Neutron Diffraction Study on Local Structure of Lithium Storage Intermetallic Compound

Hitohiko HONDA,a Hiroki SAKAGUCHI,a Toshiharu FUKUNAGA,b and Takao ESAKAa* 

aDepartment of Materials Science, Faculty of Engineering, Tottori University (Minami 4-101, Koyama-cho, Tottori 680-8552, Japan) 
bResearch Reactor Institute, Kyoto University (Sennangen, Osaka 590-0451, Japan) 

Received September 3, 2001 ; Accepted October 29, 2001 

The local structure of LixMg2Ge, which is a candidate for anode materials of lithium secondary batteries, was investigated using both X-ray diffraction (XRD) and neutron diffraction. It was found that the nearest interatomic distance of the Ge-Mg increases slightly in electrochemically lithiated Mg2Ge, (or LixMg2Ge), although any other large structural change was not obvious. The evidence suggests that lithium atoms (or ions) accommodate at interstitial sites of the Mg2Ge lattice to form a solid solution. From the Li-Ge correlation factors observed in the radial distribution functions, furthermore, lithium atoms in the lithiated Mg2Ge were supposed to occupy the sites equivalent to those of hydrogen atoms in Mg2NiH6 with an anti-fluorite structure.

Key Words : Lithium Secondary Battery, Anode Material, Mg2Ge, Lithium Storage Intermetallic Compound, Neutron Diffraction

1 Introduction

Carbon materials are commercially used as negative electrodes in lithium-ion batteries. The material such as graphite exhibits relatively small irreversible capacity loss and a good cycle life. Supposing the theoretical capacity of graphite 372 mA h g⁻¹ (ca. 800 mA h cm⁻²), however, further increase in capacity may be undesirable. Recently, there has been a considerable interest in seeking intermetallic compounds as anode materials of rechargeable lithium batteries.1–5 Considering that the intermetallic compounds make both volumetric and gravimetric capacities larger than those of the conventional materials, they would be promising anode materials.

Some types of electrochemical reactions have been proposed on the intermetallic compounds with lithium. Mao and Dahn et al. have extensively studied the Sn-Fe materials, such as SnFe and SnFe₅C,6–10 in which a substitution reaction occurred at the 1st charging, that is, the Sn-Fe compounds decompose to form LiₓSn alloy and Fe. Subsequent discharge-charge reactions are proposed to be the alloying/dealloying of lithium as to LiₓSn, while the isolated iron is inactive. In the recent papers, Kepler et al. and Dahn et al.11–13 have reported a unique lithium insertion intermetallic electrode consisting of Cu₃Sn, where lithium reacts with a two-phase reaction resulting LixCu₃Sn and Cu₃Sn.

On the other hand, some intermetallic compounds, such as Mg₂Ge and Mg₃Sn, appeared to be different types of interesting materials,14–16 in which lithium is supposed to be inserted into the lattices within the defined potential levels, and, as a result, a solid solution is formed. We have discussed the relationship between electrochemical properties of Mg₂Ge electrodes, synthesized by mechanical alloying (MA) and their internal energy. Consequently, the charge-discharge performance of the electrodes was found to be influenced by the internal energy originated from the crystallinity change and/or the introduction of lattice strain,16 that is, we needed the samples with the optimum internal energy for the best electrochemical performances. However, its electrode reaction has not interpreted satisfactorily, because the structure of lithiated Mg₂Ge has not been clarified.

In order to investigate the lithium insertion/extraction mechanism of the Mg₂Ge electrode, in situ X-ray diffraction was firstly carried out. Lithium is, however, a light element so that the X-ray experiments could not give enough information on the correlations between lithium and other metal atoms. Next, we used neutron diffraction for the same objective, because a neutron scattering experiment was used to be a powerful tool for structural analysis of the materials with a low crystallinity12–24 such as Mg₂Ge presently synthesized by MA. In this paper, the neutron diffraction data for lithiated Mg₂Ge and the lithium insertion mechanism are presented and discussed.

2 Experimental

A mixture of elemental magnesium (Goodfellow Cambridge, more than 99.8% pure, particle size ca. 50 μm) and germanium (Nilaco, 5 N% pure, particle size ca. 300 μm) powders was mechanically alloyed under an atmosphere of dry argon gas (more than 99.99%), using a high-energy planetary ball mill (Ioth, LP4-1/2) at 300 r.p.m. for 25 h and at room temperature. More details of the milling condition were described in the previous paper.15,17–18

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

Electrochemical performance of an electrode was estimated with a three-electrode cell. The electrode consisted of Mg₂Ge, acetylene black, poly(vinylidene fluoride) (PVDF) in 75: 20: 5 in wt % on a Cu mesh (1 × 1 cm²). The acetylene black 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. LiClO₄ dissolved in propylene carbonate (PC) (Kishida 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.

