Production and Characterization of MWCNTs Produced by Non-Stationary Current Regimes in Molten LiCl

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Abstract. This article presents production and characterizations of MWCNTs produced by non-stationary current regimes into lithium molten chloride. In order to improve the process of MWCNTs production, instead of applying a constant cathode potential, the method of reversing the potential was applied. It should be mentioned that during the process of electrolysis reduced lithium intercalate at graphite surface and generates a high mechanical stress that causes exfoliation of the graphite cathode. This phenomenon enables electrochemical synthesis of MWCNTs to be possible. The measurements were performed in temperature interval from 700 to 800°C. Several techniques were employed for characterization, i.e. electron microscopy (SEM and TEM), Raman spectroscopy thermo gravimetric and differential thermal analysis (TGA and DTA). SEM and TEM images show that nanotubes are mostly of curved shape with length of 1÷20 μm and diameter of 20÷40 nm. Raman peaks indicate that the crystal lenity of produced nanotubes is rather low. The obtained results suggest that formed product contains of up to 80% MWCNTs, the rest being non-reacted graphite and fullerenes. DTA curves show that combustion process of the nanotubes takes place in two stages, i.e. at 450°C and 720°C. At the lower temperature combustion of MWCNTs occurs, while at higher one fullerenes and non-reacted graphite particles burn.

Introduction

Carbon nanotubes are micro scale length grapheme tubes, with end caps' analogous to semi-fullerenes. Single walled nanotubes (SWCNTs) consist of one graphitic layer and 1-2 nm in diameter. They often aggregate together in bundles of several tens of nanotubes. Multi-walled nanotubes (MWCNTs) consist of two or more graphitic layers, with interlayer spacing of 0.34 nm, comparable to that of graphite. Generally, they have diameters of 2-20 nm [1], although those made by molten salt electrolysis have diameters of 10-50 nm and 100 nm to 20 ηm in length.

Because of their novel electrical, mechanical and chemical properties CNTs are a very promising material. Many applications have been proposed for carbon nanotubes (CNTs)and CNT composites. Their chemical stability, high thermal conductivity and high strength are beneficial properties. They are ideal for field emitters due to their small diameters and high aspect ratio. Furthermore, CNTs have a great potential to be used as fillers in polymer composites replacing carbon fibers and carbon blacks. Several applications for CNTs have been suggested in energy production and storage [2- 5]. The opportunities of the application of these novel materials, first discovered by Lijima [6], are almost infinite with new application being reported every day.

CNTs are produced by various methods [7, 8]. At the present time, mainly they are produced by evaporation of pure carbon by using strong energetic sources (electric arc or laser) or by catalytic decomposition of hydrocarbons.

The use of CNTs requires a production method that combines growth control with low costs and scalability. The method we proposed recently [9-14] based on electrolysis of molten salts, is considered as a more advantageous and economical method when compared with arc-discharge,

CVD and laser ablation methods due to the lower cost of energy, the set-up simplicity required and the large scale production of CNTs. Following the above idea, the aims of this research work was studding of electrolytic production of MWCNTs by reversing potential method and its physical characterization.

Experimental

MWCNT's were produced in alumina crucible with a volume of 150 cm3, as the container of the molten salt electrolyte. The commercial graphite rods (d = 6.5 mm), type EC4 (1.75 g/cm^2) and EC17 (1.85g/cm^2) were used as an cathode material. Molten LiCl was used as the electrolyte.
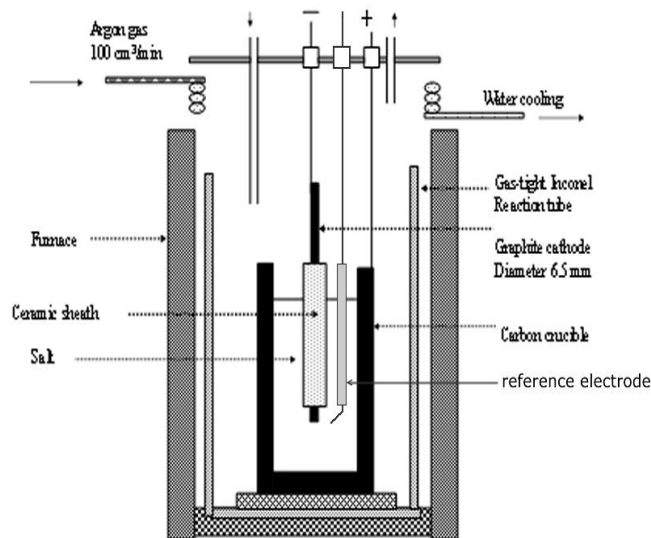

