

RECENT DEVELOPMENT IN ELECTROLYTIC FORMATION OF CARBON NANOTUBES IN MOLTEN SALTS

G. Z. Chen and D. J. Fray

Department of Materials Science and Metallurgy, University of Cambridge,
Pembroke Street, Cambridge CB2 3QZ, UK

(Received 28 december; accepted 12 January)

Abstract

This article reviews the recent research development in the electrolytic production of carbon nano-tubes in molten salts. The experimental procedure and product morphologies of the electrolytic method are described in details. Different hypotheses of the carbon nano-tube formation mechanism in molten salts, particularly its relation with the erosion of the cathode, are compared and discussed. It is anticipated that the electrolytic method can potentially become a cheap and continuous process for the production of curved carbon nano-tubes, carbon sheathed metal nano-wires and other carbon based nano-structures.

Keywords: electrolysis, molten salts, graphite cathode, carbon nano-tubes, mechanism

1. Introduction

A claim made on the web-page [1] of Hyperion Catalysis International Inc. of Cambridge, Massachusetts, indicates that, as early as (or before) 1983, a type of carbon nano-tubes (CNTs) was produced by the catalytic decomposition of hydrocarbon gases, e.g. ethylene [2]. The product of the catalytic process was then called by a different name, carbon fibrils, and the inventor of the process, Howard Tennent of Kennett Square, PA, described the product, in a US patent filed in December 1984 and published in May 1987, as “An essentially cylindrical discrete carbon fibril characterized by a substantially constant diameter between about 3.5 and about 70 nanometers, length greater than about 10^2 times the diameter, an outer region of multiple essentially continuous

layers of ordered carbon atoms and a distinct inner core region, each of the layers and core disposed substantially concentrically about the cylindrical axis of the fibril” [2]. Obviously, this description agrees very well with that of CNTs.

However, until now, the credit of Tennent’s discovery has not been very widely recognized by the scientific community. This is, at least partly, due to the fact that, before 1991, neither Tennent himself nor Hyperion had published any of their works in well known scientific journals or conference proceedings. However, they had filed a number of patents, including the one mentioned above, apparently seeking commercial benefit [3-5].

In 1991, using high resolution TEM, Sumio Iijima of NEC Corp in Tsukuba, Japan observed accidentally some tube-like structures in the carbon soot produced by electric arc during his study on the much smaller carbon structures of fullerenes [6]. He first described these unusual carbon structures as “helical micro-tubules of graphitic carbon” [6]. Seven months later, Pulickel Ajayan and co-workers [7, 8], also of NEC Corp, coined the phrase of “carbon nano-tubes” in their two publications, which immediately excited the world-wide scientific community due to the nano-tube’s unique quasi-molecular structures and remarkable material properties [9].

While it is interesting to note the eight year gap between Tennent’s and Iijima’s discoveries, the fact is that, in addition to the different preparation methods used, the two independent findings were made on two different CNTs: curved and straight, respectively. The outcomes are drastically different. Without linking to any scientific significance, Hyperion aimed to use, possibly in as early as 1983, their curved fibrils as conductive filler in conventional plastics (polymers), but reported little on the fundamental properties of their nano-materials. It was only after Iijima’s report that fundamental research on CNTs started and most reported work was carried out on the straight CNTs produced by electric arc, focusing on the structural, electrical, mechanical and other physicochemical properties. Based on these fundamental works, it was soon realized that curved CNTs such as the Hyperion fibrils had resulted from various defects on the graphitic layers of CNTs. Consequently, curved CNTs were considered to be inferior to their straight counterpart and, to a great degree, attracted much less attention of many researchers. However, recent development in research showed a promising future for using the curved nano-tubes in bulk quantities for not only electron conduction in insulating phases, but also energy conversion and storage [10-13], and catalysis of targeted chemical processes [14]. In particular, it has been demonstrated that supercapacitors based on carbon nano-tubes exhibit unprecedented high capacitance (high pulsed power) and long cycle life [10, 13]. This development is very welcomed by, for example, manufacturers of electric cars that are currently put on hold by the incapability of fuel cells and batteries to deliver sufficiently high acceleration power greater than 1 W/cm^2 (electrolyte membrane) [13]. This development, to the authors’ opinion, is the result of taking the advantage of curved CNTs being rich in surface defects which

allowed the attachment of functional molecular groups to the CNTs. This property of curved CNTs enable a much greater flexibility for chemical modifications of the nanotubes surface to suit various practical applications.

Up till now, various methods have been proposed, however, relatively bulk quantities of CNTs are still mainly obtained by the two methods used by Iijima and Tennent, i.e. electric arc assisted carbon vaporization, and catalytic decomposition of gaseous hydrocarbon at elevated temperatures. Generally speaking, although being able to produce relatively defect free and hence straight CNTs, the electric arc method produces usually contaminated by other nano-carbon materials, particularly nano-particles. On the contrast, the catalytic method is featured by its flexibility in producing either curved CNTs in bulk quantities or aligned arrays standing on an appropriate substrate, both being much purer than the electric arc product. Nonetheless, the production cost of the two methods is far from being acceptable for bulk quantity uses. To the authors' best knowledge, the cheapest catalytic CNTs could be purchased at the price between \$1500 and \$8000/kg [16], but electric arc CNTs are much more expensive. In addition to the high energy input (electric arc method) or use of relatively expensive starting materials (catalytic method), the fact that the products from the two methods come out of the gas phase adds another hurdle to introduce further improvement.

This article reviews a newly developed electrolytic method for the production of CNTs in molten salts. Pioneered by Hsu, Kroto and their co-workers in the UK in mid 1990's [17, 18], the electrolytic method is the first example of CNTs being produced in the condensed phase. While research in the electrolytic method is gathering forces around the world in the past few years [19-33], in particular, it has been shown recently by the authors that the electrolytic method can be scaled up, and has the potential to continuously produce CNTs and other carbon nano-materials [23]. More importantly, the cost for the energy consumption of electrolysis is very low in comparison with that of material consumption, i.e. graphite and molten salt, implying a significant reduction in the cost for the production of CNTs. Also included in this article are a historical view of the electrolytic method, the basic experimental set-up, characteristics of electrolytic CNTs and other carbon nano-materials, electrochemical studies of the process and a comparison of different formation mechanisms. While it is still too early to draw a conclusion about the electrolytic method, the authors believe that, with more research in this area, the future of cheap carbon nano-tubes can be very promising.

2. History of electrolytic formation of carbon nano-tubes

Unlike other areas of CNT research, the total number of published articles on electrolytic CNTs accounts for only a very small fraction of total CNT publications around the world. This is partly due to the fact that the history of electrolytic CNTs only started in 1995 and publications were, up till 1999, mainly from two UK research groups in the

Universities of Sussex and Cambridge. Since 2000, the Sussex group seems to have, at least temporarily, abandoned their program on the electrolytic method, and publications from them have not been seen in the literature. Another possible reason is that although CNTs, molten salt and electrochemistry were not unfamiliar to the scientific community, it may be rare to have the three expertise combined within one research group. The fact that electrolytic CNTs are usually rich in defects (curved) and mixed with other carbon nano-particles when separated from the solidified molten salt might have also discouraged the relevant researchers and industrial users who are usually in favor of straight CNTs. However, against the odds, the Cambridge and a couple of other research groups in Europe continued research on electrolytic CNTs. On the basis of the work of these groups, the authors strongly believe that electrolytic CNTs will become gradually more attractive because of the device and operational simplicity and feasible continuity of the electrolytic method, and hence its potential in reducing the production cost.

When Hsu and co-workers of Sussex University first reported in 1995 their work on producing CNTs in molten salts [17, 18], a condensed phase, it was against the general opinion that CNTs could only be produced in the gas phase as most of the proposed mechanisms for CNT formation include atomized carbon or C_2 species from the gas phase participating in the growth process [6-9]. While Hsu et al. did not, then, propose a mechanism, they pointed out that the carbon source for CNT formation was the high purity carbon cathode, which eroded during electrolysis. The molten salts used in Hsu's work were lithium halides, particularly $LiCl$. In addition, their findings showed the electrolytic products were a mixture of CNTs and a large proportion of carbon nano-particles and the CNTs in the product were curved in nature and had inclusions.

Stimulated by the work of the Sussex group, the authors and co-workers carried out more research in Cambridge in 1997 [19-21]. While confirming that the electrolytic CNTs were formed from the carbon cathode, the new findings included (1) the cathode could be normal graphite, (2) molten $NaCl$ was also a good media for the electrolytic preparation, (3) temperature played an important role, and (4) the formation of CNTs followed the intercalation step of alkali element into the graphite cathode.

Hsu and co-workers later in 1998 extended their findings of inclusion in CNTs (the inclusions were claimed to be metal carbides), and succeeded in using the electrolytic method to produce carbon coated metal nano-wires [22-26]. The preparation procedure included the addition of low melting point metal salt, e.g. $SnCl_2$ into the molten salt.

Also in 1998, the Cambridge team refined the intercalation mechanism, emphasizing that the erosion of the cathode was due to the fast intercalation of alkali metal cations into and their in situ reduction within the graphite layers [20]. More importantly, the refined mechanism included post-intercalation steps that were thought to be responsible for the formation of CNTs in molten salts. More details of the intercalation mechanism will be presented later.

The year of 1999 saw a few publications from the Sussex team on producing more low melting metal nano-wires, including Bi , Pb or Sn , and the $Sn-Pb$ alloy [24-26]. A

third group joined publishing research articles on electrolytic CNTs in 2000. Kaptay and co-workers in Hungary reproduced the results of the authors, and reported that the electrodeposition of *Li*, *Na*, *K*, *Mg*, *Ca* from the respective chloride salts all led to the formation of CNTs, but not *Sn* and *Ni* [27]. They also investigated the electrolytic product by atomic force microscopy, revealing some interesting nano-structures [28]. Following a quiet year of 2001, more research articles on electrolytic CNTs were published in 2002. These include a fundamental account of the intercalation process [30] and an attempt to scale up the electrolytic method by the Cambridge group [31]. A more interesting progress was the electrolytic production of single walled CNTs in molten sodium chloride by Bai and co-workers in France [32].

It should be pointed out that there are a number of less noticed oral and poster presentations at different UK conferences from the Sussex and Cambridge groups. One of these was a poster from Hsu and co-workers presented in September 1999 at the conference of NanoteC 99, University of Sussex, Brighton. They proposed a mechanism to account for the electrolytic formation CNTs in molten salt, and this will be discussed later.

3. Basic experimental apparatus

Initially, the Sussex group did their experiments in air at temperatures slightly above the melting point of *LiCl* (m.p. 601 °C) [17]. However, the use of pure carbon materials as the crucible and electrode apparently prevented them from working in air at a higher temperature for melting other salts, for example, *NaCl* (m.p. 800 °C). The Sussex group later modified their reactor to use argon to protect the carbon materials from oxidation. The Cambridge group carried out electrolysis under argon protection and succeeded in producing CNTs in *NaCl* which is much cheaper than *LiCl* [19-20]. Other groups also followed this procedure in their work.