An ex situ XRD method was also used to investigate the reaction mechanisms on Mg₂Ge. The Mg₂Ge electrode was detached from the cell after galvanostatic charging to 0 V (vs. Li/Li⁺) and dried overnight in a vacuum. Next, a lithiated Mg₂Ge sample without any carbon content was needed for the neutron diffraction measurements. In this case, only the sample mechanically alloyed was pressed into pellets under a pressure of 2000 kg cm⁻², followed by wrapping with Cu mesh. The electrode obtained was lithium galvanostatically at current densities of 0.5 mA g⁻¹.

Neutron diffraction measurements were carried out at room temperature using the high intensity total scattering spectrometer (HIT-II) installed at the spallation pulsed neutron source generated from a 500 MeV proton booster synchrotron at the High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). The samples were sealed under dry argon in the neutron zero-scattering alloy Ti-Zr cylindrical cell. Scattering intensities were measured for the samples, background, an empty cell, and a vanadium rod having the same dimension as the cell. The normalization of intensities was carried out using the intensity of the vanadium rod, which is regarded as a perfect incoherent scatterer for neutron.

The total structure factor S(Q) is defined by

\[
S(Q) = \frac{I(Q) - \left[ \sum b_i^2 - \left( \sum b_i \right)^2 \right]}{\left( \sum b_i^2 \right)^2}
\]

where \( I(Q) \) is the normalized observed intensity, \( Q = \left( \frac{4 \pi}{\lambda} \right) \sin \theta \) and \( b_i \) is the coherent scattering length of the \( i \) th nucleus, which was obtained from the literature. The conventional Fourier transform yields the total pair correlation function \( g(r) \) :\n
\[
g(r) = 1 + \frac{1}{2 \pi^2 r \rho_0} \int Q \cdot |S(Q)|^2 \sin(Q \cdot r) dQ
\]

where \( \rho_0 \) is the average atomic number density, that is, 5.26 × 10⁻⁸ atoms pm⁻³ for Mg₂Ge and 5.63 × 10⁻⁸ atoms pm⁻³ for Li₃SnMg₂Ge. The radial distribution function RDF \( r \) describes the number of atoms in the spherical shell of radius \( r \).

3 Results and discussion

Figure 1 illustrates the first charge-discharge (lithium insertion-extraction) curve of the Mg₂Ge electrode obtained by mechanical alloying. The first charge (lithium-insertion) capacity of the electrode was ca. 900 mA h g⁻¹, suggesting Mg₂Ge has a large latent power as an anode material. On the other hand, the first discharge (lithium-extraction) capacity was ca. 320 mA h g⁻¹ which translated to a volumetric capacity of 990 mA h cm⁻³ using the crystallographic density of 3.08 g cm⁻³ for Mg₂Ge. The both discharge capacities were somewhat larger than those of graphite at the first cycle at least. The electrochemical reaction of Mg₂Ge with lithium appears to be based on lithium absorption in the interstitials of Mg₂Ge lattice, and the large irreversible capacity observed at the first cycling may be due to excessive stabilized capture of lithium in the Mg₂Ge lattice. Thus, in order to clarify a mechanism of the electrode reaction, it is necessary to show to reveal the environmental condition around lithium atoms in the lithiated Mg₂Ge.

To obtain information concerning phases formed during lithiation, XRD was carried out on the samples at various Li-insertion steps. As shown in Fig. 2, the peak profiles are almost the same; especially no extra phase, such as Li-Ge alloys, appeared at any steps. In recent papers, Mao and Dahn et al. have studied the active/inactive composites electrode consisting of Sn-Fe alloys.
In the intermetallic compounds, a substitution reaction occurs to form a series of Li$_x$Sn alloys in an inactive composite matrix. Kepler et al. and Larcher et al.\(^{11-13}\) have reported a unique intermetallic insertion electrode consisting of Cu$_x$Sn$_y$; the structure was found to change from Cu$_x$Sn$_y$ to Li$_x$Cu$_x$Sn$_y$ during lithiation by their XRD data. Considering Fig. 2, the lithium insertion mechanism for Mg$_2$Ge appears to be different from that of Sn$_2$Fe or Cu$_x$Sn$_y$. In addition, diffraction peaks were observed to shift towards lower angle a little in the lithiated sample. The facts suggest a possibility that lithium atoms are present in a solid solution of the lithiated Mg$_2$Ge.

