

Development of Adsorbent for Natural Gas Storage

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ABSTRACT

Carbon adsorbent was selected as a means of efficiently storing methane, the main component of natural gas. Simulations were first employed to determine an ideal adsorptive pore structure. The results of the simulations were applied to establish a target in the development of activated carbon, with coconut shell, coal and carbon nano-materials (Buckminsterfullerene, carbon nano-tubes) as starting materials. TEM analysis confirmed that the activated carbon produced in this research possessed the ideal pore structure targeted. This activated carbon is capable of storing 0.155 NL/cm³ of natural gas at low pressure (3.5 MPa). This represents 77.5% of the capacity of high-pressure (20 MPa) compressed natural gas (CNG) storage. The material's storage capacity for adsorbed methane gas is one of the highest among reported figures.

1. Introduction

Recently, the demand to reduce automotive exhaust gas emissions and develop alternative fuels has increased from the viewpoint of global environmental issues and exhaustion of energy resources. Against this background, automobiles fueled by natural gas are cleaner vehicles that can greatly reduce exhaust gas emissions. This is accomplished simply by making minimum modifications to a gasoline based vehicle. Three methods have been devised for storing natural gas in automobiles as shown in Fig. 1. The first of these, compressed natural gas (CNG) fuel is stored at high pressure (20 MPa or 25 MPa), so a cylindrical pressure vessel is needed which reduces the degree of freedom for the vehicle body package. Liquefied natural gas (LNG) fuel is stored at the low temperature of $-162\text{ }^{\circ}\text{C}$, so a fuel container with a special dual structure is needed. This research concerned adsorbed natural gas (ANG) which can be efficiently adsorbed and stored at relatively low pressure as a method

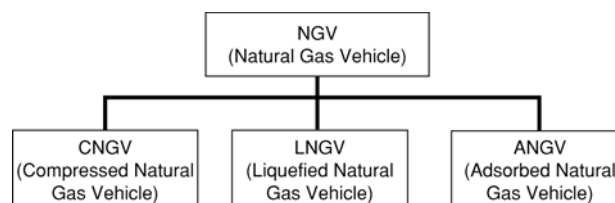


Fig. 1 Fuel storage methods for natural gas vehicles

for easily storing natural gas, and this paper describes adsorption which is the core technology for ANG.

First, the target natural gas storage capacity for the adsorption was set at 20 Nm³ (0.2 NL/cm³) for a 100 L container equivalent to the gas storage of the CNG CIVIC GX that Honda has marketed since 1998, and the storage pressure was set at 3.5 MPa.

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2. Development of Adsorption

The adsorption was developed by selecting the base materials and handling process (carbonization and activation methods), and improving the preparation conditions.

2.1. Selection of Materials

2.1.1. Activated carbon

Activated carbon raw materials that are currently used for industrial applications can be broadly classified into plant based and fossil fuel based materials⁽¹⁾. Typical plant based raw materials include coconut shell (CCS), wood and pulp. However, of these, coconut shell in particular accounts for approximately 30% of the activated carbon in the marketplace, and most of this is used for steam activated applications. Next, fossil fuel based materials can be divided into raw materials such as coal that can be converted into activated carbon without processing, and raw materials such as petroleum pitch, coal tar and synthetic polymers that undergo primary processing and are then converted into activated carbon. This research selected coconut shell, which is cheap and allows easy improvement of performance, and coal with a low impurity content as the starting raw materials.

2.1.2. Carbon nano-materials

The discovery of BuckminsterFullerene (C_{60}) in 1985 and carbon nanotubes in 1991 have stimulated efforts to research technology for synthesizing large amounts of carbon nano-materials and to develop applied technologies in recent years. Amidst this trend, numerous studies have been presented on using carbon nanotubes for hydrogen storage⁽²⁾. The authors thought that sufficient adsorption levels could be expected for methane molecules, which have greater adsorption energy than hydrogen molecules, so this research selected carbon nanotubes and BuckminsterFullerene as the raw materials.

