ENERGETIKA. 2006. Nr. 2. P. 43–46

Carbon nanotube growth and use in energy sector

Simas Račkauskas

*Lithuanian Energy Institute,
Laboratory of Combustion Processes,
Breslaujos 3, LT-44403 Kaunas,
Lithuania*

Besides the fundamental interest in the unique physical and chemical properties of carbon nanotubes (CNT), these nanostructures have a potential technological application in many industrial sectors, the energy sector included. In this work, arrays of carbon nano-fibers have been grown normal to the surface of electrically conducting supports by the simplified method of catalytic CVD. The process conditions were an open air laboratory atmosphere, and no chamber or inert gas ambient was used. The diameter and surface density of the fibers was controlled by the process parameters. A sharp decrease and again an increase in the process temperature induce significant changes in the fiber diameter.

Key words: nanotube, nano-fiber, chemical vapour deposition

1. NANOTUBES FOR THE ENERGY SECTOR

The interest in carbon nanostructure and the scope of research activities across the world on their application potential have been extraordinary in the last decade. Carbon nanotubes – graphitic cylinders 1–50 nm in diameter – due to their unique physical and chemical properties compared to conventional materials, have a potentional technological application in industry, also in the energy sector. The probable CNT applications in the energy sector are hydrogen energy, fuel cells, batteries and supercapacitors, solar cells, thermoionic power devices and coatings or special composite materials.

Pure hydrogen fuel is non-polluting, but the current methods for extracting are polluting. Employing titanium dioxide nanotubes and using the sun light as an energy source there is a possibility to extract hydrogen from water at 6.8 percent efficiency [3]. These molecular scale structures have a large active surface, so carbon nanotubes are likely to be utilized for hydrogen storage and for fuel cells. Here, the high surface area and thermal conductivity exhibited by carbon nanotubes make them useful also as electrode catalyst supports. The abundant pore structure of both individual nanotubes and nanotube bundles is particularly interesting for hydrogen storage. So far, experimental outcomes of nanotube-based hydrogen storage in gas phase look promising, but inconsistent. Mg, La, Ti or other metal-based alloys present a poor adsorbtion / desorbtion kinetics and thermodynamics, or require a high operation temperature. In addition, they are highly caustic and very sensitive to the atmosphere. Recent experiments with carbon nanotubes offer a broad assortment of results for hydrogen storage capacity, ranging from 0.02 to 8.6 wt%. Different pretreatment procedures or doping with Li or K can rise this value up to 14 or 20 wt%, but only in milligram quantities [1, 2].

The abundant pore structure of both individual nanotubes whose diameters are only 0.07 nm and nanotube bundles is also highly interesting for the storage of large amounts of lithium ions. Again, good chemical stability, large surface area, high mechanical strength and elastic modulus represent other important features prolonging the life cycle of nanotube-based batteries. Currently, the anode of Li-ion batteries is primarily made from various other carbonaceous materials, but carbon nanotubes promise to boost this rate of growth either by themselves as incorporated into an appropriate composite material. The reversible capacity of etched multi-walled carbon nanotubes reached 681 mAh/g; in the case of opened multi-walled carbon nanotubes, lithium storage capacity may get to 1281 mAh/g [1, 4].

In contrast with other active carbon fibers which exhibit mostly micropores inaccessible to electrolyte ions, carbon nanotubes contribute with a high mesopore (2–50 nm) volume and a large specific surface area. Compared to batteries, supercapacitors exhibit a higher power density. The power density of a supercapacitor is about ten times larger than that of a secondary battery. Moreover, their energy density is by 1–2 orders of magnitude higher than of conventional capacitors. Other advantages are long life cycles and short charge time. At present, high specific surface area activated carbon is normally used for the electrodes of double layer capacitors. Supercapacitors employing multi-walled carbon nanotube electrodes achieved a capacitance of 80 F/g. When the nanotubes were acid or oxide pre-treated, their specific capacitance increased to 140 F/g. The specific capacitance of impregnated ruthenium oxide on carbon nanotubes was larger than 960 F/g [1, 2].

