Journal of Alloys and Compounds 509 (2011) 4534–4537

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

^{1}H NMR study of hydrogen stored in activated carbon powder prepared by mechanical milling

K. Shindo*, T. Kondo[1], Y. Sakurai[2]

NTT Microsystem Integration Laboratories, NTT Corporation 3-1, Morinosato-Wakamiya, Atsugi-shi, Kanagawa 243-0198, Japan

ARTICLE INFO

Article history:
Received 14 April 2010
Received in revised form 18 January 2011
Accepted 18 January 2011
Available online 25 January 2011

Keywords:
Hydrogen storage
Activated carbon
Mechanical milling
^{1}H NMR

ABSTRACT

A ^{1}H NMR study was carried out using hydrogenated activated carbon powder (AC) prepared by mechanical milling in a H_2 atmosphere. Chemical shifts in the hydrogenated milled AC were observed near 0 and 2 ppm. In addition, the peak near 0 ppm was separated into two peaks (α and β) by the deconvolution of the NMR spectra; −0.6 and 0.2 ppm. This indicates that hydrogenated milled AC has three hydrogen components with different molecular mobilities. Measurement of the spin-lattice relaxation time (T_1) revealed that the hydrogen near 0 and 2 ppm consisted of two components (Components 1 and 2) and one component (Component 3), respectively. However, the activation energies (E_a) of each hydrogen component could not be estimated because the plots of inverse temperature ($1/T$) versus the logarithm of T_1 ($\ln T_1$) were scattered. We assumed that the components near 0 ppm (Component 1 and/or 2) were thermally unstable because the intensity of the chemical shift near 0 ppm decreased as the measurement temperature increased, and this might have an effect on T_1 measurements. The spin–spin relaxation time (T_2) indicated high and low molecular mobility at each chemical shift and several temperatures.

1. Introduction

Hydrogen has attracted attention as an ideal energy resource. For effective hydrogen use, we must develop a transportable system that can store hydrogen densely and safely. Compared with compressed hydrogen and liquefied hydrogen, hydrogen storage alloys have the advantage of allowing compact hydrogen storage [1]. However, there is generally a trade-off between hydrogen storage capacity and hydrogen absorption–desorption temperatures and kinetics. That is to say, alloys with large capacities absorb and desorb H_2 at high temperatures, while the alloys that desorb H_2 around room temperature absorb only a small amount of H_2. Although mechanical milling can be used to improve the characteristics of hydrogen storage alloys [2], no sufficient improvement has been reported in the hydriding/dehydriding properties of any alloys [3–5]: Mg–Ti–Ni composite with the nominal composition $(Mg_{0.8}Ti_{0.2})_2Ni$ produced by mechanical milling had a high hydrogen absorption capacity of 2.5 wt% at 100 °C, and its hydrogen desorption did not occur below 257 °C [3]. A 90Mg–6Ni–4C system of Mg–Ni–C composite prepared by mechanical milling showed the best hydriding/dehydriding properties, and absorbed hydrogen at a saturated capacity of 5.23 wt% at 100 °C and desorbed 3.74 wt% at 250 °C [4]. An 80 wt% Mg–13.33 wt% Ni–6.67 wt% Fe sample prepared by mechanical milling in a H_2 atmosphere absorbed 5.61 wt% at 320 °C and desorbed 3.92 wt% at 320 °C [5]. A high temperature of 250 °C or more is necessary for desorbing hydrogen from each alloy.