As mentioned before, X-ray experiments can not give enough information on correlations between lithium and the other metal atoms. Therefore, neutron diffraction measurements were performed to study the local environment of lithium atoms in the lithiated Mg$_2$Ge. Figure 3 shows the neutron total structure factors $S(Q)$ obtained for the Li$_x$Mg$_2$Ge ($x=0, 0.92$). The peak intensity was much larger for the lithiated Mg$_2$Ge than for the unlithiated sample, and the two peak profiles differed from one another in profiles at the shorter $Q$ side (below $5 \times 10^{-2}$ nm$^{-1}$). The change in peak profile indicates that the correlations between constituent atoms were varied by lithium insertion in Mg$_2$Ge.

Figure 4 shows a comparison of the neutron total radial distribution function (RDF) for Mg$_2$Ge with that for lithiated sample. The peaks observed commonly in both RDFs are considered to consist of the metal-metal (Mg-Mg, Mg-Ge and Ge-Ge) correlations originated from a Mg$_2$Ge phase with anti-fluorite structure. Figure 5 and Table 1 indicate the illustration of crystal structure and the structural parameters for Mg$_2$Ge, respectively. Although the local atomic structures around central magnesium and germanium atoms for the lithiated Mg$_2$Ge were similar to those for the unlithiated one, the slight but definite increase from 276 to 280 pm was observed in the interatomic distance of the nearest Ge-Mg in Mg$_2$Ge after lithiation. This tendency was also confirmed by X-ray diffraction, and the interatomic distance slightly increased from 276 to 277 pm. The results of the present neutron diffraction support the idea from the X-ray diffraction, that is, lithium atoms (or ions) accommodated at interstitial sites of Mg$_2$Ge lattice.

The peak observed at about 387 pm in the RDF of the lithiated Mg$_2$Ge reflects the correlations around central lithium atom, because the peak appeared on the negative side. Lithium nucleus exhibits the negative sign on scattering amplitude, whereas both germanium and magnesium nuclei the positive sign. Accordingly, the peaks assigned to the Li-Ge and Li-Mg correlations show the negative sign. Kim et al. reported that Mg$_2$Si with the same structure as Mg$_2$Ge electrochemically react with lithium through the following three sequential steps.\(^{3}\) Lithium accommodates octahedral sites ($b$) in Mg$_2$Si at the first step, reacts with segregated metallic Si to form Li-Si alloys, and finally reacts with residual metallic magnesium. The interatomic distance of 387 pm in the lithiated Mg$_2$Ge, however, does not agree with Li-Ge correlations originated from Li$_2$Ge alloys (LiGe and Li$_2$Ge), as shown in Fig. 4 and Table 2-a. As for Li-Mg alloys, to the best of our knowledge, structural parameters of the Li-Mg alloy phase have not been reported. From the result of the Mg$_2$Si electrode, it is difficult to consider that lithium reacts only with magnesium without reaction with germanium. In addition, no peak corresponding to the Li-Li correlations in metallic lithium (Table 2-b) was also observed in the RDF, which suggested a possibility that the lithiated Mg$_2$Ge forms a lithium solid solution.

**Table 1** Structural parameters\(^{9}\) for Mg$_2$Ge obtained by metallurgical processes.

<table>
<thead>
<tr>
<th>Metal-metal correlation</th>
<th>Ge-Mg</th>
<th>Mg-Mg</th>
<th>Mg-Mg</th>
<th>Ge-Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of M-M pairs</td>
<td>8</td>
<td>6</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>M-M distance (pm)</td>
<td>276.9</td>
<td>319.7</td>
<td>452.1</td>
<td>452.1</td>
</tr>
</tbody>
</table>

a) Under 500 pm
The relationship between electrochemical properties of the sample. Therefore, we are now planning to prepare on the basis of the above assumption, as shown in Fig. 6. The present results are not enough to clarify the local environment of lithium atoms in the lithiated Mg:Ge completely, because of a low concentration of lithium in the sample. Therefore, we are now planning to prepare the fully lithiated sample in order to obtain more information from the experiment of neutron diffraction.

