

Abstract

Chemical hydrides such as MgH_2 are known as high hydrogen containing materials. However their high working temperature and slow kinetics limit their practical application. Mg-based nano-composite materials with nano-Ni catalyst prepared by mechanical milling showed excellent properties, compared with those of Ni, a ball-milled MgH_2 or the mixture of MgH_2 and the nano-Ni catalyst, in terms of the H_2 desorption and absorption. The H_2 absorption capacity at 9 MPa and room temperature in 6 h increased from less than 0.1 wt% for the mixture to 5.0 wt % for the nano-composite material, approaching a maximum of 6.5 wt% in 70 h. The improvement in kinetics is related to the low activation barrier,

the large collision frequency, a short diffusion path length and a high driving force. Carbon-based nano-composite material was synthesized by doping with potassium in superactivated carbon. This material can adsorb 1.6 wt% of hydrogen at room temperature under 5 MPa. This absorption capacity was greater than the value of 1.0 wt% found in potassium-doped graphite. Kinetics of the hydrogen adsorption of the potassium-doped superactivated carbon was considerably improved. The high hydrogen adsorption capacity and the improved kinetics of this system may be derived from the nano-sized graphen and the high surface area.

Keywords

Magnesium, Catalyst, Potassium, Activated carbon, Nano-composite material

要 旨

MgH_2 などのケミカルハイドライドは水素貯蔵量の多い化合物として知られている。一方で高い動作温度と遅い水素吸蔵放出速度が問題である。本報告で筆者らは、ミリングによってナノNi触媒を MgH_2 中に分散させたMg系ナノ複合材料の水素の放出速度は MgH_2 や MgH_2 とナノNi触媒との混合物に比べ、著しく早くなることを見出した。水素放出後、ナノ複合材料の9MPa、室温(296K)、6時間後における水素吸蔵量は混合物の0.1wt%以下から5wt%に増加し、70時間後には6.5wt%と最大値を示した。ミリングによって小さな結晶子を

有するMgは拡散経路長を低下させ、ナノNi触媒は活性化エネルギーを減少させて衝突頻度を増し、高水素圧はMg表面のNi中に化学吸着した水素原子数を増加させて、水素吸蔵、放出速度は大きく改良されるものと考えられた。また、カリウムを活性炭にドープすることにより、炭素系ナノ複合材料を合成した。この材料の水素吸着量は5MPa、室温で1.6wt%とカリウム黒鉛層間化合物(1.0wt%)に比べ増加し、水素吸着速度も早くなった。水素吸着速度の向上はナノサイズのグラフエンと高比表面積に基づくものと考えられた。

キーワード

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1. Introduction

A fuel cell is a device that continuously converts the chemical energy of hydrogen (H_2) and oxygen (O_2) into electrical energy. Since the fuel cell has efficiency much higher than that of conventional combustion engines, a fuel cell vehicle (FCV) is expected to have high efficiency.¹⁾ A polymer electrolyte fuel cell (PEFC, PEM fuel cell) is the prime power source for an FCV. One of the most widely envisioned sources of fuel for the FCV is H_2 . Therefore, it is necessary to have a storage tank of H_2 to start the system on demand. The first FCVs were delivered on Dec. 2, 2002. These FCVs feature a 35 MPa H_2 storage tank and can travel 300-355 km on a full tank. The driving ranges of the vehicles are small compared to those of gasoline vehicles. This is the biggest hurdle for FCVs and an improvement in the range is required for a new H_2 storage system.