On the other hand, the nanostructured graphite prepared by mechanical milling in a H_2 atmosphere at room temperature had a high hydrogen storage capacity of 7.4 wt% [6]. Hydrogen in nanostructured graphite is trapped with dangling bonds created by milling, and two hydrogen components have been found [7]. Moreover, these two components may be ascribed to hydrogen in the graphite interlayer and hydrogen chemisorbed at the dangling bonds [8]. In contrast, although the hydrogen storage capacity of hydrogenated milled AC at room temperature was about 3 wt% [9], hydrogen desorption from this sample was detected at 100 °C [10], compared with the nanostructured graphite, which started hydrogen desorption at about 327 °C [11]. By using thermal desorption spectroscopy (TDS), we concluded that the hydrogen in hydrogenated milled AC might consist of two components: molecules and atoms [9]. This agreed with an analysis of deuterium desorbed from graphite [12]. We confirmed that these components might exist in hydrogenated nanocarbons prepared under the same milled conditions, independent of their host structures [13]. We are interested in whether the hydrogen stored in their nanocarbons has mobil-

---

* Corresponding author at: NTT Service Integration Laboratories, NTT Corporation 3-9-11, Midori-Cho Musashino-Shi, Tokyo 180-8585 Japan. Tel.: +81 422 59 2229; fax: +81 422 60 7855.
E-mail address: shindo.kazuhiko@lab.ntt.co.jp (K. Shindo).

[1] Present affiliation: NTT TELECON Corporation, Japan.

[2] Present affiliation: Toyohashi University of Technology, Japan.

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.01.082

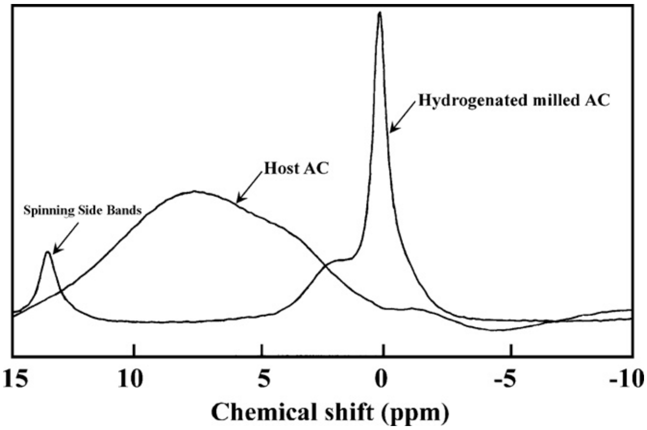

Fig. 1. ^1H NMR spectra of the host and hydrogenated milled AC at 20 °C.

ity. In this study, we prepared hydrogenated AC by mechanical milling in a H_2 atmosphere, and observed the state of the hydrogen in hydrogenated milled AC by using ^1H NMR.

2. Experimental

2.1. Sample preparation

The host AC (0.3 g) (Maxsorb; The Kansai Coke and Chemical, with a specific area of 1470 m^2/g) was degassed below 1×10^{-3} Pa at 300 °C using a turbo molecular pump before being milled. The measured sample was prepared by mechanical milling at 400 rpm for 10 h in a 45-ml steel pot with 22 steel balls each 7 mm in diameter under 0.8 MPa H_2 (high-purity hydrogen; 99.9999%) and at room temperature using a planetary ball mill apparatus (Fritsch, P7). The net hydrogen storage capacity of this sample estimated with the inert gas fusion-thermal conductivity method (HORIBA, EMGA-621W) was 1.7 wt%. The sample was handled in a glove box before and after the mechanical milling.

2.2. NMR measurements

A ^1H NMR experiment (Chemagnetics, CMX-300) was performed with magic angle spinning at 300.224 MHz at temperatures of −60, 0, 20 and 100 °C. The spectrum was observed after a 90° pulse had been irradiated using the one-pulse method. The spin-lattice relaxation time (T_1) was measured using the inversion recovery method. After reversing the magnetization with a 180° pulse and waiting for a certain time, we detected the strength of the recovering magnetization with a 90° pulse. The spin–spin relaxation time (T_2) was measured with the spin echo method. Similarly, we observed the magnetization strength by irradiating a 90° pulse, waiting for a certain time, and then irradiating a 180° pulse, and again waiting for a certain time.

