

PAPER • OPEN ACCESS

Carbon monolith from Victorian brown coal for hydrogen storage

To cite this article: B R Alfadlil *et al* 2019 *J. Phys.: Conf. Ser.* **1277** 012024

View the [article online](#) for updates and enhancements.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the [collection](#) - download the first chapter of every title for free.

Carbon monolith from Victorian brown coal for hydrogen storage

B R Alfadlil¹, G P Knowles², M R Parsa², RR D J N Subagyo¹, Daniel¹, A L Chaffee^{2*}

¹Chemistry Department, Faculty of Mathematics and Natural Sciences, Mulawarman University, Indonesia

²School of Chemistry, Monash University, Australia

*Corresponding author: alan.chaffee@monash.edu

Abstract. The application of carbon monolith from VBC (Victorian Brown Coal) for H₂ storage has been studied. The storage capacities of the monolith were measured using an isothermal adsorption process at different temperatures and pressures. In this study the adsorption capacities of monolithic carbon and those of activated carbon from other literature were compared. It was found that temperature and pressure affected the hydrogen adsorption capacity. It was also observed that density of the carbon monoliths can also have a significant effect on hydrogen storage capacity.

1. Introduction

Extensive research has been carried out on alternative energy sources such as sun, geothermal, tides, windmills, biomass, nuclear energy, hydrogen, etc [1]. Furthermore, there is increasing interest in developing gas storage systems with the aim of energy applications (e.g., storage of H₂ gas for transportation purposes) or environmental protection goals to reduce the negative effects of the greenhouse effect [2].

The storage of gases is usually performed by compression in high pressure vessels. However, the storage capacities of such devices are restricted, because of the low density of gases and pressure limitations due to safety reasons [3]. An alternative technology for gas storage is adsorption on porous materials [4]. Gas storage on sorbents is based on the physical adsorption process where adsorbate gas molecules are bound by attractive forces (e.g., Van der Waals force) to the surface of the adsorbent [3, 4]. Thus, the gas accumulates into the pores because of the attraction created between the gas molecules and the adsorbent. Thereby, the density of the gas accumulated in the porous structure of these materials is increased. Although the interaction between gas molecules and adsorbents is weak, it is sufficient to increase the amount of gas stored [5].

Given the massive scale of Victoria's brown-coal resource and the chemical properties of Victorian Brown Coal (VBC), VBC has the potential to be used for power generation, liquefaction and other applications [6]. It is also recognized that with suitable up-grading, VBC can be developed to produce carbon materials.

Porous carbon materials are considered as one of the most promising adsorbents for gas storage media because they are easily obtained from natural raw materials [7-9]. In addition, most carbon materials are not sensitive to water vapor due to their surface hydrophobicity [10, 11]. Interest in using



carbon monolithic structures for various chemical conversion and adsorption processes is increasing. The combined favourable properties of carbon and monolithic structures create a support with great potential in catalytic and adsorption processes [12]. A carbon monolith is basically a uniform block, consisting of parallel channels. Sometimes this is prepared via extrusion to give various shapes such as cylindrical, square, triangular or hexagonal, etc. Carbons with monolithic structure are able to provide good mass transfer, thermal stability, high surface area, high amenability for pore structure modification and surface functionalization. They also have good mechanical strength and can be more readily regenerated than conventional granular or powder forms [7]. This study reports the application of carbon monolith from Victorian brown coal for H₂ storage. The H₂ storage capacity of the materials were compared with that of several other carbon materials from the literature.

2. Materials and Methods

2.1. Materials

The materials used in this study were carbon monoliths from Victorian Brown Coal prepared at Monash University, Australia [13]. The carbon monoliths were activated with CO₂ at 850 °C for 1 hour. For adsorption studies, H₂ gas (99.98% purity) obtained from Air Liquide was used.

2.2. Physico-Chemical Characterisation

The density, porosity, structure and surface morphology of the carbon monoliths were all evaluated in the present study. The true density measurement was determined using an AccuPyc II 1340, Micromeritics. The CO₂ surface area was determined using an accelerated surface area and porosimeter system, Tristar II 3020, Micromeritics. The C, H and N contents were determined with TruSpec Micro, LECO Corporation by Geoservices Coal Laboratory, Indonesia. The morphology of the carbon monolith was analysed with a SEM SU3500 in Bandung Institute of Technology.

