STUDY OF MOLTEN Li₂CO₃ ELECTROLYSIS AS A METHOD FOR PRODUCTION OF CARBON NANOTUBES

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The production of carbon nanotubes (CNTs) by electrolysis in molten Li_2CO_3 was investigated by studying the effect of the electrolyte, temperature of the electrolyte and cathodic overpotential. Cyclic voltametry clearly shows that instead of the expected Li discharge of the cathode as a first reaction, some early electrochemical reaction starts at a potential of –0.1 V, as a result of which, instead of the expected process of intercalation into the graphite lattice and CNTs formation, deposition of carbon occurs with the graphite cathode acting as the substrate. The carbon deposit obtained during the process of electrolysis together with the solidified salt, after dissolving in water, filtering and drying, was inspected with scanning electron microscopy (SEM). The results show that, among the observed structures and impurities, there are no CNTs. The morphology of the product is different from others previously observed, with a shape like sheets of flowers, and very small nano-balls. The impurities are metal particles from the salt and the impurities originating from the salt. For better understanding and confirmation of these result, cyclic voltametry and electrolytic deposition of carbon on a molybdenum electrode was also investigated. Molten LiCl was used as a base electrolyte with adding of 1, 5 and 10 % of Li_2CO_3. SEM observations and cyclic voltammograms confirm that under those conditions a process of carbon deposition occurs.

Key words: carbon nanotubes; intercalation; graphite; molten salts; electrolysis; SEM

СТУДИЈА ЗА ЕЛЕКТРОЛИЗА НА РАСТОП НА Li₂CO₃ КАКО МЕТОД ЗА ДОБИВАЊЕ НА ЈАГЛЕРОДНИ НАНОЦЕВЧИЊА

Испитувано е влијанието на електролитот, температурата на електролитот и катодниот пренапон при добивање на јаглеродни наноцевчиња (CNTs) по пат на електролиза во растопен Li_2CO_3. Цикличната волтаметрија јасно укажува дека наместо очекуваниот процес на создавање на Li врз катодата како прва реакција, уште порано доаѓа до одвивање на некои електрохемиски реакции веќе при потенцијал од –0,1 V. Како резултат на ова, наместо очекуваниот процес на интеркалација во графитната решетка и создавање на јаглеродни наноцевчиња (CNTs), доаѓа до таложење на јаглерод, при што графитната катода се однесува како супстрат. Јаглеродниот депозит што е добиен за време на процесот на електролиза заедно со стврдната сол, по растворањето во вода, филтрирање и сушење, е набљудуван со скенинг-електронската микроскопија (SEM). Резултатите покажуваат дека меѓу испитуваните структури и нечистотии не се забележува постоење на јаглеродни наноцевчиња (CNTs). Морфологијата на добиениот депозит се разликува од претходната, со најчесто застапени облици на листови или цветови, и ретко со појава на многу ситни нанотопчиња. Нечистотиите се всушност метални честички од солта и нечистотии кои потекнуваат од солта. За подобро разбирање и објаснување на добиените и погоре изложени резултати беа разгледани и цикличната волтаметрија и елетродепозицијата на јаглерод врз молибденска електрода. За овие цели се користеше растоп на LiCl како основен електролит со додадени 1, 5 и 10 % од Li_2CO_3. SEM и цикличните волтамограми потврдуваат дека во вакви услови доаѓа до одвивање на процесот на депозиција на јаглерод.

Клучни зборови: јаглеродни наноцевчиња; интеркалација; графит; растоп од соли; електролиза; SEM

INTRODUCTION

Carbon nanotubes are microscale length graphene tubes, with end 'caps' analogous to semifullerenes. Single walled nanotubes (SWCNTs) consist of one graphitic layer and are 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 μm in length.

Because of their novel electrical, mechanical and chemical properties CNTs are 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 fibbers and carbon blacks. Several applications for CNTs have been suggested in energy production and storage [2–5]. They also could be used as electrode materials in lithium ion batteries, as an electrode materials in electrochemical capacitors and as individual molecules in components of miniaturized of electronic devices. The opportunities for the application of these novel materials, first discovered by Lijima [6], are almost infinite, with new application being reported every day.