H_2 can be stored in many different forms, including as compressed or liquefied H_2 in tanks,¹⁾ by adsorption on activated carbon^{1, 2)} and carbon nanotubes,^{1, 3)} as a hydrogen-absorbing alloy,^{1, 4, 5)} as chemical hydrides such as $NaBH_4$,⁶⁻¹⁰⁾ $NaAlH_4$,¹¹⁻¹⁴⁾ MgH_2 ,¹⁵⁻¹⁸⁾ $LiBH_4$ ¹⁹⁻²¹⁾ and metal nitrides,²²⁻³¹⁾ or as organic hydrides (methylcyclohexane, decalin).³²⁾ Amongst these methods, much attention has been given to thermal decomposition of light weight chemical hydrides (binary hydrides, complex hydrides), consisting of protide H^- , because of their large gravimetric H_2 densities. However, the high working temperature and the slow reaction kinetics (high activation energy) limit the practical application of chemical hydride systems.

In this review, we indicate in the following **Sec. 2**, the fact that the H_2 absorption capacities of the Mg-based nano-composite material with a nano-Ni catalyst exhibited 5.0-6.5 wt% at a high H_2 pressure of 9 MPa and room temperature (296 K). In **Sec. 3**, we demonstrate that kinetics of the H_2 adsorption of carbon-based nano-composite material (potassium-doped superactivated carbon) was considerably improved over conventional K-doped graphite (KC_8+K).

2. Magnesium-based nano-composite materials³³⁾

MgH_2 was mechanically milled with nano-Ni

46wt%/ Al_2O_3 8wt%/C 46wt% (a nano-Ni catalyst) or a Ni (Soekawa Chemicals, 0.8 μm) catalyst, yielding Mg-based nano-composite materials. The nano-Ni catalyst was prepared by a co-precipitation method. **Figure 1** compares the transmission electron micrographs of the nano-composite materials. The dark portions in Fig. 1(a) and (b) are nano-Ni and Ni whose dimensions are below 100 nm. It is revealed that the products are nano-composite materials.

The Ni crystallite size in the nano-composite materials was calculated using the Scherrer's equation. The Ni crystallite sizes in the nano-composite materials with the nano-Ni and the Ni catalysts were assumed to be 6 nm and 20 nm, respectively. The MgH_2 crystallite size of both the nano-composite materials and the ball-milled MgH_2 , as obtained from Scherrer's equation, was 10-11 nm and thus smaller than the value of as-received MgH_2 and the mixture (78 nm). The ball-milled specimens included about 10 % MgO. This contamination might originate from small leaks in the pulverizing system.

Figure 2 shows the desorption curves of the Mg-based nano-composite materials (catalyst: 5 wt%), together with the data from the ball-milled MgH_2 and the mixture. The nano-composite material with the nano-Ni catalyst could desorb 5.8 wt% of H_2 within 6 h at 473 K, followed, in order, by the nano-composite material with the Ni catalyst. The ball-milled MgH_2 and the mixture were unable to desorb

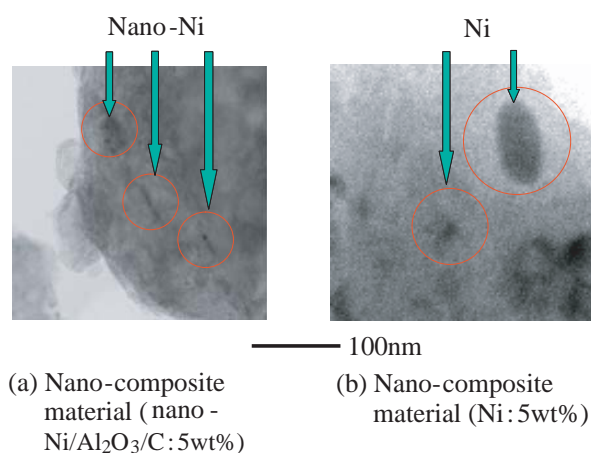


Fig. 1 TEM photographs of Mg-based nano-composite materials.

H₂ at the temperature. Furthermore, the nano-composite material containing 9 wt% nano-Ni/Al₂O₃/C desorbed 4.9 wt% H₂ at 423 K. We found that H₂ desorption is considerably improved using the nano-Ni catalyst. The maximum H₂ desorption capacities of the nano-composite materials was 6.5 wt% and this was 90 % of the theoretical value (7.2 wt%). This is due to the production of MgO during the mechanical milling.

