Application of Alkali Metal-Graphite Intercalation Compounds
to Cryosorption Material for Hydrogen Isotopes

(Received Oct. 21, 1987)

N. Akuzawa*, K. Katano*, Y. Ohmura*, T. Konishi*,
T. Amemiya*, T. Terai** and Y. Takahashi***Tokyo National College of Technology,
1220-2, Kunugida-machi, Hachioji-shi, Tokyo 193, Japan**Faculty of Engineering, University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

Behavior of hydrogen absorption by alkali metal-graphite intercalation compounds (AM-GICs) at low temperatures was investigated in order to utilize them as a cryosorption material for hydrogen isotopes. The equilibrium hydrogen pressures at the condition where fractional absorption was 0.5 were determined to be 0.32 and 0.71 Torr for CsC_{24} and RbC_{24} , respectively, which were considerably low as compared with 32 Torr for KC_{24} and 83 Torr for molecular sieve 5A (MS 5A) under the same condition. Among AM-GICs, Cs-GIC was found to be the most promising because of low equilibrium pressure. Rb-GIC was also considered to be a good absorber. In contrast with the Langmuir type absorption observed for Cs- and Rb-GICs, K-GICs showed a complicated behavior, *i.e.* the characteristic sigmoid pressure dependence in its isotherm.

The effect of heat treatment temperature (HTT) of the pristine carbon material on the absorption behavior was also examined. In the case of Cs-GICs, the GIC sample prepared from well graphitized carbon material (with high HTT value) had larger absorption capacity of hydrogen absorption than those prepared from less graphitized one. On the contrary, K-GICs prepared from material with HTT of 1500°C showed maximum capacity of hydrogen absorption in low pressure region (below 1 Torr) among those prepared from materials with HTT of 1000, 1500, 2000 and 2600°C , although it was still inferior to Cs- and Rb-GICs in absorbing ability of hydrogen gas.

KEYWORDS: Graphite, Intercalation, Insertion, Hydrogen isotopes, Absorption

1. INTRODUCTION

Alkali metal-graphite intercalation compounds (hereafter abbreviated as AM-GICs) have been known to absorb hydrogen gas at low temperatures^{1),2)}. This phenomenon has been extensively studied. Lagrange *et al.*³⁾ determined thermodynamic data for the hydrogen absorption by KC_{24} . Lagrange and Hérold⁴⁾ examined the effect of the starting carbon material of K-GICs on absorbing behavior of hydrogen gas and isotopic effect of the absorption of H_2 and D_2 . Terai and Takahashi^{5),6)} investigated the isotope separation of HT from H_2 -HT gas mixture by

low temperature absorption on KC_x . Maximum separation coefficient was obtained by the KC_x sample prepared from carbon material with heat treatment temperature of 1500°C .

Metal-hydrogen systems are considered to be used in hydrogen storage⁷⁾. However there are still some difficulties remained. For example, hydrides are disintegrated into fine powdery form during hydrogen absorption-desorption cycles⁸⁾, and impurities in hydrogen gas such as oxygen reduce considerably the ability of hydrogen absorption⁹⁾. In this respect, AM-GICs can be considered to be advantageous as a candidate material for hydrogen storage because

of its relative immunity to disintegration by the repeated absorption-desorption cycling and to oxygen attack at working temperature. In order to examine the usefulness of AM-GICs as a cryosorption material, it is important to know that to what extent they can absorb hydrogen in low pressure region (below 1 Torr). Such data have not yet been reported. This paper aims at getting these data by measuring the absorption isotherm of hydrogen isotopes in low pressure region. In addition, the influence of starting carbon materials of AM-GICs upon the hydrogen absorption behavior is also investigated.

2. EXPERIMENTAL

2.1 Materials

Carbon materials used were Grafoil (Union Carbide Co., Ltd., GTA grade), cut into tips of about $30 \times 5 \times 0.4$ mm and granular petroleum cokes with the particle size distributed from 0.18 to 0.25 mm, heat-treated at 1000, 1500, 2000 and 2600°C (hereafter abbreviated as HTT-1000, -1500, -2000 and -2600). They were degassed at around 1000°C under a vacuum of 10^{-4} Pa before use. Alkali metals were used after purification by distillation.

