Synthesis of Nanostructured Carbon Material by Electroreduction in Fused Alkali Carbonates

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Carbon fine powders were obtained by the electrochemical reduction of liquid ternary system lithium–sodium–potassium carbonates at 450 °C using nickel electrodes. The analysis of these powders by transmission electron microscopy and X-ray diffraction measurements revealed the coexistence of three different forms of carbon: graphite, amorphous carbon and carbon nanostructures. The third has an average diameter of about 10 nm and is self-organized into long "ropes".

Carbon like natural and synthetic graphites, petroleum coke, diamond, carbon fibers or mesocarbons has a particular place among the technological materials depending on temperature and method of preparation, in degree of crystallization and stacking order: for example, diamond is used for abrasive paste, graphite for its lubricating properties.

In 1991, Iijima has discovered a new form of carbon called carbon nanotubes[1] which were prepared in cathode-tip deposits during the arc-discharge synthesis of fullerenes. A nanotube is a cylinder with a graphite structure and closed generally at both ends by a fullerene type cap. The "Russian doll" model allows for describing in detail the structure of the carbon nanotubes; they are composed of graphitic sheets rolled into closed concentric cylinders. The diameter and the length of the latter are in the order of nanometers and micrometers, respectively. They constitute the ultimate carbon fibers. Depending on the detailed structure (diameter, twist etc.), these nanotubes exhibit metallic or semiconducting electrical properties. Owing to these properties, combined with their small size, a large range of micro-electronics applications is expected.

Recently, particular attention has been paid to the synthesis of such kind of carbon materials, notably since they were proposed as materials in fuel cells for hydrogen storage[2] and as anode materials in lithium-ion batteries.[3] Therefore, many efforts were devoted to find new methods for preparing large amount of nanostructured compounds. For example, carbon nanotubes can be produced by the arc-discharge method[4] and by pyrolyzing hydrocarbons.[5]

As reported previously, in order to obtain carbon coating or carbon with special electrochemical properties, it has been proposed to use the electrochemical decomposition of solid or liquid carbonates.[6–8] The carbon deposits will be influenced by preparation conditions such as temperature, carbonates composition, reduction potential, current density, and so on. In this paper, based on the electrochemical reduction of fused alkali carbonates, an approach for the synthesis of nanostructured carbon like carbon fibers, which could be assimilated to carbon nanotubes through the size and the arrangement, is presented.

The molten salt used for the preparation of carbon powders was composed of the eutectic mixture of 43.5 mol% of Li_2CO_3, 31.5 mol% of Na_2CO_3 and 25 mol% of K_2CO_3 with a melting point at 396 °C. Each constituent of the fused Li_2CO_3–Na_2CO_3–K_2CO_3 salt was previously weighted, mixed, dehydrated under vacuum at 150 °C and slowly heated to 450 °C under carbon dioxide atmosphere as described elsewhere.[6] The electrochemical cell is constituted of an outer Pyrex envelope containing a glassy carbon (Degussa) crucible. The residual pressure was less than 0.1 mm Hg. During each experimental run, carbon dioxide was kept flowing through the cell. The carbon powders were deposited electrochemically on nickel wire (Ø = 1 mm) working electrode. A CO_2–O_2/CO_3^{2-} electrode was used as a reference electrode.[6] The carbon crucible was used as a counter-electrode. Carbon powder was obtained by scratching the working electrode surface. The carbon powder was washed with hot water followed by washing with hydrochloric acid in order to remove residual carbonates, and dried at 150 °C under vacuum.

X-ray diffraction (XRD) measurements are carried out in order to examine the nature of the carbon electrodeposited using a Rigaku Rint 2200 diffractometer (Cu Kα). Transmission electron microscopy (TEM) measurements were performed (Hitachi, H-800) to observe nanometer scale structures. Powders were dispersed in ethanol using ultrasonic waves and deposited on an amorphous carbon grid supported by a Cu frame. The accelerated voltage of electron beam was 200 kV.

The electrochemical reaction involved in the carbon deposit process in fused Li–Na–K carbonates corresponds to the reduction of carbonate ions into carbon and oxide according to[6]:

$$CO_3^{2-} + 4\,e^- \rightarrow C + 3\,O^{2-}$$

Recently, Kawamura and Ito have reported some results concerning the preparation of thin carbon film on aluminum substrate by electrolysis of fused LiCl–KCl–K_2CO_3.[7] However, in their experimental conditions, the amount of deposited carbon powder was indirectly related to the carbonate ions content. So, the electrolysis of molten salt containing only carbonate ions could give rise to substantial carbon deposit.[6]

Carbon was deposited on nickel electrode at a fixed potential value (E = –1.6 V vs CO_2–O_2/reference electrode) comprised between the beginning of the reduction of carbonates and the electrodeposition of alkali. The X-ray diffraction pattern of a carbon powder obtained is presented in Figure 1. The broad peak around

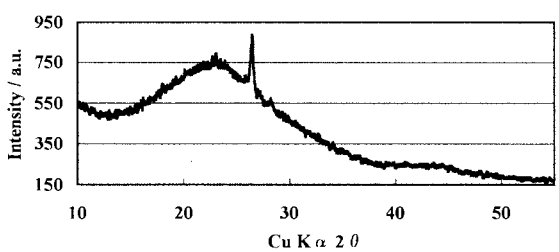

Figure 1. XRD patterns of carbon electrodeposited on nickel electrode in molten carbonates, washed with HCl aqueous solution and dried 80 °C in vacuum.