At the present time CNTs are produced by various methods [7, 8]. In 1995, Hsu and co-workers discovered one of the most promising way of producing carbon nanotubes [9, 10]. They electrolyzed molten lithium chloride using graphite electrodes. The cathode eroded during the electrolysis and nanoscale products, including multi-walled nanotubes (MECNTs) were found in the electrolyte. This was the first production route to produce nanotubes in the liquid phase.

Chen *et al.* [11, 12] connected the erosion of the cathode and formation of the products to the intercalation of alkali metals into graphite. This was further extended by Fray [13, 14] who had realized that the cathodic carbon/graphite erosion was similar to that found in the Hall-Heroult cell where alkali metals also intercalate into graphite.

Most scientists in their investigations used current control and, when voltage control was used, results were mainly expressed in terms of current. Dimitrov *et al.* [15], in their recent paper, reported that the constant voltage electrolysis, opposite to the constant current electrolysis, could improve and increase the yield of produced CNTs.

Along the same line of thought, the aim of this research work was to study electrolytic production of CNTs by electrolyses in molten lithium carbonate.

EXPERIMENTAL

The experiments in this study were divided in three groups: 1. Cyclic voltametry study, 2. CNTs production by electrolysis in molten Li_2CO_3, and 3. Electrodeposition of carbon by molten salt electrolysis.

1. The cyclic voltametry experiments were performed using a three-terminal electrochemical cell. The working electrode (WE) was a graphite rod with 6.5 mm diameter, shielded in an alumina tube and connected to a molybdenum wire of 0.5 mm diameter, likewise shielded in an alumina tube. A molybdenum wire was employed as the reference electrode (RE). A carbon crucible (external: 150 mm height and 90 mm diameter; internal: 140 mm height and 70 mm diameter), served as the container for the electrolyte and also as the counter electrode (CE). 1 %, 5 % and 10 % of Li_2CO_3 were added in molten LiCl.

2. The experiments of CNTs production by electrolysis in molten Li_2CO_3 were performed in the some crucible as described above. The crucible served as anode while a graphite rod was inserted into the electrolyte (6.5 mm diameter) to act as a cathode. As a cathode material, commercial graphite was used, EC17, with an average grain size of 0.001 mm and density of 1.9 gcm^{-3}. A 10 mm of the cathode were exposed to the electrolyte to give an initial cathodic surface area of 2.4 and 3 cm^2. In order to prevent electrical contact between the cathode and anode through the metal floating on the surface of the electrolyte, the cathode was shielded in an alumina tube. In these experiments molten Li_2CO_3 was used as electrolyte at 780 and 840 °C (Table 1).

3. The experiments of electrolytic deposition of carbon in molten LiCl + 5% Li_2CO_3 at a temperature of 700 °C were performed in the same crucible as described above. The crucible was served as anode while a molybdenum wire was

inserted into the electrolyte (0.5 mm diameter) to act as cathode. A 20 mm of the cathode was exposed to the electrolyte to give an initial cathodic surface area of 0.5 cm². The cathode was shielded in an alumina tube to prevent electrical contact between the cathode and anode through the metal floating on the surface of the electrolyte. After each experiment, the cathode was removed and washed in water and 1 M HCl.

In all three cases the cell was used inside a sealable Inconel tube reactor with water cooled jacket and heated by a vertical 1600 °C Lenton furnace equipped with a programmable controller (Fig. 1). The salt was always thermally pre-dried in an argon atmosphere inside the Inconel tube at 250 °C for at least 2.5 h and then melted in an argon atmosphere. The electrolysis was controlled by a Farnell LS30-10 autoranging power supply.