3. Results and discussion

3.1. Hydrogen in AC hydrogenated by mechanical milling

Fig. 1 shows the ^1H NMR spectra of the host and hydrogenated milled AC at 20 °C. The host spectrum exhibited broad peaks near 4 and 8 ppm. We consider that these broad peaks originate from small molecules such as H_2O and functional groups such as –OH, –COOH and –NH_2, on the AC surface. The spectrum of the milled sample exhibited three peaks near 0, 2 and 13 ppm. The peak near 13 ppm is a spinning side band that appears when measurements are made while rotating the sample; the band is a kind of dummy peak and it appears at the same position as the spinning frequency or at a position that is an integral multiple of its frequency part. Accordingly, the chemical shifts of the milled sample are two peaks observed as the near 0 and 2 ppm. These peaks proved that there was hydrogen with a different molecular mobility in the hydrogenated milled AC. The TDS spectrum of the hydrogenated milled AC showed that the two peaks are in agreement [9]. The TDS spectrum also agrees with the NMR spectrum of nanostructured graphite indicating that there are two types of hydrogen components [8].

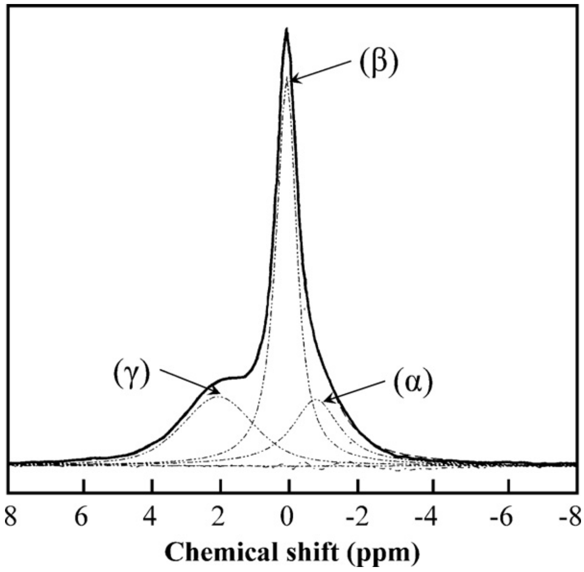

Fig. 2. Deconvolution of ^1H NMR spectra of hydrogenated milled AC at 20 °C.

The deconvolution of the ^1H NMR spectrum of hydrogenated milled AC at 20 °C using a mixed Gaussian/Lorentzian function is shown in Fig. 2. The peak near 0 ppm was separated into two peaks, −0.6 (α) and 0.2 ppm (β). These peaks and the peak near 2 ppm suggest that there are at least three hydrogen components in hydrogenated milled AC. The existence of these three hydrogen components agrees well with the three peaks in the deuterium desorption curves for graphite [12] and the three hydrogen retention sites in the graphite lattice [14].

3.2. Influence of temperature on ^1H NMR spectrum

The ^1H NMR spectra of hydrogenated milled AC were measured at −60, 0, 100 °C as well as at 20 °C. The spectra at each temperature revealed chemical shifts near 0 and 2 ppm similar to that at 20 °C. However, the peak intensities at 0 and 2 ppm differed depending on the measurement temperature. Specifically, the peak intensity at 0 ppm decreased at 100 °C. We normalized the spectrum by using a peak intensity of 2 ppm to compare the element ratios in each chemical shift. Fig. 3 shows the temperature dependence of hydro-

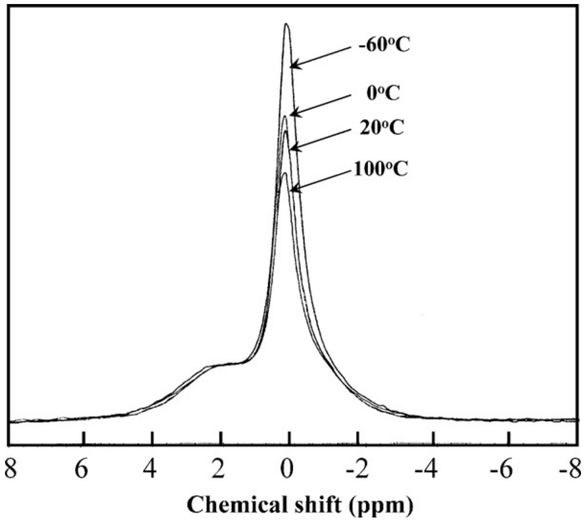

Fig. 3. Temperature dependence of ^1H NMR spectra of hydrogenated milled AC normalized at 2 ppm.