2.2 Preparation and characterization of AM-GICs

AM-GICs were prepared by the usual two-bulb technique. The composition of the sample was determined by the weight increase after the preparation and/or by the chemical analysis being performed after finishing the hydrogen absorption experiments.

2.3 Measurement of absorption isotherm

The absorption isotherm was determined at temperatures of 77 and 90 K by the constant volume method⁶⁾. Special attention was given to obtain the precise data in low pressure region, lower than 1 Torr. Thus, the hydrogen gas pressure in low pressure range (10^{-3} Torr $< p_{H_2} < 1$ Torr) was measured by a McLeod gauge. At high pressures above 1 Torr, a conventional mercury manometer was used. It was confirmed that the rate of hydrogen absorption was fairly rapid and around 20 min was enough to reach the equilibrium of absorption. Therefore, the equilibrium pressure, denoted as p_{eq} , was taken after being allowed to stand for 30 min. The fractional

absorption, θ , was defined by the absorbed amount of hydrogen normalized by saturated amount at high equilibrium pressure. When we need to compare the results of different conditions, we used relative equilibrium pressure, $P_{eq}/P_{eq}(\theta = 0.5)$ normalized by P_{eq} at $\theta = 0.5$.

Fig. 1 Absorption isotherms of hydrogen at 77 K by $KC_{21.3}$ (●), $RbC_{23.2}$ (■), $CsC_{23.8}$ (▲) and MS5A (○) as $\log(p_{eq}/\text{Torr})$ vs. $V/\text{cc}_{NTP} \cdot \text{g}^{-1}$ plots.

Fig. 2 Fractional absorption θ vs. p_{eq} plots: ●, $KC_{21.3}$; ■, $RbC_{23.2}$; ▲, $CsC_{23.8}$; ○, MS5A.

3. RESULTS AND DISCUSSION

3.1 Isotherms for K-, Rb- and Cs-GICs

Absorption isotherms of hydrogen gas by $\text{KC}_{21.3}$, $\text{RbC}_{23.2}$ and $\text{CsC}_{23.8}$ at 77 K are shown in Fig. 1 in the form of $\log(p_{\text{eq}}/\text{Torr})$ vs. $(V/cc_{\text{NTP}} \cdot \text{g}^{-1})$. GIC samples used were prepared from Grafoil. In the figure the data for MS 5A (molecular sieve 5A, synthetic zeolite) are also plotted for the comparison. The equilibrium pressures p_{eq} for $\text{CsC}_{23.8}$ and $\text{RbC}_{23.2}$ are much lower than for $\text{KC}_{21.3}$ and MS 5A in low pressure region, which suggest advantage of Cs- and Rb-GICs in the absorption of H_2 gas. The absorption capacities per 1 gram of GIC for $\text{CsC}_{23.8}$ and $\text{RbC}_{23.2}$ at 1 Torr are about 10 times larger than that for $\text{KC}_{21.3}$ and MS 5A. This is more clearly seen in Fig. 2, where fractional absorption θ is plotted against pressure in low pressure region. The equilibrium hydrogen pressures p_{eq} at the fractional absorption θ of 0.2 and 0.5 are shown in Table 1 for $\text{KC}_{21.3}$, $\text{RbC}_{23.2}$, $\text{CsC}_{23.8}$ and MS 5A.

Table 1 Equilibrium pressure p_{eq} at fractional absorption θ of 0.2 and 0.5.