As mentioned before, we have previously discussed the relationship between electrochemical properties of Mg:Ge electrodes, synthesized by mechanical alloying (MA) and their internal energies. Consequently, the charge-discharge performance of the electrodes was found to be influenced by the internal energy originated from the crystallinity change and/or the introduction of lattice strain, that is, we needed the samples with the optimum internal energy for the best electrochemical performances. The idea from the present neutron diffraction, that is, lithium atoms (or ions) accommodated at interstitial sites of Mg:Ge lattice, supports the concept that the appropriate internal energy may make the lattice expansion moderate due to relaxation of stress at lithium insertion. In this type of electrochemical reactions with lithium, we believe that the internal energy originated from the crystallinity change etc. is effective to the prolongation of cycle life as the rechargeable battery.

4 Conclusions

XRD and neutron diffraction measurements were employed to investigate the lithium insertion/extraction mechanism for Mg:Ge intermetallic compound. The interatomic distance of the nearest Ge-Mg was found to increase from 276 to 280 pm after lithium insertion without a large structural change. In addition, no phase separation or decomposition occurred during the charge-discharge cycling. These facts suppose that lithium atoms (or ions) accommodate at interstitial sites of Mg:Ge lattice. The peak with negative sign observed at about 387 pm in the RDF of the lithiated Mg:Ge is attributed to the correlation around a central lithium atom. If the lithium positions are the same as hydrogen atoms in the

Table 2-a Structural parameters for Li,Ge with orthorhombic phase.

<table>
<thead>
<tr>
<th>Number of Li-Ge pairs</th>
<th>Li-Ge distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>265.6</td>
</tr>
<tr>
<td>2</td>
<td>269.1</td>
</tr>
<tr>
<td>1</td>
<td>282.9</td>
</tr>
<tr>
<td>2</td>
<td>298.5</td>
</tr>
<tr>
<td>2</td>
<td>325.3</td>
</tr>
</tbody>
</table>

Table 2-b Structural parameters for metallic lithium with cubic phase.

<table>
<thead>
<tr>
<th>lithium-lithium correlation</th>
<th>Li-Li</th>
<th>Li-Li</th>
<th>Li-Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of Li-Li pairs</td>
<td>8</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Li-Li distance (pm)</td>
<td>303.9</td>
<td>350.9</td>
<td>496.3</td>
</tr>
</tbody>
</table>

a) Only Li-Ge correlation

An attempt is made to specify the lithium position in Mg:Ge with an anti-fluorite structure, the octahedral sites of which are empty. Huang and Kim proposed that lithium could insert in the octahedral site of Mg:Si. As mentioned above, the Mg:Si has the same structure as Mg:Ge. Therefore, Mg:Ge may electrochemically react with lithium in the same manner as Mg:Si, and the interatomic distance of Mg-Mg would be changed, if the octahedral sites are occupied by lithium, as seen in Fig. 5. However, there was no change in the interatomic distance of Mg-Mg in Mg:Ge after lithiation. Moreover, the first charge capacity of the Mg:Ge electrode, 900 mA h g\(^{-1}\), corresponded to 4.07 lithium atoms for a formula weight of Mg:Ge, which indicated that lithium does not occupy the octahedral site, but some other sites.

We noticed that the structure of Mg:Ge is similar to that of hydrogenated Mg:Si well known as a hydrogen storage alloy. Mg:Si absorbs hydrogen up to four atoms for a formula weight. Assuming that the hydrogen position in Mg:Si coincides with the lithium one in Mg:Ge (Fig. 6), the number of lithium atoms occupied almost coincide with the first charge capacity. A peak with negative sign was observed at about 387 pm in the RDF of the lithiated Mg:Ge. This agreed with the Ge-Li correlation based on the above assumption, as shown in Fig. 6. The present results are not enough to clarify the local environment of lithium atoms in the lithiated Mg:Ge completely, because of a low concentration of lithium in the sample. Therefore, we are now planning to prepare the fully lithiated sample in order to obtain more information from the experiment of neutron diffraction.

- **Fig. 6** Hypothetical structures of cubic phase Li\(_x\)Mg\(_2\)Ge.

- **Table 2-a** Structural parameters for Li,Ge with orthorhombic phase.

- **Table 2-b** Structural parameters for metallic lithium with cubic phase.
MgNiH$_3$ with an analogous structure to Mg$_2$Ge, the interatomic distance of Li-Ge would be 387 pm. This appears also to substantiate the above assumption.

Acknowledgment
We thank Dr. K. Itoh, Kyoto University, and the staff of the Booster Synchrotron Utilization Facility at KEK for their helpful advice and technical assistance in the neutron diffraction measurement. This work was supported by a grant-in-aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, and a grant from the Electric Technology Research Foundation of Chugoku and the Asahi Glass Foundation.

References