After H₂ desorption at 523 K, the H₂ absorption curves at room temperature are shown in **Fig. 3**. It

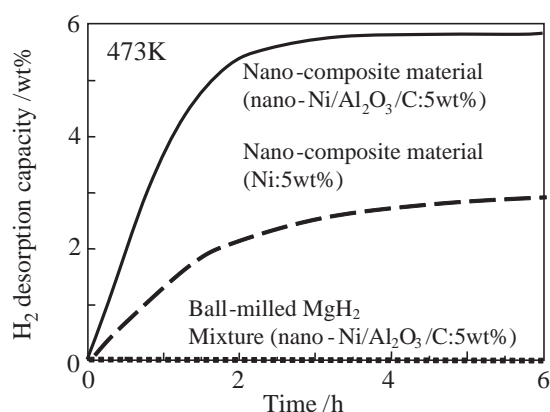


Fig. 2 Hydrogen desorption curves of Mg-based nano-composite materials together with the data from ball-milled MgH₂ and the mixture of MgH₂ and nano-Ni/Al₂O₃/C.

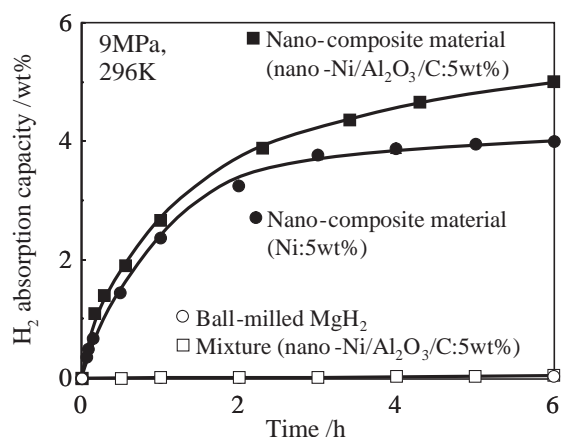


Fig. 3 Hydrogen absorption curves of Mg-based nano-composite materials together with the data from ball-milled MgH₂ and the mixture of MgH₂ and nano-Ni/Al₂O₃/C.

can be seen that the H₂ absorption capacities of the nano-composite materials are 4.0-5.0 wt% at 9 MPa and room temperature (296 K), while the H₂ absorption capacity of the ball-milled MgH₂ and the mixture are below 0.1 wt%. The H₂ absorption capacities at 296 K of the nano-composite materials with the Ni catalyst (5 wt%) and the nano-Ni catalyst (Ni/Al₂O₃/C : 5-9 wt%) in 70 h were 4.8 wt% and 6.3-6.5 wt%, respectively. At 373 K, the nano-composite materials absorbed 6.3-6.5 wt% of H₂ in 100 sec. The relation between the H₂ absorption capacities of the nano-composite materials and time were given by the first-order rate equation. The initial H₂ absorption rate (rate constant) was independent of the pressure. This result indicates that the concentration of the chemisorbed hydrogen atom in the Ni and the nano-Ni catalysts on the Mg particles linearly increases with pressure. From the Arrhenius plot of *k* with temperature, the activation energies of the absorption were obtained as 50 and 86 kJ/molH₂ for the nano-composite material with the nano-Ni catalyst and the ball-milled MgH₂, respectively. The activation energy of the nano-composite material is lower than that of the ball-milled pure MgH₂ and corresponds to the value of diffusion in Mg-2 wt% Ce alloy given by Renner and Grabke (40.0 kJ/molH₂).³⁴⁾ From the Arrhenius plot of H₂ desorption rate constant value with temperature, the activation energy of 74 kJ/molH₂ in the nano-composite material with the nano-Ni catalyst is approximately the same as the standard enthalpy change (-ΔH:74.4-76.2 kJ/molH₂).^{35, 36)} A possible interpretation of these results is that the activation barrier for dissociation of H₂ molecule and the formation of the hydrogen atom in the nano-composite material is sufficiently low and the absorption rate-limiting step is diffusion-controlled.

