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Electrochemical production of low-melting metal nanowires

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Abstract

The extent of nanotube formation arising from the electrolysis of molten LiCl, using graphite electrodes, is reduced by the addition of salts to the electrolyte. In certain cases (99% LiCl + $<$ 1% $SnCl_2$), considerable quantities of tin-containing nanotubes are formed in addition to Li_2C_2. However, the tube walls are poorly graphitised. Analogous results were obtained by adding trace amounts of Bi, Pb or Sn powder to the LiCl. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In addition to the commonly employed arc discharge technique, pyrolysis of hydrocarbons and metal-catalyzed laser ablation of graphite [1–6], a novel method for producing nanotubes and fullerene-related materials, involving the passage of a direct current through a graphite rod (cathode) immersed in a molten ionic salt (e.g., LiCl or LiBr) contained in a graphite crucible (anode) [7–9], has recently been developed. In our earlier studies [7–9], 20–40% of the carbon-based products consisted of well-graphitised multi-walled nanotubes, the remainder being amorphous carbon and polyhedral particles. A proportion of the nanotubes and particles contained encapsulated Li_2C_2 [9]. Addition of 1–50% (by weight) of $SnCl_2$ to the LiCl resulted only in amorphous carbon particles. However, when the $SnCl_2$ concentration was reduced to less than 1% by weight, tin-containing nanotubes (ca. 30–40% of the observed material) were produced [10,11]. The walls of the tubes, however, appear to be fairly amorphous.

In this Letter, we describe a detailed and extended study involving other mixed electrolytes, e.g. LiCl containing ca. 1–50% by weight of KCl, $CuCl_2$, $ZnCl_2$ or $CaCl_2$. Small amounts (ca. $<$ 1% by weight) of Bi, Co, Cu, In, Pb, Sn or Zn powder were also added to the LiCl.

2. Experimental

The electrolysis apparatus consists of a heated quartz glass tube (length, 40 cm; OD, 5 cm) with gas inlet/outlet flanges. A crucible (anode) was made by drilling a 3 cm diameter hole to a depth of 7 cm in a

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Table 1
Production of nanostructures using composite electrolytes

Electrolytes	Additive salts or metal powder in LiCl (% by weight)	Nanotubes (%)	Nanowires (%)	Metal-encapsulated particles (%)	Amorphous and polyhedral carbon particles (%)
$KCl + LiCl$	1–50	20–40			60–80
$CaCl_2 + LiCl$	10–50	1–5			> 95
$CaCl_2 + LiCl$	1–10	20–40			60–80
$CuCl_2 + LiCl$	10–50				100
$CuCl_2 + LiCl$	1–10	< 1		5–10	> 90
$ZnCl_2 + LiCl$	10–50				100
$ZnCl_2 + LiCl$	1–10	< 1		5–10	> 90
$SnCl_2 + LiCl$	10–50				100
$SnCl_2 + LiCl$	5–10			5	95
$SnCl_2 + LiCl$	1–5	< 1	1–5	1–5	90
$SnCl_2 + LiCl$	0.8–1	< 1	30–40	5–10	50–60
$Sn + LiCl$	0.8–1	< 1	30–40	10	50–60
$Pb + LiCl$	0.8–1	< 1	30–40	5–10	50–60
$Bi + LiCl$	0.8–1	< 1	20–30	5–10	50–60
$Cu + LiCl$	0.8–1	< 1		30–40	60–70
$Co + LiCl$	0.8–1	1–2		5–10	> 90
$In + LiCl$	0.8–1	< 1		10–20	80–90
$Zn + LiCl$	0.8–1	< 1		30–40	60–70

Column heading percentages based on TEM observations.

