

## Microscopic characterization of metal-carbon-hydrogen composites (metal = Li, Mg)

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(Received 2 June 2013; accepted 20 August 2013; published online 5 September 2013)

Li-C-H system, which can store about 5.0 mass% of rechargeable H<sub>2</sub>, has been reported as a promising hydrogen storage system by Ichikawa *et al.* [Appl. Phys. Lett. **86**, 241914 (2005); Mater. Trans. **46**, 1757 (2005)]. This system was investigated from the thermodynamic and structural viewpoints. However, hydrogen absorption/desorption mechanism and the state of hydrogen atoms absorbed in the composite have not been clarified yet. In order to find new or better hydrogen storage system, graphite powder and nano-structural graphite ball-milled under H<sub>2</sub> and Ar atmosphere were prepared and milled with Li and Mg under Ar atmosphere in this study. Microstructural analysis for those samples by transmission electron microscope revealed that LiC<sub>6</sub> and/or LiC<sub>12</sub> were formed in Li-C-H system. On the other hand, MgC<sub>2</sub> was found in Mg-C-H system ball-milled under H<sub>2</sub> atmosphere, but not in the system ball-milled under Ar atmosphere. These results indicated that nano-structure in composites of nano-structural graphite is different from that of alkali (-earth) metal. For these reasons, metal-C-H system can be recognized to be a new family of hydrogen storage materials. © 2013 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4820455>]

### I. INTRODUCTION

Hydrogen storage is one of the most important technologies to develop fuel cell vehicles. A lot of research on hydrogen storage materials has been reported over the past few decades.<sup>1–3</sup> At present, carbon based materials have been paid much attention as a hydrogen storage materials, because carbon is light element and abundant materials. A lot of new carbon materials such as carbon nano tubes (CNTs), activated carbon, and hydrogenated nano-structural graphite (C<sup>nano</sup>H<sub>x</sub>) have been researched to create more efficient hydrogen storage materials.<sup>4–12</sup> Among these new carbon materials, we have paid attention to hydrogenated nano-structural graphite. C<sup>nano</sup>H<sub>x</sub> is synthesized from graphite by the ball-milling under H<sub>2</sub> gas atmosphere.<sup>13–22</sup> So far, it has been reported that the hydrogenated nano-structural graphite (C<sup>nano</sup>H<sub>x</sub>) can store about 7.4 mass% of hydrogen.<sup>13</sup> C<sup>nano</sup>H<sub>x</sub> material requires heating up to more than 700 °C to release the hydrogen and desorbs hydrogen with hydrocarbons (CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>). Thus, C<sup>nano</sup>H<sub>x</sub> itself is difficult to use as hydrogen storage materials. So, Li-C-H system has recently been reported as a way to solve these problems.<sup>23,24</sup> Li-C-H system was synthesized from LiH and nano-structural graphite by ball-milling under hydrogen atmosphere, and it can reversibly absorb and desorb 5 mass% of hydrogen at 350 °C under 3.0 MPa H<sub>2</sub> gas atmosphere. Moreover, not only Li-C-H system but also Mg-C-H system has been reported as the superior hydrogen storage material than C<sup>nano</sup>H<sub>x</sub> itself.<sup>25–30</sup> However, hydrogen absorption/desorption mechanism and the state of hydrogen atoms absorbed in the composite have

not been clarified yet. It has been difficult to discuss those by using X-ray diffraction (XRD), because the crystallite sizes of the compounds in Li-C-H and Mg-C-H systems were too small or amorphous. In this paper, by using transmission electron microscopy (TEM), we have investigated the compounds in both systems to understand the reaction mechanism. Especially, we have determined the reaction formula of hydrogenation and dehydrogenation in both systems.

### II. EXPERIMENTAL PROCEDURES

Samples were prepared by ball-milling method. High purity graphite powder (99.99% purity) was milled under H<sub>2</sub> and Ar gas atmosphere (1.0 MPa pressure) for 8 h, which was labeled as HG and AG, respectively (a planetary ball-mill equipment: Fritch, P7). No-milling graphite was labeled just as G. In this way, three kinds of graphite (G, HG, AG) were prepared. Then, these three kinds of graphite were milled with Li (Li:C = 1:2, 99.9%) under Ar gas atmosphere (1.0 MPa) for 3 h to synthesize the sample of Li-C-H system. We labeled three kinds of samples as Li-HG, Li-AG, and Li-G, respectively. In the same way, graphite were milled with Mg (Mg:C = 1:4), which were labeled as Mg-HG, Mg-AG, and Mg-G, respectively. For the hydrogenation and the dehydrogenation of all samples, the heat-treatments were carried out at 450 °C for 8 h under 3.0 MPa H<sub>2</sub> gas atmospheres and at 450 °C for 8 h under vacuum condition, respectively. We observed all samples by TEM (JEM-2010, 200 keV) and high voltage electron microscope (HVEM, ARM-1300, 1250 keV). The samples were handled without any exposure

