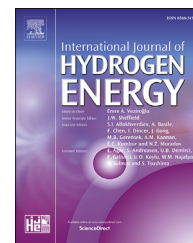




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# A study on optimal pore range for high pressure hydrogen storage behaviors by porous hard carbon materials prepared from a polymeric precursor

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## ABSTRACT

In this study, activated polymer-based hard carbons were prepared using various steam activation conditions in order to enhance their hydrogen storage ability. The structural characteristics of the activated carbons were observed by X-ray diffraction and Raman spectroscopy. The N<sub>2</sub> adsorption isotherm characteristics at 77 K were confirmed by Brunauer-Emmett-Teller, Barrett-Joyner-Halenda and non-local density functional theory equations. The hydrogen storage behaviours of the activated carbons at 298 K and 10 MPa were studied using a Pressure-Composition-Temperature apparatus. From the results, specific surface areas and total pore volume of the activated carbons were determined to be 1680–2320 m<sup>2</sup>/g and 0.78–1.39 cm<sup>3</sup>/g, respectively. It was also observed that various pore size distributions were found to be dependent on the functions of activation time. In the observed result, the hydrogen adsorption of APHS-9-4 increased about 30% more than that of as-prepared hard carbon. This indicates that hydrogen storage capacity could be a function not only of specific surface area or total pore volume, but also of micropore volume fraction in the range of 0.63–0.78 nm of adsorbents.

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## Introduction

The depletion of fossil fuels and growing environmental awareness has created the need for more eco-friendly fuels. Hydrogen is gaining increasing attention as a solution to energy and environmental problems, mainly due to its abundance, high chemical energy, and pollution-free burning.

Hydrogen combustion does not generate pollutants such as particles, nitrogen oxides (NO<sub>x</sub>), sulphur oxides (SO<sub>x</sub>), hydrocarbons, and carbon monoxide (CO). The energy density of hydrogen is three times greater than the energy density of gasoline, and it is possible to produce it from renewable energy sources [1]. However, the storage of hydrogen is still a major challenge.

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Many hydrogen storage methods have been proposed, involving liquid hydrogen [2], high-pressure hydrogen [3], metal hydrides [4], Physisorption [5–9], chemisorption, and spill-over [10]. Several means of hydrogen storage have not been proven to be practical technologies that could compete with fossil fuels. Hydrogen liquefaction is very expensive and consumes great amounts of energy. Compressed hydrogen gas is cheaper, but still requires higher volumes and heavier containers to get a practical hydrogen density. There are also risks associated with the use of hydrogen at high pressure [11].

Recently, research on hydrogen adsorption storage has focused on finding the ideal adsorbent that, used at room temperature, would allow storage of useful amounts of H<sub>2</sub> [12–14]. Physisorption on porous materials has been proposed to lower the storage pressure of compressed gas fuels such as natural gas and hydrogen [13,14]. Hydrogen adsorption using porous materials has advantages in fast adsorption and desorption kinetics, long life cycle, no need for energy to release hydrogen, and high hydrogen uptake than other methods [12–14].

Among the various adsorbents like mesoporous silica, activated alumina, zeolite, metal-organic frameworks (MOFs), and others, carbon materials [5–9] offer many advantages: abundance, heat resistance, non-toxicity, good chemical stability, good recycling characteristics, reversibility, low-cost and availability [13]. In addition, lightweight carbon with high porosity is a preferred choice for achieving a gravimetric hydrogen storage target.

Among the materials that can be used as adsorbents, carbon materials such as activated carbons [5–8], carbon nanofibers [9], carbon nanotubes [15], graphene [16], and fullerene [17] have been the subject of research. In previous studies the hydrogen storage capacity of microporous carbon materials was analyzed theoretically and experimentally for a selection of samples [18]. The results allowed us to conclude that there exist an optimum pore size for hydrogen adsorption [8,9]. Among them, activated carbons have been intensively researched as hydrogen adsorption materials, since it is easy to obtain and their porous structure is more developed than other carbon materials.