2.2. Adsorption Manufacturing Method

2.2.1. Carbonization and activation methods

The process for converting the raw materials into adsorption materials requires carbonization and activation. The carbonization process carbonizes the raw materials, and the activation process grows pores in the carbonized materials. Activated carbon is normally made using the above two processes, but carbon nano-materials are already carbonized in the raw material stage, so they can be converted into adsorption type using only activation. Activation processes can be grouped into physical activation and chemical activation processes⁽¹⁾. Physical activation uses steam, carbon dioxide gas or other gases as the activation agent, and the pore growth mechanism uses the method of gas erosion from the raw material surface. Steam activation is more economical, so this process is most widely used for industrial applications.

On the other hand, chemical activation uses KOH, phosphoric acid or other chemicals, and the pore growth mechanism uses the methods of chemical erosion and intercalation from the surface and inside of the raw materials. Chemical activation uses more expensive chemicals as the activation agency and requires a handling process after activation, so it is not used widely for industrial applications⁽¹⁾. This research fabricated adsorption substrates using the two representative methods of steam activation and KOH activation as the activation methods. Figure 2 shows the steam and KOH activation mechanisms.

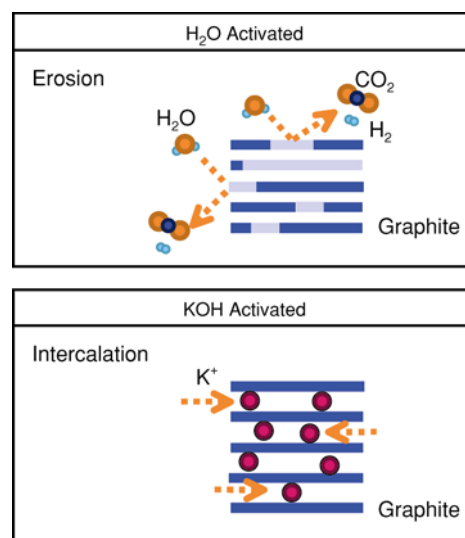


Fig. 2 Activation mechanism

2.2.2. Monolith manufacturing method

After the carbonization and activation process, the adsorbent is in powder or granulated powder form. When packaging this into a fuel container, the format must prevent damage when charging. In addition, this is an automobile mounted part, and the format must be unaffected by vibrations when cruising and changes in temperature and humidity. Furthermore, like a gasoline canister, the structure must prevent the adsorbent from breaking down into particles during repeated adsorption/desorption cycles. Therefore, the powder and granulated powder adsorbent was molded into a monolith to meet these performance requirements. Figure 3 shows the molding process.

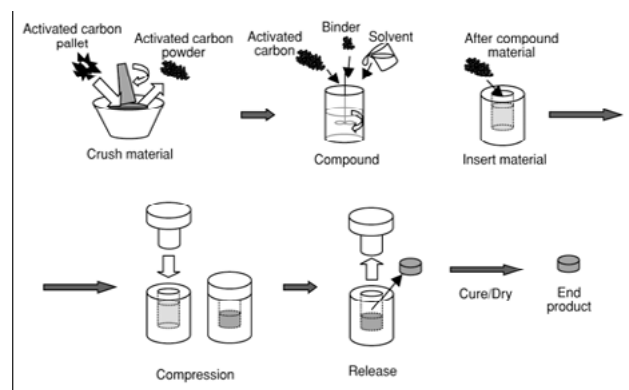


Fig. 3 Molding process of monolith

3. Adsorption Simulation

The adsorption simulation was used to predict adsorption pore structures that would be effective for methane gas storage, and to provide direction for the research. The simulation used the Cerius² made by Accelrys Inc. (USA), and adsorption performance was calculated by the monte-carlo method.

