



High density Mongolian anthracite based porous carbon monoliths for methane storage by adsorption



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HIGHLIGHTS

- Mongolian anthracite based carbon monoliths for methane storage by adsorption.
- Carbon rich anthracite was used to prepare porous carbon monolith with high density.
- Carbon monolith prepared with structurally and energetically heterogeneous surface.
- Methane storage capacity of 162 V/V achieved at 293 K and 3.5 MPa.

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ABSTRACT

Carbon monoliths for methane adsorption were prepared from Mongolian anthracite based activated carbons using carboxy-methyl cellulose as a binder under different molding pressures. Nitrogen adsorption/desorption studies were carried out to obtain the specific surface area, pore volume, pore size distribution and adsorption energy distributions of the monoliths. Methane adsorption experiments on the monoliths were conducted at isothermal condition and at pressures up to around 3.5 MPa in a volumetric adsorption apparatus. As expected, adsorption results indicated that the gravimetric methane capacities of the carbon monoliths increase with increasing surface area. On the other hand, the maximum volumetric uptake of methane was observed as 162 V/V at 293 K and 3.5 MPa on a sample, PMAC1/2-3-65, which has low specific surface area and high packing density comparing with other monoliths. This result implies that the specific surface area of adsorption media is not always a major factor in storing of gases such as methane.

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1. Introduction

The rapid growth in chemical, electronic, and manufacturing industries raises the level of carbon dioxide in atmosphere from burning of solid and liquid fossil fuels [1], which causes serious impact on global ecosystems. The worldwide consumption of gasoline and diesel for moving vehicles has also led to increasing concerns on the level of global warming gases such as carbon dioxide and unburned hydrocarbons. In last decades, a number of solutions for reducing global warming gases have been suggested. One of the potential solutions might be the use of natural gas (NG) as fuels for transportation and heating purposes [2]. NG has been considered as a possible alternative source for fuels such as coal, gasoline, and diesel since it is a cheap, clean, and also an abundant resource for

automotive and stationary applications. Moreover NG is a fuel that can be used directly on gasoline or diesel vehicles since it has a narrow flammability range, making it an inherently safe fuel [3]. Also strict safety standards make NG vehicles as safe as gasoline-powered vehicles. In addition, NG poses no threat to land or water since it is non-toxic and it does not form a vapor pool on the ground as liquefied petroleum gas (LPG) does, since it is lighter than air [4].

The major drawback with NG is extremely low volumetric energy density, only 0.12% of gasoline at standard temperature and pressure conditions [5]. Therefore, NG has been used as compressed natural gas (CNG) in most applications, especially for moving vehicles. For this purpose NG is usually compressed up to more than 20 MPa and only cylindrical type tanks are available because of extremely high pressure condition [6]. Since multiple stage compressions should be used to charge NG into fuel tanks, the charging infrastructure requires high construction and operation costs. Furthermore the use of CNG is not safe because of high charging

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pressure and it is not easy to get enough space for fuel tanks that are not conformable at high pressures. For the mass transport of NG through oceans, the liquefied natural gas (LNG) has been employed but requires the use of considerable amount of gas for keeping the temperature lower than $-162\text{ }^{\circ}\text{C}$ on the way [7]. For moving vehicles and household gas tanks for heating and cooking, LNG is not basically applicable.

The adsorbed natural gas (ANG) has been known as a modern technology wherein NG is adsorbed by porous materials at relatively low pressure around 3.5 MPa and room temperature storage conditions. Once a good adsorbent medium with sufficient working capacity is developed, ANG can be competitive technically and economically comparing with the conventional storage methods such as LNG and CNG. In order to make this ANG as a feasible commercial technology [8], the US Department of Energy (DOE) had set a storage target of 180 V/V at 3.5 MPa and 298 K in the year 2000 and recently modified this target to more than 220 V/V, which is the maximum achievable capacity based on carbon-based materials [9]. Volumetric storage capacities for methane (a major constituent of NG) have been reported in the range from 150 to 200 V/V from bench-scale experiments however there is no news that any ANG technology has been practically applied till now.

Adsorbed natural gas (ANG) storage for vehicular application has been tested and experimented for several years and yet the commercialization of the same is not successfully done due to its inherent problems including synthesis of technically more suitable adsorbent material whose production cost should also be more economical [10,11]. Several researchers have been attempting to make novel materials including Metal Organic Frameworks, Covalent Organic Frameworks and other polymer based materials for the application of ANG. Though these materials are technically very good, the issues related to their bulk production as well as the higher cost of production are still worrying factors in using these materials commercial for ANG application [12]. On the other hand, the versatile and relatively cheaper carbon materials could be used for ANG application, if they can be produced with certain specific desirable properties for the storage of natural gas [13]. The Mongolian raw anthracite (MRA), which is highly rich in carbon content, has been used to make adsorbents for gas and energy storage applications. The selection of MRA as a carbon source for this study was done due to the following reasons: (i) less ash content, (ii) exclusion of carbonization step, (iii) high bulk density, and (iv) strong physical strength. MRA is a fossil fuel and basically formed at high temperature and pressure conditions during cluster movement. Therefore MRA has intrinsically strong physical strength as well as high density, which strongly favors the high pressure adsorption processes, especially for ANG application [14].