Table 1
Position of the peak maxima obtained by the deconvolution of the NMR spectra at several temperatures.

Temperature (°C)	Position of the peak maxima near 0 ppm (ppm)		Position of the peak maxima at 2 ppm (ppm)
	(α)	(β)	(γ)
100	−0.34	0.27	2.22
20	−0.62	0.23	2.14
0	−0.37	0.26	2.23
−60	−0.35	0.19	2.38

Table 2
The ratio of each hydrogen component obtained by the deconvolution of the NMR spectra at several temperatures.

Temperature (°C)	−0.6 ppm (α) (%)	0.2 ppm (β) (%)	2 ppm (γ) (%)
100	28.1	41.5	30.4
20	21.0	52.2	26.8
0	22.2	51.1	26.7
−60	24.2	54.1	21.7

genated milled AC normalized at 2 ppm on the ^{1}H NMR spectra. The peak intensity at 0 ppm decreased as the measurement temperature increased. We assumed that part of the hydrogen components near 0 ppm may easily desorb with increasing temperature and/or the hydrogen components near 0 ppm shift to the 2 ppm component. This is because we also confirmed that the TDS spectrum of the hydrogenated milled AC showed desorbing hydrogen molecules (mass number = 2) at about 100 °C [10].

Tables 1 and 2, respectively, show the positions of the peak maxima and the ratio of three hydrogen components (α, β and γ) obtained by deconvolution at several measurement temperatures. It became clear that there were three hydrogen components because the chemical shift near 0 ppm was also separated into two peaks at several measurement temperatures.

3.3. *Temperature dependence on molecular mobility of hydrogen stored in hydrogenated milled AC*

T_1 was estimated from the peaks at 0 and 2 ppm. The T_1 value at several temperatures is shown in Table 3. In particular, we proved that the hydrogen component at 0 ppm had two T_1 elements. From the results of deconvolution and the T_1 estimation, we concluded that the hydrogen near 0 ppm clearly consisted of two different components (Components 1 and 2).

In accordance with NMR theory [15], Fig. 4 plots the inverse temperature ($1/T$) versus the logarithm of T_1 ($\ln T_1$). In an area where these plots closely resemble a straight line, the relationship between T_1 and the time of the molecular mobility τ_c is described by the Arrhenius equation as follows:

$$\frac{1}{T_1} = A\tau_c \tag{1}$$

$$\tau_c = \tau_0 \exp\left(\frac{E_a}{RT}\right) \tag{2}$$

Table 3
Relaxation time T_1 at several temperatures.

Temperature (°C)	Relaxation time T_1 at 0 ppm (s)		Relaxation time T_1 at 2 ppm (s)
	Component 1	Component 2	Component 3
100	1.050	0.929	0.434
20	0.838	0.105	0.407
0	0.967	0.156	0.408
−60	0.722	0.143	0.487

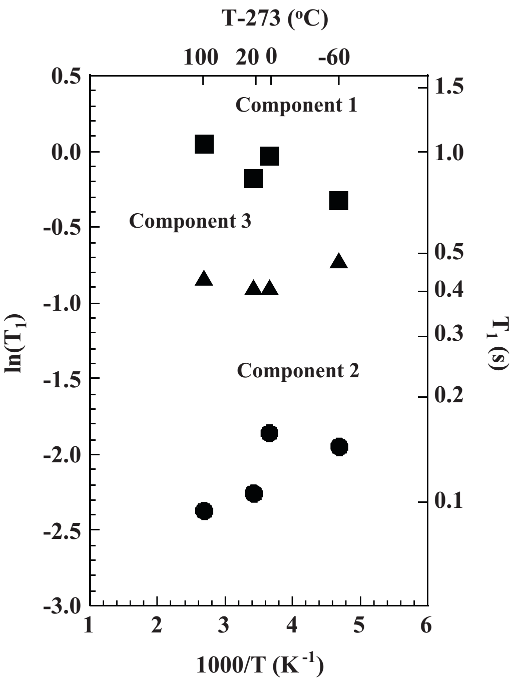

Fig. 4. Temperature dependence of relaxation time (T_1) for hydrogenated milled AC.