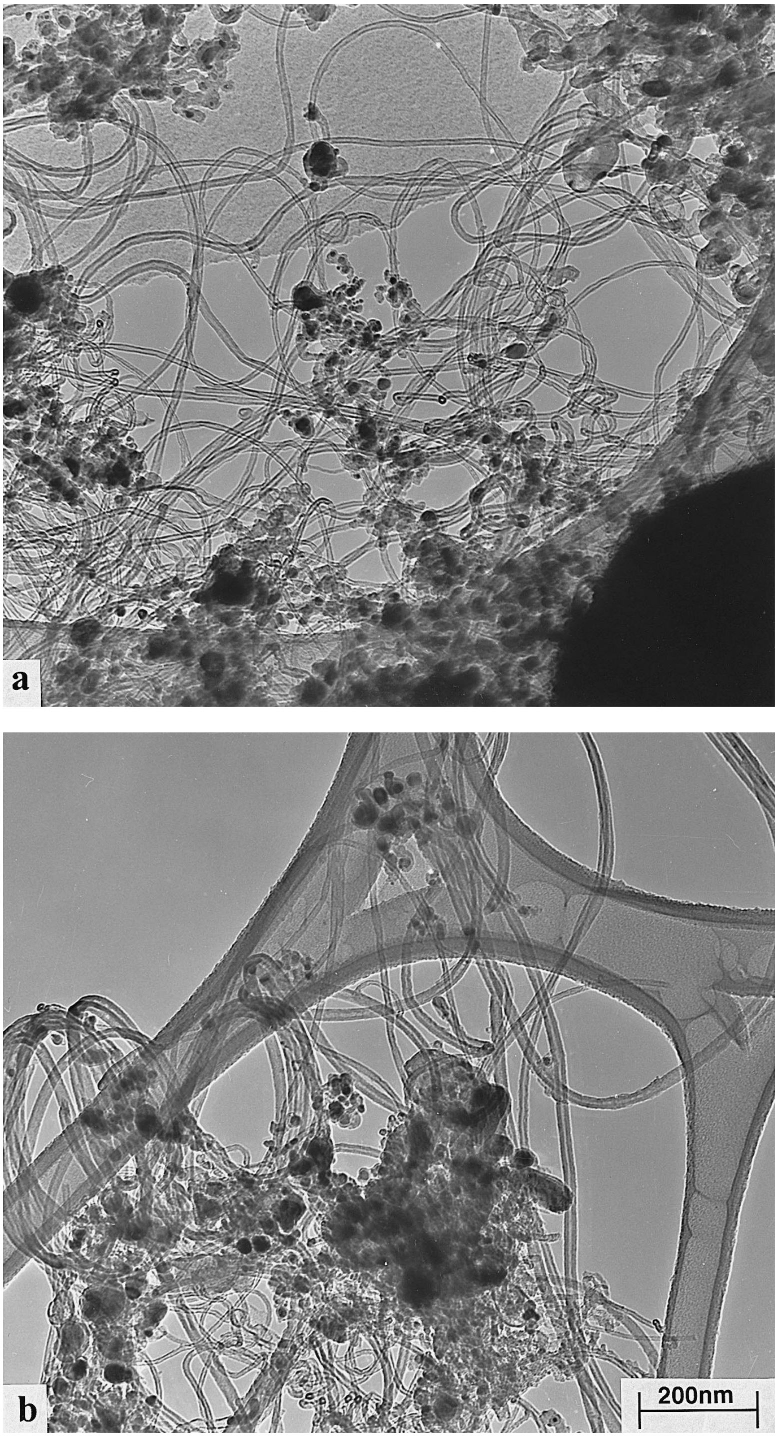

Fig. 1. Carbon nanotubes produced using: (a) LiCl as electrolyte; (b) LiCl + KCl (1–50% by weight) as electrolyte.