It would be of worth to make proper monoliths from powdered activated carbon to increase the packing density. In general, the monoliths offer the increase in density by reducing the excess void volume, compactness and easy handling. Usually, the carbon monolith is made by compressing a mixture of powdered activated carbon and binder. Several binders have been used for making monoliths [15]. In this study, the carbon monoliths were produced from the MRA-based activated carbons using carboxy-methyl-cellulose (CMC) sodium salt as a binder and used for methane adsorption. The effects of binder contents and molding pressure on the properties of carbon monoliths prepared were also studied.

2. Experimental

2.1. Preparation of carbon monoliths

Activated carbons for carbon monoliths were prepared by the chemical activation of physically mixed MRA and KOH as reported

in elsewhere [14]. The activated carbons used in this study were made by varying the mass ratio of Mongolian raw anthracite (MRA) and potassium hydroxide (KOH) from 1:0.5 to 1:4 and accordingly named as PMAC2/1, PMAC1/1, PMAC1/2, PMAC1/3 and PMAC1/4 [14]. Initially MRA and KOH powder mixture was mixed and preheated at $450\text{ }^{\circ}\text{C}$ for 2 h under N_2 atmosphere in a tubular furnace to remove moisture and volatile contaminants. Then the temperature of preheated samples was further increased to $750\text{ }^{\circ}\text{C}$ under N_2 atmosphere in order to activate the samples. The activated samples were first washed out with 0.5 M HCl and finally with deionized water until the pH of the rinse remains constant around 7. The resultant AC powder was dried for 24 h in an oven before used for monolith preparation. Coin-type carbon monoliths for ANG application were fabricated from the MRA-based activated carbons (PMACs) using CMC sodium salt as a binder. The binder contents (3, 5, and 10 wt%) and molding pressures (10, 25, 45 and 65 MPa) were varied in order to elucidate the effect of these variables on physical properties of the carbon monoliths. The activated carbon and binder were first thoroughly mixed in water. Then the water present in the slurry was removed by heating and the resultant mixture was compressed at room temperature to make coin-type monoliths [16,17]. The prepared carbon monoliths were dried in an oven for overnight at 378 K and labeled as PMAC1/2-x-xx based on binder content (wt%) and molding pressure (MPa) used as shown in Table 1. The radius and thickness of carbon monoliths are 3.15 cm and 0.5–0.6 cm, respectively.

2.1.1. Physical characterization

The physical properties of the prepared carbon monoliths were characterized using nitrogen adsorption and desorption isotherm data measured at 77 K (Micromeritics ASAP 2020, USA). Prior to the adsorption analysis, the sample was outgassed at 423 K for 12 h under vacuum condition for the removal of moisture and other impurities. The specific surface area was determined on the basis of the Brunauer-Emmet-Teller (BET) equation [18] using the relative nitrogen pressures (P/P_0) in the range of 0.01–0.05 [19]. The pore size distribution, pore volume, and average pore width were obtained by employing the density functional theory (DFT). Furthermore the Barrett Joyner and Halenda (BJH) [20] and the Horvath-Kawazoe (H-K) equations [21] were used for the calculation of mesopore (V_{BJH}) and micropore (V_{HK}) volumes, respectively. The average pore width (APW) was calculated by the following expression: $(4V_t/S_{\text{BET}})$ where S_{BET} is the BET surface area and V_t is the total pore volume [22].

2.2. Methane adsorption

The adsorption of methane was carried out in a volumetric adsorption apparatus at three different temperatures (293, 303, and 313 K) and at pressures up to 3.5 MPa. The detailed description about operating procedures, volumetric adsorption apparatus, and schematic view of adsorption set-up are available elsewhere [23]. The volumetric apparatus used in this study has two main parts, a loading cell (507 ± 1 ml) and an adsorption cell (505 ± 1 ml). After placing adsorbents in the adsorption cell, the cell was degassed completely using a vacuum pump. The accurate measurement of temperature and pressure at the equilibrium state were measured using a K type thermocouple and pressure transducers. At the equilibrium step, pressure and temperature were recorded by a mobile recorder (MV 100, Yokogawa Co.) A mass balance equation was incorporated for the calculation of adsorbed amount using the experimental data.

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