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Synthesis and anode behavior of lithium storage intermetallic compounds with various crystallinities

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Abstract

An anode active material, $Mg_{2.0}Ge$, was synthesized using mechanical alloying (MA). Electrochemical performance of the compounds having different crystallinities was examined. It was found that the first discharge capacity of the $Mg_{2.0}Ge$ with a 90% crystallinity (MA treatment for 25 h) was ca. 320 mA h g^{-1}. The lattice expansion at the insertion of Li was decreased with decreasing crystallinity, suggesting the prolongation of cycle life. On the other hand, the discharge capacity of $Mg_{2.0}Ge$ with the lower crystallinity (MA treatment for 100 h) showed an insignificant value, being ca. 25 mA h g^{-1}, but the cycle dependence of capacities was favorable. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Carbon materials, such as graphite and pre-graphitic carbon, are well known to be safe anode materials in advanced lithium secondary batteries. Poor cycle performance at a high rate and low capacities of insertion–extraction of lithium for the carbon materials are, however, an essential problem for development of the batteries. New anode materials have been continued to be proposed in order to improve the disadvantages of carbon materials [1–4]. Some intermetallic compounds, such as Mg_2Ge and AlSb, are also candidates of promising anode materials because of their large capacities in comparison with those for carbon materials [5]. The compounds, however, have a serious drawback which is the disintegration of particles caused by repeating of lattice expansion at lithium insertion.

Lower crystallinity appears to make the lattice expansion moderate. The known example of such a case is the amorphization of hydrogen storage alloys [6,7]. Mechanical alloying (MA) is suitable for synthesis of alloys with various crystallinities, especially low crystallinities [8,9]. Moreover, since it is difficult to synthesize intermetallic compounds containing Mg, such as Mg_2Ge, by conventional melting because of high vapor pressure of Mg, the

low temperature synthesis using MA is considered to be the most appropriate method.

In the present study, we have employed the technique to synthesize Mg_2Ge and to vary the crystallinity of the compounds obtained, and investigated some behaviors of electrodes consisting of the compounds.

2. Experimental

A mixture of elemental Mg (Goodfellow Cambridge, more than 99.8% pure, particle size ca. 50 μm) and Ge (Nilaco, 5 N% pure, particle size ca. 300 μm) powders at a composition of $Mg/Ge = 2.0$ put in a stainless steel vessel (80 ml) together with five balls (∅ 15) in an argon atmosphere. The weight ratio of the balls to powder was about 15:1. The vessel used was sealed with a viton O-ring to avoid air. The milling with the prescribed time interval was done using a high-energy planetary ball mill (Itoh, LP-4/2) at 300 rpm and at room temperature.

Identification of phases and structures was carried out on MA samples by X-ray diffraction (Shimadzu, XRD-6000). The XRD measurements were done with monochromatized Cu Kα radiation at a 2θ scan of 0.5 deg min^{-1}. The thermal stability of the samples was examined by means of differential scanning calorimetry (DSC) with a Rigaku DSC-8230D in a flow of argon at a heating rate of 0.083 K s^{-1}, and crystallinities of the samples were esti-

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mated from a heat of crystallization which was determined from the area of the exothermic peak [7]. ICP emission spectroscope (Shimadzu, ICPS-5000) was used to determine the chemical composition of the MA samples or impurities in the samples.

Electrochemical tests were performed in three-electrode cells. The electrode consisted of Mg_2Ge, acetylene black and poly(vinylidene fluoride) (PVDF) in 75:20:5 in wt.% on a thin Cu sheet or a Cu mesh (1×1 cm^2). To improve the electrical contact, Mg_2Ge and acetylene black powders were previously milled for 1 h. The nickel powder was also used as another conductive material. In the test cell, 2 mm thick lithium metal sheets supplied by Mitsui Mining and Smelting were used as counter and reference electrodes. Propylene carbonate (PC) with 1 M LiClO$_4$ (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. The cell was cycled between ca. 2.8 and 0.1 V vs. Li/Li$^+$ with a scan rate of 10 mV min^{-1}.