Carbon nanotubes have aroused a legitimate interest in the solar cell industry due to their excellent electrical conductivity. Also, carbon nanotubes have the advantage of being able to impart this property to various composite hosts, without impairing their optical transparency. Other attractive features are the semiconducting nature of some nanotube species and photoconduction capabilities. As conductive additives, nanotubes will hopefully deliver the price-drops that will allow solar cells to be manufactured and sold on commercial basis. Therefore, several groups have already shown an interest in the use of carbon nanotubes as electron acceptors in polymeric materials [1, 2].

Thermionic power generators represent an emerging field of applications for carbon nanotubes. Carbon nanotubes are expected to allow thermal to electric conversion even at low temperatures, commonly encountered in the majority of applications resulting in waste heat. A thermionic power converter consists of an electron emitter (cathode) and an electron collector (anode) placed in a vacuum tube. The cathode is in thermal contact with the heat source, while the anode is coupled with the heat sink. When a voltage is applied across the gap between anode and cathode, it extracts the charged thermions and produces an electrical current. Single-walled carbon nanotubes appear as very promising candidates for reinforcing both electrodes of the device, due to their low percolation threshold, combined with a high electrical conductivity and a remarkable anisotropic thermal conductivity. Early prototypes incorporating titanium films with homogeneously embedded carbon nanotubes were already demonstrated, but more efforts are still expected. Such materials could make possible the generation of electricity from waste heat of engines, also geothermal or other sources of heat [6].

There are also great promises to apply carbon nanotubes based composites for heat resistant materials, vibration absorbance [7], superhydrophobic surfaces for effective reduction of friction in fluid flow [8], carbon nanotubes foam-like ultra-strong, chemically and heat resistant films for different applications associated with heat transfer, electrical contacts and cushioning effect [9].