2.3. Adsorption study

Prior to isothermal carbon adsorption testing, approximately 2 grams of carbon monolith was crushed and then degassed at a temperature of 105 °C for approximately 6 hours under vacuum (0.01 mTorr) using a Micromeritics VacPrep 062 degasser.

The adsorption study was conducted with an HPVA II-200 from Particulate Systems using the static volumetric method to obtain high-pressure adsorption and desorption isotherms (Figure 1). The temperature was controlled by Colora Messatechnik GMBH refrigerated/heating circulator and an Edwards RV3F vacuum pump provided by Edward Corporation (UK) was used.

The volumetric technique consists of introducing (dosing) a known amount of gas into the chamber containing the sample to be analyzed. When the sample reached equilibrium with the gas, the final equilibrium pressure was recorded. These data were then used to calculate the quantity of gas adsorbed by the sample. This process was repeated at given pressure intervals until the maximum preselected pressure was reached. Then the pressure was decreased to provide a desorption isotherm. Each of the resulting equilibrium points [volume adsorbed and equilibrium pressure] was plotted to provide an isotherm. The adsorption capacity of H₂ in carbon monolith samples was measured at 273, 293 and 313 K. This temperature range was chosen as the temperature which was most widely used in hydrogen storage applications using volumetric methods. In the isothermal adsorption process the temperature was kept constant by recirculated thermal bath / dewar for optimum adsorption process. Each isotherm experiment took approximately 24 hours to complete.

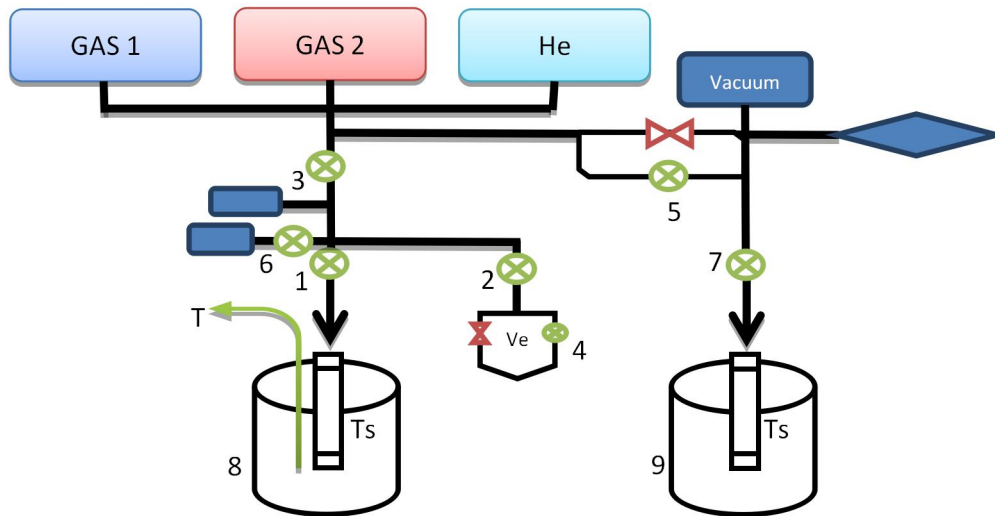


Figure 1. HPVA II-200. HP, high-pressure transducer; LP, 1000 torr pressure transducer; T, temperature probe; Ts, Tube sample; (1) analysis port valve; (2) vent valve; (3) manifold valve; (4) full vent valve; (5) full vacuum valve; (6) 1000 torr isolation valve; (7) degas port valve; (8) Analysis station bath; (9) Degas station bath.