The samples extracted from the solidified electrolytes were inspected by electron microscopy, using JEOL 6340F (SEM, 10 kV).
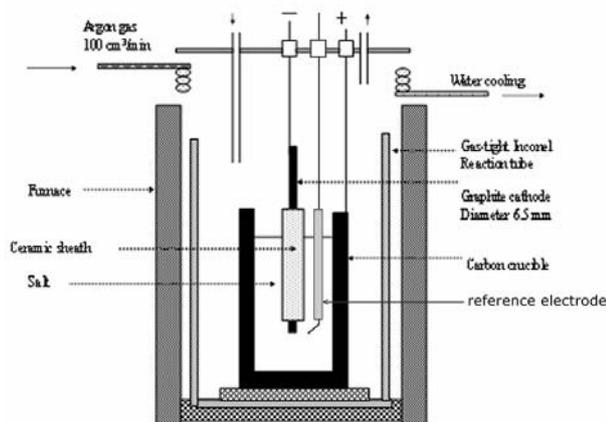
Fig. 1. A schematic diagram of the experimental set-up for molten salt electrolysis [14]

RESULTS AND DISCUSSION

The goal of this study was production of carbon nano-tubes and nano-fibers by passing an electric current through a molten ionic salt between graphite electrodes at a constant electrode potential. In our previous work [15], we have demonstrated electrolytic preparation of CNTs in molten LiCl, using a constant cell voltage. In order to control cathode current density, all experiments in this work were performed under the conditions of constant cathode potential.

Some authors [9, 10] reported that production of CNTs, using molten salts as the electrolyte, is

not possible at a temperature below 500 °C. Thus, in this work, lithium carbonate was selected as an electrolyte because of its higher melting point, 723 °C, and the absence of hydrogen ions.

Cyclic voltametry

At the beginning of this study, in order to have more information about the nature of the reactions occurring on the cathode, the method of cyclic voltametry was used. The polarization curves obtained at a scanning rate of 0.01 and 0.02 V/s in pure molten Li₂CO₃, on a molybdenum wire and a graphite rod working electrode, are shown in Figs. 2 and 3, respectively.
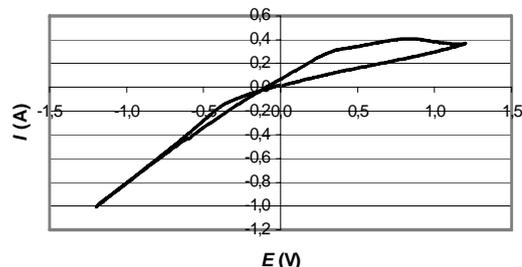
Fig. 2. Cyclic voltamogram for a molybdenum electrode in molten Li₂CO₃ at a potential scanning rate v = 10 mV/s at 840 °C
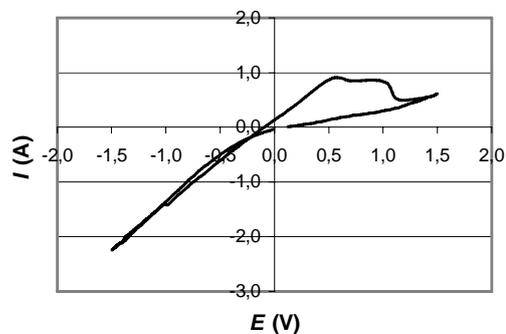
Fig. 3. Cyclic voltamogram for a graphite electrode in molten Li₂CO₃ at a potential scanning rate of v = 20 mV/s at 840 °C

The voltamograms show that discharge of Li at the Mo-electrode occurs at a potential of –0.8 V at 840 °C. When the applied potential is more positive than –0.8 V, the current vs. time plot exhibits the occurrence of some other electrochemical process at the cathode. This means that some early electrochemical reaction starts at a potential of around –0.1 V, probably as a result of carbon discharge at this potential. This preliminary explanation is also supported by the current peaks obtained

when the potential was shifted in a more positive direction. The first peak, at 0.4 V, should be re-oxidation of already reduced carbon, and the second one, at 0.8 V, re-oxidation of reduced lithium.

Furthermore, Fig. 3 shows a curve obtained under the same conditions using the graphite working electrode. The shape of the curve is very similar to the previous one shown in Fig. 2, which suggests that at the graphite electrode the same or similar electrochemical processes occur as on the molybdenum electrode. As it was mentioned before, the first reaction is discharge of carbon and occurs at –0.1 V, while the second reactions is discharge of lithium at –1.0 V. In the oxidation part of the voltamogram, re-oxidation of Li occurs at 0.5 V, and re-oxidation of carbon at 1.0 V. Comparing both experimental curves, it could be concluded that with both the molybdenum and the graphite working electrode similar or identical

processes of reduction and oxidation at potentials of –0.1 and –1.0 V occur.