3. Results and discussion

Fig. 1 illustrates the changes of XRD patterns when mechanical alloying was done on the mixture of Mg and Ge powders. Although Ge from starting materials still remained at 10 h MA, a cubic phase (CaF$_2$ type) of Mg_2Ge already appeared at the time. A single phase of Mg_2Ge was found to be obtained after 20 h MA treatment. Prolonged MA treatments resulted in broadening of the
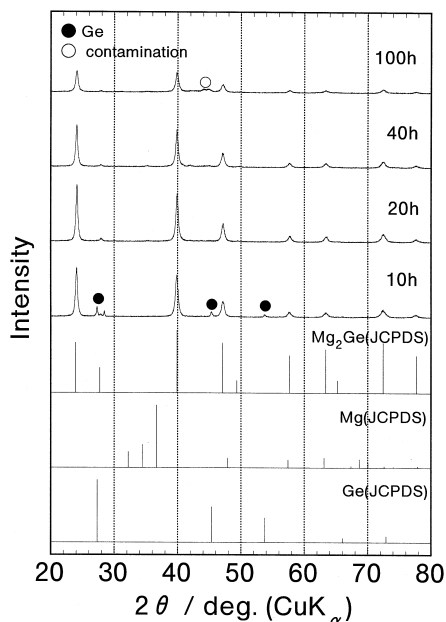
Table 1
Compositions of the samples synthesized by mechanical alloying

MA time	Composition
25 h	$Mg_{2.0}GeFe_{0.01}Cr_{0.01}Ni_{0.00}$
40 h	$Mg_{2.0}GeFe_{0.06}Cr_{0.02}Ni_{0.00}$
100 h	$Mg_{2.0}GeFe_{0.33}Cr\_Ni_{0.02}$

peaks, indicating a decrease in crystallinity. As a result of this, it was confirmed that the present technique is quite suitable both to synthesize Mg_2Ge and to vary the crystallinity of the compound.

The compositions of all samples as mechanically alloyed for 25 h, 40 h and 100 h were determined at $Mg_{2.0}Ge$. As shown in Table 1, the concentrations of impurities in the sample obtained by the 25 h MA treatment were extremely low, but the concentrations gradually increased with the MA time. Effects of the impurities at 100 h MA on electrode behaviors may not be negligible.

On the 100 h MA sample, the DSC curve had a distinct exothermic peak centered at around 600 K and the peak was an irreversible one. A smaller peak was also observed on the 25 h MA sample. The peak area was smaller for the 25 h MA sample than for the 100 h MA one. After the DSC measurements, the XRD peaks assigned to an Mg_2Ge phase obviously increased in intensity for both two samples, and the two patterns were mutually coincided. Therefore, the exotherm appears to attribute to a heat of crystallization. The heats of crystallization were 0.161 and 0.018 J g^{-1} for the 100 and 25 h MA samples, respectively. Accordingly, the crystallinity of the 25 h MA sample was estimated at ca. 90% when the crystallinity of 100 h MA sample was regarded as 0%.

Fig. 2 shows the electrochemical performance of electrodes consisting of Mg_2Ge obtained by the 25 h MA treatment. On the electrode using acetylene black as an conductive material, the first discharge (Li extraction)
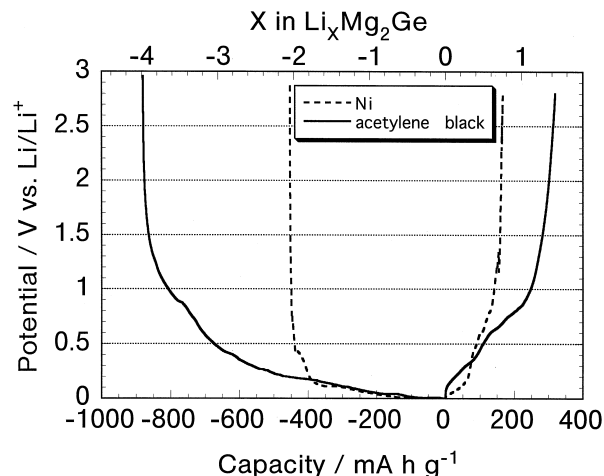

Fig. 1. Changes in XRD patterns of Mg_2Ge with mechanical alloying (MA) time.