In the HPVA II-200 measurement procedure, the gas composition in the adsorption cell after achieving equilibrium was measured during each desorption step, which could be used to calculate the adsorbed amount of gas at each desorption step to improve the accuracy of calculations. The total adsorbed amount of gas at one pressure step (Δn_{ads}) can be calculated using Equation 1.

$$\Delta n_{ads} = \Delta n_{dosed} - \Delta n_{Nads} \quad (1)$$

where Δn_{dosed} is the amount gas dosed from the manifold at that pressure step and Δn_{Nads} is the non-adsorbed amount of gas at that pressure step. Likewise, the total adsorbed amount of gas at the n^{th} pressure step (Δn_{Nads}) can be calculated using Equation 2.

$$\Delta n_{adsn} = \Delta n_{dosedn} - \Delta n_{Nadsn} = n_{An} - n_{Bn} - n_{Aadsn} + n_{Nadsn-1} \quad (2)$$

where n_{An} is the number of moles of gas in the manifold before dosing at the n^{th} pressure step, n_{Bn} is the number of moles of gas in the manifold after dosing at the n^{th} pressure step and $n_{Nadsn-1}$ is the number of moles of gas not adsorbed by the sample at the n^{1st} pressure step.

3. Results and discussion

3.1. Material characterisation

The physical and chemical characteristics of carbon monolith from Victorian Brown Coal are presented in Table 1. The value of conductivity is influenced by the amount of carbon in the honeycomb structure, with a density of 1.82 g/cm^3 . The SEM picture of the carbon monolith (Figure 2) shows that the monolithic carbon possessed interconnected macropore channels. The porous adsorbents may have high adsorption activities towards various gases, including hydrogen. This may be due to the mechanism of volume filling of pores inherent in these materials. This structure looks like a sponge with cavities that may be beneficial for use as an adsorbent material.

Table 1. Characteristics of VBC Carbon Monolith

Parameter	Value
CO ₂ Surface area (m ² /g)	973
True density (g/cm ³)	1.82
Conductivity (Ω ⁻¹ cm ⁻¹)	160.5
Carbon (%)	82.5
Hydrogen (%)	2.7
Nitrogen (%)	0.5

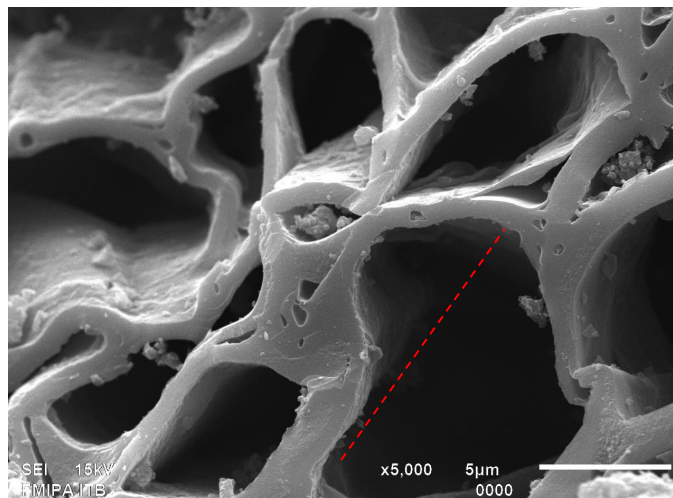


Figure 2. The SEM image of VBC carbon monolith at x5000 magnification (Red line indicates a macropore channel).

3.2. Adsorption study

The adsorption capacity of hydrogen with carbon monolith from Victorian Brown Coal was measured at three different temperatures (Figure 3). The highest adsorption capacity was obtained at 273 K (1.646 mmol/g) because the experimental temperature was the closest to the critical temperature of hydrogen (33 K). In other words, the higher the temperature used, the lower amount of hydrogen gas that can be stored in the carbon monolith. The increase of adsorption temperature to 293 K decreased adsorption capacity to 1.282 mmol / g and this value continued to decline at higher temperature (313 K) with a storage capacity of only 0.922 mmol / g.

A comparison of the hydrogen gas storage capacity, at 293 - 298 K, of several carbon materials from the literature was carried out to characterise the capability of the monolithic carbon used in this study. For this purpose, the hydrogen storage capacities of some carbon materials made from various sources and by different activation methods. The carbons compared were in various forms (i.e., monolith, powder and granular) and are presented in Table 2.