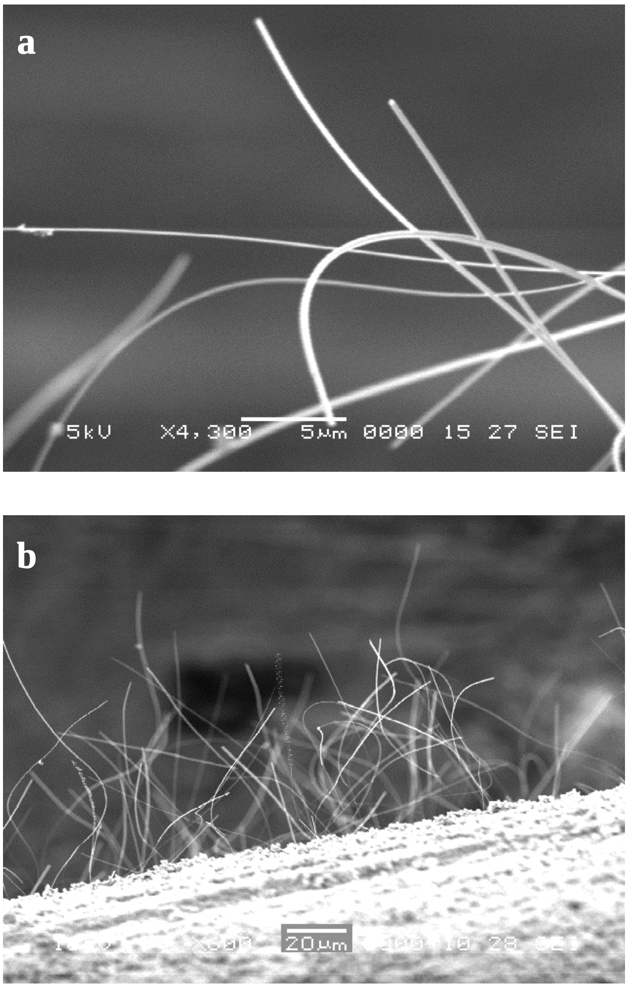

Fig. 1. SEM images of carbon nano-fiber

2. EXPERIMENT

Liquid hydrocarbon source was deposited on a heated catalytic support to produce the carbon vapour atmosphere at the surface. The only conducting support was heated by electric current during the carbon nano-fiber growth process. It allows easily to control and change the temperature and heating rate during the process. After making electric contact, support is heated and the liquid carbon source instantly vaporizes and dissolves in the catalyst. Carbon nano-fiber grows on the appropriate catalyst particle (catalyst site). Ethanol (96%) and porphyrin were used as a source of carbon by decomposition at a high temperature near the surface of the support. The process conditions were an open air laboratory atmosphere, and no chamber or inert gas ambient was used. It is thought that the presence of oxygen as a component in the reaction system, making possible the formation of carbon monoxide, reduces the tendency to deposit nonfibrous carbon [10]. No fiber was found carrying the process in the inert atmosphere conditions. The nichrom wire (80% Ni, 20% Cr) was used without pre-treatment as a combined catalyst and supporting material. The produced carbon nano-fiber diameter varies in the range of 50 to 100 nm and the length up to a hundred of micrometers. The diameter and surface density of the fibers produced is controlled by the process parameters. The process temperature was in the range of 1030–1070 ^{0}C. If the process temperature is out of the optimal range, the surface density and the length of fibers is less or they do not form at all due to the inappropriate rate of hydrocarbon decomposition and solution in the catalyst. The length of a hundred of microns was obtained within several minutes from the ethanol source (Fig. 1 a, b). The change of temperature strongly influenced the diameter of carbon nano-fibers. The sharp decrease and again an increase in the process temperature by 40 ^{0}C change of the fiber diameter more than twofold – from 305 nm to 110 nm (Fig. 2 a); the diameter can be increased similarly.

The measurement procedure, mechanical properties and its values are described elsewhere [11].

In order to get a dense layer of vertically aligned carbon nanotubes, a chemically prepared catalyst was used. We intend to apply these structures in high temperature hydrogen separation membranes.

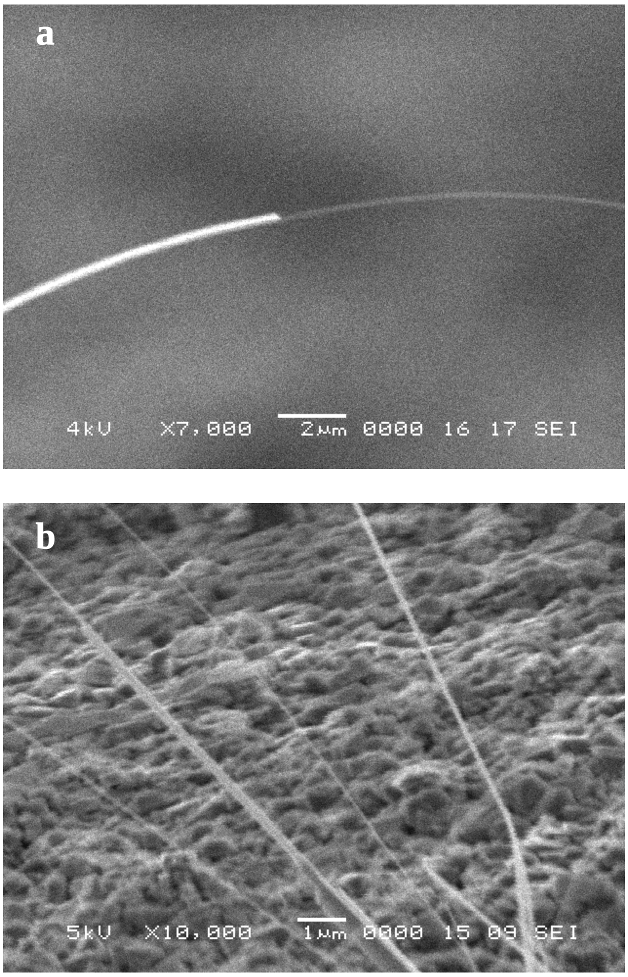

Fig. 2. Sharp changes of the diameter

3. CONCLUSIONS

Nanotubes are most likely to be applied in energy storage and conversion. Whether their potential for hydrogen storage will be confirmed or not, nanotube-reinforced composites and nanotube-based catalyst supports will likely improve electrodes and proton exchange membranes in fuel cells. Electrodes for lithium batteries are also a sure target and a huge market at the same time. The third major field of research is represented by the solar cell industry, where nanotubes are expected to boost the performances and to significantly lower the costs. Unlike more exotic applications (such as carbon–carbon batteries or thermionic power devices), nanotube-based fuel cells, photovoltaic cells and batteries are expected to hit the market within a decade, as nanotube prices will surely drop.