3.1. Activated Carbon

Figure 4 shows the basic simulation model. The simulation calculated the methane adsorption capacity for different pore sizes using this model⁽³⁾. Figure 5 shows the adsorbed status for each pore size. The calculation results showed that a graphite layer distance (distance between graphite layer centers) of approximately 11 Å provided the ideal adsorption for methane molecules. Figure 6 shows these results in terms of pore size and gas storage capacity. These calculation results showed that the ideal pore structure for methane storage was a peak pore size of 7.8 Å, and the specific surface area at that time is 2 630 m²/g.

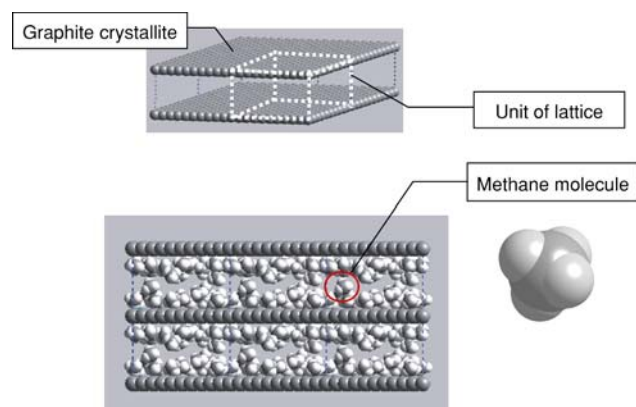


Fig. 4 Basic model of adsorption

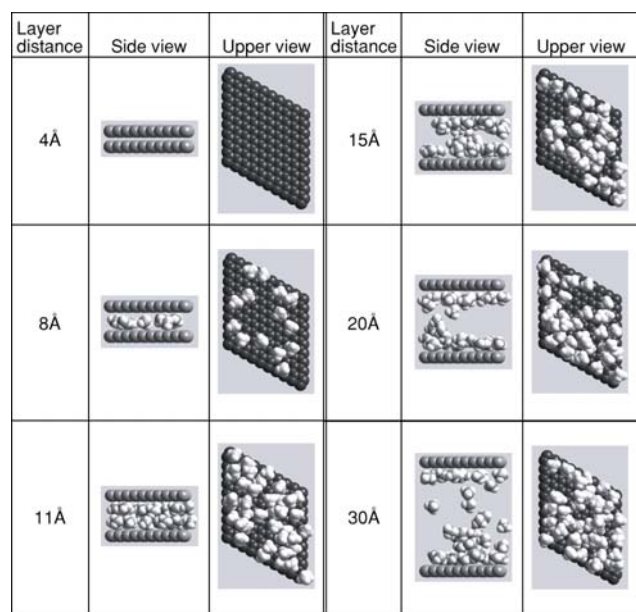


Fig. 5 Status of adsorption with change in layer distance

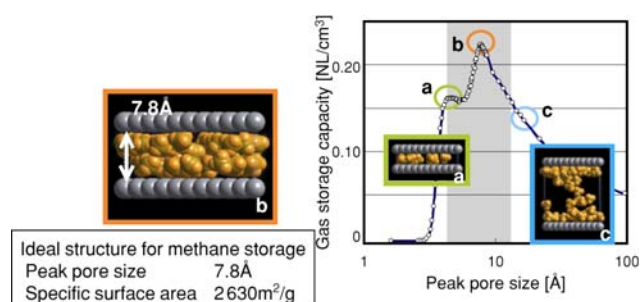


Fig. 6 Pore size and storage capacity

3.2. Carbon Nano-materials

An adsorption model was constructed and simulations were performed for carbon nano-materials in the same manner as activated carbon. Figure 7 shows the simulation model. There are still many unknowns in terms of model creation and simulation methods for BuckminsterFullerene and carbon nanotubes, so the simulation was conducted using the same setting conditions for activated carbon⁽⁴⁾⁽⁵⁾.