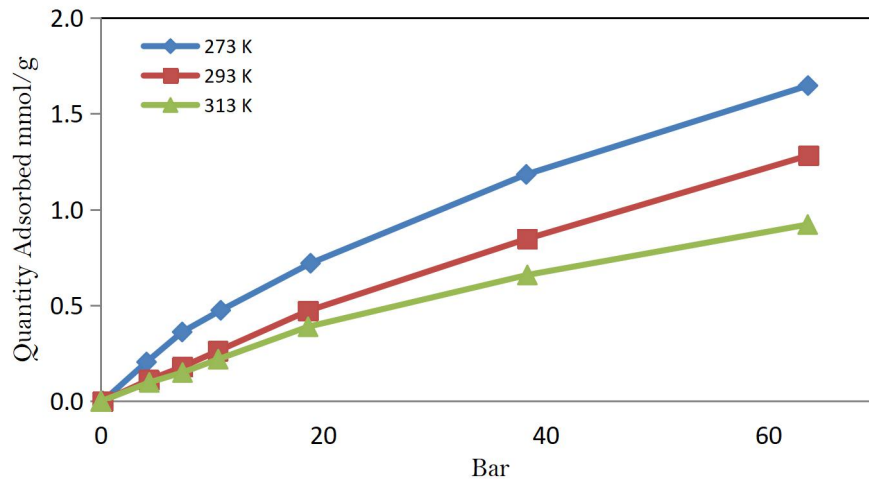


Figure 3. H₂ adsorption isotherm with carbon monolith from Victorian brown coal (CO₂ surface area= 973 m²/g) at different temperatures.

Table 2. Hydrogen storage capacity of carbon monolith materials [1, 4, 9] at 298 K and CM-VBC at 293 K, 60 bar pressure

Sample	CO ₂ Surface area (m ² g ⁻¹)	Density (g cm ⁻³)	H ₂ adsorption (mmol/g)	Reference
M-A1	928	1.00	1.9344	[1, 4, 9]
M-A336	1367	0.87	2.0833	
M3M	2610	0.42	1.1746	
MOF-210	6240	0.25	0.4960	
D10 PACK	2259	0.62	3.7301	
D10 TAP	2259	0.36	2.9761	
D7 PACK	2364	0.63	3.2241	
D7 TAP	2364	0.34	2.8769	
M-ACF15	1127	0.69	2.8521	
ACF15 PACK	1193	0.94	2.8422	
ACF15 TAP	1193	0.24	2.3690	
M-ACF20	2068	0.54	2.9265	
M-ACF25	1838	0.54	2.5793	
CM-VBC	973	1.82	1.2823	

Table 2 and Figure 4 show that VBC carbon monolith material possessed higher hydrogen adsorption capacity than some carbon materials with higher surface area. However, compared to carbon materials with much higher surface area, the hydrogen adsorption capacity of the VBC carbon monolith is inferior. The result indicated that high surface area is not the only determining factor for materials to possess high adsorption capacity, but material density is also one of the factors that can increase adsorption capacity.