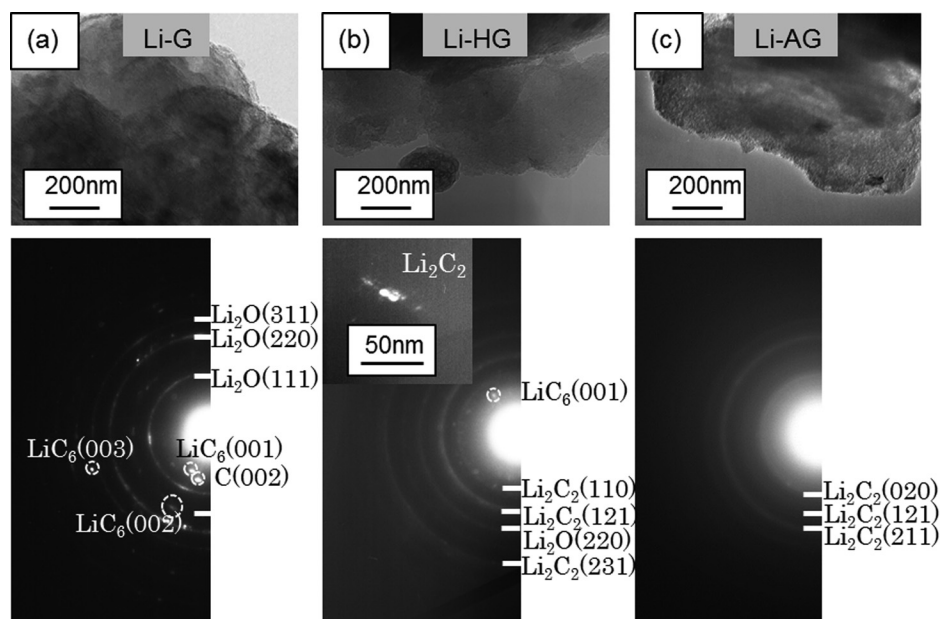


FIG. 1. BF and DF images and diffraction patterns of as-synthesized samples: (a) Li-G, (b) Li-HG, and (c) Li-AG.

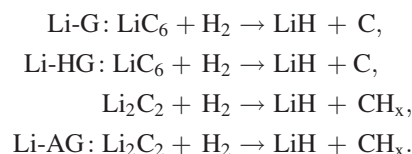
to air in whole process. The sample powder was placed on a micro-grid, and the grid was set into a heating specimen holder in the glove box under Ar gas atmosphere. The sample holder was put into a plastic bag under Ar gas atmosphere and loaded into TEM equipment in order to prevent the oxidation.<sup>29</sup> The high resolution TEM (HRTEM) images were analyzed by fast Fourier transformation (FFT) and inverse FFT (IFFT).

### III. RESULTS AND DISCUSSION

#### A. Li-C-H system

Figures 1(a)–1(c) show the bright field (BF) images and diffraction patterns of as-synthesized samples of Li-G, Li-HG, and Li-AG, respectively. From the BF images, it seems that the particle sizes of Li-G, Li-HG, and Li-AG are from several tens nm to several hundred nm. Additionally, the crystallite size of  $\text{Li}_2\text{C}_2$  in Li-HG was around 30 nm, as shown in the insetted dark field (DF) image of (b). From the diffraction patterns, the diffraction spots from  $\text{LiC}_6$  (003),  $\text{LiC}_6$  (001),  $\text{LiC}_6$  (002), C (002) and the diffraction rings from  $\text{Li}_2\text{O}$  (111),  $\text{Li}_2\text{O}$  (220),  $\text{Li}_2\text{O}$  (311) were indexed in Li-G. In cases of Li-HG and Li-AG, the diffraction spots from  $\text{LiC}_6$  (001), and no spots, the diffraction rings from  $\text{Li}_2\text{C}_2$  (110),  $\text{Li}_2\text{C}_2$  (121),  $\text{Li}_2\text{C}_2$  (231),  $\text{Li}_2\text{O}$  (220), and  $\text{Li}_2\text{C}_2$  (020),  $\text{Li}_2\text{C}_2$  (121),  $\text{Li}_2\text{C}_2$  (211), were identified, respectively, as listed in Table I. Two kinds of compounds between Li and C are identified. One is a graphite intercalation compound (GIC) of  $\text{LiC}_6$ , the other is  $\text{Li}_2\text{C}_2$ , which has been