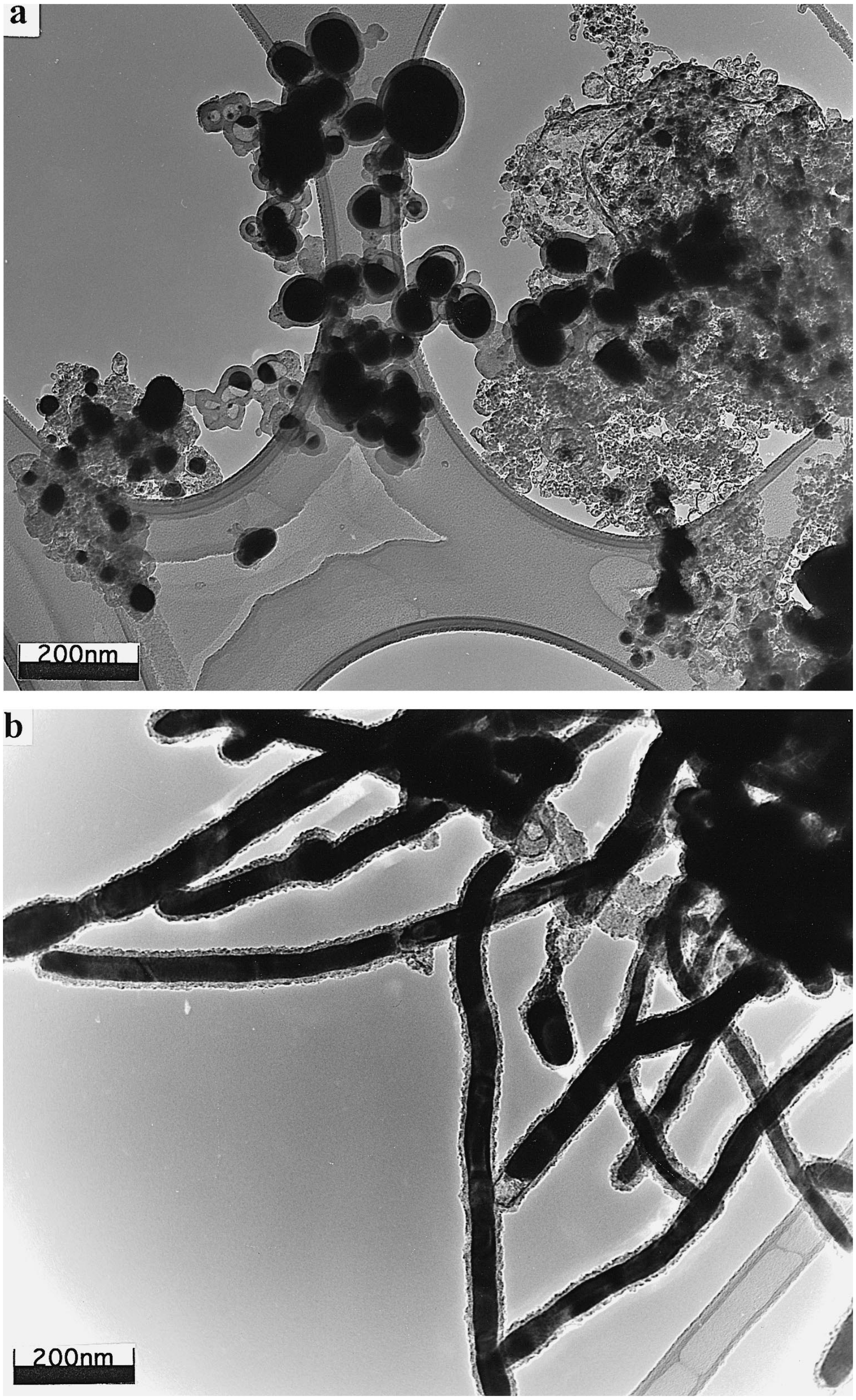

Fig. 2. (a) Encapsulated particles produced from LiCl + $CuCl_2$ (1 ∼ 5% by weight). X-ray diffraction measurements confirm the presence of pure Cu within the carbon cage. (b) Sn nanowires produced from LiCl + $SnCl_2$ (0.8–1% by weight). EDX and X-ray diffraction analyses confirm the presence of β-Sn containing nanowires.

cylindrical block of high-purity graphite (length, 10 cm; OD, 4 cm; Le Carbone, Portslade, UK). The cathode consisted of a 3 mm diameter carbon rod positioned at various depths within the crucible by means of a screw mechanism. The crucible was filled with the ionic salts/powder (ca. 50 g) and the apparatus was evacuated and purged with argon (100–150 Torr). The oven temperature was then raised (20°C/min) until the ionic salts melted (ca. 600°C). The current was varied by carefully adjusting the voltage (0–20 V at 3–5 A). For the sake of uniformity, the current was maintained for 2 min in each electrolysis experiment and the cathode immersion depth was set at 2 cm.