In this work, straight and sufficiently long carbon nano-fiber arrays attached to the surface of electrically conducting supports were grown by the simplified method of catalytic CVD, without using a complex catalyst preparation. Catalyst particles or active catalytic sites were formed during catalyst heating in air. The role of oxygen is important: it induces catalyst surface breakup processes through which catalytic sites occur, and also promotes catalytic activity by avoiding formation of amorphous carbon. AFM observations showed that surface breakup processes caused by mismatches in catalyst lattice produce grains of different sizes and smoothness on the surface. Carbon nano-fiber grows on the appropriate grain (catalyst site). The optimal temperature of the process is quite high (1050 ^{0}C on the surface); this may be due to the low ambient temperature and consequently a low temperature of supplied gaseous reagents.

Sharp changes (over twofold) in nano-fiber diameter during growth are possible by controlling the process conditions.

Received 14 April 2006

References

1. Application of the Month: Energy Storage and Convertion // Carbon Nanotubes Monthly – December 2005.
2. Nanotubes for the Energy Market // Cientifica. April 2005.
3. Nanotubes Crank out Hydrogen – the Latest Technology Research News 02.09.2005 – www.trnmag.com
4. Nanotubes Juice Super Batteries– the Latest Technology Research News 23.03.2005 – www.trnmag.com
5. Nanotechnology Could Promote Hydrogen Economy – Eurekalert 28.03.2005 – www.eurekalert.org
6. Scientists Discover Better Way to Generate Power from Thermal Sources – Eurekalert 28.03.2005 – www.eurekalert.org
7. Adding Nanotubes Makes Ordinary Materials Absorb Vibration – Science Daily 13.02.2006 – www.sciencedaily.com
8. A Superhydrophobic Surface – Physics News Update 06.02.2006 - www.aip.org
9. Engineers Create Super Compressible Carbon Nanotube Foam-like Films – Physorg.com 24.11.2006 – www.physorg.com
10. Li Y. L. Kinloch I. A. Windle A H 2004 Science 304 276
11. Rackauskas S., Snitka V. Method for the simple catalytic carbon nano-fibers growth in air // Microelectronic Engineering. 2006.

Simas Račkauskas

ANGLINIŲ VAMZDELIŲ SINTEZĖ IR PANAUDOJIMAS ENERGETIKOJE

Santrauka

Angliniai nanovamzdeliai dėl unikalių savybių, lyginant su naudojamomis medžiagomis, perspektyvoje bus pritaikyti daugelyje pramonės šakų, taip pat energetikoje. Šiame darbe aprašoma anglinių nanovamzdelių sintezė ant elektrai laidaus substrato paviršiaus, statmenai, taikant supaprastintą cheminį katalitinį garų nusodinimo metodą. Anglinių nanovamzdelių sintezės metu buvo kaitinamas tik substratas, leidžiant per jį elektros srovę. Taip galima lengvai reguliuoti ir keisti proceso temperatūrą. Inertinė aplinka nenaudota, procesas vykdytas atviroje laboratorijos aplinkoje. Gautų struktūrų skersmuo kontroliuojamas keičiant proceso parametrus.

Raktažodžiai: nanovamzdelis, nanopluoštas, cheminis garų nusodinimas

Симас Рачкаускас

СИНТЕЗ И ПРИМЕНЕНИЕ УГЛЕРОДНЫХ НАНОТРУБОК В ЭНЕРГЕТИКЕ

Резюме

Углеродные нанотрубки благодаря своим уникальным свойствам (по сравнению с используемыми в настоящее время материалами) перспективны для применения во многих отраслях промышленности и в энергетике. В данной работе описан метод синтеза углеродных нанотрубок на электропроводном субстрате, применяемый одновременно с химическим каталитическим методом осаждения пара. При синтезе углеродных нанотрубок нагревался только субстрат. Это позволяет легко регулировать температуру. Процесс осуществлялся в открытом лабораторном воздухе без использования инертной среды. Диаметр полученных структур контролируется изменением параметров процесса.

Ключевые слова: нанотрубки, нанопучок, химическое осаждение пара