reported in Refs. 27 and 29. The crystallinity of C in Li-G and Li-AG is the highest and the lowest. Therefore, it could be considered that  $\text{LiC}_6$  was generated from Li and C with high crystallinity (graphite), meanwhile  $\text{Li}_2\text{C}_2$  was from Li and C with low crystallinity. Then, the samples were hydrogenated at 450 °C for 8 h under 3.0 MPa  $\text{H}_2$  gas atmospheres. Figure 2 shows the BF and DF images and diffraction patterns of hydrogenated samples: (a) Li-G, (b) Li-HG, and (c) Li-AG. The compounds identified from the diffraction patterns are listed in Table I. LiH was observed in the all hydrogenated samples; on the other hand, C was observed in the hydrogenated samples of Li-G and Li-HG. The DF images show the crystallites of LiH with the size of around 200 nm, 50 nm, and 30 nm in the hydrogenated samples of Li-G, Li-HG, and Li-AG, respectively. From those results, the hydrogenated reaction of Li-G, Li-HG, and Li-AG can be considered as follows:



Here,  $\text{CH}_x$  is hydrocarbon such as  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_2\text{H}_4$ . As reported in Ref. 29, the hydrogenation reactions of Li-G, Li-HG, and Li-AG occur around 200 °C, 130 °C and 200 °C, and 130 °C. Considering this result, it can be indicated that  $\text{LiC}_6$  and  $\text{Li}_2\text{C}_2$  are hydrogenated at around 200 °C and 130 °C, respectively.

TABLE I. Temperature for hydrogenation, compounds identified by electron diffraction patterns in as-synthesized samples, compounds identified by electron diffraction patterns in hydrogenated samples, and compounds identified by electron diffraction patterns in dehydrogenated samples of Li-G, Li-HG, and Li-AG.

Sample	Temperature for hydrogenation (°C)	Compounds in as-synthesized	Compounds in hydrogenated	Compounds in dehydrogenated
Li-G	130	C, $\text{LiC}_6$ , $\text{Li}_2\text{O}$	C, LiH	$\text{LiC}_{12}$ , LiH
Li-HG	130, 200	$\text{LiC}_6$ , $\text{Li}_2\text{C}_2$ , $\text{Li}_2\text{O}$	C, LiH, $\text{LiC}_6$	$\text{LiC}_6$ , $\text{Li}_2\text{C}_2$
Li-AG	200	$\text{Li}_2\text{C}_2$	LiH, $\text{Li}_2\text{O}$ , LiOH	$\text{Li}_2\text{C}_2$

