

Hydrogen storage in the carbonized conducting polymer

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Abstract

The conducting polymer was carbonized for the hydrogen storage. The carbonization of the conducting polymer was carried out at each temperature. Hydrogen adsorption capacity of the carbonized conducting polymer was measured using the PCT method at each pressure. The measurement temperature was 173-308K. The maximum hydrogen storage capacity of PCM-1 was 0.54 wt.% at 50atm and 223K, and that of PCM-2 was 1.09 wt.% at 50atm and 223K. The maximum hydrogen storage capacity of PCM-3 was 4.0 wt.% at 70atm and 173K.

The reiteration experiment of the hydrogen adsorption and desorption was carried out for the evaluation of the stability of the carbonized conducting polymer.

Key words; Carbonization, Conducting polymer, Hydrogen storage, Gas adsorption, Gas desorption

1. INTRODUCTION

Hydrogen is an attractive fuel for the future because it is renewable as an energy resource and it is also flexible as an energy carrier. Hydrogen energy is spotlighted as one of the clean energies and secondary energy source. Specially, if hydrogen used as a fuel, it do not release the earth environmental pollution materials such as carbon dioxide (CO₂) and sulfur dioxide (SO₂). However, hydrogen storage with a safety, high storage capacity and cheap system is crucial for a transportation and utilization of hydrogen.

Recently, carbon materials have been widely investigated for the hydrogen storage, and very attractive results for various carbon nanotubes or nanofibers. Hydrogen storage

capacity of carbon materials is determined by physical properties such as pore geometry, surface area and appearance of grapheme sheets which are influenced by synthetic methods.

Kaiser et al. (Kaiser et al., 2001) reported that the electronic transport properties of the conducting polymers show remarkably similar behavior patterns, and some aspects of this behavior are also seen in mats of single-wall carbon nanotubes and bundles of polymer fibers. Polymer chains may extend through several crystallites regions, or they may be folded back on themselves within the crystalline regions. In either case, the ordered crystallites are interconnected by amorphous regions. It is clear that if a similar morphology occurs in conducting polymers, electronic states would tend to become localized first in the amorphous fringes separating more highly conducting crystalline regions, greatly affecting the conductivity. Beau et al. (Beau et al., 1999) also reported that the material would be composed of two kinds of regions: 1) well-ordered regions, crystalline or para-crystalline, with metallic conductivity and 2) amorphous regions in which conduction is of quasi-1D hopping type. Joo et al. (Joo et al., 2001) reported that the size of crystalline regions, and polymer chain alignment in the disordered regions, supporting the establishment of mesoscopic metallic regions. They propose an inhomogeneous disorder model for this system in which ordered (crystalline) regions, described by three-dimensional metallic states, are connected through amorphous regions of polymer chains where one-dimensional disorder-induced localization is dominant.

If the hydrogen storage property of carbon nanotube is determined by the metallic properties, the conducting polymer, which showed similar behavior to single-wall carbon nanotubes, might be showed that the conduction electron made by conjugated bond interacted between the hydrogen molecular. And, the amorphous regions in the conducting polymer would be influenced the hydrogen storage properties.

In this study, the conducting polymer was carried out the acid treatment for the primary experiment and carbonized to increase the amorphous region. And, the hydrogen storage properties of the carbonized conducting polymer were examined by PCT (pressure composition temperature) method.