Experiments were conducted using various salt ratios, e.g., KCl/LiCl, $CaCl_2$/LiCl, $CuCl_2$/LiCl, and $ZnCl_2$/LiCl. In addition, experiments were carried out in which trace amounts ($<$ 1% by weight) of metal powders, e.g., Bi, Co, Cu, In, Pb, Sn and Zn (325 mesh, 99.8%., Aldrich Chem.), instead of metal salts, were added to the LiCl. After electrolysis, the apparatus was set aside to cool. Distilled water was added to the crucible and the mixture was worked up in order to obtain the carbonaceous products (ca. 20–30 mg) (see Refs. [7–9] for a detailed description of this procedure). The results of these experiments are given in Table 1.

3. Results

Electrolysis of LiCl/KCl mixtures, containing up to 50% (by weight) KCl, gave results identical to those obtained using pure LiCl, i.e., 20–40% nanotubes (Fig. 1). Addition of $CaCl_2$ (10–50% by weight) to LiCl, however, led to a decrease in nanotube formation (to ca. 1–5%). Reduction of the $CaCl_2$ content to below 10% by weight lead to the reestablishment of the nanotube yield. Addition of

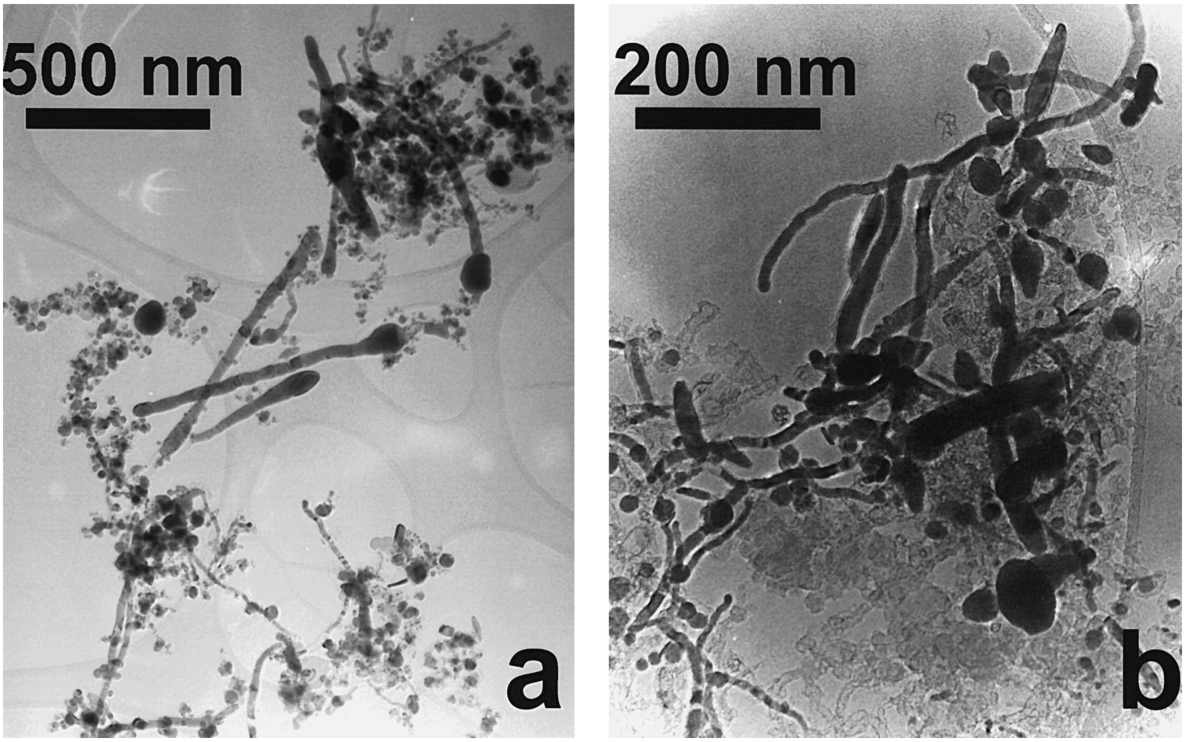

Fig. 3. (a) Pb nanowires produced from LiCl + Pb (0.8–1% by weight). (b) Bi nanowires produced from LiCl + Bi (0.8–1% by weight) mixtures.