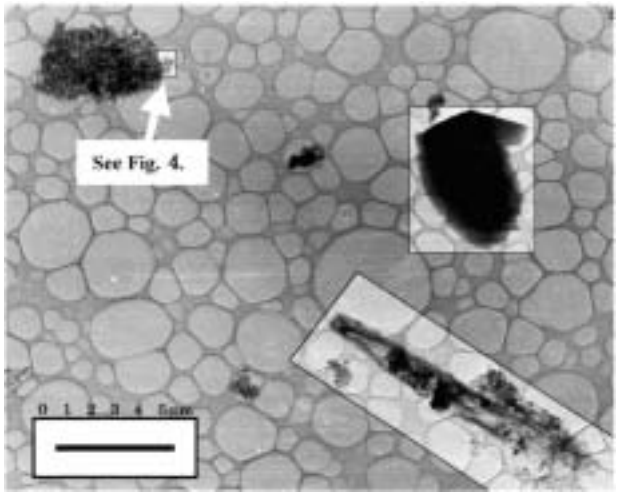

Figure 2. TEM image of three kinds of carbon compounds obtained by electroreduction of molten ternary carbonates (Li–Na–K) at 450 °C. Scale bar: 5 μm.

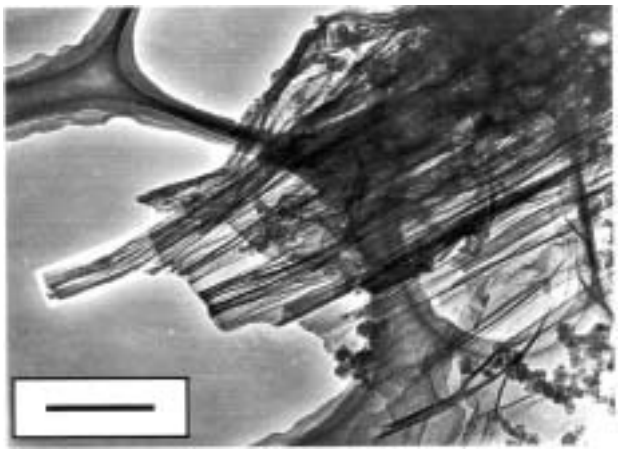

Figure 3. TEM image of carbon fibers obtained by electrochemical reduction of liquid ternary system (Li–Na–K) carbonates. Scale bar: 200 nm.

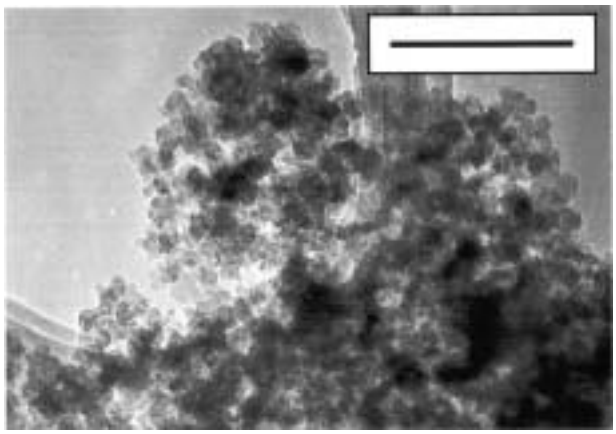

Figure 4. TEM image of amorphous carbon obtained by electrochemical reduction of liquid ternary system (Li–Na–K) carbonates. Scale bar: 200 nm.

$2\theta = 24°$ is characteristic of amorphous carbon. The (002) peak at $2\theta \approx 26.5°$ related to the graphite structure is clearly observable.

The results obtained by X-ray diffraction showing the presence of graphite and amorphous carbon were confirmed by TEM analyses (Figure 2). These TEM analyses have also revealed the presence of the third kind of carbon fibers with an average diameter of around 10 nanometers (Figures 2 and 3). These nanostructures have a nearly-uniform size and are self-organized into long "ropes" in which parallel nanofibers are bound together. The diameter of a "rope" was comprised between 100–500 nm corresponding to 10–50 tubes per "rope". The dark particles observed in Figure 3 can be explained by the coexistence of amorphous carbon which surrounds carbon nanofibers. As illustrated in Figure 2, this amorphous carbon particle (around 5 μm) consists of clusters of smaller particles around 10 nm size (Figure 4). These results were in good agreement with our previous results.[6] These authors have reported that the specific surface area determined by the B.E.T. method is generally high and comprised between 450 and 650 m^2/g, depending on the applied potential value in molten Li_2CO_3–Na_2CO_3–K_2CO_3. These high values suggest that agglomeration of nano-sequence (5–10 nm) in an amorphous carbon cluster occurs.

Finally, in our experimental conditions, the growth of the ropes seems to be limited; their length reaches a finite value of 1 μm. Nevertheless, one cannot exclude that this limitation may be due to the washing procedure of the carbon powders with hot water and HCl aqueous solution which could break these ropes into shorter one. The electrolysis of molten lithium–sodium–potassium carbonates gives rise to substantial production of carbon powders. The analyses of these powders by TEM and XRD have revealed the presence of carbon nanofibers with an average diameter of about 10 nm. However, this preparation condition is until now not selective and also gives rise to amorphous carbon and graphite. Nevertheless, by controlling electrolysis conditions and washing treatments, we believe possibility of designing micro- and nano-structure of carbon deposits.

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