Petroleum and Coal

Article Open Access

COAL PYROLYSIS PRODUCTS UTILISATION FOR SYNTHESIS OF CARBON NANOTUBES

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Received February 3, 2019; Accepted April 3, 2019

Abstract

Coal pyrolysis products are to be a good substitute for existing carbon sources. They are applied in carbon nanotubes synthesis in the role of the raw materials due to their abundance and cheapness. This publication reveals the possibility of using coal pyrolysis products to produce various carbon nanomaterials such as carbon nanotubes and carbon whiskers via the plasma arc method. The obtained carbon nanomaterials have been investigated by means of SEM and TEM. As the global recent approach to the application problem for carbon nanotubes derived from coal pyrolysis products is in their use as the anode material in lithium-ion batteries, the currently reported studies has targeted this problem. They have evidenced that the carbon nanotubes vs. conventional anode materials can increase the reversible capacity, the rate capability, and improve cyclability.

Keywords: *Carbon nanomaterials; Carbon nanotubes; Plasma-arc method; Coal pyrolysis products; Lithium-ion battery.*

1. Introduction

Nanotechnology is a rapidly growing industry of a global economy value, it includes the development and production of nanoscale engineering particles, fibres and coatings, generally often called nanomaterials. The nanomaterials belong to the type of those materials, which have at least one dimension less than 100 nanometers. In particular, for the particles, it is the size characteristics that is the principle one to attribute a particle to the class of nanomaterials and to name it as a nanoparticle. With their unique properties, nanomaterials are used for the industrial and the consumer applications. Their various types have found their place in a multitude of sectors: agriculture, energy, aerospace, cosmetics, food, medicine, construction, transport, electronics, etc. Most of the nanomaterials, promised for the production in large volumes or for significant volumes on the nanomarket of the nearest future, will consist specifically of the following main materials: soot in the amount of 9.6 million tons, silicon dioxide (amorphous and crystalline) - 1.5 million tons, aluminium oxide - 200 000 tons, barium titanate - 15 000 tons, titanium dioxide - 10 000 tons, cerium oxide - 10 000 tons, zinc oxide - 8 000 tons, carbon nanotubes and carbon nanofibers - 100-3000 tons and silver nanoparticles - 20 tons [1].

The precursors for synthesis can play a pivotal role for the viability of nanotechnology. Most conventional methods use expensive carbon materials, for instance, graphite and hydrocarbons (methane, acetylene, etc.). Coal and its pyrolysis products have a great potential as a substitute for all the named, as shown in the review article [2]. This review article reveals the recent developments in the production of a large number of carbon-based nanomaterials from different types of coal (lignite, bituminous, anthracite) with the purpose to apply them as the synthesis precursors and to outlines their potential applications in the energy engineering, the environmental spheres and the biomedicine. Moreover, the thereof publication highlights the results of the coal pyrolysis products application, namely, those with coal tar to obtain quantum dots via the chemical oxidation method.

Generally, among the synthesis approaches, the plasma-arc method has shown advantages in the mass production of high-quality carbon-based nanomaterials such as single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs) [3], double-walled carbon nanotubes [4], branched carbon nanotubes [5], bamboo shaped carbon tubes [6], graphene [7], carbon nanofibers [8], and carbon dots [9].

One of the instances how a plasma-arc method can serve with a conventional carbon precursor for nanomaterials obtaining has been shown in the paper [10]. It reports on obtaining carbon nanomaterials, including fullerene, graphene and nanorods from the inside of the chamber using different gaseous atmospheres, namely, argon, nitrogen and hydrogen at a constant electric current. They also write concerning both anode and cathode, which were the graphite rods with the diameter of 10 mm and the purity of 99.999%.

The feasibility to obtain carbon nanomaterials from coal was first demonstrated by the synthesis of C_{60} and C_{70} [11]. It is important to note here that coal has limitations in its application, since it is not possible to obtain a conductive material directly from coal and to enjoy the characteristics suitable for electrodes. Therefore, all works related to the nanomaterials production include the step of coal carbonisation with the objective to prepare semi-coke or coke. Further, the electrode preparation is carried out in the temperature range of 400-500°C from non-caking coal (for example, anthracite) or, alternatively, semi-coke can be manufactured from the mixture of coal and binder (for instance, pitch or coal tar) or from a caking coal without any additives. Then, the carbonisation process is carried out and it takes several hours in a stream of an inert gas at the temperatures of 1000-1200°C to obtain the conductive electrode. In some cases, they apply a hollow graphite high purity anode filled in certain techniques with powders of coal, or carbon black, or coal plus catalyst [5]. The coal pyrolysis products are usually used as a binder in the preparation of the anodes for further use in the arc discharge.