Figure 8 shows the simulation results for activated carbon and carbon nano-materials. At a pressure of 3.5 MPa, the gas storage capacity was 0.205 NL/cm³ for the carbon nano-tube(CNT), and 0.216 NL/cm³ for activated carbon. This indicated that the adsorption with the most ideal pore structure was activated carbon.

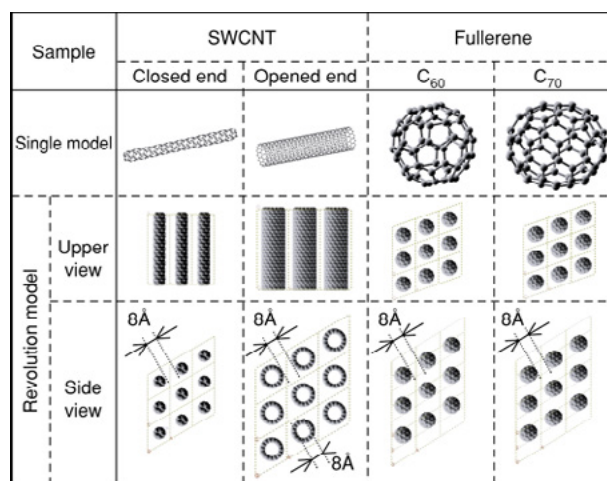


Fig. 7 Adsorption model for nano-carbon materials

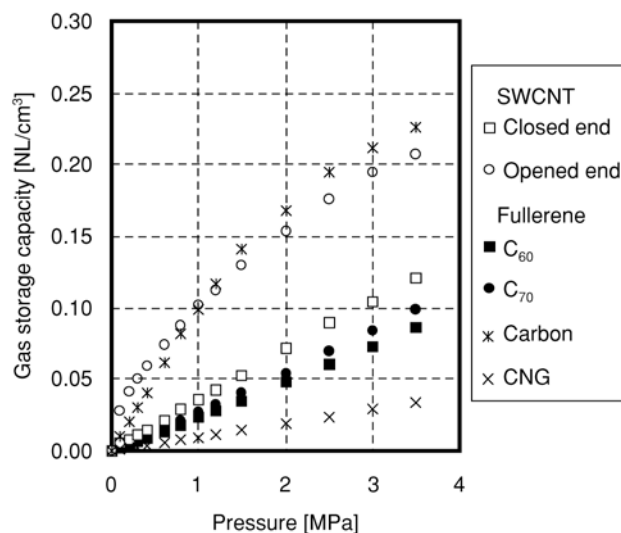


Fig. 8 Results of simulation

4. TEM Surface Observation

The purpose of TEM surface observation was to obtain a relative comparison of the internal structures of the adsorbents used in the tests. In addition, the pore status can also be understood by performing image analysis on the TEM images.

4.1. Activated Carbon

TEM surface analysis was performed for the two types of activated carbon (coconut shell/steam activation, coal/KOH activation) evaluated by this research. Figure 9 shows the analysis results. These results confirmed that the activated carbon made using coal and KOH activation could be fabricated to values near the peak pore size of 7.8 Å and specific surface area of 2 630 m²/g which were the ideal pore structure obtained by the adsorption simulation. In contrast to this, coconut shell and steam activation resulted in a smaller specific surface area (obtained using the BET method) at the ideal peak pore size, and conversely a larger than ideal peak pore size at the ideal specific surface area. This indicated that the combination of coconut shell and steam activation is not suitable for methane adsorption.