$CuCl_2$, or $ZnCl_2$ (10–50% by weight) to LiCl produced only amorphous carbon, whereas the presence of less than 10% of $CuCl_2$ or $ZnCl_2$ resulted in the formation of some encapsulated particles and amorphous carbon (Fig. 2a) to the exclusion of nanotubes. In none of these experiments were metal-containing nanotubes observed.

In previous papers we demonstrated that tin-containing nanotubes were formed by the electrolysis of LiCl-containing $SnCl_2$ ($< 1\%$ by weight) [10,11]. We have now shown that replacement of $SnCl_2$ by tin powder ($< 1\%$ by weight) gives the same result (Fig. 2b). Experiments using powdered Bi or Pb also generated the corresponding metal-containing nanotubes (Fig. 3a,b). By contrast, the addition of Co, Cu, In or Zn powder to LiCl yielded predominantly amorphous carbon, accompanied by encapsulated (metal) particles but negligible amounts of nanotubes.

The nanotube length varies from metal to metal, e.g., 3–5 μm for Sn and Pb and 1–3 μm for Bi. HRTEM images (Fig. 4a,b) (ED-X analyses) of Bi- and Pb-containing nanotubes, respectively, confirm that only the metals, and not their halides, were present. A previous report described the movement of encapsulated tin within nanotubes under the influence of electron irradiation [10,11]. Similar behavior was observed for Pb but not for Bi.