2. Experimental

2.1. Acid treatment of the conducting polymer

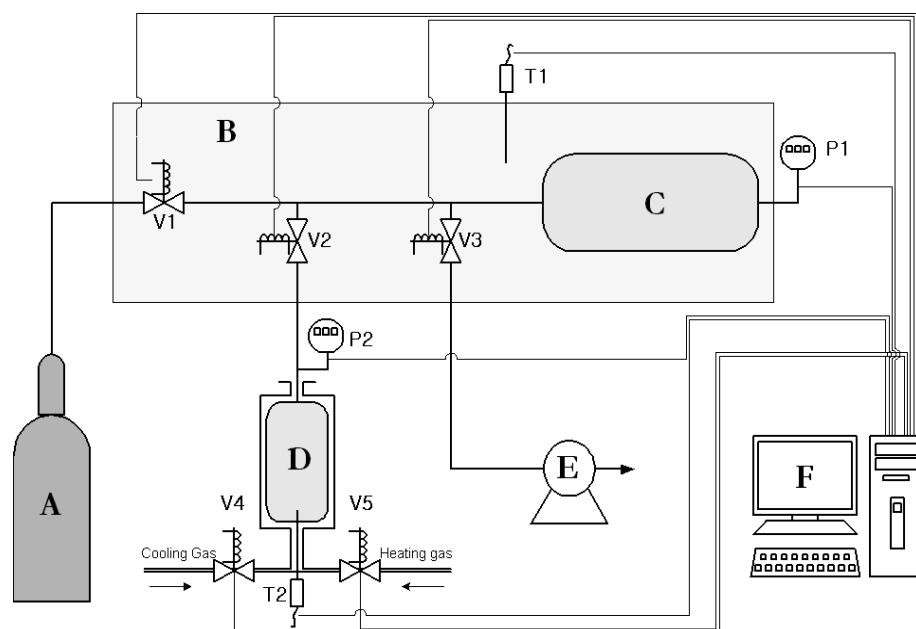
Pani (polyaniline, supplied by Aldrich co.,) was used as a conducting polymer. CSA (camphor sulfonic acid) was mixed with Pani (molar ratio of CSA:Pani = 0.5:1). 1g of the

mixture was dissolved in 30ml of HCl solution (37 wt.%), and then aged during 24 hrs at the room temperature to obtain slurry phase. The obtained slurry phase was filtered with the distilled water, and then washed with the mixture solution of ethanol and HCl solution (ethanol:HCl=1:5 wt.%). The washed precursor was dried in the oven at 110°C during 24hrs. The acid treated conducting polymer is named as PCH.

2.2. Carbonization

The acid treated conducting polymer was fixed in a quartz reactor and placed in an electric furnace. The carbonization was carried out at 300~800°C with an air gas flow rate of 30 ml/min. The carbonized conducting polymer is named as PCM.

The carbonized conducting polymers at each temperature were analyzed by Fourier Transform IR (Thermo Electron Co., Nexus FT-IR Spectrometer) and atomic absorption spectrometry (Leco Co., CHN-100 elemental analyzer).



A: H₂ gas cylinder, B: Chamber, C: Buffer tank, D: Reactor, E: Vacuum pump
 F: System control & data acquisition, V: Solenoid valve, T: Thermocouple
 P: Pressure transducer

Fig. 1 Schematic diagram of the PCT apparatus.

2.3. Hydrogen storage

Fig.1 shows a schematic diagram of the PCT apparatus.

The volumes of the pressure reservoir C and the sample reservoir D was 320.5 and 65.5cm³, respectively. The measurement was automated by using a personal computer

for pressure and temperature measurements, and with a relay board for solenoid valve operation. The principal part of the apparatus (pressure reservoir, solenoid valve) was contained in a chamber. Its temperature, measured at the transducer with a thermocouple (T1), is held at -0.5°C and 17.0°C according to the measurement temperature in the reactor (T2), respectively. Hydrogen gas used a high purity one (99.9995%). To minimize the leakage, the pressure reservoir and the sample cell were connected with using a metal gasket face seal. To avoid adsorbed impurities, all system was treated to a vacuum by the rotary pump during 10 minutes before start the test.

A several hundred milligrams of the carbonized conducting polymers were loaded in the reactor shown in Fig.1. Blank experiment was done first to check out gas leakage. The obvious decrease of pressure indicated hydrogen storage. The real gas law of Redlich-Kwong bi-parameters empirical equation was used to calculate the hydrogen adsorption capacity because hydrogen is non-polar (Zhu et al., 2003):

$$\{P + a/[T^{0.5}V_i(V_i+b)]\} \{V_i-b\} = RT \quad (1)$$

$$a = 0.42748 R^2 T_c^{2.5}/P_c, \quad b=0.08664 RT_c/P_c$$

$$\text{excess adsorption} = M_{\text{H}_2}/M_C \quad (2)$$

where P is the hydrogen pressure in the reactor, T is the temperature of the reactor, V_i is the molar volume of the hydrogen, $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$, a and b are the two parameters for matter properties of hydrogen, T_c and P_c are the two critical parameters, for hydrogen, $T_c=33.25\text{K}$, $P_c=12.8 \text{ atm}$.

The real hydrogen storage value was calculated by subtract blank value. To minimize the error value, the experiment was carried out five times.

3. Results and discussion

3.1. Carbonization of the conducting polymer

Table1 shows the weight change before and after the carbonization.