Activated carbon can be prepared from a wide range of raw materials including coal [19], pitch [20], biomass [5–7,21], and polymeric resins [22,23]. The polymer precursor has specificity with a uniform chemical structure and can be control the crystallinity of the hard carbon during the carbonization process. Polymer-based hard carbon with controlled crystallinity can produce activated carbon with an optimized pore structure for hydrogen storage [8,9,23].

Recent hydrogen storage studies show that the hydrogen adsorption capacity of activated carbon is less than 1.0 wt% at room temperature [5,6]. Activated carbons with very high specific surface area (over 3000 m<sup>2</sup>/g) have only hydrogen adsorption capacity of about 4.5–0.6 wt% at room temperature [6]. Metals used as catalysts for hydrogen storage may play a role in the hydrogen uptake [10,24]. M. Zielinski et al. [24] clearly show that metal catalysts supported on activated carbon could store significant amounts of hydrogen at room temperature and high pressure (up to 0.53% at 30 bars against 0.1% for the activated carbon). The specific surface area and hydrogen adsorption capacity of the activated carbon without

metal catalysts are only 1000 m<sup>2</sup>/g and 0.1 wt%, respectively. It is known that at room temperature and high pressure, the hydrogen spill-over species are most probably stored on the micropore of activated carbon. This is the reason why an optimized pore structure for hydrogen adsorption of activated carbon is required.

In this work, activated polymer-based hard carbons (APH) with high surface area were prepared from various steam activated contents and the effects of specific surface area and micropore fraction on hydrogen uptake were investigated. The pore characteristics of activated carbon were observed through analysis of crystal structure.

## Experiment

### Preparation of activated hard carbon

Polymeric precursors (Aekyung Petrochemical Co., Ltd.) were used as the starting materials. The polymeric precursors were heated to 900 °C at 10 °C/min in a self-made cylindrical furnace (SiC heater: 100 × 1000 mm) under N<sub>2</sub> gas (99.999%, 300 mL/min), and kept at a target temperature for 1 h to obtain carbonised polymer-based hard carbon (HC). Then, the gas flow was switched to H<sub>2</sub>O at a rate of 0.5 mL/min while the temperature was raised to 1000 °C and held for 20 min (APHS-9-2), 40 min (APHS-9-4) or 60 min (APHS-9-6). The samples were allowed to cool under N<sub>2</sub> gas (300 mL/min). The yield of activated sample was determined from the weight of the sample before and after activation.

### Characterizations

The structural changes that occurred after the H<sub>2</sub>O activation of the hard carbon were investigated using X-ray diffraction (XRD) spectroscopy and Raman spectroscopy. XRD patterns were collected within the diffraction angles from 5° to 60° with a speed of 2°/min with a customized automount and a Cu K $\alpha$  radiation source. Raman spectra were measured at constant room temperature using 523 nm wavelength. The laser was focused through a microscope with a 100 $\times$  objective. Raman spectra presented in this study corresponds to accumulation of 3 spectra's recorded from 0 to 3500 cm<sup>-1</sup>. For all the XRD and Raman spectra, a linear baseline correction was conducted, and the peak analysis was performed with the OriginLab Pro 8.5 (USA).

The N<sub>2</sub> adsorption isotherms at 77 K were measured using BELSORP-max (BEL Japan). For pore analysis, each sample was degassed for approximately 5–6 h at 573 K, with the residual pressure maintained at 10<sup>-3</sup> torr, or less. The specific surface area was calculated in the relative pressure interval of 0.04–0.17 using the Brunauer-Emmett-Teller (BET) method [25]. Pore size and distribution were calculated by the Barrett-Joyner-Halenda (BJH) method [26] and non-local density functional theory (NLDFT) integrated cylinder-shaped pore model from isotherm curves [27]. Micropore volume were calculated using the Dubinin-Radushkevitch (DR) equations to the N<sub>2</sub> adsorption isotherm at P/P<sub>0</sub> < 0.1 [28].

High-pressure hydrogen adsorption measurements at 298 K and 10 MPa were carried out in an automated high-

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