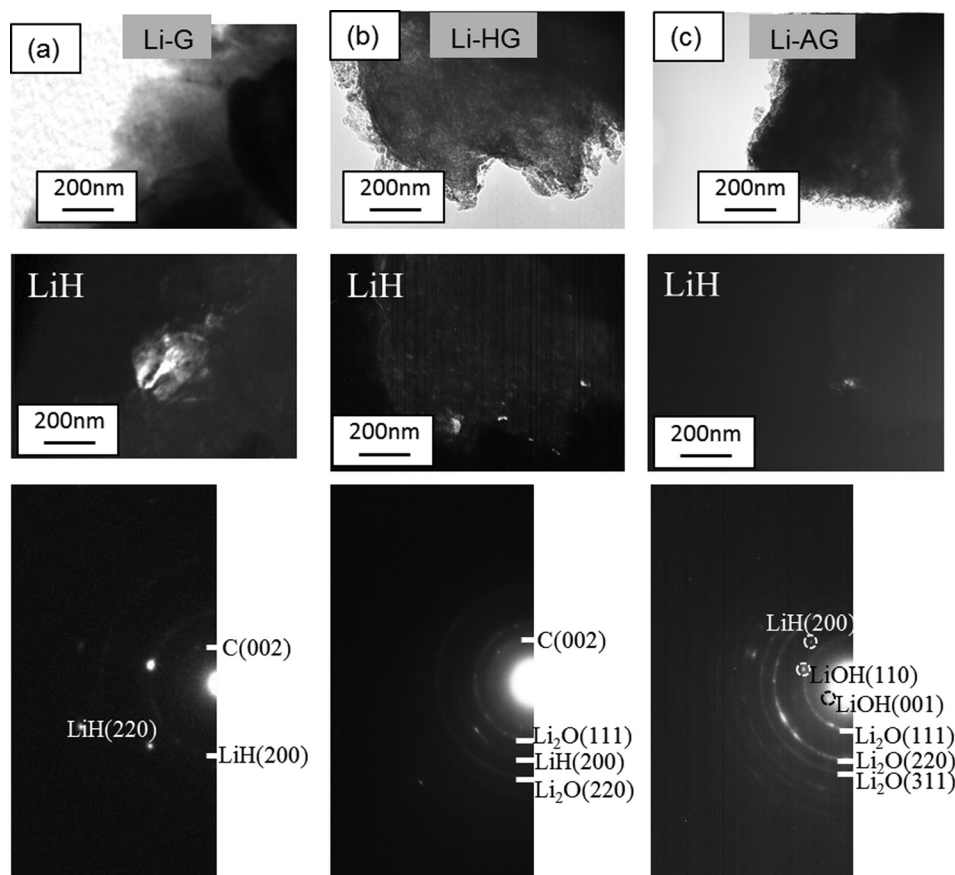


FIG. 2. BF and DF images and diffraction patterns of hydrogenated samples: (a) Li-G, (b) Li-HG, and (c) Li-AG.

The BF and DF images and diffraction patterns of dehydrogenated samples are shown in Figure 3(g) Li-G, (h) Li-HG, and (i) Li-AG. After dehydrogenation, the graphite intercalation compound of  $\text{LiC}_{12}$  appeared in Li-G and Li-HG. And  $\text{Li}_2\text{C}_2$  appeared in Li-HG and Li-AG, as listed in Table I. The DF images show the crystallites of  $\text{LiC}_{12}$  and  $\text{Li}_2\text{C}_2$  in the dehydrogenated samples. The crystallite size of  $\text{LiC}_{12}$  in Li-G was relatively larger than that in Li-AG, and the crystallite size of  $\text{Li}_2\text{C}_2$  was comparable to that in Li-AG. This result would indicate that carbon (graphite) with relatively large crystallite and carbon (amorphous like) with small crystallite changed to  $\text{LiC}_{12}$  and  $\text{Li}_2\text{C}_2$ , respectively. From those results, the hydrogenated reaction of Li-G, Li-HG, and Li-AG can be considered as follows:

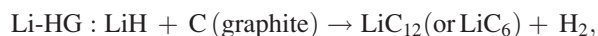
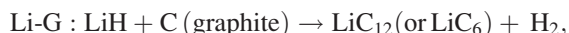


Figure 4 shows (a) BF, (b) DF images, and (c) diffraction pattern of the dehydrogenated sample of Li-G. In the diffraction pattern, a couple of diffraction spots were assigned to  $\text{LiC}_{12}$  (002). In the DF image, layer structure due to the crystallite of  $\text{LiC}_{12}$  was observed. Here, the Li atoms were intercalated into graphite structure, however, we found LiH particle in the sample after hydrogenation (Fig. 2(d)). Li atoms should move to outside of graphite from intercalated sites, when LiH forms. To clarify the formation site of LiH,

we obtained the HRTEM image of the hydrogenated sample of Li-G, as shown in Figure 5(b). FFT image was analyzed from (a) HRTEM image, and (c) IFFT image was analyzed from (b). Finally, (a') image shows the location of graphite and LiH. From this result, it was indicated that Li atoms could move along in-plane direction of graphite and could form LiH at the edge of graphite. Now stage, although we are not sure the driving force of Li atoms moving, it was confirmed that hydrogenation of GIC proceeded with generating LiH at the edge site of graphite.

## B. Mg-C-H system

Figures 6(a)–6(c) show the BF images and the diffraction patterns of as-synthesized samples of Mg-G, Mg-HG, and Mg-AG, respectively. From the BF images, it seems that the particle sizes of Mg-G, Mg-HG, and Mg-AG are from several tens nm to several hundred nm. From the diffraction patterns, the diffraction spots from Mg (101),  $\text{MgC}_2$  (210), and the diffraction rings from C (002), MgO (200) were indexed in Mg-G. In Mg-HG, and Mg-AG, the diffraction spots from Mg (101), Mg (102),  $\text{MgC}_2$  (210),  $\text{MgC}_2$  (311),  $\text{MgC}_2$  (400), and  $\text{MgC}_2$  (200), the diffraction rings from C (002), MgO (200), and no spots, the diffraction rings from C (002), MgO (200), were identified, respectively, as listed in Table II. The result of diffraction patterns of Mg-G was almost similar with the result of Mg-HG.  $\text{MgC}_2$  was generated from the solid-solid reaction between C and Mg during ball-milling. Parts of Mg and graphite remained without any reactions. MgO, which was composed of much small

