

PRE-TREATMENT OF NATURAL GRAPHITE AS STARTING MATERIAL FOR CARBON NANOTUBE SYNTHESIS.

Madzlan Aziz¹, Suhaila M. Sanip¹, and Noraziah Buang¹.

¹Chemistry Department,
Faculty of Science,

University Technology of Malaysia,
81310 UTM Skudai, Johor

²Membrane Research Unit (MRU),
Faculty of Chemical and Natural Resources
Engineering,
Universiti Technology Malaysia,
81310 Skudai, Johor.

ABSTRACT

In the push for renewable energy and cleaner fuels, hydrogen is an ideal candidate for this purpose. This is due to the high-energy value and lack of environment pollution generated on combustion, compared with conventional fossil fuel sources. Several researches have been done on Carbon Nanotube (CNT) as potential hydrogen storage material. This research was conducted to determine the suitable base material to synthesis CNT. The effects of heat treatment were looked into for natural graphite. The materials were heated at 400 °C and 800 °C for 4 to 24 hours. The surface area and composition of natural graphite were studied before and after treatment. The surface area analyses were carried out using Nitrogen Gas Adsorption technique, while the percentage carbon composition were determined using Energy Dispersive X-ray Analysis (EDAX). Heat treatment resulted in the change of surface areas with the increment of temperature and time. The percentage of carbon content in natural graphite after heat treatment at 800 °C still remain in the range of 90%, indicating the stability of graphite. Conclusively, natural graphite is suitable to be use as starting material for CNT.

Keywords: heat treatment; Nitrogen Gas Adsorption; surface area

ABSTRAK

Dalam usaha untuk memperolehi sumber bahan api yang bersih, hidrogen didapati berpotensi bagi tujuan ini. Pemilihan hidrogen sebagai bahan api adalah kerana ia mampu menghasilkan tenaga yang tinggi dan dapat mengurangkan pencemaran alam sekitar semasa pembakaran di dalam enjin. Beberapa penyelidikan telah dijalankan untuk mengenalpasti bahan asas yang sesuai bagi penghasilan nanotub karbon. Kesan pra-rawatan haba telah dilakukan ke atas 'natural graphite'. Sampel dipanaskan pada suhu 400 °C dan 800 °C selama 4 hingga 24 jam. Luas permukaan dan komposisi 'natural graphite' telah dikaji sebelum dan selepas rawatan. Analisis luas permukaan dilakukan menggunakan teknik Penjerapan Gas Nitrogen manakala peratus komposisi karbon diperolehi daripada teknik Analisis Penyerakan Tenaga Sinar-X (EDAX). Didapati, rawatan haba memberikan perubahan pada luas permukaan dengan pertambahan tempoh rawatan dan kenaikan suhu perawatan. Kestabilan grafit telah dibuktikan dimana pada suhu 800 °C peratus komposisi karbon masih di sekitar 90% ke atas. Kesimpulannya, natural graphite sesuai digunakan sebagai bahan asas bagi penghasilan nanotub karbon.

INTRODUCTION

Hydrogen is an ideal candidate as it is available from domestic renewable sources, and pollution free. The discovery of carbon nanotubes (CNT) in 1991 by Iijima has stimulated research on a large variety of physical properties of the nanotubes. Carbon nanotubes are formed by rolled graphite sheets, with an inner diameter starting from 1 nm up to several nm and a length of 10 – 100 μm . Tubes formed by only one graphite layer are called single wall Nanotube (SWNT). Tubes consisting of multiple concentric graphite layers are called multi-wall nanotubes (MWNT).

In graphite, each c-atom is covalently bonded to three c-atom to give trigonal geometry. Each c-atom in graphite is sp^2 -hybridized. Basic trigonal units unite together to give basic hexagonal ring. In graphite these rings form flat layers. These layers are arranged parallel, one above the other. These layers 3.35 Å apart and held together by weak Van de Waals forces. Carbon material is preferred due to their high electrical conductivity, low cost, high surface area, adsorption behavior, processability and their chemical and electrochemical resistivity. For this purpose, a wide variety of commercial and specialty carbon have been tested as possible sorbents for hydrogen storage.

The scope of the analysis is to study the influence of heat treatment on surface area and carbon content of natural graphite. Changes in surface area and carbon content have been recorded.

MATERIALS AND METHODS.

Heat treatment was done on natural graphite as starting material for CNT synthesis. Natural graphite was supplied by Superior Graphite Co.

Generally, heat treatment can be divided into a 3 step experiment:

1. Preparation of sample.
2. Heat treatment on sample.
3. Characterization on sample using Nitrogen Gas Adsorption technique and Energy Dispersive X-Ray Analysis (EDAX).

Natural graphite was heated at 400 °C and 800 °C for 4 to 24 hours. The surface area and carbon content of natural graphite were studied before and after treatment. Surface areas of natural graphite were measured using single-point PulseChemisorp Micromeritics 2705. The samples were degassed using nitrogen gas for 1½ hour at 350 °C. The nitrogen adsorption-desorption was carried out in liquid nitrogen. The BET surface area was calculated from the equation below,

$$\text{BET surface area (S) m}^2\text{g}^{-1} = \frac{\text{Peak area, m}^2}{\text{Sample weight, g}}$$

The EDAX technique provides valuable information for the percentage of carbon content. Both before and after treatment of samples were also analyzed as comparison.

RESULTS AND DISCUSSIONS

The surface area of BET method and carbon content before and after treatment are shown in table 1.

TABLE 1 Surface area and carbon content before and after treatment.