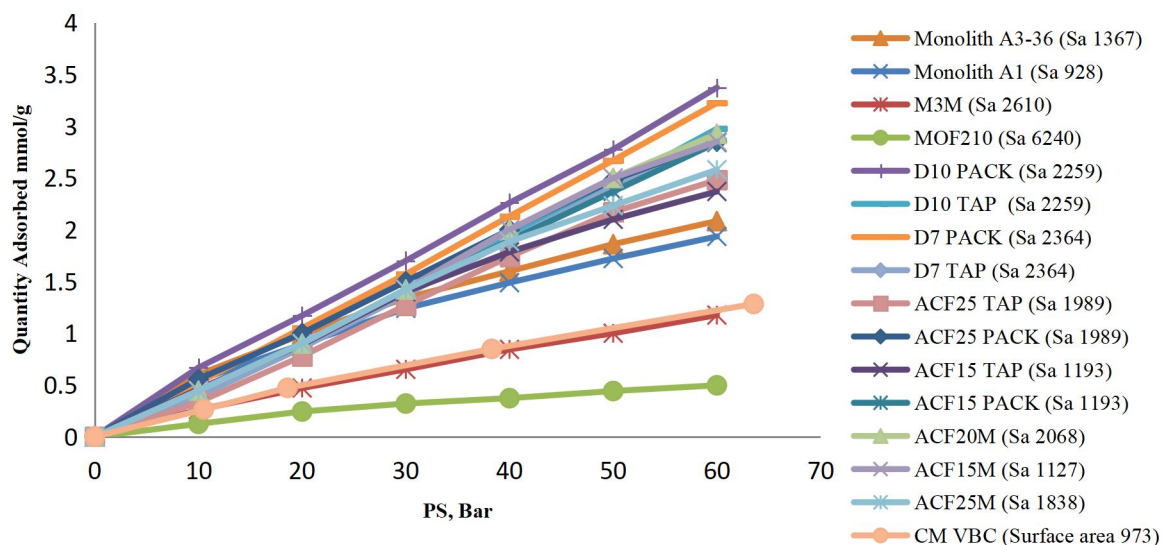


Figure 4. Comparison of H_2 adsorption isotherms of several carbon materials at 298 K [1,4,9] (for CM-VBC, the isotherm was obtained at 293 K)

4. Conclusion

Carbon monolith prepared from Victorian Brown Coal has potential as a material for hydrogen storage. The maximum adsorption capacity of hydrogen gas was 1.646 mmol/g which was obtained at 273 K with 60 bar pressure. It was found that material density was one key factor for hydrogen storage capacity.

Acknowledgements

We would like to acknowledge Ministry of Research, Technology and Higher Education of the Republic of Indonesia for the financial support of the project through the Master's Thesis Research Scheme (Contract number: 220/UN17.41/KL/2019).

References

- [1] Marco-Lozar J P, Kunowsky M, Suárez-García F, Carruthers J D and Linares-Solano A 2012 Activated carbon monoliths for gas storage at room temperature *Energy & Environmental Science* **5** pp 9833-42
- [2] Biradha K, Ramanan A and Vittal J J 2009 Coordination Polymers Versus Metal–Organic Frameworks *Crystal Growth & Design* **9** pp 2969-70
- [3] Morris R E and Wheatley P S 2008 Gas storage in nanoporous materials *Angewandte Chemie (International ed. in English)* **47** pp 4966-81
- [4] Marco-Lozar J P, Kunowsky M, Carruthers J D and Linares-Solano Á 2014 Gas storage scale-up at room temperature on high density carbon materials *Carbon* **76** pp 123-32
- [5] Lennard-Jones J E 1932 Processes of adsorption and diffusion on solid surfaces *Transactions of the Faraday Society* **28** pp 333-59
- [6] Perry G J, Allardice D J and Kiss L T 1984 *The Chemistry of Low-Rank Coals*: American Chemical Society) pp 3-14
- [7] Ma X, Zou B, Cao M, Chen S-L and Hu C 2014 Nitrogen-doped porous carbon monolith as a highly efficient catalyst for CO_2 conversion *Journal of Materials Chemistry A* **2** pp 18360-6
- [8] Zhang Y, Chi Y, Liu S, Xing W, Wang L and Song Y 2016 Competitive adsorption/desorption of CO_2/CH_4 mixtures on anthracite from China over a wide range of pressures and temperatures *RSC Advances* **6** pp 98588-97
- [9] Kunowsky M, Marco-Lozar J P and Linares-Solano Á 2014 Activated Carbon Fibre Monoliths

- for Hydrogen Storage *Advances in Science and Technology* **93** pp 102-11
- [10] Yeon S-H, Knoke I, Gogotsi Y and Fischer J E 2010 Enhanced volumetric hydrogen and methane storage capacity of monolithic carbide-derived carbon *Microporous and Mesoporous Materials* **131** pp 423-8
- [11] Zacharia R, Cossement D, Lafi L and Chahine R 2010 Volumetric hydrogen sorption capacity of monoliths prepared by mechanical densification of MOF-177 *Journal of Materials Chemistry* **20** pp 2145-51
- [12] Vergunst T, Linders M J G, Kapteijn F and Moulijn J A 2001 Carbon-based Monolithic Structures *Catalysis Reviews* **43** pp 291-314
- [13] Parsa M R, Chaffee A L 2018 Carbon Monoliths and a Process for Producing Same WO2018213890A1