Electrolysis

The investigation was continued and set of experiments by electrolysis in molten Li_2CO_3 were performed.

The experimental parameters for the electrolyses are summarized in Table 1. The experiments were conducted at different temperature and cathodic potential. In order to make comparisons between the experiments, the other parameters where kept constant at values already known to be optimal. The anode, in all experiments until now, including this one, showed no signs of erosion during any of the electrolyses. Also, it should be noted that only commercial graphite EC17 was used as the electrode material.

T a b l e 1

Experimental condition of electrolysis in molten Li_2CO_3

Exp. No	Salt	Temp. (^{o}C)	Cathodic potential η (V)	Immersion (mm)	Li_2CO_3 (g)	Graphite $D = 6.5$ mm
1	Li_2CO_3	780	–1.5	10	100	EC17
2	Li_2CO_3	780	–2.0	10	100	EC17
3	Li_2CO_3	840	–1.5	10	100	EC17
4	Li_2CO_3	840	–2.0	10	100	EC17

The process of electrolysis was not changed. As previously discussed, the immersed part of the cathodes supposed to corrode and produce carbon material. But at this instance, the process does not occur. Instead of cathode erosion, there is a different process, i.e. carbon deposition that prevails.

Figs. 4 and Fig. 5 show curves, current as a function of time, for different values of cathodic potentials and reaction temperatures. Further, Figs. 6 and 7 show an image of the sample obtained from experiment 2 (Table 1), and its cross section. It is obvious (Fig. 4 and 5), that the imposed electrode potential at the cathode and the applied temperature influence the current passed through the cell. Due to the process of carbon deposition at the cathode, as opposite of the cathode erosion, the current did not decline with time.

The deposit formed at the cathode is shown in Fig. 5. The morphology of the deposit is more

clearly seen on the cross section, Fig. 6. The cross section shows two phases formed at the cathode, a black one and a gray one. The black one is deposited carbon containing impurities of the salt, and the gray one is solidified salt containing carbon impurities. It is also worth noticing that this deposit is formed inside the crucible, during the process of electrolysis at the temperature of 780 ^{o}C.

The carbon deposit produced together with the solidified salt was dissolved in water, filtered, dried and inspected with a scanning electron microscope (Fig. 8 and 9). It was found that, among the observed structures and impurities, there are no CNTs. The obtained product morphology is different from previous those observed previously, with the shape like sheets of flowers, and very small nano-balls. Impurities are metal particles originating from the salt.
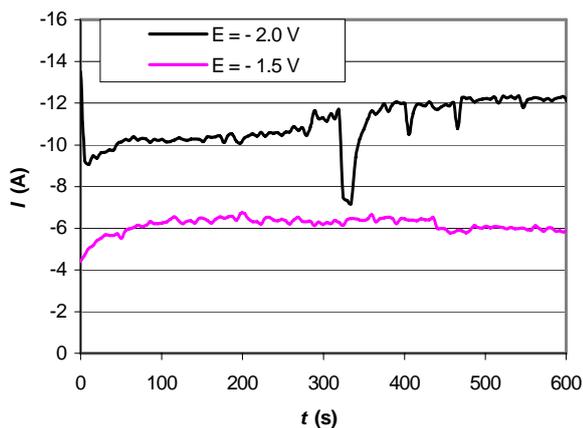
Fig. 4. Current-time plots of electrolysis in molten Li_2CO_3 at 780 °C, under argon using a graphite rod cathode, graphite crucible anode. Applied cathodic potential,
a) $\eta = -2.0$ V, b) $\eta = -1.5$ V
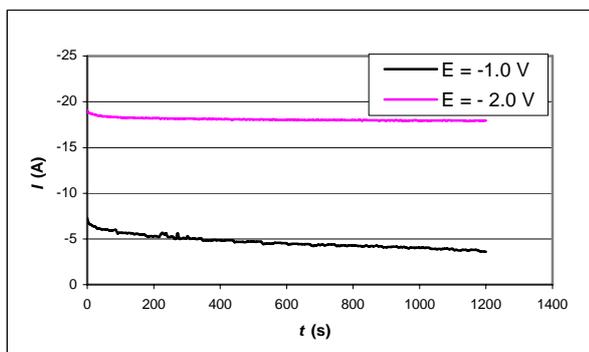
Fig. 5. Current-time plots of electrolysis in molten Li_2CO_3 at 840 °C, under argon using a graphite rod cathode, graphite crucible anode. Applied over-potential,
a) $\eta = -1.0$ V, b) $\eta = -2.0$ V