Time (Hrs)	Temperature (°C)	BET (m ² /g)	EDAX (%C)
Without treatment		7.74	86.68
4	400	7.37	95.26
8	400	7.46	95.67
16	400	6.87	95.65
24	400	7.48	94.85
4	800	7.40	93.87
8	800	7.57	95.55
16	800	6.65	95.20
24	800	8.77	92.23

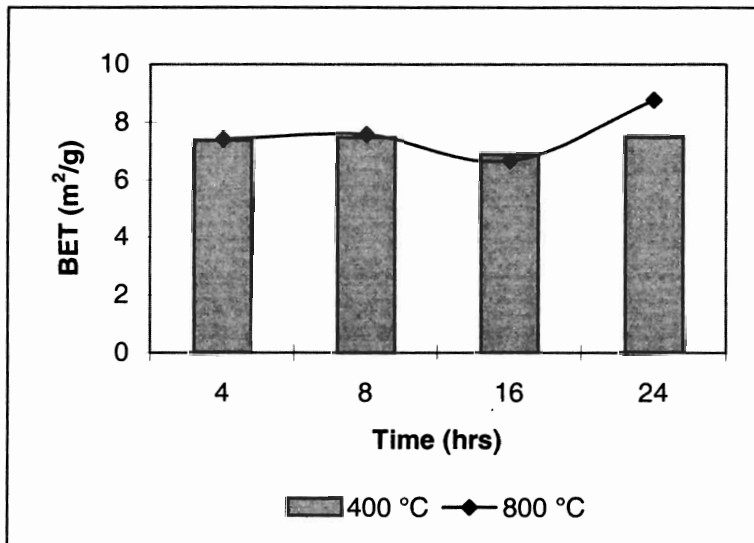


FIGURE 1 Surface area derived from BET method for natural graphite.

Heat treatment resulted in the changes of surface area with the increment of temperature and time. At 400 °C, the surface area of the natural graphite have not shown substantial increase compared to before treatment as shown in table 1. However, upon heat treatment for 24 hours at 800 °C the surface area showed a significant increase, implying that the changes in surface areas was due to the opening up of the porosity and release of internal surface area. The structure of graphite are flat layers, held together by weak Van de Waals forces only. These layers are able to slide over one another as a result of heat treatment. Thus, it was indicated by the increment of nitrogen adsorption on the surface area.

The overall percentage of carbon content in natural graphite after heat treatment still remain in the range of 90% at high temperature. From the EDAX

results only carbon and oxygen were present. It showed that the graphite is stable and highly resistant to oxidation at high temperature. Heat treatment of graphite at high temperature also reduces the sulfur content.

CONCLUSIONS

1. Heat treatment resulted in changes of the natural graphite surface area. Thus, the BET- surface area increase is a function of the temperature and time.
2. Heat treatment proved the stability of natural graphite
3. Natural graphite is a stable material and highly resistant to oxidation even at high temperature.

ACKNOWLEDGEMENT

To the Ministry of Science, Technology and Environment of Malaysia and IRPA
Vot. No. 74525.

REFERENCES

- C. Dillon, K.E.H. Gilbert, J. L. Alleman, T. Gennett, K.M. Jones, P.A. Parilla and M. J.Heben. 2000. Carbon Nanotube Materials For Hydrogen Storage, in Proceeding_of The 2001 DOE Hydrogen Program Review.
- Massooud Pirjamali, Yohannes Kiros. 2002. Effects Of Carbon Pretreatment For oxygen Reduction in Alkaline Electrolyte. *J. Power Sources*.**109**. 446-451
- Shaobin Wang and G.Q. (Max) Lu. 1998. Effect Of Acidic Treatments On The Pore And Surface Properties Of Ni Catalyst Supported On Activated Carbon. *Elservier Science*. **36**.283-292.
- Vahan V. Simonyan, J. Karl Johnson 2002, Hydrogen Storage in Carbon Nanotubes and Graphitic Nanofiber, *Journal of Alloys and Compound*, **330-332**, 659-665.
- Nelly M. Rodriguez. 2000. Synthesis, Characterization and Properties of Catalytically Grown Graphite Nanotubes, in Proceeding of The International Winterschool of Electronic Properties of Novel Material: Molecular Nanostructures, Hans Kuzmany, Jöng Fink, Michael Mehring, Siegm Roth, 495-499.

- A. Züttel, Ch. Nützenadel, P. Sudan, Ph. Mauron, Ch. Emmenegger, S. Rentsch, L. Schlapbach, A. Weidenkaff, T. Kiyobayashi. 2001. Hydrogen Storage in Carbon Nanotubes And Other Carbon Nanostructures, *J. Of Alloys And Compounds*. 1-7
- Sumio Iijima. 1991. Helical Microtubules of Graphitic Carbon. *Nature*, **354**, 56-58
- F. Lamari Darkin, P. Malbrunot, G.P. Tartaglia . 2002. Review of Hydrogen Storage by Adsorption in Carbon Nanotubes, *International Journal of Hydrogen Energy*, 193-202.
- R. Ströbel, L. Jörissen, T. Schliermann, V. Trapp, W. Schütz, K. Bohmhammel, G. Wolf, J. Garche. 1999. Hydrogen Adsorption on Carbon Material, *Journal of Power Sources* **84**, 221-224
- Scott Hynek, Ware Fuller and Jeffrey Bentley. 1997. Hydrogen Storage by Carbon Sorption, *International Journal of Hydrogen Energy*, **Vol. 22**, Issue 6, 601-610