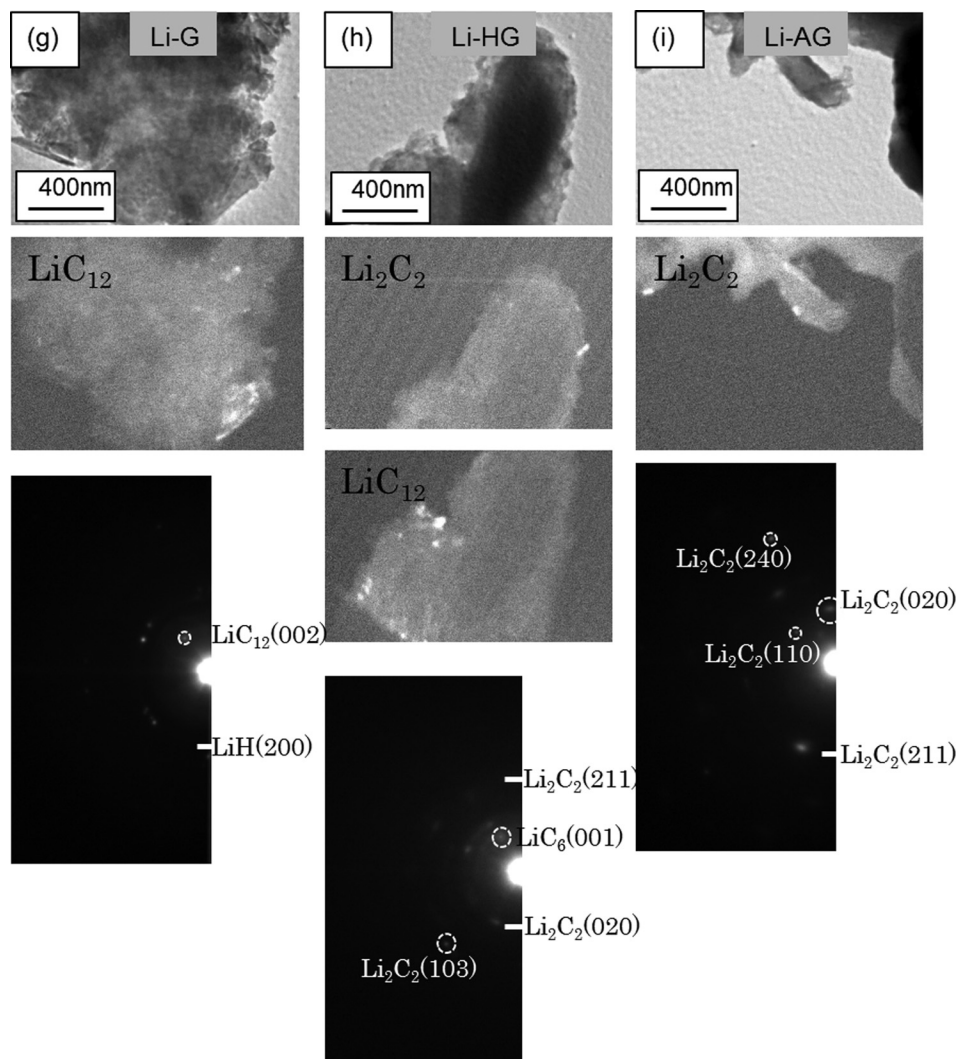


FIG. 3. BF and DF images and diffraction patterns of dehydrogenated samples: (g) Li-G, (h) Li-HG, and (i) Li-AG.

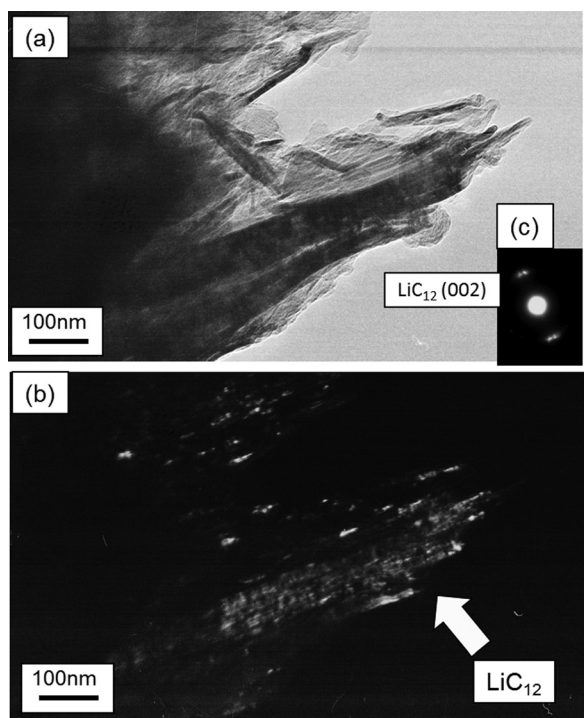


FIG. 4. (a) BF images, (b) DF images, and (c) diffraction pattern of the dehydrogenated sample of Li-G.