Fig. 6. Image of carbon deposit produced in molten Li_2CO_3 at cathodic potential, $\eta = -1.5$ V, and temperature of 780 °C. Table 1, exp no. 1

Fig. 7. Cross section of image 6.
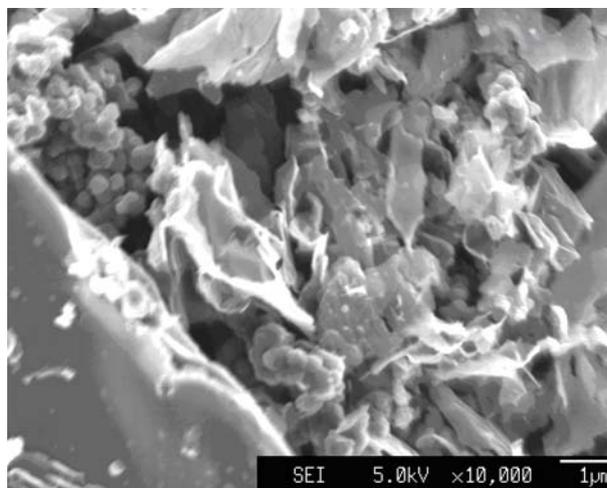
Fig. 8. SEM image of graphite nanoparticles produced in molten Li2CO3 at over-potential, $\eta = -1.0$ V, and temperature of 780 °C. Table 1, exp no. 1
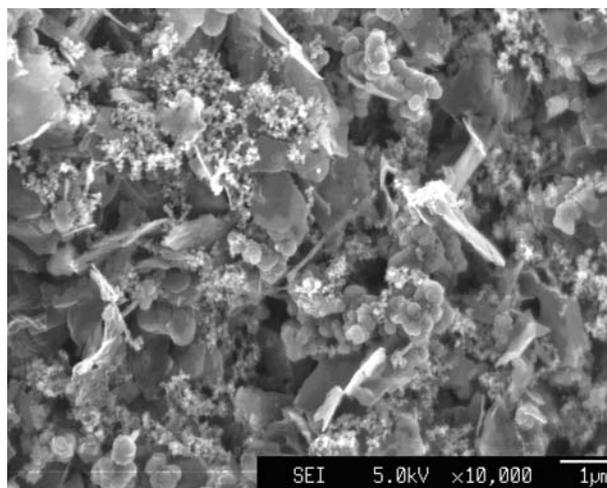
Fig. 9. SEM image of graphite nanoparticles produced in molten Li_2CO_3 at over-potential, $\eta = -1.5$ V, and temperature of 780 °C. Table 1, exp no. 2

It can be concluded that under these conditions, instead of the expected intercalation into the graphite lattice followed by corrosion of the cathode, deposition of carbon occurs with the graphite cathode acting as the substrate. This is the reason why production of CNTs and nano-fibers did not occur under these circumstances.

For better understanding of this phenomenon, an additional cyclic voltametry study was performed. The experiments were performed with LiCl as the base electrolyte with additions of 0, 1, 5 and 10 % of Li_2CO_3 by weight. Figures 10, 11, 12 and 13 show cyclic voltamograms obtained under these conditions, using a scanning rate at 0.1 V/s at the molybdenum wire. It is obvious from Fig. 10 that lithium discharge on the molybdenum electrode occurs at a potential of –1.8 V at 840 °C.