Fig. 1 Schematic of experimental set-up used for the production of MWCNTs

The cell was used inside a sealable Inconel tube reactor with a water-cooled jacket and heated by a vertical 1600 ^{o}C Lenton furnace. The salt was always thermally pre-dried in an argon atmosphere at 250 ^{o}C for at least 2 h and was then melted in an argon atmosphere. After the each experiment, the cathode was removed and the electrolyte was left to solidify overnight. Typically, the solidified salt was then dissolved in distilled water with the aid of mechanic stirring, and left for the solvents to phase-separate. Properties of the graphite materials used as the cathode in the electrolysis experiments are shown in Table 1.

The experiments conducted under reversing potential method are presented in Table 1. The data presented in the table 1, show that only varied parameter during the electrolyses were the values of the cathode over potential. It should be noticed also that the over potential was reversed between the electrodes manually.

Table 1. Conditions of experiments performed with reversing potential method.

NO	SALT	TEMP. [^{o}C]	CATHODE POTENTIAL [V]	TIME OF PULSE [SEC]	GRAPHITE
1	LiCl	780	-2.0	60	EC4
2	LiCl	780	-2.5	60	EC4
3	LiCl	780	-3.0	60	EC4
4	LiCl	780	-2.0	60	EC17
5	LiCl	780	-2.5	60	EC17
6	LiCl	780	-3.0	60	EC17

The samples were inspected by electron microscopy, using JEOL 6340F, TGA/DTA analysis using Perkin Elmer thermogravimetric/differential thermal analyzer in temperature range of 0 to 1200 °C with heating rate of 10 °C·min^{-1}. Structural characteristics were studied by means of Raman Spectroscopy (Renishaw Ramascope 1000).

Result and Discussion

The electrochemical route offers possibility for accurate control of various parameters, such as applied voltage, current density, temperature and morphology of starting material. Thus, the yield and quality of CNTs could be improved. This study is a continuation of the previous our work [9, 11].

   Reversing Potential Method. The main goal of this study was to compare the result obtained by constant potential method [9] and assess the influence of reversing over potential and the type of graphite material on the final, possibly CNTs containing product. Furthermore, the second goal of this study was the improvement of the process of CNT production. Figs. 2-4 shows the dependence of the current as a function of time at a value of potential –2.0, -2.5, and –3.0 V reversed manually between the working and contra electrode.
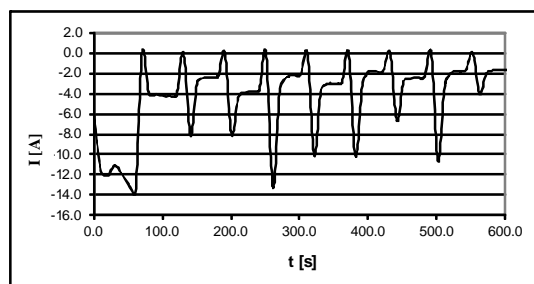

Fig. 2 Dependence of current as a function   Fig. 3. Dependance of current as a function of
   of applied time at reversing potential –2.0 V.   applied time at reversing potential of -2.5 V.

   It should be notice that in all conducted experiments the time of switching of the electrode polarity and the time of duration of the electrolysis were constant. Analyzing the curves presented on Figs. 2-4 we can see that almost each electrode potential change cause appearance of higher current peaks.