Figures 1a and 1b present the experimental apparatus used in Sussex and Cambridge, respectively. Although the two types of set-up look very different in structure, they are actually the same in terms of electrochemical principle. Of course, each of the two apparatus may have advantages in some cases but disadvantages in others. For example, the Sussex set-up is simple and convenient to construct. However, without any measure to secure sealing and water cooling, high temperature experiment may not be carried out safely. In addition, the use of a quartz tube is convenient for work on a small scale, and helps to maintain clean environment around the electrolytic cell. Due to its high cost and manufacturing difficulty, quartz tube is not very practically desirable if the apparatus needs to be scaled up. Although more complex in structure and tedious to construct, the Cambridge set up is much safer to use. The view and torch glasses on the Cambridge set up enable direct observation of changes in the cell during electrolysis. The torch glass allows the use of a torch to shine light into the reactor when the experiment is operated

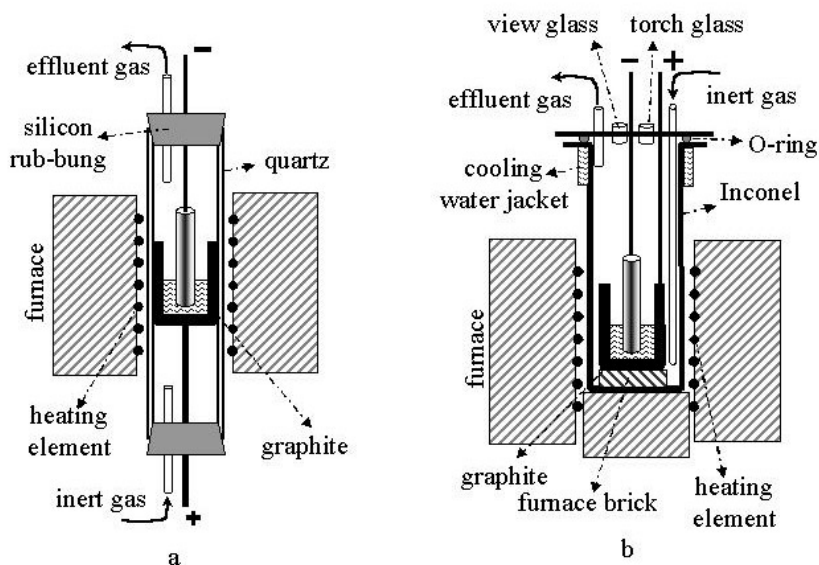


Figure 1. Schematic diagrams showing the experimental set-up used in (a) Sussex University and (b) Cambridge University for the electrolytic preparation of carbon nano-tubes in molten salts.

at low temperatures (<750 °C). Inconel (or stainless steel) is also much cheaper than quartz and readily available. However, because chlorine is anodically produced during electrolysis, corrosion of the metal can be a potential problem of long term use. A solution to the corrosion problem may be the addition of some alkali metal oxide into the molten salt so that chlorine evolution can be replaced by oxygen (or carbon oxides) evolution. Nevertheless, it should be pointed out that, for short time laboratory use, both of the Cambridge and Sussex set up were proven to be satisfactory.

The key element in the apparatus is the electrolytic cell. The cell has, in most cases, a simple two-electrode configuration with a graphite crucible as the cell and also the anode, and a carbon rod, often graphite, as the cathode. Two examples used in Cambridge are shown in Figure 2. These cells were simply made by drilling a hole of desired diameter and depth in a graphite rod. The wall thickness is an important parameter and is usually greater than 1 cm. This is because a thinner wall cannot withstand the stress caused by the contraction and expansion of the solidified molten salt during cooling and heating. Alternatively, the cell can be made from inert ceramic or metallic materials if an independent anode is .

A reference electrode can also be added to the cell, and is desirable for more accurate control of the electrolysis. In their work on molten salt electrochemistry, the Cambridge group has been using simply a metal wire or foil or graphite immersed in the molten salt as a pseudo-reference electrode and the potential is calibrated against known electrode

reactions, such as cathodic metal deposition, e.g. $Na^+ + e^- = Na$, or anodic anion discharge, e.g. $2Cl^- = Cl_2 + 2e^-$. The use of such pseudo-reference electrodes is satisfactory for short time work, up to a couple of hours, but the challenge is to maintain their long time stability, particularly when the composition of the molten salt system changes with time.

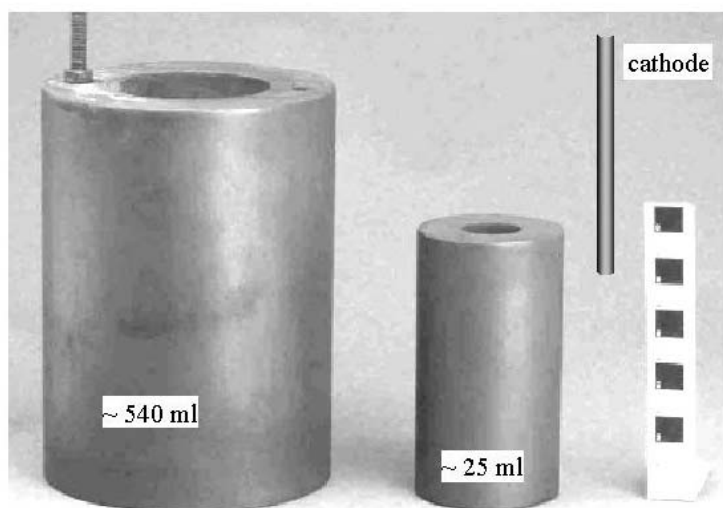


Figure 2. A photograph of two graphite crucibles of different sizes used in Cambridge for the electrolytic formation of CNTs in molten salts. The larger cell was used as a scaled up version of the smaller cell. Both cells have the same wall thickness for the sides and bottoms. The graphite rod shown in the picture was used as the cathode in most cases. Each scale on the ruler on the far right is one centimeter [31].

Based on findings showing that the cathodically deposited alkali metal, e.g. *Li* and *Na*, could dissolve into and float on the surface of the molten salt, and hence conduct electrons through the electrolyte or short the electrodes, the Cambridge group modified their cell by introducing a ceramic sheath surrounding the cathode at the interfacial region between the molten salt and atmosphere, and a ceramic base underneath the cathode to ensure similar, if not identical, cathode insertion lengths. Figure 3 shows the configuration of one of the Cambridge cells adopting this idea.

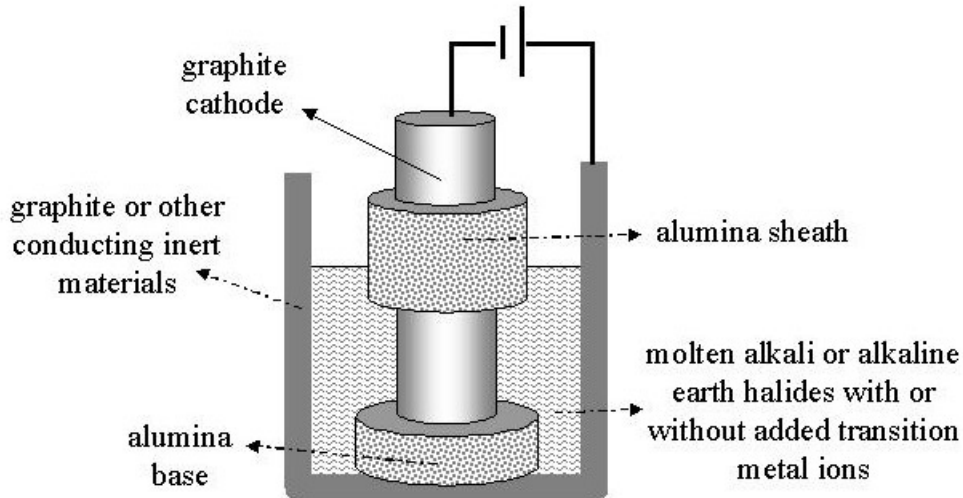


Figure 3. A schematic diagram showing the cell arrangement involving the use of an alumina sheath around the cathode to prevent cathodically formed alkali metal from shorting the electrodes, and also an alumina base underneath the cathode to control insertion depth [31, 33].

4. Preparation for electrolysis

Since its discovery, the electrolytic method for CNT preparation in molten salts has attracted attention of many CNT and carbon scientists, as evidenced by the fact that many review or research articles on CNTs published after 1996 have cited and commented the electrochemical work [34-36]. However, as it was discussed previously, research in electrolytic CNTs is far less than in other CNT research areas. One of the reasons is possibly the lack of confidence for many researchers to carry out research in molten salt electrochemistry. As a matter of fact, the original inventors of the electrolytic method, Hsu and co-workers did very little research in molten salt electrochemistry prior to their discovery. Their courage in working with molten salts came from their experience in using electric arc for CNTs preparation.

Indeed, the electrolytic method is not complicated at all. It follows a common and practically used procedure for material synthesis in molten salts. With the aim of encouraging more groups to join the research on electrolytic CNTs, this review describes the method in details, including (1) preparation (this section), (2) electrolysis, (3) post-electrolysis processing, and (4) extraction of nano-materials. Characterization and analysis of electrolytic CNTs are fundamentally the same as for CNTs prepared by other methods.

4.1. Furnaces and DC power supply

Construction of the electrolytic set up accounts for the major part of the preparation work for molten salt chemistry and electrochemistry in general, and CNT preparation in particular. Furnaces and electrochemical equipment are mostly available from commercial sources, although suppliers do appreciate input from users, if their listed products may not meet the requirement. For the preparation of electrolytic CNTs, a vertical tube furnace and a DC power supply are the basic equipment. According to all reported work up to date, the tube of the furnace has an internal diameter 70~150 mm, and a length of about 400~600 mm. The furnace must be able to provide a uniform heating zone (length) of 150~250 mm in the middle of the tube with the maximum temperature reaching at least 1000 °C. (It is noted by the authors that most furnace manufacturers use 1200°C as the threshold to determine the price of their products. The next temperature range for pricing is 1200°C to 1600°C.) A desired furnace for carrying out the work properly should be equipped with a temperature controller capable of programmed heating. Depending on the complexity of the required programming function, the temperature controller's price ranges widely, up to a few times more expensive than that of the furnace. The DC power supply also needs to provide a sufficiently wide range of currents and voltages. In the Cambridge laboratory, the maximum current and voltage used for producing CNTs are 10 A and 50 V. Unlike the furnace which is often individually manufactured upon users' requirement, a DC power supply can usually be purchased according to the product list of many manufacturers of electric/electronic devices.