where A and τ_0 are constant, E_a is the activation energy and R is the gas constant (=8.314 J/mol K). From expressions (1) and (2),

$$\frac{1}{T_1} = A\tau_0 \exp\left(\frac{E_a}{RT}\right) \tag{3}$$

$$\ln T_1 = -\ln A\tau_0 - \frac{E_a}{RT} \tag{4}$$

we derive expression (4). Expression (4) corresponds to the plots in Fig. 4. The activation energy (E_a) is estimated from the slope of the straight line.

The $1/T$ versus $\ln T_1$ plot for each hydrogen component was more scattered than we expected. The scatter plot for one of the hydrogen components near 0 ppm (Component 2) was particularly noticeable. We consider that the instability of the hydrogen components near 0 ppm (Component 1 and/or 2) with regard to temperature originated as shown in Fig. 3. Accordingly, we did not estimate the E_a values for each hydrogen component because it is essential to consider at least the effect of temperature. Moreover, NMR measurements might be needed at different NMR frequencies [8]. We will consider the above in a future study.

On the other hand, the T_2 spectra were broad and the chemical shifts exhibited two peaks near −11 and 2 ppm because the T_2 values were measured without magic angle spinning. We consider that these components correspond to the components near 0 and 2 ppm, respectively, which were measured with magic angle spinning. Table 4 shows the T_2 values of hydrogen components near −11 and 2 ppm. It became clear that the T_2 of each hydrogen component had two elements. This indicated that hydrogen stored in

Table 4
Relaxation time T_2 at several temperatures.

Temperature (°C)	Relaxation time T_2 at −11 ppm (ms)		Relaxation time T_2 at 2 ppm (ms)	
100	1.08	0.03	1.46	0.07
20	1.81	0.04	1.36	0.04
0	1.38	0.04	1.47	0.07
−60	0.828	0.01	0.923	0.02

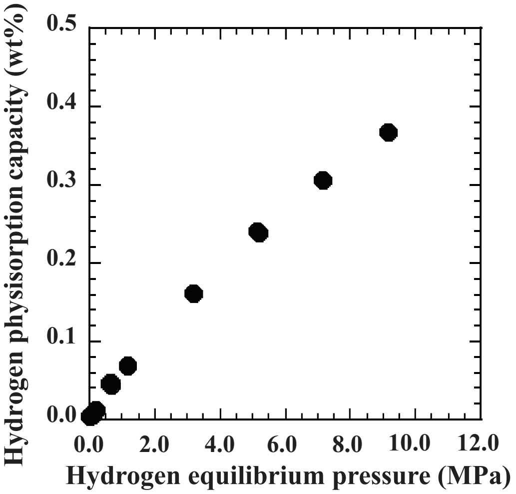

Fig. 5. Typical PCT curve of the host AC at 20 °C obtained using a gravimetric method.

hydrogenated milled AC consists of different components with high and low molecular mobilities.

3.4. Presumption of hydrogen storage mechanism

The existence of three hydrogen components in the milled AC became clear from these NMR measurements.