Further, the curves in Figs. 11, 12 and 13, clearly illustrate that addition of carbonate causes marked changes in the experimentally obtained voltamograms. This suggests the occurrence of an early electrochemical reduction process. The process has a cathodic current peak at approximately –0.6 V that is directly proportional to the added concentration of Li_2CO_3.
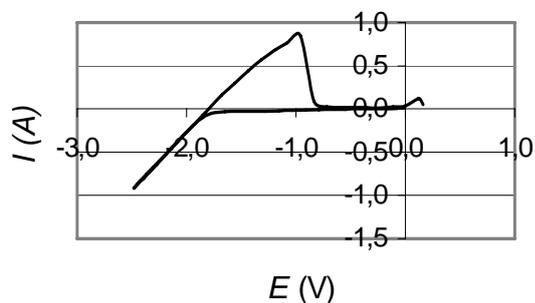
Fig. 10. Cyclic voltamogram for a molibdenum electrode in molten LiCl at a potential scan rate of $v = 100$ mV/s at 700 °C
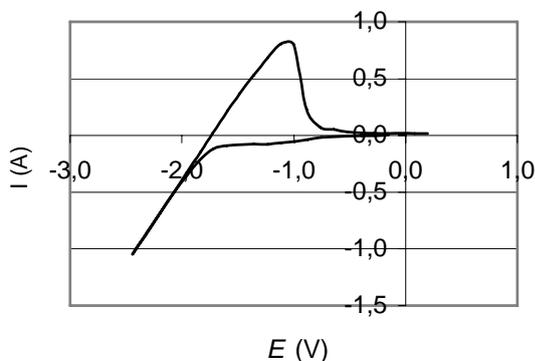
Fig. 11. Cyclic voltamogram for a molibdenum electrode in molten 99% LiCl + 1% Li_2CO_3 at a potential scan rate of $v = 100$ mV/s at 700 °C
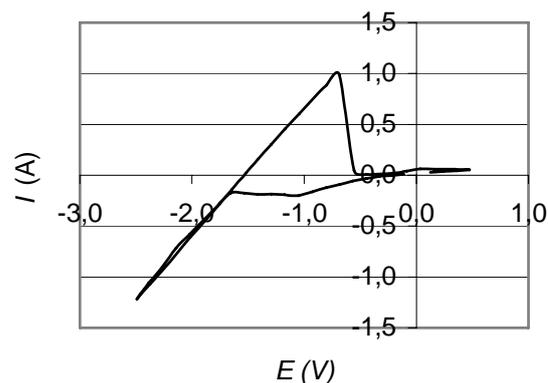
Fig. 12. Cyclic voltamogram for a molibdenum electrode in molten 95% LiCl + 5% Li_2CO_3 at a potential scan rate of $v = 100$ mV/s at 700 °C
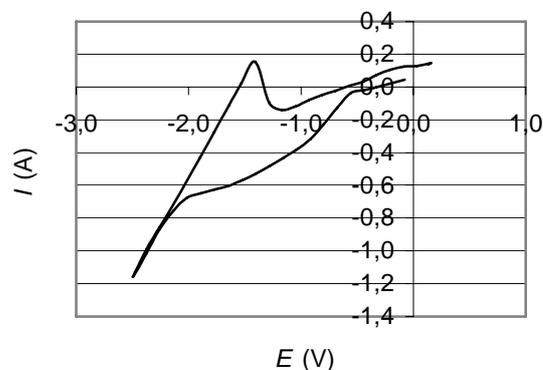
Fig. 13. Cyclic voltamogram for a graphite electrode in molten 90% LiCl + 10% Li_2CO_3 at a potential scan rate of $v = 100$ mV/s at 700 °C

Before discussing a particular reaction mechanism, it is again worth emphasizing that the cyclic voltamograms (Figures 10–13) confirm the same general conclusion that a discharge of carbon is the first electrochemical step that occurs in the process. The proposed electrochemical mechanism [16,17] could be possible, in two steps or in one step, as follows:

