Formation of Carbon Nanostructures in Electrolytic Production of Alkali Metals


Innovations of Leningrad Institutes and Enterprises Closed Joint-Stock Company, St. Petersburg, Russia
Ioffe Physicotechnical Institute, Russian Academy of Sciences, St. Petersburg, Russia
St. Petersburg State University, St. Petersburg, Russia
State Institute of Applied Chemistry, St. Petersburg, Russia

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Abstract—Carbon-based solid phase containing open and closed multiwalled carbon nanotubes (up to 5% of the total carbon) was found in the waste from industrial production of metallic lithium by electrolysis of lithium chloride melt with graphite electrodes.

The electrochemical method of preparation of carbon nanostructures [1, 2] and, in particular, carbon nanotubes (CNTs) was developed and studied somewhat later than the electric arc method [3] and virtually simultaneously with that CVD method (chemical vapor deposition, i.e., chemical decomposition of volatile carbon-containing substances in the presence of catalysts [4, 5]) and HIPCO [6]. Chen et al. [2] studied the structure of a nanomaterial in relation to a salt used in the electrolysis, and Bai et al. [7] considered in detail this process with the most readily available salt in the CNT synthesis, sodium chloride. It was found that, under definite conditions, the carbon constituent of the product accumulating in the electrolytic tank may contain up to 50% nanocarbon material. The quality of the thus obtained CNTs may be close to that of nanotubes synthesized in the arc, and their amount is substantially larger than that of multiwalled nanotubes generated in the arc without catalysts [3] and comparable with the CNT content in “cobweb” prepared in the arc, using catalysts. However, in contrast to the latter process, both multiwalled nanotubes (MNT) and single-walled nanotubes (SNT) by electrolysis can be successfully synthesized without catalyst, and hence its subsequent removal is not required.

Unfortunately, the electrolysis as a method of purposeful synthesis of CNTs has not been developed. This is caused by the fact that it is difficult to organize the electrolysis as a continuous process similar to arc synthesis [8]. Coking of an electrolytic tank with the products of graphite electrode degradation rapidly causes breakdown, and tank cleaning is required, so that, e.g., under laboratory conditions, the working time of the electrolyzer (actually, electrochemical cell) was no more than 10–15 min.

In this context, the goal of our study was to examine the possibility of CNT synthesis in the course of industrial production of alkali metals by electrolysis of their salts. In this case, the problem of coking of the electrolytic tank becomes less pressing, because all dimensions of the apparatus are larger by two to three orders in magnitude as compared to the laboratory device. An idea of CNT synthesis under such conditions was published in [1], however, we could find no information on its implementation.

EXPERIMENTAL

In production of alkali metals (lithium), a eutectic melt of lithium and potassium chlorides (Khimkonsentrat plant, Novosibirsk, Russia) serves as a starting material. The anode consisted from four 30 × 30 × 180-cm graphite blocks immersed in the melt approximately to a depth of 1 m. The direct current was 25 kA. The total surface area of the graphite anode was about 2 × 0.3 × 1 × 4 = 2.4 m². The electrolyzer operates for 1–1.5 years. During this time, each graphite block wears out approximately by half.
A steel cathode is used under the industrial conditions. During the electrolysis, the anode material rapidly converts into a graphitized coke.

We took 5–100-g coke samples from different points of the tank and found that they contain up to 20–30 wt % lithium and potassium chlorides and 30–40 wt % lithium and barium carbonates. To eliminate soluble chlorides, the coke was treated with water for 1 h at 60°C under stirring with a magnetic stirrer and filtered through a “blue tape” paper filter. To separate carbonates insoluble in water, the residue was treated with dilute hydrochloric acid (10 wt %) for 13 h with stirring at room temperature, or boiled in concentrated HCl (36 wt %) for 2 h. The weight of the residue thus obtained amounted to 12–20% of the initial slime.

The samples obtained were examined with a JEM-100S (JEOL) transmission electron microscope at 100 000–100 000 magnification after ultrasonic disintegration in toluene.

A typical TEM image of the sample is shown in Fig. 1. MNT bundles 50–70 nm in diameter (d) and separate MNTs 10–40 nm in diameter and 1–2 μm long (L) are clearly seen. In contrast to electron micrographs shown in [1, 2, 7], a substantial part of CNTs have open ends, e.g., MNT with d ≈ 20 nm projecting from MNT bundle (Fig. 2). The formation of open CNTs is of interest, since, in accordance with reference data, no opening of CNT is observed when a CNT-containing material is treated with dilute acid at room temperature. This fact suggest that at least a part of nanotubes remain open during growth.

The length L of CNTs shown in Figs. 1 and 2 is 1–2 μm. At the same time, short nanotubes with L ≈ 100 nm are also seen (Fig. 3). Their number is relatively low. Single-walled CNTs were not observed.