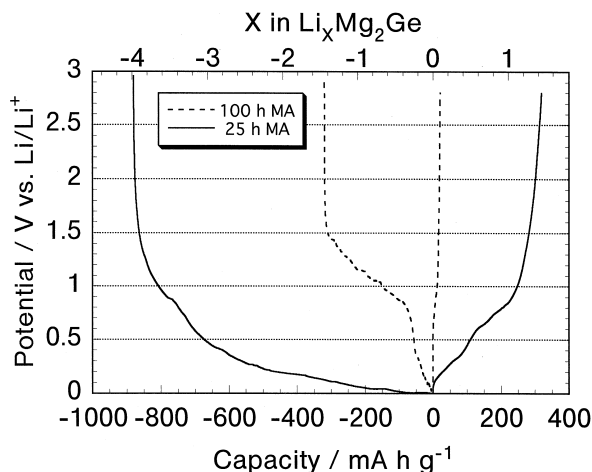Fig. 2. The first charge–discharge curves of Mg_2Ge electrodes including different conductive materials.

Fig. 3. The first charge–discharge curves of electrodes consisting of Mg_2Ge with different crystallinities.

capacity at a current density of 0.1 mA cm^{-2} was ca. 320 mA h g^{-1} which is much larger than that of carbon materials. As for the discharge capacity, acetylene black was preferable to nickel as an conductive material. The electrode using the nickel powder, however, may have the advantage of stable potential.

The first charge–discharge curve of the 100 h MA sample is illustrated in Fig. 3. A significant decrease in capacity was observed on the sample. Although this is an undesirable tendency, it is indicated that the electrochemical performance of Mg_2Ge electrode is strongly affected by variation in crystallinity. We also should pay attention to the relationship between impurities in the compound and electrode behaviors.

Fig. 4 shows the XRD patterns of Mg_2Ge in different lithium insertion states (200 and 950 mA h g^{-1} charged samples). Slight peak shifts in diffraction angle toward lower angle sides were observed in the charged samples
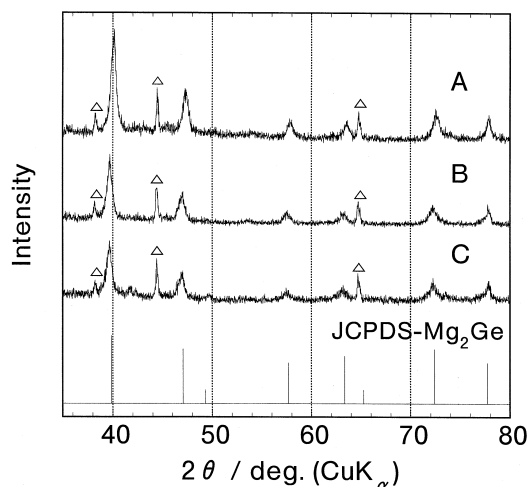
and the magnitude of the shift increased with charge capacities (sample B → sample C). This suggests that Li was inserted into the Mg_2Ge lattice. In addition to this, the scanning electron microscopic examination revealed no precipitates of dendritic Li on the surface of the electrodes. The lattice expansion caused by the Li insertion was evaluated from high angle peaks. The value on the 950 mA h g^{-1} charged sample (sample C) was 0.34% which is about 30% smaller than that for the sample synthesized by conventional melting. The smaller value of lattice expansion observed on the MA sample appears to be due to lower crystallinity, and suggests the possibility of improvement in cycle life as an anode.

Fig. 5 gives the comparison of charge–discharge cycle characteristics between 25 and 100 h MA samples. As shown in Fig. 5b, the small decrement of capacity with the number of cycle was noticed on the 100 h MA sample, though these capacities were essentially small. This also suggests there is a relationship between the crystallinities of Mg_2Ge and the capacities.