The activation energy of desorption for the ball-milled MgH₂ is 144 kJ/molH₂, which is a little smaller than that of unmilled MgH₂ previously reported (156 kJ/molH₂).³⁷⁾ The activation energy of desorption is, at 162 kJ/molH₂, approximately the sum of the standard enthalpy change (76 kJ/molH₂) and the activation energy of absorption (86 kJ/molH₂).

The height of the activation barrier depends on the

surface elements. Without using the catalysts, the activation energy of absorption corresponds to the activation barrier for the dissociation of H_2 molecule and the formation of a hydrogen atom. The activation energies of the H_2 absorption and desorption for the nano-composite material with the Ni catalyst were 52 kJ/molH_2 and 71 kJ/molH_2 , respectively. These values are similar to those for the materials with the nano-Ni catalyst, but the rate constant with the nano-Ni catalyst has a higher value. It is suggested that the collision frequency between H_2 molecules and Ni increases with the decreasing size of the Ni catalyst.

It is worth recalling that the milling of the MgH_2 , itself, improves the desorption and absorption kinetics over those of the unmilled MgH_2 because of the smaller crystallite size.³⁷⁾ **Figure 4** shows the concept of a Mg-based nano-composite material and

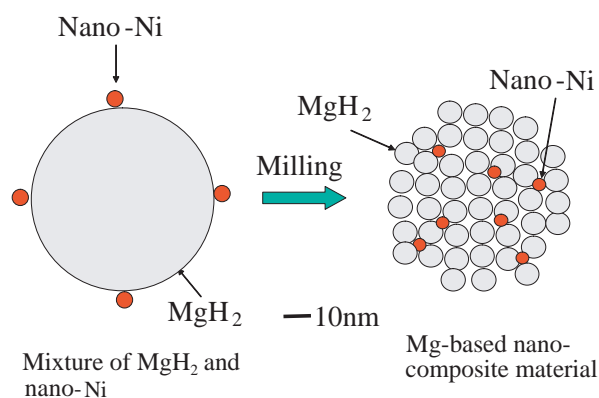


Fig. 4 Conceptual models of Mg-based nano-composite material and the mixture of MgH_2 and nano-Ni.

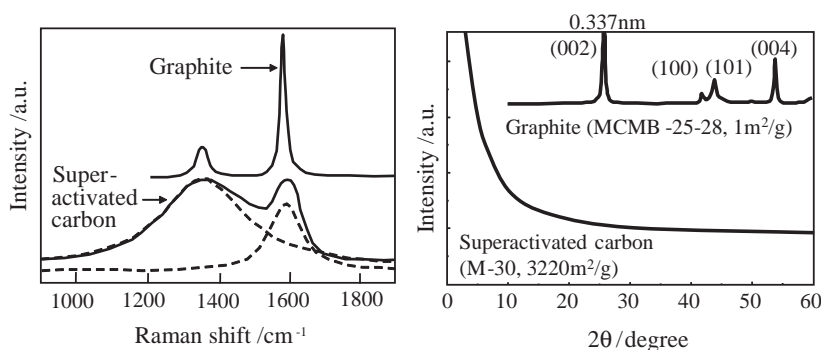


Fig. 5 Raman spectra and X-ray diffraction intensity curves of super-activated carbon and graphite.

the mixture of MgH_2 and the nano-Ni catalyst. The combination of MgH_2 (Mg) with the smaller crystallites, the nano-Ni catalyst and the high H_2 pressure gives rise to the excellent absorption/desorption kinetics. Recently, in-situ TEM observations of the decomposition and the hydrogenation of the Mg-based nano-composite material has been carried out at 200 kV and 1300 kV TEM.³⁸⁾ The in-situ TEM observation will be useful in analyzing the mechanism of the H_2 desorption and absorption in nano-composite materials.