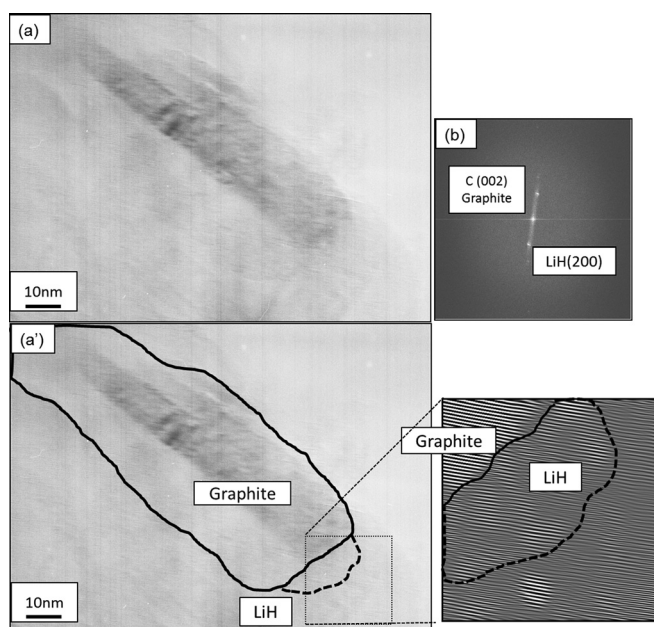


FIG. 5. (a) HRTEM image of hydrogenated sample of Li-G, (b) FFT image from (a), (c) IFFT image from (b), (a') and (a) with indication of crystallites of graphite and LiH.

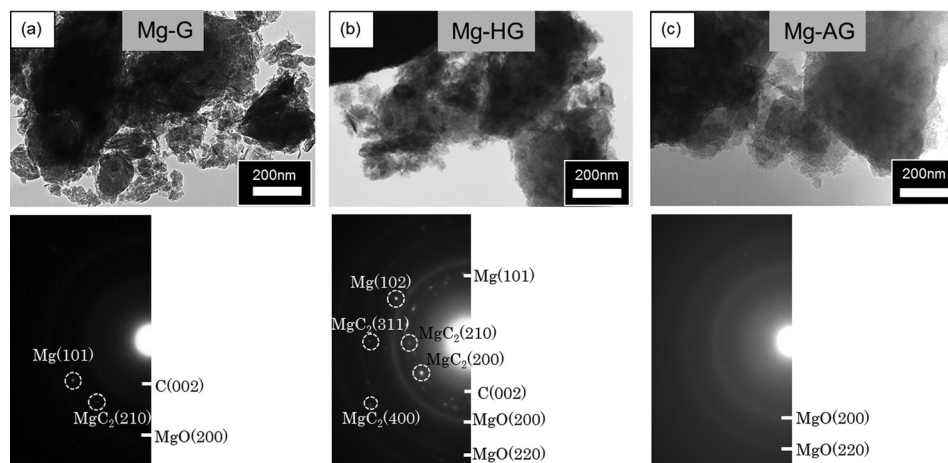


FIG. 6. BF images and diffraction pattern of the as-synthesized samples: (a) Mg-G, (b) Mg-HG, and (c) Mg-AG.

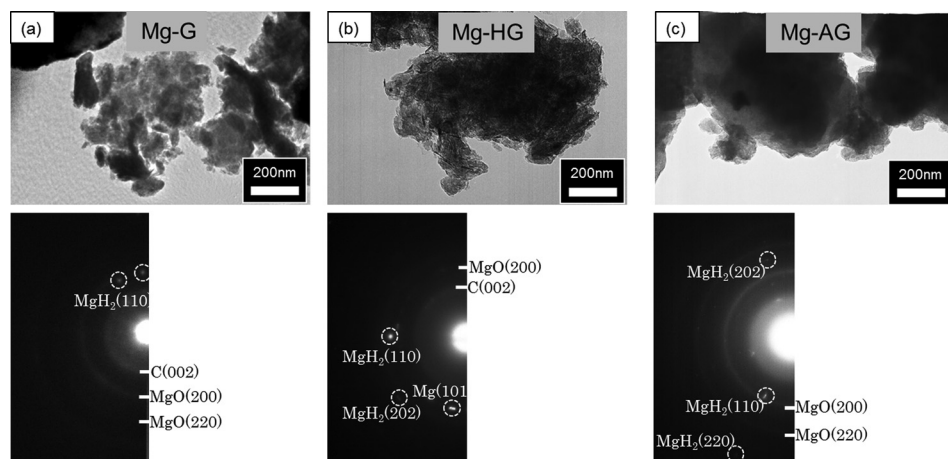


FIG. 7. BF images and diffraction pattern of hydrogenated samples: (a) Mg-G, (b) Mg-HG, and (c) Mg-AG.