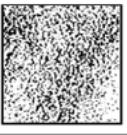
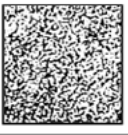
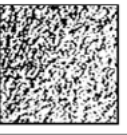
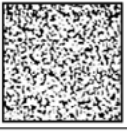
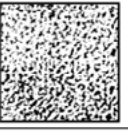
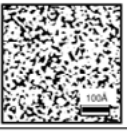
		Specific surface area [m ² /g]		
		1 800	2 600	3 000
Coal + KOH	TEM image			
	Peak pore size [Å]	8	8.8	10
CCS + H ₂ O	TEM image			
	Peak pore size [Å]	10.6	11.6	14

Fig. 9 TEM image of activated carbon

4.2. Carbon Nano-materials

In its synthesized state, C₆₀ has an extremely stable structure comprised of hexagonal and pentagonal faces⁽⁵⁾. It has been reported that effective methane adsorption sites can be obtained by applying activation to this stable structure⁽⁶⁾. This research compared the surface status before and after activation to confirm the changes produced by activation. Figure 10 shows the TEM analysis results for C₆₀.

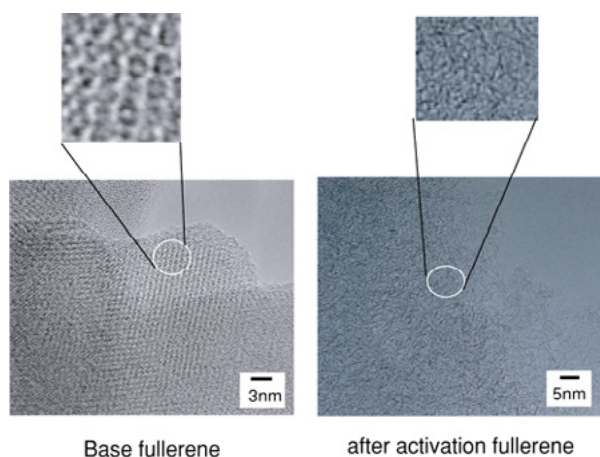


Fig. 10 TEM image of fullerene

While a neat and orderly graphite crystal lattice can be confirmed before activation, this cannot be confirmed at all after activation. These results are thought to indicate that C₆₀ does not maintain a neat soccer ball structure after activation, and instead the carbon atoms decompose into an amorphous form. Why this amorphous structure is effective for methane adsorption has not yet been theoretically solved at present, but a clear structural change can be confirmed. Figure 11 shows the Buckminsterfullerene measurement results for different activation conditions.

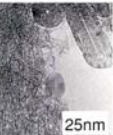
Specific surface area (m ² /g)	1 122	1 363	2 346	2 594
Storage capacity (NL/cm ³)	0.115	0.105	0.111	0.113
Adsorption ability (NL/g)	0.13	0.14	0.20	0.25
Bulk density (g/cm ³)	0.699	0.565	0.413	0.335
TEM image				

Fig. 11 Analysis of pore structure for activated fullerene

Next, Fig. 12 shows the TEM analysis results for carbon nanotubes. Carbon nanotubes are classified into single wall (SWCNT), double wall (DWCNT) and multi wall (MCNT) according to the number of tube layers⁽²⁾. However, simulation results showed that SWCNT are the most effective in terms of methane adsorption capacity relative to carbon density. However, it is extremely difficult to synthesize only SWCNT, and it is not uncommon for MWCNT and C₆₀ to also be present. Therefore, TEM analysis was performed to confirm the quality of the test materials evaluated by this research (Fig. 12). The results confirmed a small amount of catalytic residue, but the material was synthesized with an even tube size of 15 Å, and the test material quality was confirmed to be extremely high, with almost no MWCNT or other types present.