3. Potassium-doped superactivated carbon³⁹⁾

The Raman spectra of superactivated carbon (M-30, Osaka Gas Chemicals Co., Ltd., Japan) and synthetic graphite (MCMB-25-28, Osaka Gas Chemicals Co., Ltd., Japan) are shown in **Fig. 5**. The Raman band observed at 1610 cm^{-1} in single crystallite of graphite is assigned to doubly degenerate deformation vibrations of the hexagonal ring. The additional band at 1340 cm^{-1} is attributed to the size effect in the direction of polycondensed aromatic plane. The crystalline diameter of the carbon in the direction of the polycondensed aromatic plane (diameter of the graphen), L_a , was obtained by the equation reported by Tuinstra et al.⁴⁰⁾ The L_a of the superactivated carbon was 3.3 nm, and about one seventh of that of synthetic graphite (L_a : 22 nm). The specific surface areas of the superactivated carbon and the synthetic graphite are $3220 \text{ m}^2/\text{g}$ and $1 \text{ m}^2/\text{g}$, respectively. It should be noted that the maximum specific surface area for carbonaceous materials is well

known to be $2630 \text{ m}^2/\text{g}$ when both sides of graphen are effective for adsorption.⁴¹⁾ The synthetic graphite exhibits sharp XRD peaks, as shown in Fig. 5. The peak at 2θ of 26.4° results from the 002 reflection of the graphite crystallites. Three characteristic peaks of the synthetic graphite, marked by Miller indices (100), (101) and (004), are also observed in the 2θ range from 40° to 60° . The diffraction peaks are not detected in the superactivated

carbon. These results suggest that a graphen sheet is dispersed in the carbon. Weighed amounts of superactivated carbon or graphite and K were collected in an inert atmosphere and placed in a self-sealing cell made of stainless steel. The C/K ratio was 4. The cells were then thermally treated at 573 K for 20 h, yielding K-doped carbonaceous materials.

In **Fig. 6**, the amount of H₂ adsorbed in K-doped superactivated carbon at 296 K is shown as a function of time. The H₂ adsorbed attained a value of 1.6 wt% in 10 seconds. When the pressure was reduced to 0.01 MPa, the H₂ desorbed was only 0.1 wt%. Figure 6 also shows the H₂ adsorption capacity of K-doped graphite over time. The capacity gradually increases with time, approaching to a constant value of 1.0 wt%. On decreasing the pressure, H₂ was not desorbed from the graphite. Kinetics of the H₂ adsorption and the H₂ adsorption capacity of the K-doped superactivated carbon were improved with respect to the conventional K-doped graphite. It seems that H₂ adsorption capacity correlates with the structure of the carbon materials. Compared with the graphite, the superactivated carbon used in this work consists small-sized graphen (La: 3.3 nm) and possesses a large specific surface area (3200 m²/g). These features favor the high adsorption capacity and the improved kinetics of the K-doped superactivated carbon. Compared with 0.4 wt% or zero H₂ adsorption, respectively,

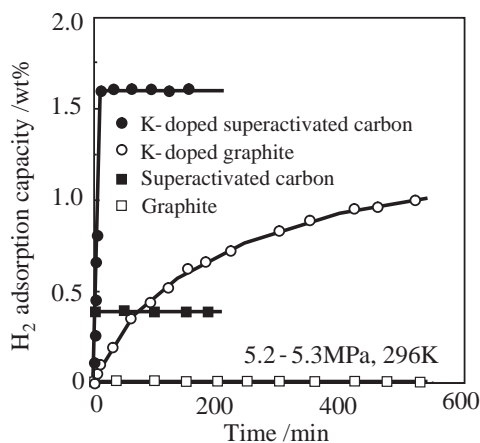


Fig. 6 H₂ adsorbed of K-doped superactivated carbon, K-doped graphite, superactivated carbon and graphite as a function of time.

measured for the same superactivated carbon and graphite without K-doping as shown in Fig. 2, the high H₂ adsorption may result from the properties of K.