The report by Iijima and Ichihashi [12] was the first to demonstrate the feasible for the fabrication of SWCNTs in catalytic arc synthesis with graphite electrodes in the helium atmosphere. Their anode had a cavity, which was filled with a catalyst (Fe, Co, Ni). In order to generate the arc on the electrodes, the current of 200 A was supplied with the voltage of 20 V. As a result of the arc synthesis, SWCNTs with the diameters in the range of 0.7-1.65 nm were obtained.

As the another instance can serve Williams *et al.* [13] who used bituminous coal with a carbon content of 73.25%, subjected to hot pressing along with the binder. Further, the anodes obtained were subjected to carbonisation in the stream of N_2 at 1200°C. The resulting electrodes were characterised with the diameter of 8 mm, the length of 75 mm and the electrical resistance of 1 Ohm. The graphite was used as the cathode. The arc was formed at the current of 100 A and the voltage of 30 V in an atmosphere of helium at the pressure of 66 kPa. These researchers concluded that from the web-like material, the output of SWCNTs was higher than that of a more dense material from the walls of the chamber.

Additionally, Qiu *et al.* [4] conducted the studies with one of the types of Chinese anthracite. Firstly, the samples of coal were crushed and were screened to the value of less than 150 μm. Secondly, the carbon powder was mixed with Fe catalyst (less than 200 μm) and binder (coal tar) in the ratio of 3:1:1 by weight. Finally, the obtained mixture was subjected to the pressure and the subsequent carbonisation at the temperature of 800°C for two hours to form carbon rods. Obtained after the synthesis, the double-walled carbon nanotubes had the outer diameters of 1.0-5.0 nm and the interlayer spacing in the walls of nanotubes about 0.41 nm.

Recently, Li *et al.* [14] reported on the synthesis of bamboo-structure carbon nanotubes from Bitumite by arc discharge in the presence of a Ni-Sm_2O_3 catalyst. The results showed that the nanotubes obtained had a surface area of 23 m^2g^{-1} and consisted of empty compartments that were separated at a distance of 50-100 nm with graphite layers.

The coke utilisation as a carbon precursor is much less commonly used to fabricate carbon nanotubes. However, Mathur *et al.* [15] made the research with the mixture of graphite, coke, coal tar pitch and catalyst Ni+Co (8.6 % by weight) and obtained sufficiently long and flexible SWCNTs and MWCNTs.

In addition, Pang *et al.* [16] described the production of fullerenes from the laboratory coke and the industrial coke. In this study, using the laboratory coke, the maximum yield of fullerene structures was obtained as much as 8.6 % compared to 3.3 % from the industrial coke.

The carbon nanotubes prepared from coal or the products of its pyrolysis are generally equal by their characteristics to those carbon nanotubes, which are produced by means of the conventional approaches and raw materials. One of the advanced carbon nanotubes applications that has recently gained momentum is their use in the role of an anode material for lithium-ion batteries [17-19]. Indeed, some of the most interesting innovations at improving lithium-ion cell anodes have come from the attempts to combine carbon nanotubes with various deposits. It is reported that carbon nanotubes are characterized by high conductivity of 10^6 S/m and 10^5 S/m for SWCNTs and MWCNTs, respectively, and high tensile strength up to 60 GPa. For instance, SWCNTs can have reversible capacities from 300 $mAhg^{-1}$ to 600 $mAhg^{-1}$. This means SWCNTs capacity can be significantly higher than the capacity of graphite (320 $mAhg^{-1}$), a widely used battery electrode material. Furthermore, mechanical and chemical treatments to the SWCNTs can further increase the reversible capacities up to 1000 $mAhg^{-1}$ [20].

Eventually, it can be evidenced that the carbon nanotubes utilisation as the anode material for lithium-ion batteries is a promising prospect to improve energy storage.