   Fig. 5 shows SEM images of the final products obtained by reversing potential electrolysis. The value of the potential, reversed manually between the electrodes was – 2.5 V, which was the optimum potential found in our previous investigation applying constant cathode potential. The morphologies are very similar to those obtained by constant cathode potential. Also, it should be notice that SWCNTS were again not found in the material produced by reversing potential. Furthermore, Fig. 6 show the material produced by reversing potential method using the commercial graphite EC17 as a cathode material.
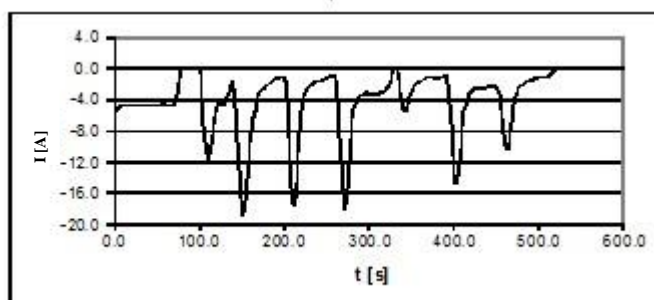

Fig. 4 Dependence of current as a function of applied time at reversing potential –3.0 V.

The nano-tubes observed by SEM are curved and multiwall, but shorter in the length than previous ones produced by constant cathode potential. The size of nanotubes varied, and ranged between 5 and 10 µm in length and 20–50 nm in diameter. The images show that the sample contains a fairly large amount of MWCNTs, more than 70%, Fig. 5.

The morphologies shown on those images are completely different from the morphology of the material produced with graphite type EC4. There are no CNTs or only very small quantities. The structure of carbon particles has the shape of small balls, sheets and some of them are MWCNTs. Finally, this result reveals that commercial graphite type EC17 is not proper material for this s
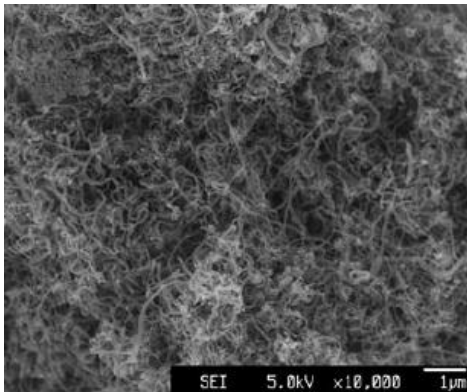

Fig. 5. SEM image of CNTs produced with reversing current method in molten LiCl at cathodic potential, η = - 2.5 V. Graphite EC4.

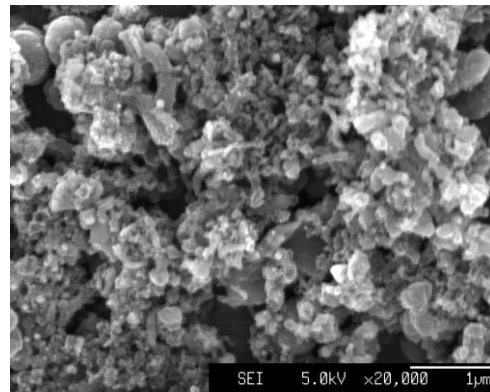Fig. 6. SEM image of CNTs produced with reversing current method in molten LiCl at cathodic potential, η = - 2.5 V. Graphite EC17.

Thermogravimetric Analysis and Raman Spectroscopy. Shown in Figure 7 are TGA/DTA thermograms of the carbon nanotubes produced by molten salt electrolysis (Fig. 7 a) and commercial graphite EC4 (Fig. 7 b) which was used as a cathode. The analyzed carbonaceous materials were heated under oxygen flow whereat they oxidize at different temperatures. DTA curves directly reflect variation in the weight with temperature, thus more attention we will turn on the DTA curves for comparison of the analyzed materials. DTA curve for commercial graphite EC4 was shows two peaks at about 500 $^\circ$C and 950 $^\circ$C (Fig. 7 b). This means that the oxidation process of the graphite occurs in two stages. The corresponding DTA curve for produced carbon nanotubes indicates that the process of thermal oxidation occurs also in two stages, the first one bellow 465°C and the second one at 720 $^\circ$C (Fig. 7 a). The curve indicates that probably MWCNTs oxidize at the temperature below 465 $^\circ$C, because the first peak can be attributed to the oxidation of the amorphous carbon, and the second peak at 720 $^\circ$C correspond to the temperature of oxidation of carbon fullerenes and unreacted graphite particles. Lower oxidation temperatures registered for the obtained MWCNT (around 400 $^\circ$C) indicate that some defects and derivatization moieties are present in the nanotubes walls that can cause the lower thermal stability.