The X-ray diffraction intensity curves of the K-doped carbon materials are shown in **Fig. 7**. Before H₂ adsorption, the K-doped graphite exhibits XRD peaks corresponding to KC₈ and K. The X-ray diffraction peak of hydrogenated K-doped graphite is observed at 2θ of 33° due to KC₄H_{0.8} (003 reflection).⁴²⁾ **Figure 8** shows the schematic diagram of the layer structure in K-graphite intercalation compounds (KC₈ and KC₄H_{0.8}). The intercalation of K and H₂ into KC₈ in the first layer

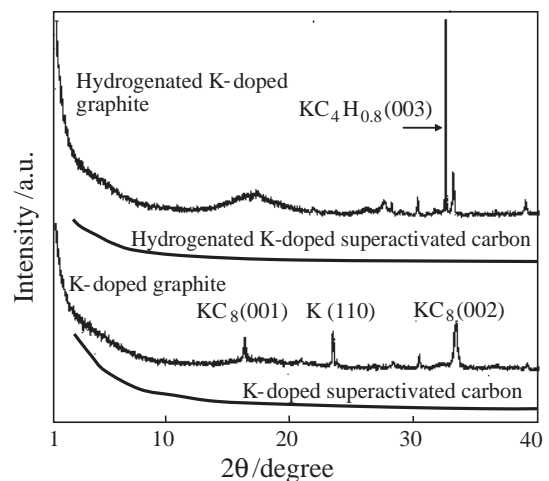


Fig. 7 X-ray diffraction intensity curves of K-doped graphite, hydrogenated K-doped graphite, K-doped superactivated carbon and hydrogenated K-doped superactivated carbon.

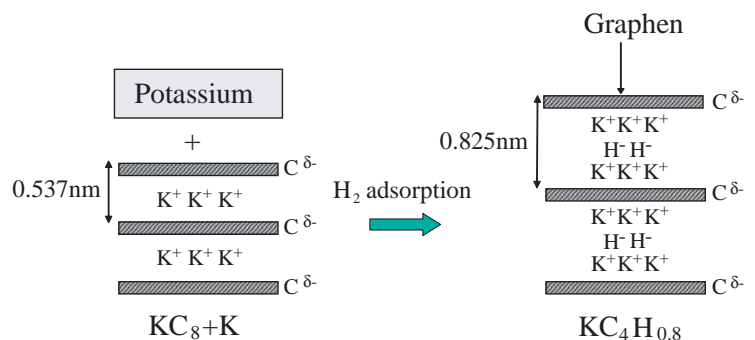


Fig. 8 Schematic diagram of the layer structure in K-graphite intercalation compounds (KC₈ and KC₄H_{0.8}).

leads to $KC_4H_{0.8}$ in that layer. The compound has a triple atomic layer of K-H-K between graphene planes. X-ray diffraction intensity curves of the K-doped superactivated carbon and the hydrogenated K-doped superactivated carbon were also measured. It is indicated that those specimens possess an amorphous structure, as shown in Fig. 7. The H_2 desorption peak temperatures of the hydrogenated K-doped superactivated carbon (peaks: 567, 649, 773, 1108 K) were different from those of $KC_4H_{0.8}$ (peaks: 532, 697, 884, 1173 K). This can be explained by the fact that the K-doped superactivated carbon includes a new intercalation compound.

4. Conclusions

We investigated H_2 absorption (adsorption) and desorption using nano-composite materials. The Mg-based nano-composite material and K-doped superactivated carbon showed excellent kinetics. The kinetics were improved by producing materials possessing a nano-sized phase.

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