crystallites, could be considered as an impurity in the starting material of Mg. In the previous report,<sup>30</sup> compound between Mg and C has never been found in XRD results. However, in this study,  $\text{MgC}_2$  has been identified in the samples of Mg-G and Mg-HG. Figures 7(a)–7(c) show the BF images and the diffraction patterns of as-hydrogenated samples of Mg-G, Mg-HG, and Mg-AG, respectively. From the BF images, it seems that the particle sizes of Mg-G, Mg-HG, and Mg-AG are the almost same as the as-synthesized samples. From the diffraction patterns, the diffraction spots from  $\text{MgH}_2$  (110) and the diffraction rings from C (002), MgO (200), MgO (220) are indexed in Mg-G. In Mg-HG and Mg-AG, the diffraction spots from  $\text{MgH}_2$  (110),  $\text{MgH}_2$  (101),  $\text{MgH}_2$  (202), Mg (101), the diffraction rings from C (002), MgO (200), and the diffraction spots from  $\text{MgH}_2$  (110),  $\text{MgH}_2$  (202),  $\text{MgH}_2$  (220), the diffraction rings from MgO (220), MgO (200), were identified, respectively, as listed in Table II. From Table II, we can consider that  $\text{MgH}_2$  is hydrogenated

from Mg and/or  $\text{MgC}_2$  in Mg-G and Mg-HG. In case of Mg-AG, no crystalline was found in as-synthesized sample, and  $\text{MgH}_2$  was found in as-hydrogenated sample. Therefore, Mg-AG could be totally different from Mg-G and Mg-HG. Meanwhile, the crystallite size of graphite in Mg-G is slightly different from that in Mg-HG, as shown in Figure 8. Figure 8 shows HRTEM images of graphite in as-synthesized Mg-G, Mg-HG, and Mg-AG with their average size. Compared with Mg-G and Mg-HG, there was no crystalline compounds in Mg-AG. Those results about the crystallinity of each sample obtained by TEM experiment were agreeable with the previous results obtained by XRD,<sup>30</sup> except for identifying the Mg-C compound, that is, this is the first report on  $\text{MgC}_2$  existing in Mg-C-H system.

With respect to the hydrogenation reaction of Mg-C-H system, it has been reported that the hydrogenation reactions of Mg-G, Mg-HG, and Mg-AG happened at about 220 °C, 220 °C, and 400 °C, respectively. As is listed in Table II, we

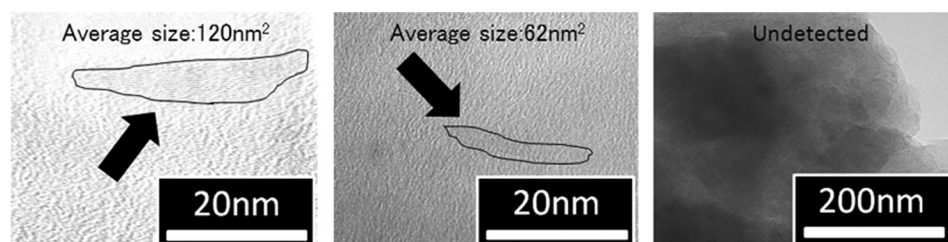
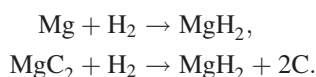


FIG. 8. HRTEM images of graphite: (a) Mg-G, (b) Mg-HG and (c) Mg-AG.

TABLE II. Temperature for hydrogenation, compounds identified by electron diffraction patterns in as-synthesized samples, and compounds identified by electron diffraction patterns in hydrogenated samples of Mg-G, Mg-HG, and Mg-AG.