(a)   (b)
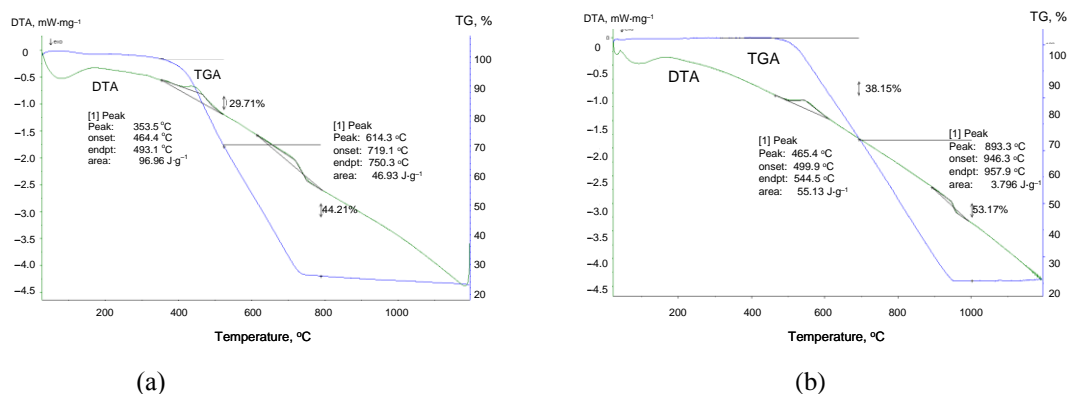
Fig. 7. TGA/DTA thermogram of the CNTs produced by electrolysis at a non-stationary regime

Also, less thermal stability suggests that the produced carbon nanotubes samples have smaller diameters. A smaller diameter implies a high degree of curvature which means increased contact with the air and subsequently a higher reactivity toward oxygen. This was observed also for C_{60} [15].

The crystalline structure of the studied material was analysed by Raman spectroscopy. Raman spectrum of the studied material is shown in Figure 8. This spectrum is characteristic for multiwall carbon nanotubes [10]. It consists of two pronounced peaks characteristic for carbonaceous materials: D peak at position near 1345 cm^{-1} attributed to disorders in the crystals and G peak near 1575 cm^{-1} attributed to in-plane vibration of the C-C bonds.
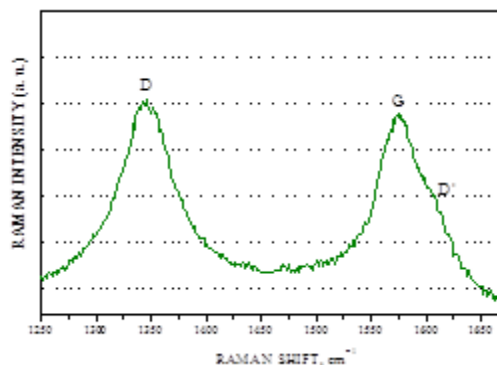

Fig. 8. Raman spectra of the CNTs produced by electrolysis at a non-stationary regime

The pick D indicates disordered carbon atoms referred to defects as pentagons and heptagons in graphite, edges of the graphite crystal and amorphous carbonaceous products [16, 17]. The peak G is characteristic for highly oriented graphite [18]. On the right side of G-line a no well pronounced shoulder peak appears at the position of near 1610 cm−1 and denotes as D'-peak. The appearance of D'-peak points out that these carbon nanotubes are multiwall [10]. The ratio of intensities of the D and G maximums (ID and IG) gives an indication of the crystallinity of the studied material.

The lower value of I_D/I_G points out on higher crystallinity, while the higher ratio suggests on the higher disorder within the crystalline structure [19]. It was calculated that $I_D/I_G = 1.05$ for the produced MWCNTs. This indicates the extent of defects and impurities in the produced material.

Summary

MWCNTs were produced by non-stationary current regimes into lithium molten chloride using the method of reversing the potential. The obtained results suggest that formed product contains of up to 80% MWCNTs, the rest being non-reacted graphite and fullerenes. DTA curves show that combustion process of the nanotubes takes place in two stages, i.e. at 450°C and 720°C. At the lower temperature combustion of MWCNTs occurs, while at higher one fullerenes and non-reacted graphite particles burn.

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