable cathodic current peak appeared at 0.5–2.0 V vs. Li/Li^+ in the first reduction half-cycle. The result would also deny the formation of Li-Sn alloys.

Figure 5 displays the relationship between discharge capacity and charge-discharge cycle number, *i.e.* cycle life of the Mg_2Sn electrode together with the previous data concerning Mg_2Ge and Mg_2Si . The abrupt capacity change observed between 10th and 11th cycle is due to exchange of electrolyte and Li electrodes. It was noteworthy that the Mg_2Sn electrode exhibited an excellent cycle life compared with the Mg_2Ge and Mg_2Si electrodes. In the case of the Mg_2Ge electrode, the electrode shape was bent due to Li insertion. Such phenomenon was, however, never seen in the Mg_2Sn electrode. There may be a mechanism of relaxation of internal stress in the Mg_2Sn electrode.

Fig. 4 Cyclic voltammogram (10 mV min^{-1}) for the Mg_2Sn electrode with a mixed phase.

Fig. 5 Dependence of discharge capacity on charge-discharge cycling for the Mg_2Sn electrode with a mixed phase. The previous data concerning Mg_2Ge and Mg_2Si were also indicated.

According to the above result, the good performances were obtained for the mixed phasic Mg_2Sn . So, next, we examined the performance of the electrode with each phase separately. Figure 6 gives the result of cycle life on the cubic and orthorhombic Mg_2Sn electrodes. There is a big difference between the mixed phasic and cubic Mg_2Sn electrodes. At least, the cubic phase gave obviously no contribution to the discharge capacity of the mixed phasic electrode. On the other hand, the orthorhombic Mg_2Sn electrode exhibited the similar result as mixed phasic one, though the electrode showed a little bit lower performance than the mixed phasic Mg_2Sn one.

As a result, the mixed phasic electrode showed the longest cycle life among the electrodes obtained. This appears to be due to the cooperative effect of cubic and orthorhombic phases. The orthorhombic phase may contribute to large capacity, while the cubic phase may assist the relaxation of internal stress generated at lithium insertion.

To discuss the reason why there is the difference of electrochemical performance between cubic and orthorhombic Mg_2Sn electrodes, we focused on the structural difference of the two phases. Figure 7 illustrates the structures of lithiated cubic and orthorhombic Mg_2Sn phases. In the structures, Li atoms are put in most feasible but hypothetical positions, because the structure of lithiated Mg_2Sn has never been reported. As for the cubic Mg_2Sn , although there exist some sites to be occupied by Li atoms and diffusion paths, the sites appear to be too narrow. On the contrary, the orthorhombic phase has a layered structure and the distance between the layers is enough to accommodate Li atoms. Consequently, Li atoms (or ions) may be able to insert into between these layers. This idea is no more than a guess in the present stage. We are now planning to examine the structure of lithiated Mg_2Sn using neutron diffraction.

Mg_2Sn has two crystal systems, *i.e.* cubic and orthorhombic phases, as mentioned above. The effects of the crystal systems on electrochemical behaviors of lithium insertion-extraction have never been investigated in the past, and this paper must be the first report. The interesting crystallographic features of the Mg_2Sn system bid

Fig. 6 Dependence of discharge capacity on charge-discharge cycling for the Mg_2Sn electrodes with cubic and orthorhombic structures compared with that with mixed phase.

Fig. 7 Hypothetical structures of (a) cubic phase and (b) orthorhombic phase $\text{Li}_x\text{Mg}_2\text{Sn}$.

fair to open up new routes for developing superior electrode materials to carbon ones.

4 Conclusion

We succeeded in synthesizing a new lithium storage intermetallic compound, $\text{Mg}_{2.0}\text{Sn}$, using mechanical alloying. The compound had two crystal systems of cubic and orthorhombic depending on MA time. The reversible insertion-extraction of lithium was observed on the Mg_2Sn electrode. No phase separation or decomposition occurred during the cycle, suggesting that lithium accommodated at interstitial sites of the Mg_2Sn lattice. The electrode consisting of cubic and orthorhombic mixed phasic Mg_2Sn exhibited the best electrochemical performance. As for the mixed phasic electrode, the discharge capacity exhibited $250\text{--}300\text{ mA h g}^{-1}$ even after 20 times cycling, which is fairly larger than those of the

Mg_2Ge and Mg_2Si electrodes after many cycle numbers. The capacity of the mixed phasic electrode may be due to the layered structure of orthorhombic phase and that the coexistence of cubic phase decreases the internal stress generated at lithium insertion.

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