4.2. Reactor

The vapor pressure of a molten salt may be significantly increased by increasing temperature. Therefore, prevention of the salt vapor from attacking the heating element of the furnace is often needed. This is usually achieved by confining the molten salt within a container or reactor, see Figure 1. The materials that can be used for making the reactor include quartz, alumina and, most commonly, corrosion (oxidation) resistant metals/alloys, such as Inconel and stainless steel. For CNT preparation at temperatures higher than 700 °C, the reactor needs to be sealed and continuously purged with argon to protect the carbon (graphite) electrode and cell from oxidation by oxygen in air. More details about gas protection are given later.

4.3. Electrolytic cell and electrodes

The carbon electrode (cathode) and cell can be purchased with desired dimensions and, in many cases, used straight away. If cleaning is desired, it can be done easily by abrading on the surface of the electrode and cell. A great advantage of working with

molten salts at elevated temperatures is the removal of most organic contamination from the system upon heating.

The most readily available carbon material is graphite. In their early work [17], the Sussex team used a high purity carbon cathode, but their work was soon found to be repeatable with normal graphite [19]. In Cambridge, the EC4 grade graphite rod from Graphite Technologies (UK) is frequently used, although electrolytic CNTs were prepared from many other graphite materials, e.g. the used carbon block from the Hall-Heroult cell [37].

Electric connection between electrodes and the DC power supply is usually realized by nickel, molybdenum, stainless steel or Kanthal wires. The wire is attached to the carbon either by tightly wrapping the wire around the carbon, or by threading the wire (male) and the carbon (female). When the threading method is used, corrosion of the metal wire could occur if the joining region is exposed to the salt vapor. This problem can be avoided or reduced to a satisfactory level by covering the joining region with a few alumina sheaths (collars), or a layer of dried alumina paste (simply mixing alumina powder with water) or the commercially available high temperature cement.

4.4. Molten salts

Alkali and alkaline earth chloride salts are usually hygroscopic. Thermally drying the salt in air can usually be satisfactory for CNT preparation. However, it should be pointed out that thermal drying in air, particularly at a high speed, could lead to hydrolysis of the chloride salt, resulting in the formation of oxide. Although oxide presence in the molten salt may not affect the electrolysis, however, it should be avoided if accurate electrochemical data are to be collected, e.g. by cyclic voltammetry. Once dried, the salt is ready to melt.

The amount of salt to be melted depends on the final depth of the molten salt required for carrying out the electrolysis. While the amount can always be calculated from the density of the salt, a simple rule of thumb is that to obtain one unit depth of molten salt, three-unit height of the dry salt powder is needed in a single melting process. For CNT preparation, because of the use of graphite crucible, melting the salt should be conducted under argon.

4.5. Inert gas protection and effluent gas processing

In addition to the separation of the reaction system from the furnace, the reactor, if sealed appropriately with a lid and O-ring, plays other important roles. For example, it enables the use of an inert gas, usually argon, to provide a desired gaseous environment within the container so that the electrochemical elements and the process are protected from the attack by constituents of air, such as oxygen, moisture and, in some cases,

nitrogen. For laboratory safety, the effluent gas from the reactor should be processed before releasing into atmosphere. For the electrolysis of a chloride salt, the effluent gas will contain anodically formed chlorine gas, which should be absorbed by, for example, a solution of relatively concentrated *NaOH*.

For these purposes, in-let and out-let gas lines are attached to the reactor. For laboratory uses, the in-let gas line includes the gas cylinder, gas flow meter of a measuring range of 0~300 ml/min, and drying columns filled with respectively self-indicating granules of silica gel and molecular sieve, and the out-let gas line includes the same drying columns as the in-let gas line, buffer bottle (empty, preventing back flow of downstream liquids), and bottles containing solutions of concentrated H_2SO_4 and *NaOH*, respectively. The end of the out-let gas line is fed into a fume-hood. In Cambridge the gas (argon) flow rate is usually 100 ml/min for a cylindrical reactor of 10 cm diameter and 60 cm height (internal).

4.6. Accessories and tools

In addition to general purpose facilities and tools used in any chemical laboratories, the special items for preparing CNTs in molten chloride salts include alarms for *CO* and Cl_2 gases, thermal protection gloves, face shield, long leg tones (assisting placing and removing items in the reactor), torch (shining light into the reactor), alumina tiles and cotton, sand bucket and etc.

5. Electrolysis

In all the reported work on electrolytic preparation of CNTs in molten salts, the electrolysis was carried out under the mode of either constant current or voltage, using a two-electrode cell. In the constant current mode, the applied current density was in the range of $10^3\sim 10^5$ A/m² with reference to the surface area of the cathode before starting the electrolysis. Constant current electrolysis has the convenience of allowing the calculation/estimation of the starting current density and total charge passed during electrolysis. It is also the preference of the industry. However, because of gradual erosion, the cathodic current density increases with electrolysis time, which is undesired, giving rise to many problems as will be discussed later. In their first report on electrolytic CNTs, the Cambridge team described that the cell voltage changed with time in a way that depended on the type of molten salt, but usually decreased slightly at the early time of electrolysis, and then increased quickly [19]. The voltage increase was thought to have resulted from the fact that the cathode was gradually eroded [19]. However, it was later suspected that, due to the use of a small cell, the short separation distance between the cathode and anode could have helped the entrapment of the anodically formed chlorine bubbles of similar sizes to the cathode-anode distance and hence blocked the current

passages between the two electrodes [20]. The entrapment of anodic gas bubbles became more likely when, at the later stage of electrolysis, more carbonaceous materials entered, and hence increased the viscosity of the molten salt. Consequently, a great increase of cell resistance and hence cell voltage would follow. Indeed, if terminated shortly to allow the chlorine bubble to escape, the electrolysis could be resumed successfully [33, 38]. Also, when the electrode separation was increased by using a larger cell or the anode current density is reduced by using a large anode, voltage surge was rarely observed [31, 37].

In their more recent work, the Cambridge team used the constant voltage mode to perform the electrolysis. The applied cell voltages were in the range of 3–9 V, considering the voltage loss due to electrolyte and circuit resistance. When a significantly large surface area ratio (>10) of anode to cathode is used, the current density on the anode will be sufficiently small and not cause any significant polarization of either electron transfer or mass transport or both. This will enable the anode potential to remain approximately the same as the equilibrium potential of the anodic reaction (which is the chloride ion discharge to form chlorine gas). Consequently, by applying a constant cell voltage, the cathode potential is also relatively fixed, disregarding the variation of the surface area of the cathode. Indeed, with a sufficiently large separation distance and surface area ratio between anode and cathode, it was observed that in response to the applied constant cell voltage, the current decreased with time steadily, which is attributable to the erosion of the cathode. Figure 4 shows some examples of the current–time plots recorded during constant voltage electrolysis [31, 33]. The recent attempt to scale up the electrolytic method was also performed by voltage control [31].

It should be mentioned that in either constant current or voltage electrolysis, if the applied voltage or current were high, discrete cracking noises were audible, accompanied by fluctuation of the voltage or current. (These changes are not shown in Figure 4 because they were too fast to record manually.) This phenomenon is believed to result from the cracking of the graphite cathode due to fast intercalation of the alkali metal [20]. Evidence of cracked cathode will be shown later.

The temperature and time of electrolysis are also two important parameters contributing significantly to the nature of results. According to reported data, in terms of producing CNTs, optimal values exist for both parameters for a given molten salt [18–20]. In addition, the Cambridge group reported that in comparison with *LiCl* and *NaCl*, much less CNTs were produced in molten *KCl* at the same temperatures, and they had attributed this result to the low boiling point of potassium metal [19, 20]. Unlike many other cases of electrolytic production of materials where the product is deposited from the solution onto the electrode, the electrolytic CNTs are prepared by converting the solid carbon (electrode) into CNTs that then enter the solution phase. Such a process will terminate naturally after the electrode has been consumed completely. For this reason, in all the early work on electrolytic CNTs, the time of electrolysis in the two-electrode cell

usually lasted for only a few minutes [17-20]. The Cambridge team recently reported their work on repetitive feeding the cathode into the cell during electrolysis [31, 33]. However, the time of electrolysis can still be limited by the saturation of the molten salt with the product. Obviously, the solution to continuous electrolysis is to feed the cathode and, at the same time, remove the product, but the latter still remains a laboratory challenge.

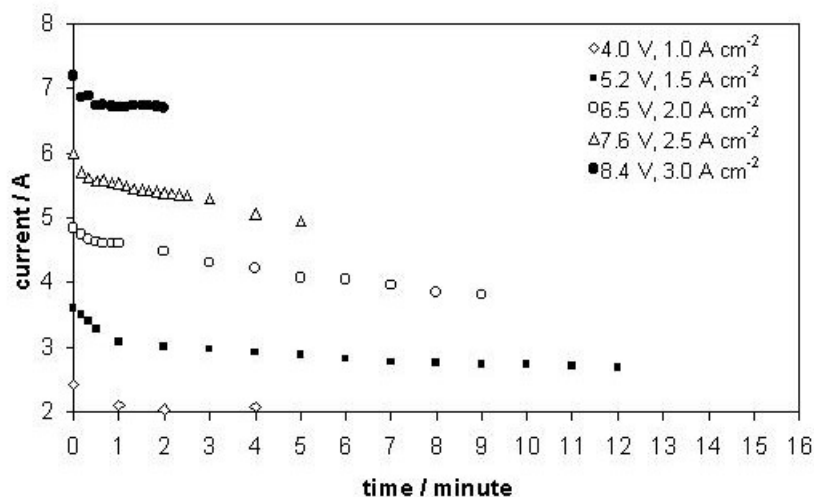


Figure 4. Current–time relations of constant voltage electrolysis in molten LiCl at 700 °C under argon using a graphite rod cathode and a graphite crucible anode. The applied cell voltage and calculated current density at the beginning of electrolysis are indicated. Cathode diameter, 0.65 cm, insertion depth, 1.0 cm; anode surface area, 150 cm²; anode-to-cathode separation,

In the simple cell configuration shown in Figures 2 and 3, the immersion depth of the cathode and its separation from the anode (cell wall) are the other two factors affecting electrolysis. In Cambridge and Sussex, the immersion depth is usually 5–10 mm which is not too different from the diameter of the graphite rod cathode (6.5 mm). The separation of the cathode from the cell wall is determined by the internal diameter of the graphite crucible (cell), ranging from less than 5 mm to greater than 25 mm. However, if the cell configuration includes an independent anode, the anode-cathode separation can be adjusted.

Interestingly, it was found by the Cambridge team that increasing the electrolysis

time produced more carbon nano-materials, however, the proportion of CNTs in the product decreased [33, 38]. In the constant current mode, the decrease in CNT proportion was thought to be related with the increase of current density at the cathode whose surface area decreased with time due to erosion, assuming that there was an optimal current density for the formation of CNTs [20, 31, 33]. However, even under the voltage control, the CNT proportion in the product was still observed to decrease with electrolysis time. This will be discussed later.