Sample	Temperature for hydrogenation (°C)	Compounds in as-synthesized	Compounds in hydrogenated
Mg-G	220	C, Mg, MgC <sub>2</sub> , MgO	C, MgH <sub>2</sub> , MgO
Mg-HG	220	C, Mg, MgC <sub>2</sub> , MgO	C, Mg, MgH <sub>2</sub> , MgO
Mg-AG	440	Amorphous, MgO	C, MgH <sub>2</sub> , MgO

found MgC<sub>2</sub> in as-synthesized sample and MgH<sub>2</sub> in as-hydrogenated sample of both Mg-G and Mg-HG. So, we expected that Mg and MgC<sub>2</sub> absorbed hydrogen at 220 °C to be MgH<sub>2</sub>. The hydrogenation reactions of Mg and MgC<sub>2</sub> were considered as follows:



In general, Mg can absorb hydrogen over 300 °C. It would be indicated that MgC<sub>2</sub> somehow helped Mg absorbing hydrogen. Actually, it was confirmed that MgC<sub>2</sub> phase was located nearby Mg phase. (Figure 9 shows (a) HRTEM image of Mg-G, (b) FFT pattern of a boxed part of (a), and (c) IFFT pattern obtained from spots of Mg and MgC<sub>2</sub> in (b).) Meanwhile, it was reported that Mg-AG can absorb hydrogen at 440 °C.<sup>30</sup> In Mg-AG, amorphous materials or composite with poor crystallinity, which called (Mg-C)<sup>nano</sup> in Ref. 30, absorbed hydrogen to be MgH<sub>2</sub>. However, the reaction mechanism of Mg-AG has not clarified yet in this report, it would be different from that of Mg-G, Mg-HG.

#### IV. CONCLUSION

In this study, we have investigated the compounds in the Li-C-H and Mg-C-H systems to understand the reaction

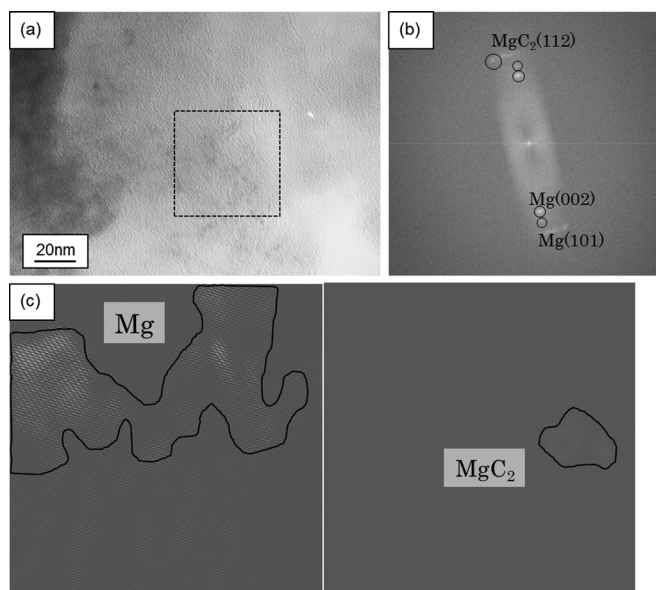
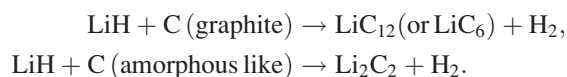
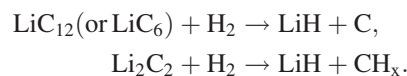


FIG. 9. (a) HRTEM image of Mg-G, (b) FFT pattern of a boxed part of (a), and (c) IFFT pattern obtained from spots of Mg and MgC<sub>2</sub> in (b).

mechanism. Conclusively, we have determined the reaction formula of the hydrogenation and dehydrogenation in both systems. In the L-C-H system, we identified two kinds of compounds between Li and C. One was LiC<sub>6</sub> (LiC<sub>12</sub>) of GIC, the other was Li<sub>2</sub>C<sub>2</sub>. The hydrogenation reaction formula of each compound were determined as

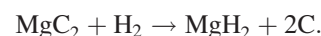


And the dehydrogenation reaction formula of each compound were determined as



Here, it should be noticed that de/hydrogenation Li<sub>2</sub>C<sub>2</sub> is irreversible because of emission of CH<sub>x</sub>. Additionally, we have discussed the hydrogenation mechanism of GIC, namely, it has been indicated that the hydrogenation of GIC proceeded with generating LiH at the edge site of graphite.

In the Mg-C-H system, we identified the MgC<sub>2</sub> as the compound between Mg and C. MgC<sub>2</sub> absorbed hydrogen at 220 °C to be MgH<sub>2</sub>



According to this reaction equation, MgC<sub>2</sub> can theoretically absorb and desorb 4.1 mass% of hydrogen at around 200 °C. Additionally, Mg with MgC<sub>2</sub> can absorb and desorb hydrogen at around 200 °C, though Mg itself absorb and desorb hydrogen at around 400 °C. The mechanism of this improvement has not clarified yet in this study, however, we confirmed that metal-C-H system has high potentials for promising hydrogen storage materials.

#### ACKNOWLEDGMENTS

This work has been partially supported by HYDRO STAR (NEDO) and L-station (Hokkaido Univ.).

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