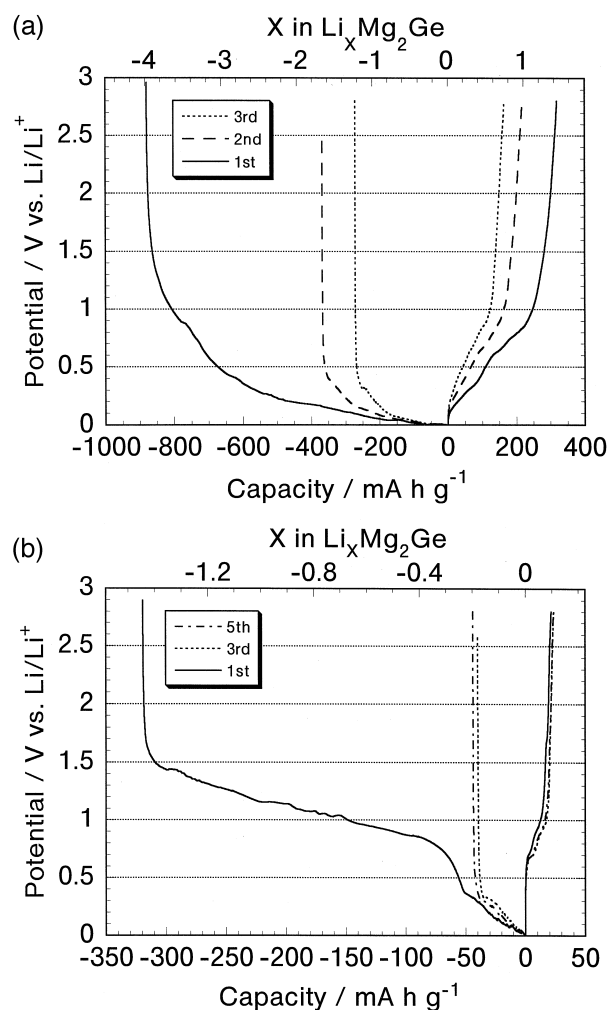Fig. 4. Changes in XRD patterns of Mg_2Ge with Li insertions. (A) Before Li insertion, (B) After Li insertion (200 mA h g^{-1}), (C) After Li insertion (950 mA h g^{-1}), ($\triangle$) Cu substrate.

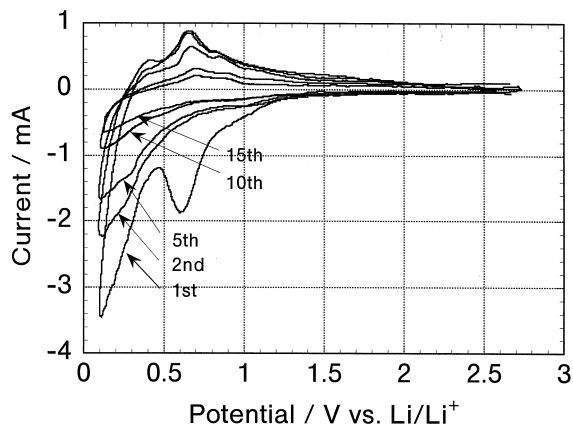Fig. 5. Dependence of charge–discharge cycle on capacities of Mg_2Ge electrodes. (a) 25 h MA Mg_2Ge electrode, (b) 100 h MA Mg_2Ge electrode.

Fig. 6. Cyclic voltammograms (10 mV min^{-1}) of the 25 h MA Mg$_2$Ge electrode.

Cyclic voltammograms of the 25 h mechanically alloyed sample are shown in Fig. 6. A large cathodic current peak was observed at around 0.6 V vs. Li/Li$^+$ in the first reduction half-cycle of Mg$_2$Ge, whereas the peak was absent in the second cycle. This behavior is analogous to that observed on graphite anodes. For the graphite anodes, it has been explained that the behavior is associated with a formation of solid electrolyte interface (SEI) on the surface of graphite electrode [10]. The Mg$_2$Ge electrodes may be covered with the SEI as well as the graphite electrodes.

4. Conclusions

We succeeded in synthesizing a new anode active material, Mg$_{2.0}$Ge, using mechanical alloying (MA). The Mg$_2$Ge electrode obtained by a 25 h MA treatment was found to have a discharge capacity of ca. 320 mA h g^{-1} in the first cycle. A crystallinity of the 25 h MA Mg$_2$Ge was determined at about 90%, and the low crystallinity comparing with that of the sample synthesized by melting decreased the lattice expansion at the insertion of Li, suggesting the prolongation of cycle life. The discharge capacity for the 100 h MA sample was only ca. 25 mA h g^{-1}, but the cycle dependence of capacities was small.

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