Up to date, all reported work on electrolytic CNTs has been carried out in the two electrode cell in which controlling and maintaining the cathode potential can be, as stated previously, approximated by using a large ratio of the surface areas between anode and cathode. However, the cathodic potential can be much better controlled and maintained by using a three-electrode cell, and carrying out constant potential electrolysis. The Cambridge group had predicted the advantages in using the three-electrode cell for CNT preparation [20]. Particularly, they have used the three-electrode cell to identify cathode reactions [20, 30] and study the lithium intercalation into graphite [30] by cyclic voltammetry and chronoamperometry. While more results of these experiments will be presented in separate publications, their work shows that, by using the three-electrode cell and applying an appropriate cathodic potential, the electrochemical processes occurring at the cathode can be more accurately controlled and even selected.

6. Post-electrolysis processing

After terminating electrolysis, the remaining cathode is removed from the reactor. Upon removal from the furnace, it was usually observed that the lower end of the recovered cathode was eroded with the nature and degree of erosion depending on experimental conditions. The erosion occurred in two different ways. Under high current density or voltage, the remaining cathode showed some features (e.g. flat surfaces and cracks) that apparently resulted from cracking. If a relatively small current density or voltage was applied, the erosion could be very uniform, and the cathode only became thinner. Figure 5 presents two photographs of the eroded cathodes due to cracking and thinning respectively [33, 38].

After removal of the cathode, the furnace is allowed to cool naturally to room temperature or a temperature below 300°C so that, once taken out of the reactor, the graphite cell containing the solidified salt can be safely and quickly cooled in air. Because the reactor is linked to bottles containing H_2SO_4 and $NaOH$, it is important to prevent these solutions from being sucked into the reactor whose internal pressure would decrease during the cooling process. In practice, this could be done either by valves, or simply passing a small flow of argon (<5 ml/min) through the reactor to compensate the pressure drop.

In their early work, Hsu and co-workers used a relatively small cell, and the removal

of the solidified salt, which contained the electrolytically produced CNTs and other carbon nano-particles, from the cell was achieved by adding water into the cell, followed by ultrasonication. In Cambridge, it was noticed that, possibly due to the use of a less powerful ultrasonic bath, this procedure had to be repeated many times to achieve complete dissolution of the solidified salt [19]. Interestingly, during these operations, it was noticed that the solidified salt was not always blackened completely but some time only partially in the top region.

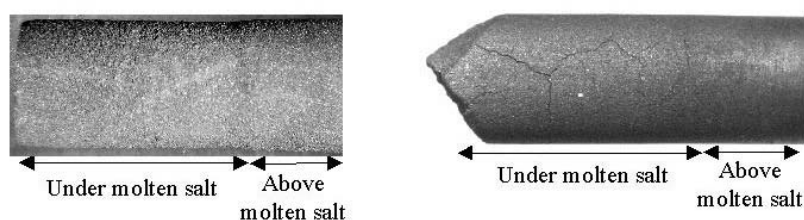


Figure 5. Photographs showing eroded graphite cathodes caused by (left) thinning at 3.5 V and (right) cracking at 6.5 V. The electrolysis was carried out under argon in a NaCl melt at 820 °C for 10 minutes [33, 38].

The slowness of using the ultrasonic bath to assist dissolving the solidified salt was found to be particularly problematic for a relatively large cell. Complete dissolution could take 10 hours or even longer. On the contrary, the Cambridge team found that fast and complete dissolution of the solidified salt could be achieved by adding hot water (60~80 °C) to the cell followed by mechanical stirring [20, 31, 38]. In doing so, dissolution of the salt could be completed within a couple of hours, resulting in a black aqueous suspension, which was further processed as described below.

7. Extraction of the electrolytic nano-materials

As revealed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX), the black aqueous suspension obtained from the above procedure often contained various forms of carbonaceous materials, including CNTs, carbon nano-particles, amorphous carbon and carbon debris of micrometer and larger sizes, and also chloride and oxide of the alkali metal. The oxide could be formed from the cathodically formed alkali metal via reaction with water and/or oxygen in air [31]. Therefore, an appropriate method capable of effective extraction/separation of the nano-materials from the rest of the electrolytic product is required.

Hsu et al are the first to use toluene to separate or extract the carbon nano-materials from the rest of the electrolytic product [17, 18]. They reported that the separation was due to that the carbon nano-materials entered or were extracted into the toluene phase in which small fullerene molecules are often soluble [17, 18]. However, in an early report, the Cambridge team showed that the carbon nano-materials were actually aggregated at the interfaces of toluene-water and toluene-glass [19]. They later observed that direct addition of toluene to the unwashed black aqueous suspension often resulted in a product that still contained too much salt [31]. The salt content could be reduced by washing and filtering the extracted carbonaceous materials, but complete removal of the salt was difficult.

The inclusion of the salt in the extracted product was first thought to be due to the solidified salt being entrapped in the agglomerates of the carbon nano-materials and not accessible by water [31]. The observation that the electrolytic carbon nano-materials aggregated at the interface of toluene-water suggests the existence of either separated hydrophobic and hydrophilic groups on the surface of the carbon nano-materials or, more likely, of very different wetting abilities between water and toluene on the surface of the carbon nano-materials. Consequently, in either case, some micelle like or more complex forms of closed water-carbon-toluene structures could have formed, entrapping the salt containing water in the center of the structure.

The Cambridge team then refined the extraction process, introducing washing steps. These include repeated combination of stirring, ultrasonication and filtration. The black suspension was either left to stand overnight to allow precipitation of the carbonaceous materials, followed by decanting the clear water or simply filtered through filter paper. The obtained black precipitate or powdery product was further washed with water under stirring and ultrasonication followed by decanting or filtration. The washing step was sometimes repeated to achieve more complete removal of the salt from the carbon product. The total amount of water used for the washing process is about a few times as much as that in a saturated solution of the salt [31].

The washed carbonaceous materials were added to a mixture of 1:10 toluene/water contained in a separation flask and well mixed with the aid of ultra-sonication. The sonication step helped to break down the agglomerates of carbon nano-materials and closed water-carbon-toluene structures to liberate the entrapped salt and further separate the carbon nano-materials from those carbon pieces of micrometers or larger sizes [31]. The mixture was then allowed to go through phase separation. Afterwards, most of the water phase was discarded. For a better result, clean water could be added to the separation flask again, followed by repeating the sonication mixing and phase separation steps. (For economical operation, the water can be collected after phase separation and used in the dissolution and washing processes). In the end, the toluene phase, carbon nano-materials, and the small amount of water left in the separation flask were transferred into storage bottles. The mixture could be further dried or analyzed directly. During drying, the evaporated toluene could be collected for re-use.

8. Characterization and analyses of the electrolytic nano-materials

There are two aspects of analysis of the electrolytic product: (1) properties of the various forms of the electrolytic carbon and (2) the proportional content of each. In particular, the proportional content and structure of CNTs are the two most wanted parameters. Like other areas of CNT research, the CNT concentration in mixed carbon nano-materials is mostly measured by scanning or transmission electron microscopy (SEM or TEM) and the result provides an approximated volume proportion. In references [33] and [38], a procedure of using TEM for measuring CNT purity is described. Because the measurement strongly depends on how the microscopic sample is prepared, and who carries out the measurement, the error in the SEM or TEM result is high. Therefore, a more reliable method for the determination of the CNT content in the electrolytic product is required.

Based on SEM or TEM estimations of different research groups [17-20, 27, 31-33], the electrolytic carbon nano-materials contain CNTs in the range of 5 to 50 vol. %, with the rest being mostly nano-particles (onions or amorphous). Apart from voltage, current density, electrolysis time and temperature, the type of salt was found to influence the nature of the product significantly. Under similar conditions, the total amount of extracted carbon nano-materials was found to follow the order of $KCl > LiCl > NaCl$ [19]. However, the dominant form in the product from KCl was micro-particles, and this was thought to have resulted from the fact that the electrolysis temperature was higher than the boiling point of potassium metal [20].

Typical morphologies of the electrolytic carbon nano-tubes and nano-particles are demonstrated in Figure 6. High-resolution TEM investigations confirmed that nano-tubes similar to those shown in Figure 6 were composed of a few to a few tens of walls with a space of 0.34 nm between neighboring walls. Electrolytic CNTs are usually bent, indicating the presence of defects. These features of electrolytic CNTs are similar to those of catalytically prepared CNTs. However, the lengths of electrolytic CNTs were found to range from sub-micrometer to a couple of tens of micrometers, significantly shorter than their catalytic counterpart.

In addition, foreign crystalline substances were often observed inside the nano-materials. For CNTs, the inclusions were located more likely at the tip and bent regions of the tubes (see Figure 6b). This differs from the catalytic CNTs in which catalyst particles were only seen at the end of the nano-tubes. While the inclusions in electrolytic CNTs were more often observed in the product from molten lithium halides, later studies in molten sodium chloride also showed similar results, although the total amount of inclusions was much less [33, 38]. These inclusions were thought to be either the metal [20] or carbide [25] of the alkali element, which implies the participation of the alkali element in the formation mechanism.

Until 2002, all SEM and TEM investigations revealed only multi-wall nano-tubes of

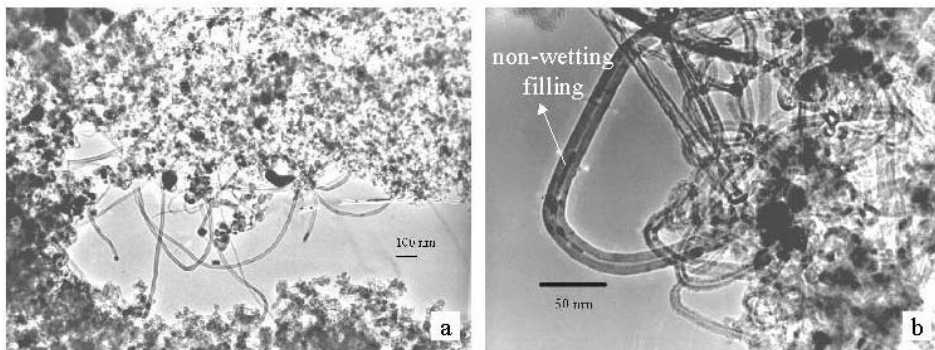


Figure 6. TEM images of carbon nano-tubes and nano-particles prepared in molten LiCl by constant current electrolysis at 820 °C, showing two sampled areas that were respectively dominated by nano-particles (a) and nano-tubes (b).

different diameters in the electrolytic products, together with various other forms of carbonaceous materials. Figure 7 shows examples of some unique nano-structures. These observations imply that the electrolytic method is capable of producing many different forms of carbon nano-materials, and there is no reason to exclude single wall nano-tubes (SWNTs). Based on these observations, some mechanisms (see later for details) were proposed to account for the formation of various types of carbon nano-structures, including SWNTs [20, 25].