2. Experimental

In order to obtain carbon nanomaterials in the arc discharge, the anodes have been prepared using coal pyrolysis products. For this purpose, pitch coke, coal tar, pitch and NiO (II)-Fe catalyst were pressed at the pressure of 69 kPa in the matrix. The resulting rods were placed in the oven and were heated with the step of 10°C/min up to 500°C. After reaching the required temperature, the heat treatment was further performed for 1 hour. Then the electrodes were carbonised up to 900°C. After reaching the final temperature, the anode was subjected to further heat treatment for 6 hours.

For the production of carbon nanomaterials, a plasma arc reactor was used and it was operated in the following way. Two electrodes, the anode and the cathode, placed in the plasma arc reactor, were connected to an external energy source of 80-90 A DC and the voltage of 20-25 V. When the distance between the electrodes reached 1-2 mm, the arc was formed in the argon atmosphere under the pressure of 69 kPa. The apparatus walls cooling was carried out through the circulation of water through the pipes. The durations of the experiments in the set were approximately 20-30 minutes, resulting in soot on the chamber walls, as well as the solid deposit on the cathode, and the carbon "web" was also formed.

The obtained carbon nanotubes were examined by a scanning electron microscope (Jeol JSM 840) and by a transmission electron microscope (TEM 125K), equipped with a digital output system for the image of SEO-SCAN.

3. Result and discussion

As a result of arcing evaporation for the carbon black, the carbon "web" and the carbon deposit have been obtained. The examination of the carbon black has revealed the presence of C_{60} and C_{70}. Subsequently, the samples of carbon "web" were subjected to burning soot and acid wash (HCl). Further, the carbon nanotubes have been found both in the treated carbon "web" and in the treated carbon deposit.

The developed composition was worked to shape the anodes and it has produced the SWCNTs with the diameters ranging within 35-40 nm and lengths of 2.1-2.3 μm (refer to Fig. 1 a, b).

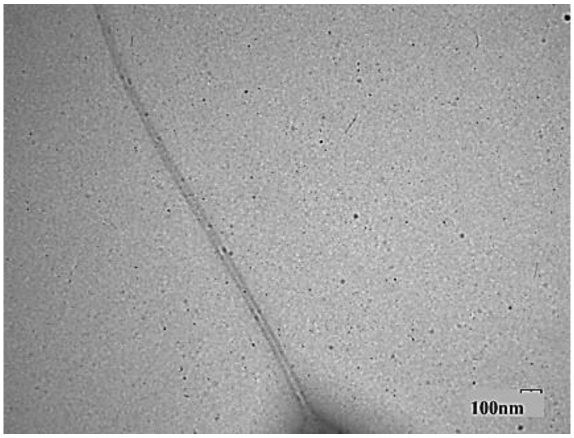

Figure 1a. TEM images of SWCNTs (x10000)

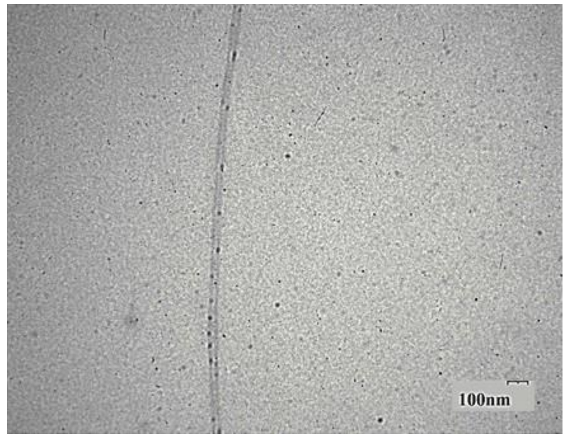

Fig. 1b.

Fig. 2 shows the SWCNTs obtained by the electric arc method. Their lengths are within 3.4-3.5 μm while their diameters are 15 nm on average.

The TEM image evidences that the obtained MWCNTs consist of several concentric cylindrical layers of graphene (refer to Fig. 3): the length of 345-504 nm, the outer diameters of 28-50 nm and the inner diameters of 6.2-8.5 nm. For these MWCNTs with a rather rigid structure, the greater tensile strength is inherent.