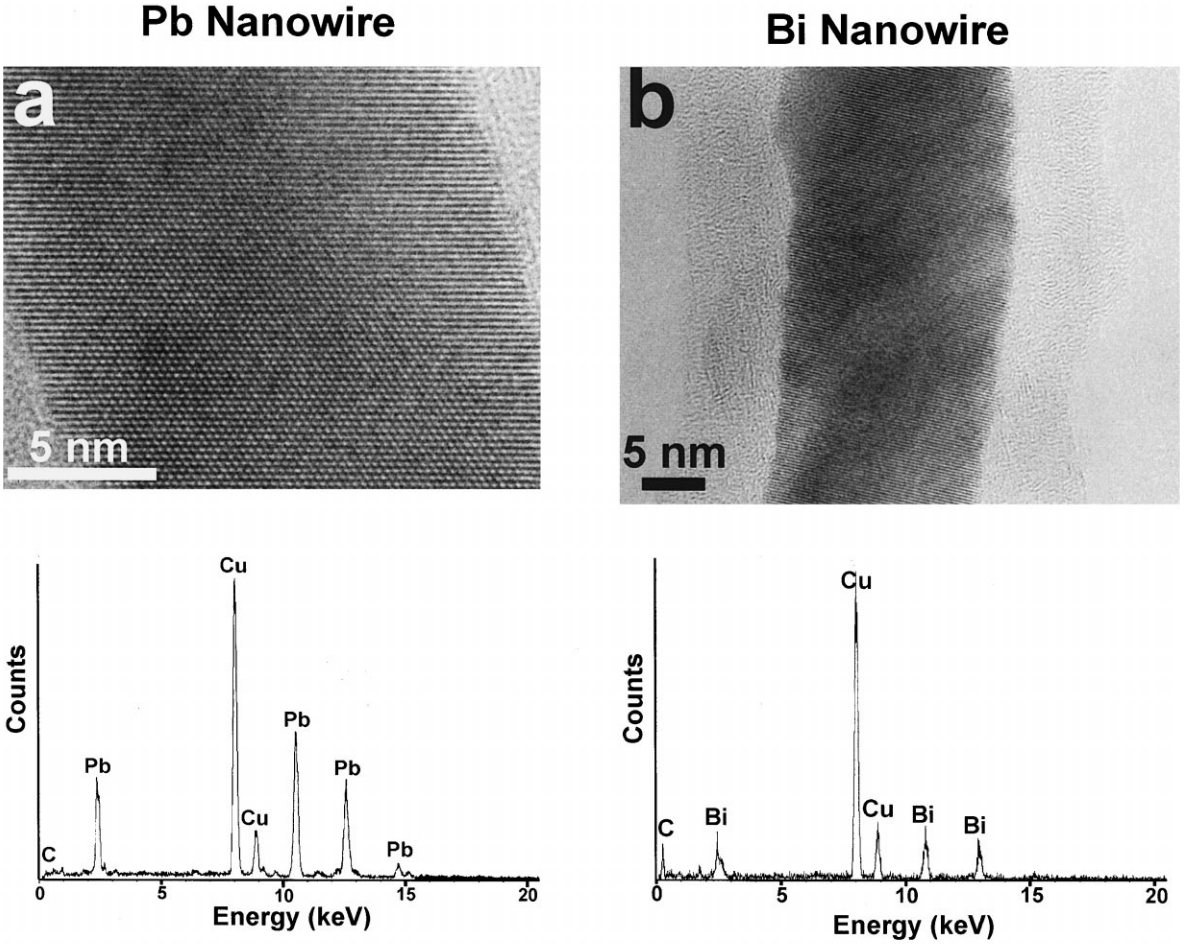

Fig. 4. HRTEM images: (a) a single Pb-containing nanowire; (b) a single Bi-containing nanowire. The EDX spectrum of the individual wires is shown in the insert. The Cu profiles were built up from a TEM copper grid.

4. Discussion

The fascinating discovery that during electrolysis of molten lithium chloride in a single compartment cell with a graphite cathode (rod) and graphite anode (crucible), well-graphitised nanotubes are formed is not an obvious or the expected result, nor one that is easy to explain.

The prerequisite for Li^+ reduction, the observation of Li_2C_2 formation, and the inhibition of nanotube formation when ions with a more positive discharge potential (Ca^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Sn^{2+}, Pb^{2+}, etc.) are present at high concentration in the molten salt provides an insight into the electrochemistry of nanotube formation which is now considered. The experimental data in Table 1 suggests that reduction of lithium cations at the graphite cathode plays a crucial role in the formation of nanostructures. Thus when easily reducible metal cations (Cu^{2+}, Zn^{2+}, Sn^{2+}) are present at high concentration, they are discharged as the free metals in preference to Li^+ and the formation of nanostructures is prevented. The presence of KCl does not interfere in the process because Li^+ is preferentially reduced. Intermediate behaviour is observed with Ca^{2+}. At high concentration this cation is preferentially discharged and the formation of nanotubes is thus inhibited, lowering the loading of Ca^{2+} and re-establishing Li^+ as the major charge carrier. The yield of nanotubes consequently increases.

The question now arises: what is the nature of the cathodic reaction of lithium cations which leads to dissolution of graphite and re-formation of carbon nanostructures? The two obvious cathodic reactions of Li^+ are reduction to the metal at the surface and intercalation of Li between graphitic layers. At temperatures above 600°C, graphite dissolves in molten Li to give a thermodynamically very stable Li_2C_2 phase. The material, identified by electron diffraction [9], was found to be encapsulated within well-graphitised carbon nanotubes, suggesting that the formation of Li_2C_2 may be a key step in cathode dissolution and subsequent nanotube formation (Reaction (1)):

$$2Li^+ + 2e^- + 2C_{\text{graphite}} \rightarrow Li_2C_2 . \qquad (1)$$

Slugs of Li_2C_2 are often found encapsulated within the well-graphitised carbon nanotubes and we estimate that ca. 10% of available nanotube inner core volume is filled with this material. That the material is *within* the nanotubes prompts the suggestion that C atoms extrude or segregate as an ordered hexagonal array, resulting in graphitic nanotubes. A somewhat analogous process has been suggested in order to explain the metal-catalysed gas-phase formation of boron nitride (BN) nanotubes [12]. In this experiment, amorphous BN material reacts with a metal (Ta) to form a crystalline Ta/BN particle. Subsequently, segregation or extrusion of *ordered* BN from the alloy facilitates the formation of hexagonally infrastructured nanotubes.