The weight was decreased with an increase of treatment temperature. It seems that $-\text{CH}$ and $-\text{Benzene}$ chain in the PCH was decomposed by the carbonization, and $-\text{C}-\text{C}-$ chain remained in the polymer led to the weight decrease, with an increase of treatment temperature. This phenomenon was confirmed by analysis of Fourier Transform IR (FT-IR).

The carbon content was 64.5%, 69.4%, 68.5% and 74.1% for PCH, PCM-1, PCM-2 and PCM-3, respectively, measured by the atomic absorption spectrometry. The results showed that the carbonization of the conducting polymer could be carried out at high

temperature from the viewpoint of carbon content.

Table 1. Weight change before and after carbonization.

Name	Carbonization temp.(°C)	Treatment time (hr)	Weight before carbonization (g)	Weight after carbonization (g)	Weight change ratio (%)
PCM-1	300	2	3.03	1.59	48.6
PCM-2	500	1.5	1.5	0.59	61.9
PCM-3	800	2	40.76	0.37	91.1

Table 2. Hydrogen storage capacity of the each material.

Name	Hydrogen storage capacity (wt.%)								
	20 atm			50 atm			70 atm		
	308 K	223 K	173 K	308 K	223 K	173 K	308 K	223 K	173 K
PCM-1	-	0.25		0.16	0.54		0.30	0.1	
PCM-2	-	0.27		-	1.09		0.35	0.77	
PCM-3	0.11	0.14		-	1.13	1.3	0.35	1.03	4.0

- : non hydrogen storage, Blank : non-measure

3.2. Hydrogen Storage capacity

Table 2 shows the hydrogen storage capacity of the each material.

Hydrogen storage capacity of the each carbonized conducting polymer increased with an increase of the measurement pressure and with a decrease of the measurement temperature.

The maximum hydrogen storage capacity of PCM-1 was 0.54 wt.% at 50atm and 223K, and that of PCM-2 was 1.09 wt.% at 50atm and 223K. The maximum hydrogen storage capacity of PCM-3 was 4.0 wt.% at 70atm and 173K. At 50atm and 223K, the hydrogen storage capacity of PCM-3 was higher than the other materials. It would be supposed from those results that the carbonization of the conducting polymer at the high temperature might be suitable from the viewpoint of the hydrogen storage capacity.

3.3. Hydrogen adsorption and desorption capacity

Table 3 shows the hydrogen adsorption and desorption capacity of PCM-3.

The hydrogen adsorption and desorption experiment was carried out as a following; PCM-3 set up in the PCT apparatus and hydrogen adsorption experiment proceed at 70atm, 173K during 2h, and then hydrogen desorption experiment proceed at 373K during 2h.

Table 3. Hydrogen adsorption and desorption capacity of PCM-3.

Name	Hydrogen adsorption capacity (wt.%)			Hydrogen desorption capacity (wt.%)			Desorption capacity (%)		
	1 Cycle	2 Cycles	3 Cycles	1 Cycle	2 Cycles	3 Cycles	1 Cycle	2 Cycles	3 Cycles
PCM-3	3.5	6.0	5.0	2.5	2.8	2.7	71	47	54

The hydrogen adsorption capacity was 3.5~6.0wt.%, and desorption capacity was 2.5~2.7wt.% during cycle test. The hydrogen adsorption capacity increased with an increase of cycle time. This would be explained by the following possibility. The remained –CH chain or –C–C– bond after the carbonization treatment decomposed or modified to 2 or 3-bond at the cycle test condition (desorption temperature, measurement pressure and high temperature different), and hydrogen easily combined with those chains. The hydrogen desorption capacity was the almost same during the cycle test.

Future study is necessary to clarify the cycle test of the carbonized conducting polymer.

4. Conclusions

- (1) The conducting polymer was carried out the acid treatment for the primary experiment and carbonized. The carbonization was carried out at 300~800°C with an air gas. And, the hydrogen storage properties of the carbonized conducting polymer were examined by PCT (pressure composition temperature) method.
- (2) The carbon content was 64.5%, 69.4%, 68.5% and 74.1% for PCH, PCM-1, PCM-2 and PCM-3, respectively.
- (3) The maximum hydrogen storage capacity of PCM-1 was 0.54 wt.% at 50atm and 223K, and that of PCM-2 was 1.09 wt.% at 50atm and 223K. The maximum hydrogen storage capacity of PCM-3 was 4.0 wt.% at 70atm and 173K.

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