First, the hydrogen introduced into the milling pot physisorbs AC pores before milling. This is the first component. Moreover, pores are destroyed by milling and physisorbed hydrogen may be taken into the milled AC. This is similar to nanostructured graphite, where hydrogen is present in a graphite interlayer [7,8]. However, it is considered that hydrogen has a small physisorption capacity because the hydrogen physisorption capacity for AC in a 1 MPa H_2 atmosphere and at 20 °C obtained by the gravimetric method was only 0.4 wt% as shown in Fig. 5 [10]. Next, the dangling bonds that originate in a defective AC structure may be reactivated by milling and hydrogen may be chemisorbed with these bonds. This is the second component. Hydrogen chemisorbed at dangling bonds is similar to that in nanostructured graphite [7,8]. Two hydrogen states, molecules and atoms, similar to those mentioned above, are also revealed by TDS measurements [9,13].

The third hydrogen component is assumed to have adsorbed physically and/or chemically weakly onto the milled AC surface. Because the desorption of the hydrogen molecules (mass number = 2) from the milled AC in the TDS measurement started at about 100 °C [10], and this temperature is close to that of deuterium desorption from graphite [12], this component may correspond to Component 2, which is thermally unstable. The bonding state of Component 2 may be weaker than that of other components (Components 1 and 3).

4. Conclusions

The state of hydrogen stored in AC prepared by mechanical milling in a H_2 atmosphere has been investigated by using ^{1}H NMR. Chemical shifts were observed near 0 and 2 ppm. The peak near 0 ppm was separated into two peaks by the deconvolution of the NMR spectrum. It became clear that there were three hydrogen components in hydrogenated milled AC because an estimation of T_1 indicated that hydrogen near 0 ppm clearly consisted of two different components. However, the E_a of each hydrogen component could not be estimated because T_1 measurements might be influenced by the thermal instability of the hydrogen components near 0 ppm. T_2 measurements indicated that the hydrogen components at each chemical shift had high and low molecular mobilities. We also assumed three hydrogen components from the hydrogen storage mechanism. One is hydrogen that physisorbs the pores of the host AC. Another is hydrogen that chemisorbs the dangling bonds of the milled AC. The third is hydrogen adsorbed weakly onto the milled AC surface.

References

[1] L. Schlapbach, A. Züttel, Nature 414 (2001) 353.
[2] S. Orimo, H. Fujii, Intermetallics 6 (1993) 185.
[3] A.V. Borissova, S. Deledda, B.C. Hauback, J. Alloys Compd. 481 (2009) 24.
[4] Y. Zhu, Z. Liu, Y. Yang, H. Gu, L. Li, M. Cai, Int. J. Hydrogen Energy 35 (2010) 6350.
[5] M.Y. Song, S.H. Baek, J.-L. Bobet, S.-H. Hong, Int. J. Hydrogen Energy 35 (2010) 10366.
[6] S. Orimo, G. Majer, T. Fukunaga, A. Züttel, L. Schlapbach, H. Fujii, Appl. Phys. Lett. 75 (1999) 3093.
[7] T. Fukunaga, K. Itoh, S. Orimo, M. Aoki, H. Fujii, J. Alloys Compd. 327 (2001) 224.
[8] G. Majer, E. Stanik, S. Orimo, J. Alloys Compd. 356–357 (2003) 617.
[9] K. Shindo, T. Kondo, M. Arakawa, Y. Sakurai, J. Alloys Compd. 359 (2003) 267.
[10] K. Shindo, T. Kondo, Y. Sakurai, J. Alloys Compd. 379 (2004) 252.
[11] S. Orimo, T. Matsushima, H. Fujii, T. Fukunaga, G. Majer, J. Appl. Phys. 90 (2001) 1545.
[12] H. Atsumi, S. Tokura, M. Miyake, J. Nucl. Mater. 155–157 (1988) 241.
[13] K. Shindo, T. Kondo, Y. Sakurai, J. Alloys Compd. 372 (2004) 201.
[14] S.L. Kanashenko, A.E. Gorodetsky, V.N. Chernikov, A.V. Markin, A.P. Zakharov, B.L. Doyle, W.R. Wampler, J. Nucl. Mater. 233–237 (1996) 1207.
[15] W. Emsley, J. Feeney, L.H. Sutcliffe (Eds.), High Resolution NMR Spectroscopy, Pergamon Press, Oxford, 1965 (Chapter 2).