GIC	gas absorbed	Equilibrium pressure $p_{\text{eq}}^*/\text{Torr}$	
		$\theta = 0.2$	$\theta = 0.5$
Cs-GIC	H_2	0.05	0.32
	D_2	0.04	0.25
Rb-GIC	H_2	0.16	0.71
	D_2	0.05	0.20
K-GIC	H_2	8.9	32
MS 5A	H_2	11	83

* at 77 K

The observed difference in the absorption behavior between AM-GICs used may be explained as follows. The isotherms of hydrogen absorption by MC_{24} ($M = \text{K, Rb, Cs}$) at 77 K are replotted in Fig. 3 as θ vs. $p_{\text{eq}}/p_{\text{eq}}(\theta = 0.5)$. All the data for CsC_{24} and RbC_{24} fall on a single line given by Langmuir equation. On the other hand, the data for KC_{24} deviate significantly from this line. It is reported²⁾ that in the course of hydrogen absorption interplanar distance

Fig. 3 Absorption isotherms of hydrogen at 77 K by $\text{KC}_{21.3}$ (●), $\text{RbC}_{23.2}$ (■) and $\text{CsC}_{23.8}$ (▲), where equilibrium pressure is expressed by $p_{\text{eq}}/p_{\text{eq}}(\theta = 0.5)$, that is, equilibrium pressure normalized by that at $\theta = 0.5$.

along the c-axis increases from 5.4 Å for KC_{24} to 5.69 Å for $\text{KC}_{24}(\text{H}_2)_2$, while those of CsC_{24} or RbC_{24} are effectively unaltered. Therefore KC_{24} needs extra energy for expanding along c-axis. If this extra energy is fairly large, we may observe a threshold pressure as seen in absorption of methane by CsC_{24} ²⁾. In the case of hydrogen absorption by KC_{24} , it is considered that the extra energy is not too large to induce the threshold, but it causes sigmoid pressure dependence of H_2/K observed here.

Fig. 4 $(\text{H}_2/\text{Cs})/(\text{H}_2/\text{Cs})_{300 \text{ Torr}}$ vs. p_{eq} plots for CsC_x : ■, HTT-1000 ($\text{CsC}_{28.7}$); ○, HTT-1500 ($\text{CsC}_{28.7}$); ▲, HTT-2000 ($\text{CsC}_{33.6}$); ●, HTT-2600 ($\text{CsC}_{37.1}$).

3.2 Effect of heat treatment of carbon materials

In order to compare the effect of the heat treatment temperature (HTT) of pristine carbon materials on the absorption behavior, cesium and potassium GICs were prepared from granular petroleum cokes of HTT-100, 1500, 2000 and 2600. Their absorption isotherms in low pressure region are shown in Fig. 4 for Cs-GIC and Fig. 5 for K-GIC, respectively, where the amounts of H_2 absorbed were normalized by those at the pressure of 300 Torr for each sample. It can be seen from Fig. 4 that as heat treatment temperature (HTT) of the pristine material increases the amount of H_2 absorbed increases steeply with pressure. Thus the well graphitized material is advantageous to give large capacity of hydrogen absorption to the resulting CsC_{24} .

Fig. 5 $(H_2/K)/(H_2/K)_{300\text{Torr}}$ vs. P_{eq} plots for KC_x : ■, HTT-1000($KC_{15.7}$); ○, HTT-1500($KC_{19.8}$); ▲, HTT-2000($KC_{19.4}$); ●, HTT-2600($KC_{15.5}$).

In the case of KC_{24} , on the contrary, the maximum capacity of hydrogen absorption is attained by HTT-1500 material as shown in Fig. 5. As HTT decreases the sigmoid pressure dependence tends to be modified towards Langmuir type. It is interesting to note that the similar behavior has been observed in the isotope separation phenomena in the absorption of H_2 - D_2 gas mixture by K-GIC: The maximum isotope separation coefficient for H_2 - D_2 and H_2 -HT gas mixture was attained by KC_{12} prepared from HTT-1500 material^{5),6)}. Furthermore, the remarkable reactivity of KC_8 prepared from HTT-

1500 material against water vapor has been reported¹⁰⁾. Such observations sustain that somewhat disordered structure is advantageous to give large capacity of hydrogen absorption to resulting KC_{24} . It has to be mentioned that although KC_{24} prepared from HTT-1500 material showed somewhat increase in hydrogen absorption capacity, the fractional absorption at 1 Torr is still $1/3 \sim 1/4$ times of that for CsC_{24} prepared from HTT-2600 material.

