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Influence of current density on the erosion of a graphite cathode and electrolytic formation of carbon nanotubes in molten NaCl and LiCl

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ABSTRACT

The electrochemical deposition of sodium and lithium from their respective molten chlorides onto a graphite cathode as the first step of carbon nanotube electrolytic production has been investigated. It has been shown that in the case of both sodium and lithium, as the cathodic current density increases, the cathode weight first increases and then decreases, i.e. the dependence of cathode weight change vs. cathodic current density passes through a maximum. The value of cathodic current density corresponding to the maximum increase in the cathode weight in the case of sodium is approximately 4 times as high as that in the case of lithium, which is explained by a higher solubility of sodium metal in molten sodium chloride compared to that of lithium metal in molten lithium chloride. The higher sodium metal solubility causes a higher electronic conductivity of the molten electrolyte, while the ratio of intercalated to dissolved sodium will be lower as compared to lithium. Curved multi-walled carbon nanotubes of an outer diameter of 20–50 nm with a wall thickness of 5–10 nm (molten NaCl) and of 20–100 nm with a wall thickness of 5–40 nm (molten LiCl) have been synthesized.

1. Introduction

There exist several experimental techniques to obtain carbon nanotubes (CNTs). Among other methods, CNTs are synthesized electrolytically in molten alkali/alkaline-earth halides, which involves electrochemical insertion of molten alkali/alkaline-earth metals into the graphite cathode.

The electrolytic method of CNT production was discovered in 1995 by Hsu and co-workers of the University of Sussex [1,2]. They electrolyzed molten lithium chloride with carbon electrodes. The average diameter of multi-walled nanotubes (MWNTs) obtained by these authors was 25–30 nm with the distance between graphene sheets being 0.34 nm. The CNTs were curved and had inclusions; depending on the electrolysis conditions, the CNT content in the electrolytic product ranged from 2 to 30%. Hsu et al. were first to synthesize metal filled CNTs [3–6]. The electrolyte used for such preparation contained a low melting point salt (e.g. $SnCl_2$); the outer diameter of CNTs in these experiments was 30–50 nm. These authors also succeeded in synthesizing CNTs from molten $CaCl_2$. The Sussex team proposed a carbide mechanism of electrolytic CNT formation, whose first step is the formation of alkali carbide, which then decomposes to lithium metal and CNTs.

Fray and co-workers of the University of Cambridge [7–9] confirmed that electrolytic CNTs are formed from a carbon (graphite) cathode. Most of the tubes were 10–50 nm in diameter and 100 nm to 20 μm long, while the maximum content of CNTs in the electrolytic product was 5, 30 and 50% for potassium, lithium and sodium chloride, respectively. The majority of the tubes were curved ones. The Cambridge team proposed an intercalation mechanism of electrolytic CNT formation [8,10], whose first step is fast intercalation of alkali cations into the graphite lattice and their in situ reduction inside the lattice. In works [11,12] Fray and co-workers made an attempt to scale up the electrolytic method of CNT production and showed that CNTs and other nanomaterials can be produced continuously on industrial scale by this method. In paper [13] it was found that the percentage of CNTs fell as the electrolysis of molten NaCl in galvanostatic regime was run for longer periods of time. The electrolysis was also inhibited by the anode effect and the formation of a sodium layer on the top of the electrolyte. In work [14] the Cambridge team investigated the electrochemical reduction of tin (II) and lithium ions from a LiCl–$SnCl_2$ molten salt. They showed that tin metal being deposited on the graphite surface does not intercalate in between the graphene sheets, which is related rather to electronic than to geometric factors.

The authors of the present paper reported that the electrodeposition of Li, Na, K, Mg and Ca from the respective molten chlorides all led to the formation of CNTs, but not Sn and Ni [15]. They also investigated the electrolytic product by atomic force microscopy, revealing some interesting nanostructures [16]. The authors intro-

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duced the term of material balance reversibility and showed that sodium and calcium intercalation into graphite is irreversible, while lithium intercalation is a reversible process [17–19]. Also, the influence of temperature on the electrochemical deposition of lithium was studied and it was shown that the rate of lithium intercalation into graphite increases when increasing temperature [20].

Bai et al. [21] report the formation of both single-walled carbon nanotubes (SWNTs) and MWNTs by electrolysis of molten NaCl at 810 °C in the range of current intensities from 2 to 10 A. The MWNTs synthesized by them have an average outer diameter of 10 nm and thin walls (about 3 nm thick), while the SWNTs are estimated to be 1.3–1.6 nm in diameter. The influence of very fine catalyst particles (Fe, Ni, Co), which originate from the impurities of the salt, is assumed by the authors and this assumption is confirmed by TEM observations.

Volkov et al. [22] obtained a mixture of spherical carbon nanoparticles (5–10 nm in diameter), nanofibers (20–50 nm in diameter, 1–20 μm long) and MWNTs (5–10 nm inner diameter) by electrolysis in molten NaCl–KCl using a graphite cathode with artificially increased lattice parameter at a temperature of 750 °C and cathodic current density of 0.1–10 A cm^{-2}. The authors mention that the CNTs are curved open-ended ones being partly filled with the alkali metal. The formation of CNTs is explained by intercalation of the alkali metals into the graphite lattice.