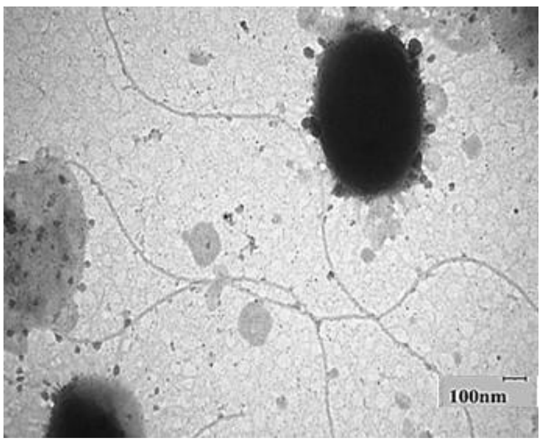

Figure 2. TEM image of SWCNTs (x10000)

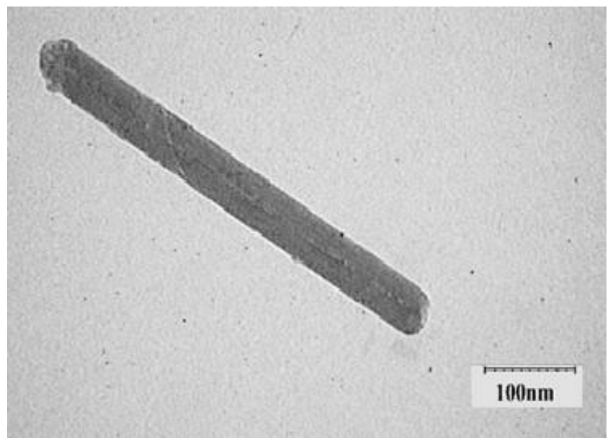

Figure 3. TEM image of MWCNTs (x40000)

In the arc discharge, whiskers have been also obtained (Fig. 4) and selected from the carbon "web" as shiny, rather rigid threads.

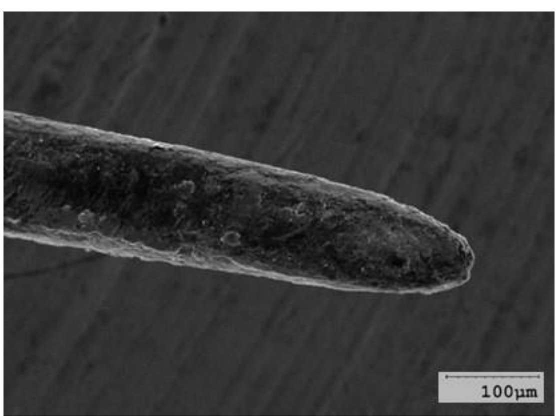

Figure 4. SEM image of carbon whiskers (x200)

The lengths of some whiskers reach 12 mm, and the diameters are about 135-200 μm. By zooming x200, it can be seen that the structure of whiskers is formed from a continuously twisted carbon structure in the form of a scroll.

The resulting carbon nanotubes with the above mentioned characteristics can increase the specific power of lithium-ion batteries to 187.4 mAh/g at a charge-discharge rate of 50 mA/g and good cyclability, they can also enhance the Coulomb efficiency up to 101.9% after 50 cycles, as shown in the work [21].

4. Conclusions

Coal pyrolysis products are a unique source of raw materials for obtaining various types of carbon nanomaterials, for example, carbon nanoparticles, quantum dots, graphene, graphene oxides, SWCNTs, MWCNTs and other types of nanotubes. The results of the reported research make it possible to conclude that for the production of carbon nanomaterials in electric arc synthesis it is possible to use the anodes made from coal pyrolysis products instead of expensive conventional materials. This has the potential to reduce the cost of the final product and to expand the possibilities of practical application of various coal processing products.

Carbon nanotubes derived from coal pyrolysis products have excellent prospects for being used in lithium-ion batteries as anode material. The carbon nanotubes utilisation in lithium-ion batteries allows increasing the reversible capacity, increasing the rate capability, and improving cyclability. Eventually, the carbon nanotubes can greatly enhance the lithium storage capacity of the composites electrode as a surface template and a conductive frame with the high specific capacity.

Acknowledgments

The publication is produced within the framework of the project entitled "The Development of Techniques to Apply the Carbon Materials Produced from Renewable Raw Materials in the Metallurgy", 0117U003919. The author would like to acknowledge Dr. Volodymyr Shmalko for his kind support in carrying out this work.

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