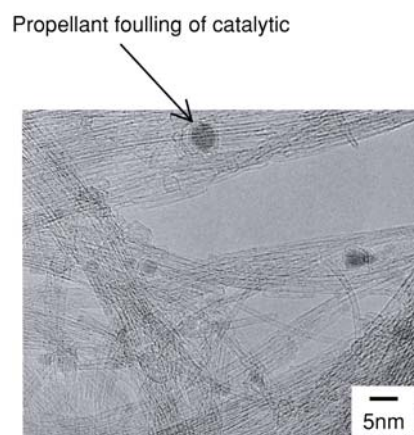


Fig. 12 TEM image of CNT

5. Pore Analysis

Image processing was performed on the TEM images, and Fig. 13 shows the activated carbon pore distribution calculated from the image processing results. The calculation results show that the ideal case in the simulation is an even peak pore size of 7.8 Å, but the pore size for actual activated carbon has a distribution, and this distribution must be taken into account when predicting the gas storage capacity. The analysis results confirmed that the peak pore size for activated carbon made using coal and KOH activation is the same 7.8 Å as the ideal peak pore size, and that a sharper pore size distribution can also be achieved than that for coconut shell and steam activation. This is thought to indicate that activated carbon made using coal and KOH activation is closer to the ideal.

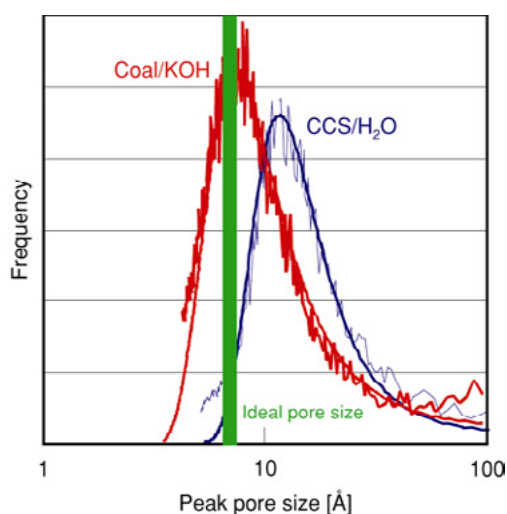


Fig. 13 Pore size distribution

6. Evaluation of Adsorption Ability

6.1. Activated Carbon

Figure 14 shows the methane adsorption test results for activated carbon molded into a monolith. Improvement of the activated carbon is broadly divided into three steps, and the conditions (temperature, time, etc.) for activation, which is the core technology, are expressed as the degree of activation. This degree of activation has an extremely high correlation with the bulk density of the activated carbon. First, in step 1 the degree of activation was improved using coconut shell and steam activation. The results clearly show the coconut shell tendency, and make it possible to ascertain the adsorption ability.

Next, in step 2 the raw materials and activation method for the activated carbon were changed, and a vast improvement in ability was confirmed compared to step 1. Therefore, in step 3 the coal raw materials and degree of activation were further reviewed compared to step 2. As a result, the activated carbon achieved a methane storage capacity of 0.155 NL/cm³, which is 77.5% of the target gas storage capacity.