Indeed, experimental evidence of the presence of SWNTs in the electrolytic product was reported in 2002 by Bai and co-workers in Paris, France, who observed for the first time bundles of SWNTs in the electrolytic product from molten sodium chloride [32]. In addition to TEM evidence, they also confirmed the presence of single wall nano-tubes by Raman spectroscopy. It should be pointed out that Bai's work is exceptional for that it is commonly accepted that SWNTs could only be formed with the aid of a catalyst, which was used in all the previously reported methods for producing single wall carbon nano-tubes. However, Bai et al. used essentially the same method and set-up as the Cambridge team, and a NaCl salt of 99% purity without any added catalyst. However, the hypothesis that SWNTs could be prepared without using a catalyst needs further verification because Bai et al. did imply the possible catalytic role of the trace amount of impurities (e.g. 10 ppm of Fe) in the molten salt.

The chemical composition of the electrolytic product has been analyzed by energy dispersive X-ray analysis (EDX) which is usually equipped on the electron microscopes. Although this method may not be very accurate quantitatively, it can provide useful qualitative information of the elemental composition of the sample, except for very light

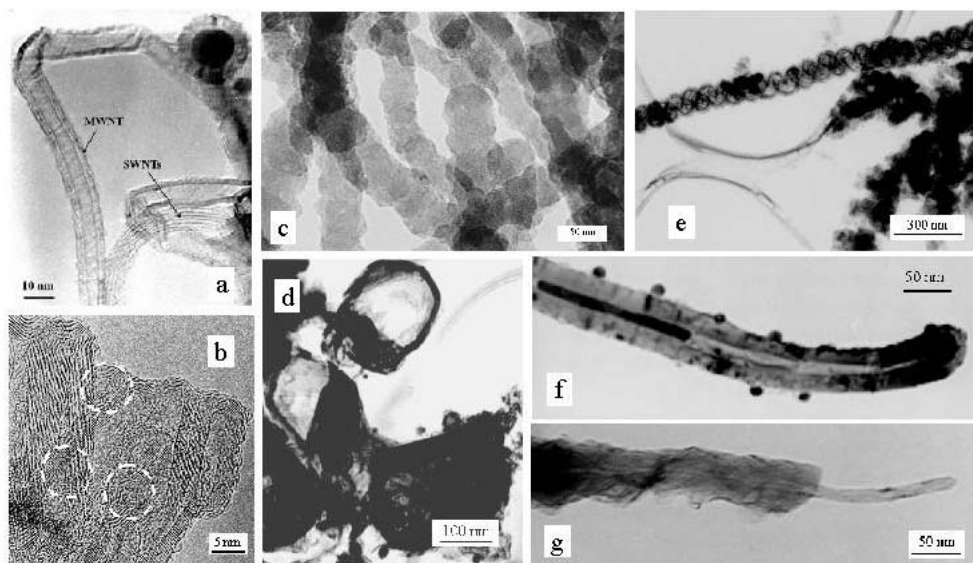


Figure 7. Transmission electron microscopic images of various electrolytic carbon forms (a) multi- & single-wall nano-tubes [32], (b) onion like nano-particles (circled with dashed line) [20], (c) nano-fiber (particle chains) [38], (d) tambourines [19, 38], (e) double helix [19, 38], (f) non-wetting inclusion & external decoration [20, 38], and (g) amorphous coating [38].

elements (e.g. *H* and *Li*). More importantly, the method can be applied to either a spot on individual nano-tubes and nano-particles, or a large collection of different constituents of the sample. Using this function of EDX, one can easily identify the nature, location and origin of an impurity, such as the salt. In general, before thorough washing, carbon, chlorine and oxygen were usually the dominant elements detected in the electrolytic product from molten lithium chloride (lithium is excluded from the analysis because of its lightness). A typical composition is 9 wt.% *C*, 41 wt.% *Cl*, and 50 wt.% *O* [31]. Using the washing process described above, the chlorine level could be reduced to below the detection limit of EDX. However, the amount of oxygen was not changed significantly by washing. The oxygen was suspected to have resulted from a number of origins, e.g. the carboxylic group on the surface of the carbon nano-particles and tubes, and water molecules that were trapped by hydrogen bonds between carbon nano-structures [31].

An interesting study of the electrolytic product by atomic force microscopy was jointly reported in 2001 by two Hungary groups led by George Kaptay [28]. In addition to findings similar to that from SEM of the product from the solidified-

ly, tori of about 300~400 nanometers in diameter and 10~15 nm in height were observed on samples originated from the surface of cathode, see Figure 8. Interestingly, if one compares the tori in Figure 8 with the tambourine in Figure 7d (and that reported in reference [19]), the two structures seem not to be so different. If so, the fact that this structure could be formed in different molten salts (pure *LiCl* [19], *NaCl* [38] and mixed *NaCl* and *MgCl₂* [28]) suggests strongly an electrochemical origin. It should be noticed that the AFM result was obtained indirectly from the cathode surface, and hence deserves more but cautious attention of its significance to the history of and physico-chemical changes on the cathode.

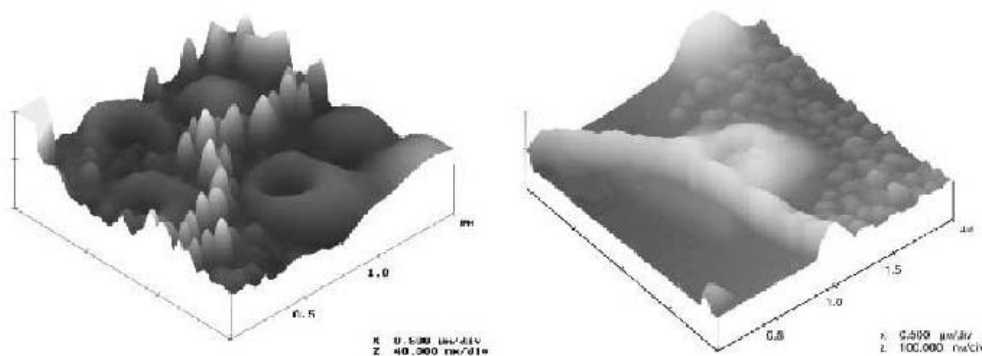


Figure 8. Two 3D AFM images of some tori (left) and a single torus underneath a thick nano-tube (right) observed in samples separated from the surface of electrode from electrolysis of *NaCl*-5% *MgCl₂*.

The other method used for the characterization of the electrolytic product is Raman spectroscopy. In addition to confirming the presence SWNTs [32], the Raman spectroscopic analysis also showed a similarity between the electrolytic CNTs and the catalytic CNTs in terms of structure and crystallinity [33, 38]. This is in agreement with the SEM and TEM analyses.

9. Production of metal nano-wires

Filling in the internal cavity of fullerenes and CNTs has been an intensive research effort since the bulk production of these empty nano-materials, aiming at producing, for example, catalysts nano-particles [14] or metal nano-wires [22-26]. The methods include the two-step and one-step processes. In the two-step process, the ends of the nano-tubes were first opened by selective oxidation. Then, the opened tubes were mixed together

with the element to be filled under certain conditions (e.g. heating), and filling was achieved by the capillary effect. The capillary filling could also be achieved by heating closed nano-tubes together with the element under a controlled oxidizing atmosphere (e.g. controlled oxygen partial pressure). The one-step process was carried out by arc discharge of a carbon anode that was drilled and packed with the element to be filled. In doing so, filled nano-tubes were formed in situ.

However, in most of the reported work, complete filling of the nano-tubes was not very successful until 1998 when Hsu et al. [22, 23] reported that the electrolytic method could also be used to make fully filled nano-tubes. Their first work seems to have a link with the observation that electrolytic CNTs usually contain encapsulated materials that partially fill the nano-tubes. They first prepared in situ tin fully filled carbon nano-tubes by adding less than 1 wt.% SnCl_2 to LiCl [22]. This work was later extended to the production of other low melting metal or alloy filled CNTs [23-26]. Figure 9 shows two TEM images of the produced carbon sheathed Sn-Pb nano-wires, and the EDX analysis of the composition on each of the spots on a single nano-wire (labeled in Figure 9b). Interestingly, they observed that the production of the tin filled CNTs was not successful in a pure SnCl_2 melt, neither in a mixed melt of SnCl_2 and LiCl with the content of SnCl_2 being greater than 1 wt.% [22, 25].

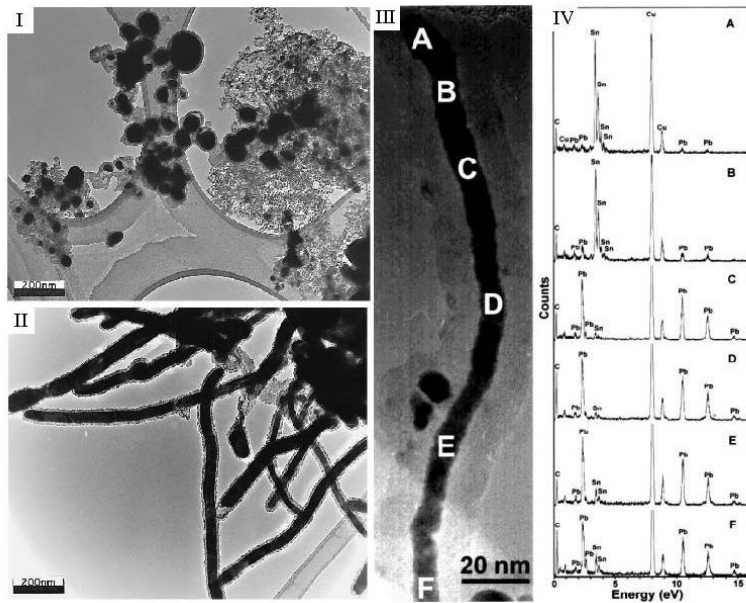


Figure 9. TEM images of the electrolytically produced carbon sheathed (I) copper nano-particles, (II) Sn nano-wires and (III) a single Sn-Pb nano-wire. The insert EDX spectra on the far right (IV) show the composition of each of the labeled spots on the Sn-Pb nano-wire shown in (III). The copper signals in (IV) are due to the TEM copper grid (sample holder).

In 2002, the Cambridge team also reported their work on producing tin filled CNTs [31]. In addition to repeating the results of Hsu et al. on a much larger scale, the Cambridge team actually used SEM to observe the tin enclosed in the CNTs. Unlike the TEM images (see Figure 9), the SEM image presented in Figure 10 shows the nanowires with a brighter core and a dark wall. This indicates that the core contains a significantly heavier, or higher atomic number, element than the wall. EDX analysis further confirmed that the nano-tubes were indeed composed of tin and carbon. It is unusual that such a contrast shown in Fig. 10 can be directly detected by the secondary electron beam, but the observation may be understandable considering that the carbon walls of the CNTs were of only a few nanometers to a few tens of nanometers in thickness.



Figure 10. An SEM image of tin filled CNTs produced similarly as those shown in Figure 9b, but the electrolysis was on a much greater scale.

10. Mechanisms of the electrolytic formation of carbon nano-structures in molten salts

Generally speaking, because CNTs can be produced under very different conditions, various formation mechanisms have been proposed. However, since these mechanism

studies have focused on the gas phase processes, the understanding may not necessarily apply to the electrolytic process in molten salts.