Novoselova et al. [23,24] synthesized CNTs from CO_2 dissolved under excessive pressure in molten NaCl–KCl or NaCl–KCl–CsCl using either a glassy carbon or platinum cathode at a temperature of 550–850 °C. The electrolysis was carried out both in galvanostatic and potentiostatic regimes (range of cathodic current densities: 0.005–0.2 A cm^{-2}, range of potentials: −1.40 to 2.07 V vs. platinum quasi-reference electrode). The authors proposed the following mechanism of carbon dioxide reduction: first stage $CO_2 + 2e^- = CO_2{}^{2-}$, second stage $CO_2{}^{2-} \rightarrow CO + O^{2-}$, and third stage $CO + 2e^- \rightarrow C + O^{2-}$. Depending on the bath composition and electrolysis conditions, the CNT content of the electrolytic product ranged from 5 to 40 vol.%, their outer diameter varied from 5 to 250 nm, while the inner diameter varied from 2 to 140 nm. The authors found that the majority of the CNTs are multi-walled curved ones, partly filled with the electrolyte. Most of the tubes agglomerate into bundles. Except MWNTs the cathodic product contains carbon nanofibers, nanographite and amorphous carbon. The formation of CNTs from elemental carbon deposited on the cathode surface is explained by the catalytic role of nanosized iron and platinum particles also present in the electrolytic product.

Kushkhov's research group [25] and Devyatkin [26] successfully obtained CNTs by electrolysis of carbonate melts being under CO_2 pressure. Kushkhov and co-workers used for this purpose a NaCl–KCl–CsCl–Li_2CO_3 (5 wt.%) molten salt at a temperature of 550 °C, while Devyatkin electrolyzed a Li_2CO_3–$Al_4B_2O_9$ molten salt at a temperature of 750 °C. Along with nanosized amorphous carbon, the cathodic product contained CNTs of 100–200 nm in diameter. Kushkhov and co-workers explained the formation of carbon products in a way similar to that of Novoselova et al., while Devyatkin proposed a mechanism including carbon and lithium metal co-deposition on the cathode surface with the formation of LiC_6 compound, whose subsequent decomposition leads to the formation of CNTs.

Alekseev et al. [27–29] report the formation of MWNTs in an industrial lithium metal electrolyzer with a steel cathode and graphite anode in a lithium chloride–potassium chloride eutectic melt. They observed both bundles of MWNTs (single nanotubes in them are 50–70 nm in diameter and 1–2 μm long) and individual MWNTs (10–40 nm in diameter and 1–2 μm long) in the anodic slime. The fraction of CNTs was about 5 wt.% of the weight of carbonaceous material, while a significant part of the tubes had open ends.

Huang and co-workers [30] obtained Sn-filled CNTs from a LiCl–1% $SnCl_2$ molten salt at 700 °C in the range of cathodic current densities 2.55–6.76 A cm^{-2} for 3 min. The number of nanotubes formed was quite high, while most of the CNTs were filled with tin metal nanoparticles and nanorods; some nanotubes were filled with long continuous nanowires. The metal-filled nanotubes were typically straight, being 75–125 nm in diameter and more than several micrometers long. The size of the nanoparticles and nanorods varied from several to tens of nanometers. The authors explain the formation of filled nanotubes by oxidation of primarily formed intercalation compounds Li_xC_y by Sn^{2+} cations with subsequent formation of tubule carbon, which tends to wrap tightly around the tin droplets.

In this contribution, an attempt to establish a correlation between cathodic current density, the rate of alkali metal intercalation into graphite and the amount of graphite eroded from the cathode surface will be made.

2. Experimental

The measurements were carried out in an air-tight electrolytic cell made of an INCOLOY superalloy. Lithium chloride and sodium chloride (both reagent grade, Sigma–Aldrich) were used for the measurements. Prior to experiments, the salts (one at a time) were placed in the electrolytic cell and thoroughly dried in vacuum at a temperature of 393 K for 40 h. After that the temperature was raised to 573 K and held for 1 h. To enhance the moisture removal, periodic flushing with purified dry argon gas was applied. It is known that lithium chloride is capable of absorbing and retaining moisture even at elevated temperatures. To remove as much moisture from it as possible, after keeping the salt at 573 K it was heated up to 773 K in an argon atmosphere and kept at this temperature for another hour. During this period, the cell was evacuated and filled with argon several times. The same procedure was repeated at 873 K. After that the salts were melted in argon. All electrochemical measurements were performed at a temperature of 1123 K (sodium chloride) and 973 K (lithium chloride), respectively.

Cyclic voltammetry measurements were carried out in a three-electrode cell using molybdenum, glassy carbon and graphite working electrodes. A glassy carbon rod of 3.5 mm in diameter served as the quasi-reference electrode (GC Q.R.E.). A glassy carbon crucible was used both as the auxiliary electrode and container for the electrolyte. Cyclic voltammograms were recorded in the range of scan rates ν from 20 to 0.01 V s^{-1}, starting typically with potential $E_1 = +0.2$ V relative to the potential of the GC Q.R.E. The reversal potential E_2 varied from −1.0 to −2.0 V vs. the potential of the GC Q.R.E.

Open-circuit potential (OCP) measurements in molten NaCl and LiCl were carried out in the three-electrode cell described above using a graphite working electrode and a GC Q.R.E. Before each measurement, the working electrode was polarized galvanostatically by a cathodic current density of 45.5 mA cm^{-2} (90.9 mA cm^{-2}) for 3.1–12.4 s.

Electrolysis was performed in galvanostatic regime. The electrolytic cell generally comprised 3 electrodes: graphite rod cathode, glassy carbon crucible anode, glassy carbon quasi-reference electrode. In certain cases, when the current intensity applied was above 1 A, the electrolysis was done in a two-electrode cell (graphite rod cathode, glassy carbon crucible anode). A VoltaLab 40 "dynamic electrochemical laboratory" and a Konstanter SSP 120-40 power supply were used in this work. The initial active surface area of the cathode was 0.44 cm^2. The cathodic current density and time of electrolysis varied so that the electrical charge passed through the circuit and related to it theoretical weight of the deposited metal was constant. All other experimental conditions were the same in each of the series. After the electrolysis was completed, the molten