In two steps

$$CO_3^{2-} + 2e \rightarrow CO_2^{2-} + O^{2-}$$

$$CO_2^{2-} + 4e \rightarrow C^- + 2O^{2-}$$

In one step

$$CO_3^{2-} + 4e \rightarrow C + 3O^{2-}$$
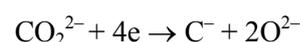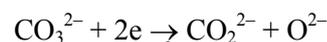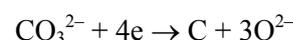
Because of the evidence obtained by cyclic voltametry and suggested mechanism of carbon reduction at the cathode, it could be assumed that lithium carbonate is not a convenient electrolyte

for production of CNTs and nano-fibers by electrolysis. In order to confirm this assumption, additional experiments of the electrolytic deposition of carbon in molten LiCl + 5% Li_2CO_3 at a temperature of 700 °C were performed.

Electrolytic deposition of carbon

The preceding results show that the reduction of CO_3^{2-} ions occurs in a potential range of –0.8 to –1.7 V. In order to confirm the reaction around this potential and to characterize the possible electrolytic carbon deposits, some potentiostatic electrolysis runs were carried out at a potential of –1.3 V and temperature of 700 °C on molybdenum wire

as a cathode. The electrolysis time was limited at 30 and 60 seconds.

The morphology of the obtained deposit, washed with distilled water, is shown in Fig. 14. From SEM images of the carbon deposit it seems that the whole surface of the molybdenum is covered. Fig. 14 also shows that the morphology of the deposit or the film formed at the cathode surface is quite smooth but with surface cracks. The observation shows that after the cooling of the cathode, a thick mixed film of carbon and salt is formed on the surface. To avoid this problem the method of washing and the solution used for it were changed. The next samples were washed with 1M HCl in ultrasonic bath. The results obtained are shown in Fig. 15.
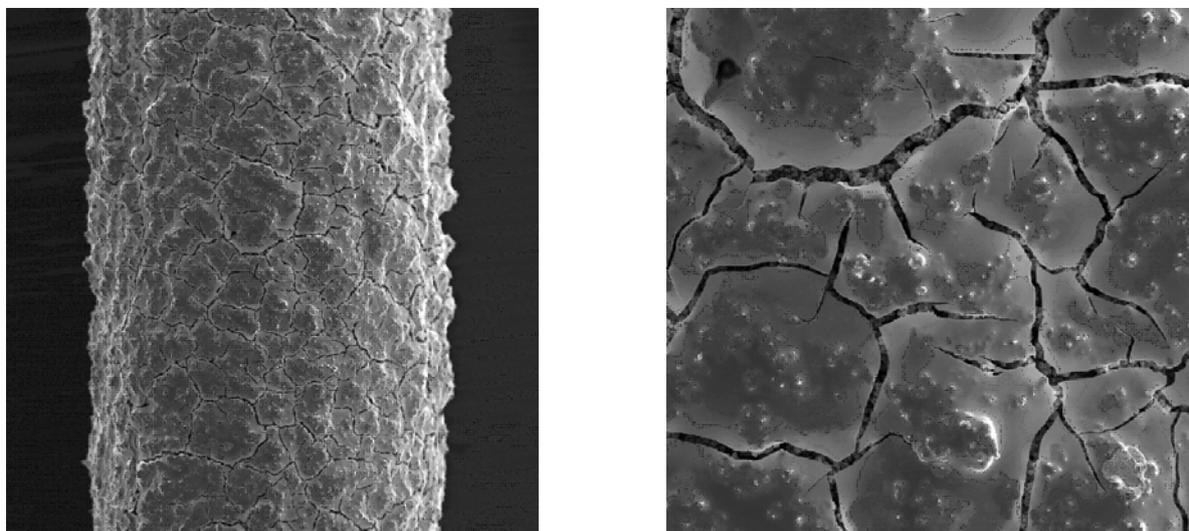
Fig. 14. SEM images of Carbon film obtained on molybdenum wire in electrolyte of LiCl + 5% Li_2CO_3
at temperature of 700 °C. The film is washed with water. Magnification: a) 100× and b) 500×. Time of deposition 30 seconds.
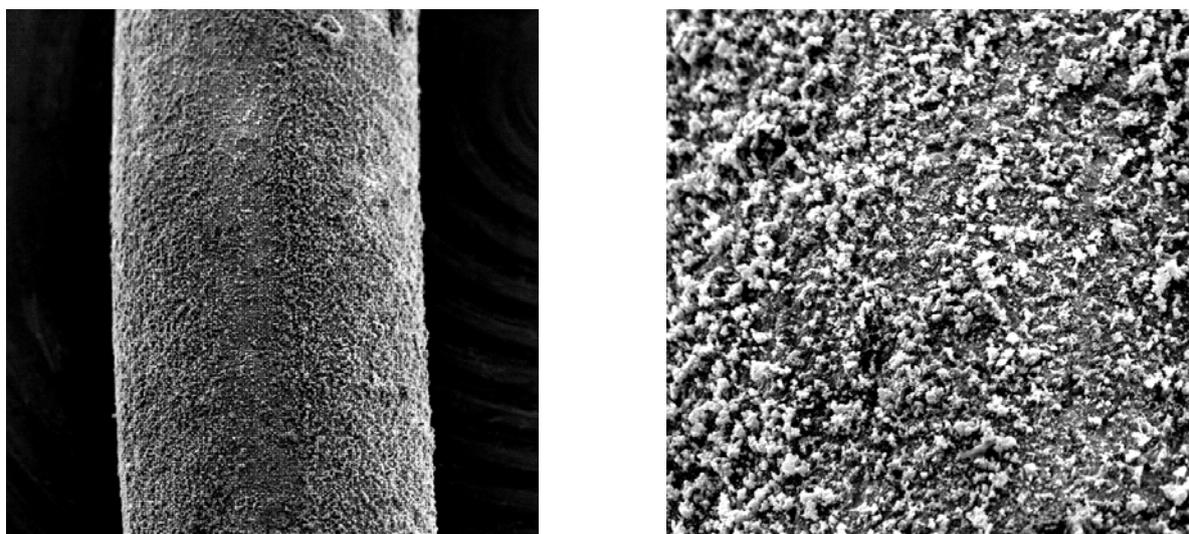
Fig. 15. SEM images of Carbon film obtained on molybdenum wire in electrolyte of LiCl + 5% Li2CO3 at temperature
of 700 °C. The film is washed with 1M HCl. Magnification: a) 100× and b) 500×. Time of deposition 30 seconds.