In their first report, the Sussex team pointed out that the “high purity carbon” cathode provided the carbon source for the electrolytic CNT formation in molten salt [17, 18]. This was based on the observation that the carbon cathode eroded after the electrolysis, and carbon nano-materials were collected from the molten salt. While this view has been supported by the results from all laboratories, the questions are (1) how the erosion occurs, (2) what are the erosion products, (3) how the erosion products form the nano-materials, particularly CNTs, and (4) whether the formation takes place on the surface of the cathode or in the molten salt.

10.1. The Cambridge intercalation mechanism

Within the Cambridge team, Fray [19, 21] was the first to point out that the erosion of the graphite cathode is commonly observed in the Hall-Heroult cell where the intercalation of alkali metals, particularly sodium, into the carbon cathode is known to lead to cathode expansion, cracking and erosion. He then postulated that the intercalation of the alkali metal into the graphite must have extruded carbon out of the graphite structure to form CNTs directly on the surface of the cathode. This postulation had not been experimentally confirmed in the Cambridge laboratory and others [17-26], until recently when Kaptay et al. reported their observation of a carbon micro-tube on the surface of a graphite cathode [27].

Based on the facts that CNTs were collectable from the solidified salt phase and also the CNT yield depended strongly on electrolysis current and temperature [17-20], Chen et al proposed [20, 29] that, driven by a sufficiently negative electrode potential, the alkali metal ion (M^+) intercalates into the graphite lattice where it is then reduced in situ. Because of the significantly larger size of metal atom than metal cation, the alkali metal formed in situ then expands the graphite lattice and more strain is put into the lattice as the amount of metal increases, until the lattice fragments. The carbon based fragments (M_xC_y) may then enter the molten salt and, without the protection of the graphite lattice, undergo through an inter- and/or intra-fragment re-combination process, leading to the formation of various carbon nano-particles and nano-tubes in the electrolyte [20, 29]. Figure 11 illustrates schematically this hypothesis.

It is interesting to point out that both the extrusion and the fragment re-combination mechanism emphasize that the cathode erosion is caused by the intercalation of alkali metal element, but describes differently the post-intercalation processes that are responsible for the CNT formation. In fact, the two post-intercalation processes can be considered essentially the same if the extruded CNTs or their precursors can fall into and grow further in the electrolyte or the inter- and/or intra-fragment re-combination may occur on the cathode surface.

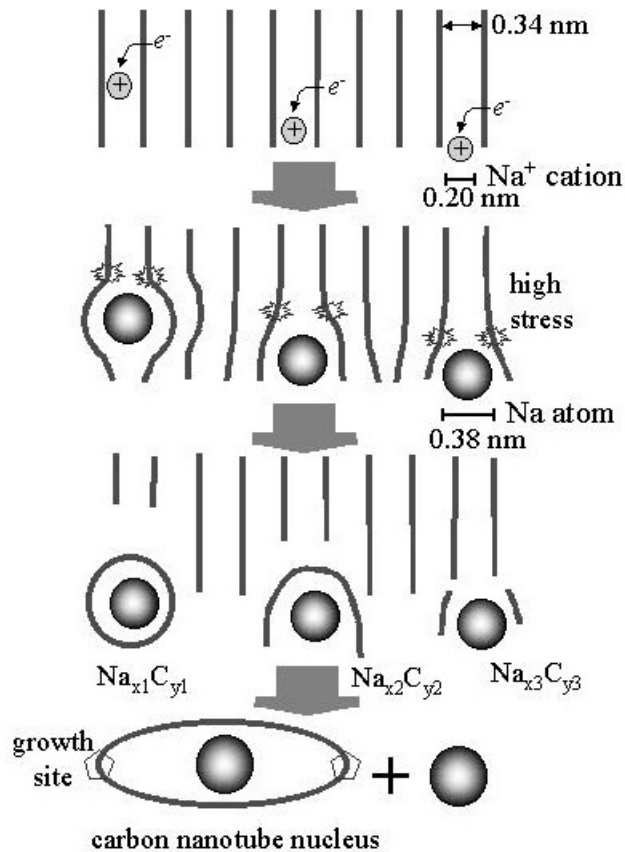


Figure 11. The intercalation and fragment re-combination mechanism for the formation of electrolytic CNTs in molten salts.

The Cambridge team's CNTs formation mechanism was generally advocated by Kaptay et al. [27]. They reported the results of an interesting experiment in which NaCl was mixed with 5 wt. % of a bi-valent metal chloride (MgCl_2 , CaCl_2 , SnCl_2 and NiCl_2) and the electrolysis was performed under a cathodic current density that was kept below the limiting current density of the bi-valent metal [25]. They then found CNTs in the two alkaline earth metal chlorides, but not the two transition metal chlorides. This observation was attributed to the fact that the alkaline earth metals can intercalate into graphite, while the transition metals cannot. This is strong evidence that intercalation plays an important role in the electrolytic formation of CNTs in molten salts. In addition, they argued that once suspended in the molten salt, tube formation was driven by the attractive "interfacial" forces between the two edges of the suspended graphite planes

having broken carbon bonds. (This process is the same as the intra-fragment recombination process.) They also claimed that the process could be assisted by small chlorine bubbles rising through the molten salt and bending the horizontally situated graphite sheets due to buoyancy force.

In two recent publications [30, 33], the Cambridge team reported their fundamental studies of the electrolytic process in greater depth. In the first paper [30], an intercalation model was developed from two fundamental assumptions: (1) lithium intercalation into graphite was driven by the lithium concentration gradient present on the graphite side of the graphite-molten salt interface; (2) the lithium concentration at the graphite-salt interface was governed by the Nernst equation. It should be pointed out that these two assumptions differ from the intercalation step illustrated in Figure 11 that emphasizes the in situ reduction of the lithium cation within the graphite lattice.

The mathematical solution of this model was derived for the double-potential step chronoamperometric experiment. The solutions for the forward and backward potential steps are given below.

$$\text{forward step: } I(t) = FS \frac{c_{Li}^*}{r_{Li}} \sqrt{\frac{D_{Li}}{\pi}} \exp\left(-\frac{E - E^o}{RT} F\right) \frac{1}{\sqrt{t}}$$

$$\text{backward step: } I(t) = -FS \frac{c_{Li}^*}{r_{Li}} \sqrt{\frac{D_{Li}}{\pi}} \exp\left(-\frac{E - E^o}{RT} F\right) \left(\frac{1}{\sqrt{t - \tau}} - \frac{1}{\sqrt{t}}\right)$$

where S is the electrode's geometric surface area; c_{Li}^* , r_{Li} and D_{Li} are the saturation concentration, Henrian activity coefficient and diffusion coefficient, respectively, of the lithium in the graphite phase; τ is the time when the potential steps backward. (GZC acknowledges that Dr. Rongshan Qin helped to find the mathematical solutions, but was not mentioned in the original paper.) The model was found to agree well with the results obtained from experiments in which the electrode potential was stepped to values less negative than the lithium metal deposition potential (determined by cyclic voltammetry). Figure 12 presents the experimental and theoretical results for the forward and backward potential steps. However, it was also observed that, after these potential step experiments, the electrode recovered from the molten salt exhibited no visible erosion, even though the recorded current-time curves confirmed that lithium intercalation into the graphite electrode indeed took place. The absence of graphite erosion in these experiments is not surprising, because the applied electrode potentials were possibly not negative enough to drive lithium cations into the graphite lattice and subsequently reduce them in situ to lithium metal, and/or to force a fast intercalation process that can lead to stress increase within the graphite lattice.

Upon stepping the potential to more negative values, the current was observed to first

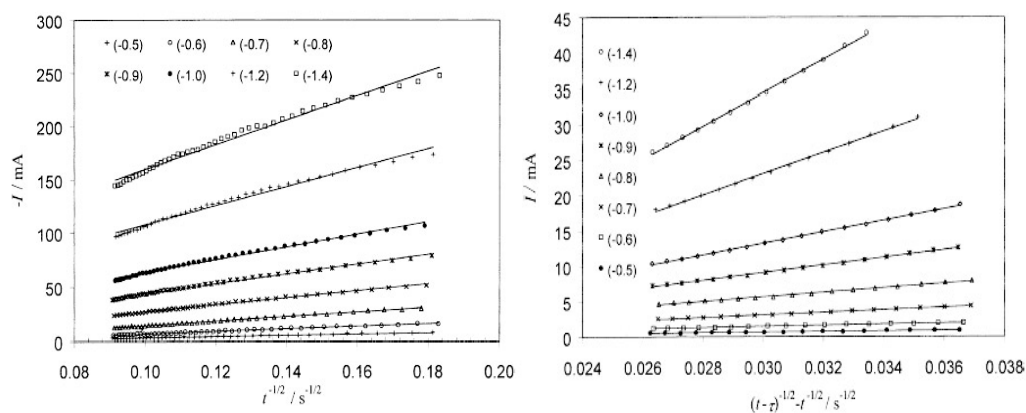


Figure 12. Experimental (symbols) and theoretical (fitted lines) results [30] showing the linear relations predicted by the intercalation model for the forward (left) and backward (right) potential steps on a graphite disk electrode in molten lithium chloride at 775 °C. Data given in parentheses are electrode potentials with reference to a molybdenum wire immersed in the same melt.

follow a pattern showing the simultaneous occurrence of both lithium intercalation and deposition (-2.0~ -3.8 V vs. *Mo*), and then to fluctuate irregularly, indicative of cracking/exfoliation of the electrode surface. Figure 13 plots the current-time curves, showing the irregular current fluctuations. Upon visual inspection after the experiment, electrode erosion was evident. An interesting phenomenon is that, as shown in Figure 13, the current fluctuation depended on not only the potential but also the time. While the fluctuation occurred earlier with stepping to more negative potentials, the length of the fluctuation shortened, followed by a steady constant current. Such behavior was linked to the formation of a continuous layer of the deposited lithium metal that then physically separated the graphite electrode from the molten salt. However, the termination of the current fluctuation, and hence the exfoliation of the graphite electrode by the coverage of lithium metal was somehow unexpected because the intercalation of lithium should have continued. The implication is that, if it indeed took place, lithium metal intercalation into graphite might have proceeded in a way that is very different from the process described in Figure 11 which emphasizes the intercalation of lithium cation and its in situ reduction to the metal within the graphite lattice.

It was previously observed in both Cambridge and Sussex that the CNT proportion (yield) in the electrolytic product was very low if the applied voltage or current was either too small or too large, indicating the existence of an optimal cathodic current density or potential for the electrolytic formation of CNTs in molten salt [17-20]. This empirical prediction can be explained by the Cambridge intercalation mechanism. It

states that, at different electrode potentials, different graphite intercalation compounds, M_xC_y , form and there exists a crucial range of values of x and y for the M_xC_y fragments that can undergo inter- or intra-fragment combination into CNTs or the nuclei that subsequently grow into CNTs.