6.2. Carbon Nano-materials

Figure 15 shows the adsorption test results for carbon

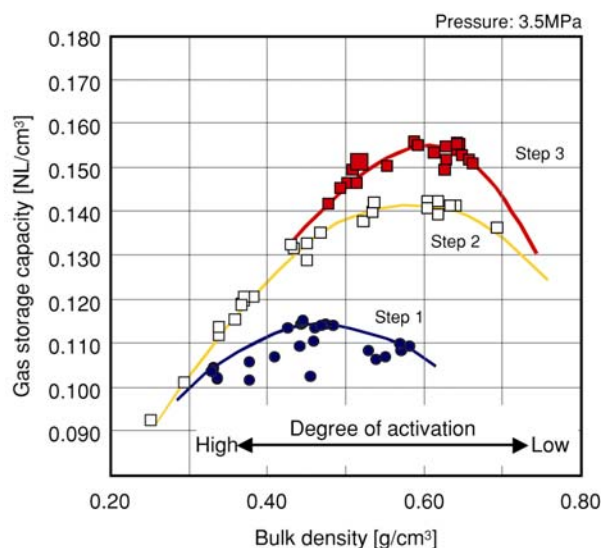


Fig. 14 Adsorption performance of activated1 carbon

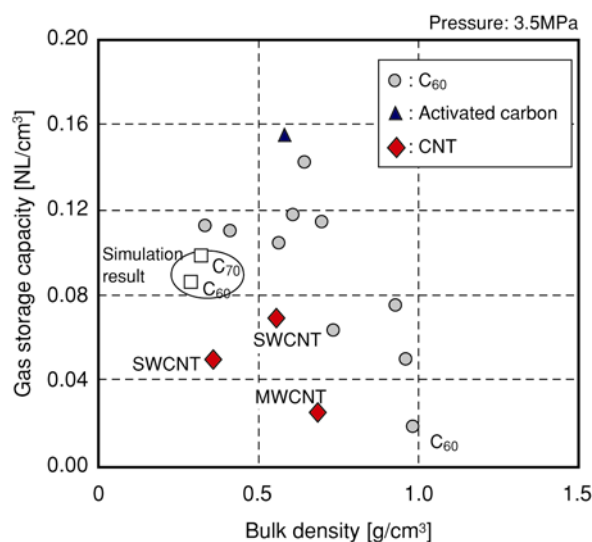


Fig. 15 Adsorption performance of nano-carbon

nano-materials. Carbon nano-materials are carbonized by the synthesizing process in the raw material stage, so the adsorption was fabricated using only activation. The adsorption test results for carbon nano-materials showed that SWCNT and MWCNT could only obtain gas storage capacities approximately 50% that of activated carbon, but C₆₀ achieved roughly the same value as activated carbon.

7. Adsorption Performance Achievement Level

Figure 16 shows a comparison of storage capacity for various methane adsorption systems^{(7) - (10)}. Like hydrogen storage, there is no global evaluation standard for methane adsorption, so there may be some deviation based on the measurement method. However, comparison with values reported in research thus far confirmed that the results achieved by this research are among the world's highest.

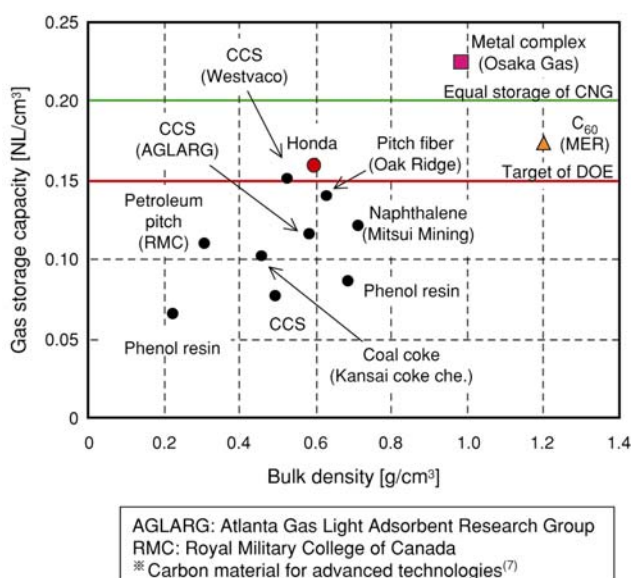


Fig. 16 Comparison of methane storage capacity

8. Conclusion

The results achieved by this research are as follows.

- (1) The methane storage capacity using activated carbon was 0.155 NL/cm³ at a pressure of 3.5 MPa. This represents 77.5% of the gas storage capacity for CNG for a 100 L container at a pressure of 20 MPa and which is the target for this research.
- (2) Research to apply carbon nano-materials as the adsorption obtained C₆₀ performance roughly equivalent to activated carbon.
- (3) Adsorption simulation calculation results showed that the methane storage capacity of the ideal graphite structure is 0.216 NL/cm³, and that the pore structure at that time has a peak pore size of 7.8 Å and a specific surface area of 2 630 m²/g.

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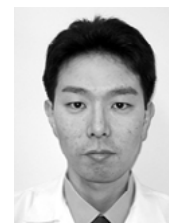
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