It is obvious from the SEM that with this method, the salt is successfully removed from the electrode surface and the electrode is covered only with carbon. This confirms that the thin film of salt was formed due to rising of the molybdenum wire from the electrolyte

Fig. 15 shows that the whole surface is covered with carbon deposit but the morphology of the deposit is different than that of the one shown in Fig. 14 (the surface in Fig. 15 looks polycrystalline, and in Fig. 14 it does not). It appears that the differences between the deposits are mainly due to the cooling time after electrolysis and the type of solution used for washing. Finally, with this evidence, it can be once again concluded that the production of CNTs and nano-fibers by electrolysis in molten lithium carbonate as a electrolyte is not convenient.

CONCLUSIONS

In summary, several conclusions can be drawn about the production of CNTs using the molten salt electrolysis. Three major investigations were conducted in this work:

– *Cyclic voltametry study.* Several types of salts were used as the electrolyte, Li_2CO_3, and LiCl as the basic electrolyte with additions of 0, 1, 5 and 10 % of Li_2CO_3 by weight. The results obtained by this study confirm that discharge of carbon is the first electrochemical step that occurs in the process.

– *Production of CNTs by electrolysis:* As a result of above evidence, production of CNTs is impossible under the applied conditions. Reduction and deposition of carbon occur instead of lithium discharge and intercalation into the cathode.

– *Electrolytic deposition of carbon:* The results obtained during this process confirm that production of CNTs and nano-fibers by electrolysis in molten lithium carbonate is impossible under applied conditions. Instead, reduction and deposition of carbon occur at the cathode, and as a result, a thin film of carbon is formed at the molybdenum wire.

The produced material was investigated with SEM. The data obtained by these techniques give sufficient evidence that the observed samples do not contain any CNTs.

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