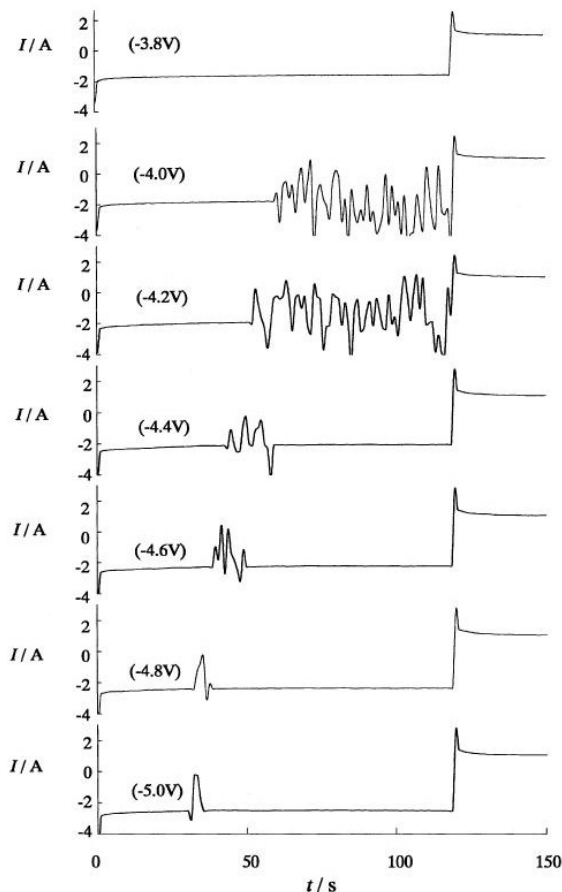


Figure 13. The current ~ time curves of a graphite electrode in molten LiCl responding to the indicated potential steps at 775 °C. (Note the current fluctuations due to fast intercalation caused exfoliation of the electrode.)

In their second recent paper, the Cambridge team reported a thorough study of the electrolytic process in molten sodium chloride [33]. Two of the results are re-plotted in Figure 14. The upper plot (Figure 14a) shows that, for 10 minute electrolysis in the constant voltage mode, the CNT yield increased drastically from 3.5 V to 4.5 V but declined with further increasing the cell voltage up to 9.0 V. It is acknowledged that the cell voltage variation is not the same as that of the cathodic potential, but the two parameters may still be linked by an approximate linear relation, given the fact that the

experiment was performed in a cell with a large anode-to-cathode surface area ratio (see Figures 1, 2, and 3). Therefore, it is reasonable to consider the CNT yield–cell voltage relation shown in Figure 14a as indirect confirmation of the expected maximum CNT yield against the cathodic potential or current density. The lower plot (Figure 14b) presents the relationship between CNT yield and the total charge passed through the cell during electrolysis. In addition to showing that the voltage influence was accompanied by passing more charge, the data demonstrate unexpectedly that increasing electrolysis time also decreased the electrolysis efficiency, even though at the same “optimal” voltage.

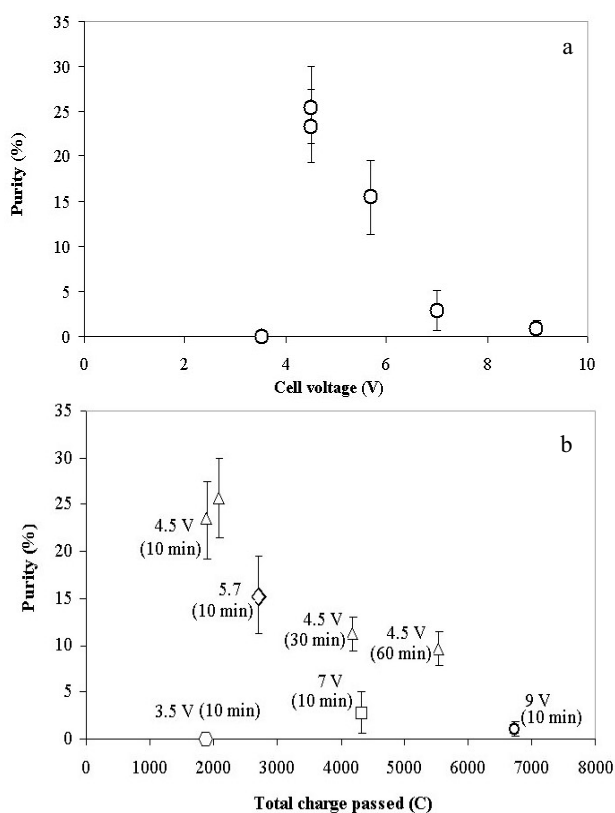


Figure 14. Dependence of the proportion of CNT in the electrolytic product (purity) on (a) the cell voltage (fixed electrolysis time of 10 minutes) and (b) the total charge passed (electrolysis time as indicated). Results were obtained from electrolysis in NaCl at 820 °C.

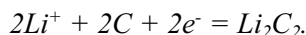
It should be pointed out that the “optimal” cell voltage, 4.5 V, included the iR drop from the cell and electric circuit, and hence could not have led to a cathodic potential as much negative as those used to record Figure 13. Furthermore, it was observed that the

total amount of carbon nano-materials increased with the electrolysis time. Apparently, in this case, the decrease in CNT yield with electrolysis time could not be due to the coverage of the cathode by a continuous layer of the electrodeposited alkali metal. The Cambridge team attributed the result to a number of reasons but mainly electronic conduction through the melt via dissolved or floated sodium metal and the chemical reaction between the dissolved sodium and the carbon nano-structures. While the chemical reaction is a very plausible explanation, however, to avoid the reaction or reduce its effect will be a challenge to the further development of the electrolytic process.

10.2. The Sussex carbide mechanism

In fact, as discussed in the previous section, Hsu et al. [22-26] reported earlier that all their attempts to prepare metal nano-wires failed in pure $SnCl_2$ or $LiCl$ mixed with more than 1 wt. % of $SnCl_2$, $CuCl_2$, or $ZnCl_2$. The products contained neither any CNTs, but mostly amorphous or polyhedral carbon particles. Unlike Kaptay et al, the Sussex team performed their electrolysis under similar conditions as preparing CNTs, i.e. the applied current was sufficiently higher than the limiting current of the transition metal. Hence, both lithium and transition metal cations in the mixed melt must have been reduced at the cathode. They also observed that when adding $CaCl_2$ into $LiCl$ from 0 to 50 wt.%, the proportion of CNTs in the product decreased significantly. However, when adding into $LiCl$ a small amount, 0.8~1 wt.%, of the transition metal powder, including Sn , Pb , Cu , Co , Bi , In and Zn , the corresponding nano-wires were obtained again.

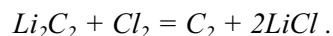
Hsu et al interpreted their results by considering the electrodeposition of the transition metals, particularly at high concentrations, being in preference to that of lithium, and hence concluded that the reduction of lithium cation played an important role in the formation of carbon nano-structures. While acknowledging the reduction of lithium cation could lead to lithium intercalation into the graphite layers, they excluded this process from contributing to the formation of nano-structures. Instead, they proposed that the cathode dissolution (erosion) and the subsequent formation of CNTs started from the electrochemical reduction of lithium cation at the graphite cathode to form lithium carbide, i.e.



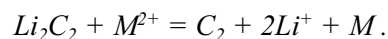
They further postulated that, under the applied experimental conditions, the decomposition of the carbide to lithium metal and CNTs might occur, which is similar to the post-intercalation steps of the Cambridge intercalation mechanism in which the graphite intercalation compounds, M_xC_y ($x \leq y \leq 2$), include not only the simple 2:2 carbide but also more complex stoichiometries [20].

Alternatively, Hsu et al. suggested that the chemical oxidation of the carbide, i.e. the chemical reverse of the above electrode reduction by an oxidant, led to carbon regener-

ation or graphitization. This was possible in two ways. First, part of the chlorine gas was formed at the bottom or lower part of the side wall of the crucible anode, and would sparge through the molten salt to oxidize the carbide as



Second, the oxidant could be the transition metal cation in the mixed melt and the reaction not only regenerated carbon but also the transition metal,



Note that the above two reactions differ slightly from those in the original paper [25].

If chlorine was the oxidant, the regenerated carbon could form a sheath around Li_2C_2 . This conducting sheath then functioned as an electron transfer medium for the further oxidation of Li_2C_2 within the carbon sheath by the reduction of either chlorine or the transition metal cation outside the sheath. As the carbon sheath was formed, Li_2C_2 was somehow extruded out of the sheath, forming a fresh Li_2C_2 surface for further regeneration of the carbon, thus propagating tubule growth.

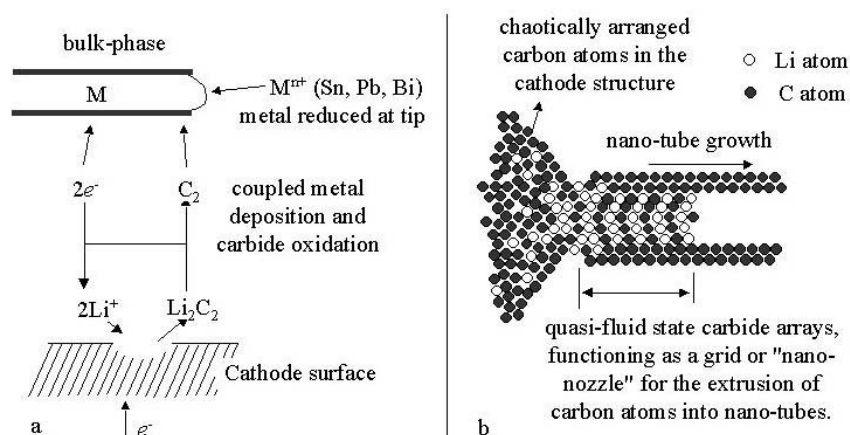


Figure 15. The Sussex carbide mechanism for the electrolytic formation of (a) amorphous carbon coated metal nano-wires [25] and (b) carbon nano-tubes [39]. Note that in (b) the carbide is depicted as a well ordered fluid (quasi-fluid) that facilitates the passage/extrusion of carbon atoms into nano-tube.

When the carbide was oxidized by the metal cation, the latter was reduced and formed metal particles on which the regenerated carbon then deposit to form the carbon

sheath. When such coupled reactions continued the growth of separated carbon and metal phases occurred, see Figure 15a. Because the deposition of the regenerated carbon blocked part of the surface of the metal particle, the growth of the metal phase was restricted in a particular direction, leading to the formation of the metal nano-wires. Hsu et al. argued that when metal powder was added to the molten salt, the metal could be oxidized by the chlorine gas to form the corresponding chloride salt, and the in situ formed transition metal chloride could function in the same way as the added chloride salt [25].