Absorption rate by CsC_{24} prepared from HTT-2600 material is quite fast and virtually absorption equilibrium is attained in a few minutes. In addition, this CsC_{24} sample did not show any indications of disintegration by the 20 times of repeated absorption-desorption cycling. This is in contrast to metal-hydrogen system in which disintegration by the repeated absorption-desorption cycling has been recognized to be a serious problem⁸⁾.

4. CONCLUSION

- (1) Absorption of hydrogen by MC_{24} ($M = K, Rb, Cs$) at 77 K was investigated in order to apply MC_{24} as a cryosorption material for hydrogen isotopes. It was found that CsC_{24} is the most promising as a cryosorption material.
- (2) As HTT increased, amount of H_2 absorption in low pressure region increased for CsC_{24} . In the case of KC_{24} , on the contrary, the maximum capacity of hydrogen absorption was attained by HTT-1500 material.

Acknowledgement

This work was supported in part by Grant in Aid for Scientific Research of Japanese Government, Project No. 62550572.

References

- 1) K. Watanabe, M. Soma, T. Onishi and K. Tamaru, *Nature Phys. Sci.* **233**, 160 (1971)
- 2) K. Watanabe, T. Kondow, M. Soma, T. Onishi and K. Tamaru, *Proc. Roy. Soc. Lond.* **A333**, 51 (1973)
- 3) P. Lagrange, A. Metrot and A. Herold, *C. R. Acad. Sci. Paris* **C275**, 765 (1972)
- 4) P. Lagrange and A. Herold, *C. R. Acad. Sci. Paris* **C281**, 381 (1975)
- 5) T. Terai and Y. Takahashi, *J. Nucl. Sci.*

- Technol.* **18**, 643 (1981)
- 6) T. Terai and Y. Takahashi, *Carbon* **22**, 91 (1984)
- 7) J. J. Reilly, *Z. Phys. Chem. N. F.* **117**, 155 (1979)
- 8) H. Ishikawa, K. Oguro, A. Kato, H. Suzuki and E. Ishii, *J. Less-Common Metals* **107**, 105 (1985)

- 9) T. Hirata, *J. Less-Common Metals* **107**, 23 (1985)
- 10) N. Akuzawa, T. Seino, A. Yugeta, T. Amemiya and Y. Takahashi, *Carbon* **25**, 691 (1987)

炭素材料学会編

炭素材料アドバンスドシリーズ No. 1

炭素繊維の展開と評価方法

著者 松井醇一氏 (東レ(株)ACM技術部部長)

A5判 300頁 昭和63年 9月発刊予定

炭素材料学会員特別価格

6,000円 (送料350円)

定価 7,800円 (送料350円)

第1章 炭素繊維の発展

1. 炭素繊維の発明から量産まで
2. 炭素繊維の用途の展開
3. CFRPの性質
4. 1次構造部材としてのCFRP-再弱層設計思想の基礎
5. 次世代複合材料の展望

第2章 炭素繊維およびその複合材料の品質管理

1. 品質管理制度の発展
2. 品質管理制度の内容
3. 品質管理制度の運用
4. CFRPの品質安定化のために

第3章 標準化

1. 炭素繊維試験方法標準化の歴史
2. 日本の現状
3. 米国の現状
4. 欧州の現状
5. 国際的な活動
6. 標準化の問題点

第4章 炭素繊維の評価方法

1. 炭素繊維用語の意味
2. 炭素繊維の形態
3. 炭素繊維の構造
4. 炭素繊維の化学組成
5. 炭素繊維の表面
6. 炭素繊維の機械的性質
7. 炭素繊維の熱的性質
8. 炭素繊維の電気的性質
9. 炭素繊維の化学的性質

予約受付中

ご希望の方は、『炭素繊維の展開と評価方法』と題記して、(1)住所、(2)勤務先の名称・所属部課名、所在地、電話番号、(3)氏名 をご記入の上、はがきまたはFAXにてお申し込み下さい。できあがり次第、現品に請求書を添えてご送付いたします。

申込先: (株)リアライズ社

東京都文京区湯島 2-16-13 斉藤ビル2F
〒113 電話 03-815-8511
FAX 03-815-8529