While the decomposition of Li_2C_2 to graphite nanotubes and Li metal *might* occur under the condi-

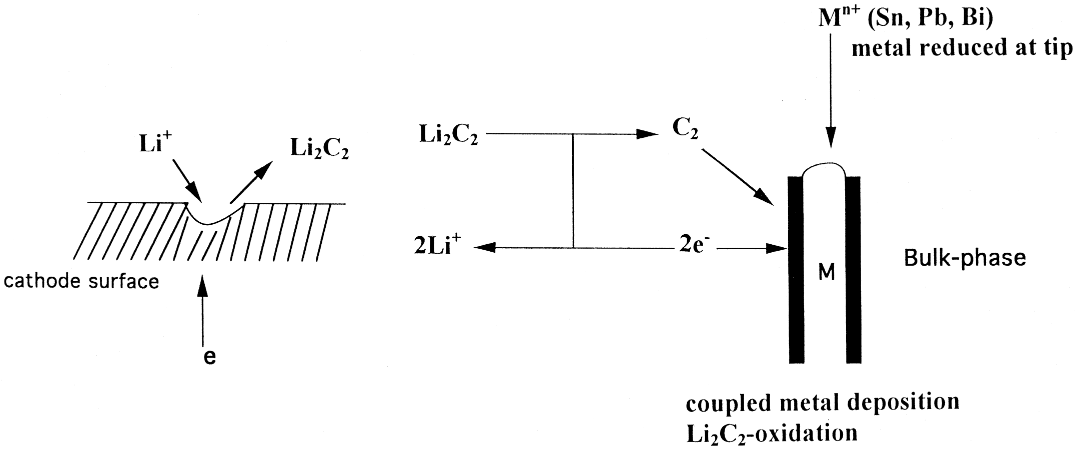

Fig. 5. Plausible scheme for electrolytic formation of amorphous carbon-coated metal nanowires.

tions of our experiments, an alternative possibility is oxidation of Li_2C_2 leading to graphitisation, i.e., reversing Reaction (1). The most likely oxidant in the system is chlorine which is generated at the (lower) anode and sparges through the melt (Reaction (2)).

$$Li_2C_2 + Cl_2 \rightarrow C_2 + 2Li + 2Cl^- . \qquad (2)$$

The formation of a *conducting sheath* around Li_2C_2 suggests a growth mechanism whereby chlorine is reduced on the graphite surface by oxidation of the carbide interior, i.e., a short-circuited electrochemical cell. As graphite is deposited on the surface Li_2C_2 is extruded forming a fresh surface for graphitisation, thus propagating tubule growth.

The presence of easily reducible metal halides of Sn, Pb or Bi provides alternative oxidants to chlorine (Reaction (3)).

$$Li_2C_2 + M^{2+} \rightarrow 2C_{\text{graphite}} + 2Li^+ + M . \qquad (3)$$

In such cases the encapsulated material is the metal itself, not the carbide. However, the same concept can be applied to the self-assembly of nanowires. Sn or Pb cations are discharged at the interior metal surface by electrons furnished by oxidation of adsorbed Li_2C_2. Thus coupling of oxidation of the carbide and deposition of metal would produce a graphite sheet around a molten metal core by further adsorption of the carbide, oxidative graphitisation and metal deposition (Fig. 5).

In the second type of experiment studied here, trace quantities ($<$ 1% by weight) of Sn, Pb and Bi, introduced into the LiCl electrolyte, are liberated as nanoscale metal wires almost completely encapsulated in tubes whose walls consist of disordered carbon. These metals are likely to be oxidised at least in part by liberated chlorine, thereby allowing the same mechanism of nanowire formation as suggested for their salts.

It may be significant that well-graphitised nanotubes are formed in the presence of metals which are known to form *carbides*. The observation of nanotube-like structures with very poorly graphitised walls in the presence of *metallic* Sn (which is reluctant to form a carbide [10]) lends circumstantial support to the mechanistic schemes suggested here.

In our study, it is noteworthy that the metals, which preferentially form nanowires, posses low melting points (200–300°C) so that the molten state of metal may facilitate nanowire generation. This behaviour would account for the presence of metal-encapsulated particles, instead of nanowires in experiments involving high-melting-point Co and Cu. The preferential formation of metal-encapsulated particles in the presence of low-melting-point metals, such as Zn and In, remains to be explained.

Acknowledgements

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