Later in a poster presentation [39], Hsu et al. reinforced their carbide mechanism by postulating a “nano-nozzle” concept, see Figure 15b. Considering the relatively high working temperature of 610 °C, they treated the lithium carbide formed on the cathode surface as a well ordered fluid or quasi-fluid that can function as a “grid”. This grid, flexible to some degree, permits the passage of incoming carbon atoms (originally chaotically arranged in the cathode) via the d-spacing of the carbide crystallite to become an ordered aggregate at the rear of the carbide grid to form nano-tubes. Hsu et al. imaged the entire process as carbon being extruded through the ‘nano-nozzle’ as depicted in Figure 15b [39].

11. Prospect of the electrolytic process and final remarks

In their first and successful attempt to scale up the electrolytic process (a factor greater than 20 in cell volume, see also Figure 2) [31], the Cambridge team found that, under the applied conditions, the charge and energy consumption for the cathode erosion was 0.28 kWh/kg and 4.1 kWh/kg, of which 60~70 % were for producing nanomaterials (nan-tubes: > 30 vol. %). Such a low energy consumption (for electrolysis only) was unexpected but is exciting, because it can be calculated that the electricity cost for producing electrolytic CNTs can be negligible, even in comparison with the costs for the raw materials, i.e. graphite and the molten salt, which are themselves very cheap. It is worth mentioning that the authors have experience of purchasing catalytic CNTs at a price of \$ 8000/kg for laboratory use. This price can be compared with \$ 0.3~0.7/kg for natural and synthetic graphite. It is acknowledged that the market for carbon nanomaterials in general and CNTs in particular is far from being developed, and hence the high price for CNTs may only be a reflection of the manufacturers pursuing commercial benefit, but the real manufacturing cost is unknown.

Nevertheless, in addition to the low energy consumption and use of cheap raw materials, the electrolytic method has the advantage of being a potentially continuous process. The scaling up trail performed in Cambridge has been successful in feeding the cathode manually, implying a continuous feed of the cathode in a future cell. In addition to the benefit from the view point of production, as was discussed before, continuous feed of the cathode at the same rate as that of cathode erosion will be more desirable,

because the cathode surface area and hence the cathode current density can be maintained, which is crucial for controlling the product quality (CNT morphology and purity).

The other two major remaining technical issues for developing a continuous electrolytic process are first the removal of products from the molten salt system and second the addition of the molten salt that was consumed by electrolysis. The products of the electrolysis include chlorine gas (anode), alkali metal (cathode) and carbon nano-materials (cathode). At present, in the laboratory work, the chlorine gas was carried out from the reaction system by the argon flux, and hence gave little effect on the process. However, the cathodically produced alkali metal was accumulated in the molten salt, leading to firstly electronic conduction through the electrolyte and secondly possible reactions with the formed carbon nano-materials. The more important issue of removing the product is to harvest the carbon nano-materials directly from the molten salt. The fact that the Cambridge team had used filtration in their post-electrolysis processing suggests the use of a filter for harvesting the carbon nano-materials directly from the molten salt. Regarding addition of the molten salt that is consumed during electrolysis, adding more fresh salt to the system will not be expensive. However, theoretically, it is possible to use the anodically produced chlorine gas to react with the cathodically formed alkali metal, and hence to regenerate the molten salt in situ, but this possibility has not yet been researched.

There still remain many fundamental challenges about the electrolytic process, particularly the formation mechanism of the carbon nano-materials. The inclusion of metallic element, either in the pure or compound form, in the electrolytic CNTs is another advantage of the electrolytic method, but understanding is very needed for the production CNTs filled with different elements. There has been very little work done on the characterization of the electrolytic CNTs, which will determine in what areas the electrolytic CNTs can be applied.

To end this review, the authors believe that, with more results being gradually accumulated, the electrolytic method for CNT preparation can have a promising future and compete with other CNT production technologies. Particularly, the authors hope that the detailed description of the electrolytic method and the estimated low production cost presented in this review will encourage more molten salt and CNT researchers to make a joint effort to bring the electrolytic method into commercial reality.

References

1. Hyperion Catalysis International Inc., <http://www.fibrils.com/default.htm>.
2. H.G. Tennent (Hyperion Catalysis International, Inc), US Patent 4663230, publication: May 1987, first filing: December 1984.
3. H.G. Tennent, J. J. Barber, and R. Hoch (Hyperion Catalysis International, Inc),

- US Patent 5165909, publication: November 1992, first filing: October 1990.
4. H.G. Tennent, J. J. Barber, and R. Hoch (Hyperion Catalysis International, Inc), US Patent 5578543, publication: November 1996, first filing: June 1995.
 5. R.D. Creehan (Hyperion Catalysis International, Inc), US Patent 5445327, publication: August 1995, first filing: June 1992.
 6. S. Iijima, *Nature*, 354 (1991) 56.
 7. P.M. Ajayan, S Iijima, *Nature*, 358 (1992) 23.
 8. T.W. Ebbesen, P.M. Ajayan, *Nature*, 358 (1992) 220.
 9. R.E. Smalley, From dopyballs to nano-wires, *Mater. Sci. Eng. B-Solid State Mater. Adv. Technol.*, 19 (1993) 1.
 10. C. M. Niu, E. K. Sichel, R. Hoch, D. Moy, H. Tennent, *Appl. Phys. Lett.*, 70 (1997) 1480.
 11. E. Frackowiak, K. Jurewicz, S. Delpoux, F. Beguin, *J. Power Sources*, 97-8 (2001) 822.
 12. M. Hughes, G.Z. Chen, M.S.P. Shaffer, D.J. Fray, A. H. Windle, *Chem. Mater.*, 14 (2002) 1610.
 13. M. Hughes, G.Z. Chen, M.S.P. Shaffer, D.J. Fray and A.H. Windle, *Proc. 202nd Meeting Electrochem. Soc.*, Salt Lake City, USA (2002) (accepted).
 14. J.Z. Luo, L.Z. Gao, Y.L. Leung, C.T. Au, *Catal Lett.*, 66 (2000) 91.
 15. G.F. McLean, T. Niet, S. Prince-Richard, N. Djilali, *Int. J. Hydrogen Energy*, 27 (2002) 507.
 16. (1) Guangzhou York Point New Energy, <http://www.gzenergy.com/pic/plist.jpg> (Product quality has been confirmed in the authors' laboratory.)
(2) SunNanotech Co Ltd, <http://www.sunnano.com/> (Sample product is being supplied by the company to the authors' laboratory for test.)
 17. W.K. Hsu, J.P. Hare, M. Terrones, H.W. Kroto, D.R.M. Walton, P.J.F. Harris, *Nature*, 377 (1995) 687.
 18. W.K. Hsu, M. Terrones, J.P. Hare, H. Terrones, H.W. Kroto, D.R.M. Walton, *Chem. Phys. Lett.*, 262 (1996) 161.
 19. G.Z. Chen, X. Fan, A. Luget, M.S.P. Shaffer, D.J. Fray, A.H. Windle, *J. Electroanal. Chem.*, 446 (1998) 1.
 20. G.Z. Chen, I. Kinloch, M.S.P. Shaffer, D.J. Fray, A.H. Windle, *High Temp. Mater. Processes*, 2 (1998) 459. (Also see: *Advances in Molten Salts – From Structural Aspects to Waste Processing*, Edited by M. Gaune-Escard, Begell House, Inc., 1999, 97-107).
 21. D.J. Fray, *High Temp. Mater. Process*, 3 (1999) 67. (Also see: (1) *Molten Salts Bulletin*, 66 (1999) 2; (2) *Advances in Molten Salts – From Structural Aspects to Waste Processing*, Edited by M. Gaune-Escard, Begell House, Inc., 1999, 196-207).
 22. W.K. Hsu, M. Terrones, H. Terrones, N. Grobert, A.I. Kirkland, J.P. Hare JP, K. Prassides, P.D. Townsend, H.W. Kroto, D.R.M. Walton, *Chem. Phys. Lett.*, 284

- (1998) 177.
23. M. Terrones, W.K. Hsu, A. Schilder, H. Terrones, N. Grobert, J.P. Hare, Y.Q. Zhu, M. Schwoerer, K. Prassides, H.W. Kroto, D.R.M. Walton, *App. Phys. A-Mater. Sci. & Proc.*, 66 (1998) 307.
 24. W.K. Hsu, S. Trasobares, H. Terrones, M. Terrones, N. Grobert, Y.Q. Zhu, W.Z. Li, R. Escudero, J.P. Hare, H.W. Kroto, D.R.M. Walton, *Chem. Mater.*, 11 (1999) 1747.
 25. W.K. Hsu, J. Li, H. Terrones, M. Terrones, N. Grobert, Y.Q. Zhu, S. Trasobares, J.P. Hare, C.J. Pickett, H.W. Kroto, D.R.M. Walton, *Chem. Phys. Lett.*, 301 (1999) 159.
 26. M. Terrones, N. Grobert, W.K. Hsu, Y.Q. Zhu, W.B. Hu, H. Terrones, J.P. Hare, H.W. Kroto, D.R.M. Walton, *MRS Bulletin*, 24 (8) (1999) 43.
 27. G. Kaptay, I. Sytchev, J. Miklosi, P. Nagy, P. Poczik, K. Papp, E. Kalman, *Progress in Molten Salt Chem.*, vol. 1, Elsevier, Paris, (2000), p. 257.
 28. J. Miklosi, P. Poczik, I. Sytchev, K. Papp, G. Kaptay, P. Nagy, E. Kalman, *Appl. Phys. A*, 72 (2001) S189.
 29. G.Z. Chen, D.J. Fray, *Proc. 6th Inter. Symp. Molten Salt Chem. Technol.*, Chen Nianyi, Qiao Zhiyu (Editors), Shanghai University Press, Shanghai, China, 2001, p. 79.
 30. Q. Xu, C. Schwandt, G.Z. Chen, D.J. Fray, *J. Electroanal. Chem.*, 530 (2002) 16.
 31. A.T. Dimitrov, G.Z. Chen, I.A. Kinloch, D.J. Fray, *Electrochim. Acta*, 48 (2002) 91.
 32. J.B. Bai, A.-L. Hamon, A. Marraud, B. Jouffrey, V. Zymala, *Chem. Phys. Lett.*, 365 (2002) 184.
 33. I.A. Kinloch, G.Z. Chen, J. Howes, C. Boothroyd, C. Singh, D.J. Fray, A.H. Windle, *Carbon*, accepted.
 34. A. Huczko, *Appl. Phys. A-Mater*, 70 (2000) 365.
 35. L.M. Dai, *Polym. Advan. Technol.*, 10 (1999) 357.
 36. L. Kavan, *Chem. Rev.*, 97 (1997) 3061.
 37. I.A. Kinloch, G.Z. Chen and D.J. Fray, *unpublished results*
 38. I.A. Kinloch, Ph.D. Thesis, University of Cambridge, March 2001.
 39. W.K. Hsu, M. Terrones, H.W. Kroto, D.R.M. Walton, Poster at Nanotec 99, University of Sussex, Brighton, UK, September 1999.