~~Inexpensive~~ Transformation of the greenhouse gas CO₂ by molten electrolysis into a wide controlled selection of carbon nanotubes

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ABSTRACT

This paper demonstrates a highly favored route for the synthesis of controlled nanostructures at high rate, high yield, and low cost by molten carbonate electrolysis splitting of CO₂. We show the wide, portfolio of carbon nanotubes (CNTs) that can be produced by controlling the electrolysis conditions in this one-pot synthesis. For example solid core carbon nanofibers are formed with C-13 isotope CO₂, whereas hollow core CNTs are formed with natural abundance CO₂ (which contains 99% C-12 and 1% C-13). Shown are the first doped electrosynthesized carbon nanotubes, prepared with added electrolytic LiBO₂ for boron doping, and salts for phosphorous, nitrogen or sulfur CNT doping are probed. Boron doping greatly enhances conductivity of the CNTs. Electrolytic CaCO₃ produces thin-walled CNTs, while excess electrolytic oxide yields tangled CNTs. Addition of up to 50 mol% Na₂CO₃ to a Li₂CO₃ electrolyte, decreases electrolyte costs and improves conditions for intercalation in Na-ion CNT anodes. Addition of BaCO₃ increases electrolyte density. Longer electrolysis time leads to proportionally wider diameter CNTs. Synthetic components (steel cathode, nickel anode and inorganic carbonate electrolyte) are available and inexpensive. Advantages include (1) production is limited only by the cost of electrons (electricity) providing a substantial cost reduction compared to conventional CVD and polymer spinning syntheses and (2) the only reactant consumed in the formation of the CNTs is CO₂, transforming this greenhouse gas into a stable, valuable product and providing an economic incentive to the removal of anthropogenic CO₂ from flue gas or from the atmosphere.

KEYWORDS: carbon nanotubes; electrosynthesis; boron doping; conductivity; global warming

INTRODUCTION

Carbon nanofibers (CNFs) or carbon nanotubes (CNTs) which are CNFs with hollow cores, have great potential as a material resource, with applications ranging from reinforced composites,^{1,2} capacitors,³ Li-ion batteries,⁴ nanoelectronics,⁵ and catalysts⁶ to the principal component of lightweight, high strength building materials due to their characteristic superior strength, electrical and thermal conductivity, flexibility and durability. Organo-metallic reactants using chemical vapor deposition, or arc discharge synthesis, or polymer pulling/carbonization synthesis are amongst the principal worthwhile, but costly methods of production of carbon nanofibers or nanotubes.⁷⁻⁸ We synthesized CNFs or CNTs formed from CO₂ as the reactant.¹⁰⁻¹⁶ This can contribute to lower greenhouse gases, for example by consuming, rather than emitting CO₂. This converts and stores carbon in a compact, stable form that can be used for carbon composite materials, and providing an alternative to steel, aluminum, and cement, whose productions are associated with massive CO₂ emissions.¹⁷⁻¹⁹ Increased availability of carbon composites will decrease CO₂ emissions by facilitating, both wind turbines and lighter weight vehicles for land, air and water transportation;²⁰ however CNFs or CNTs synthesized by contemporary CVD and polymer pulling technologies for composites requires 30 to 100 fold higher ~~production~~ energy compared to aluminum production.^{21,22}

In 2009, we provided a theoretical derivation that CO₂ can be split by electrolysis at high solar efficiency,²³ and demonstrated this high efficiency in 2010 through solar electrolysis of CO₂ in molten alkali eutectic carbonate or lithium carbonate to either solid (amorphous, or graphitic) carbon at $T < \sim 850^{\circ}\text{C}$ and to carbon monoxide, CO, at $T > \sim 850^{\circ}\text{C}$.²⁴ In the lower temperature domain, CO₂ removal occurs by the electrolytic reduction of tetravalent carbon in proximity to the cathode to solid, zerovalent carbon. The concentration of tetravalent carbon available for reduction is much higher as the electrolytic carbonate species than as airborne or soluble CO₂. Molten carbonate, such as Li₂CO₃(liquid), contains ~ 10 molar

moles of reducible tetravalent carbon / liter. Air contains 0.04% CO₂, equivalent to only 1x10⁻⁵ ~~molar~~ moles of tetravalent carbon / liter. Hence, molten carbonates formed by the dissolution of atmospheric CO₂, and its conversion to carbonate, provide a spontaneous, million-fold concentration increase of reducible tetravalent carbon sites per unit volume, compared to air, facilitating the direct conversion of atmospheric CO₂.

Until recently, CNTs had not been produced at low energies, nor had they been produced in high yield from CO₂. In 2015 we introduced the efficient transformation splitting of CO₂ by electrolysis in molten carbonates to form carbon nanotubes and nanofibers at high yield. The electrolysis occurs at low electrical energy and high coulombic efficiency (~4 Faraday per mole CO₂).¹⁰ For other synthetic approaches in forming CNTs, elements doped into the carbon such as ~~in-B~~ to produce boron doped CNF/CNTs have displayed enhanced physical/chemical properties, i.e. conductivity, oxidation resistance, or superior performances in oxygen reduction compared to pure CNTs.^{9, 25-26}

In 2015 we demonstrated that specific transition metals at the cathode, such as Ni, Co, Cu and Fe, act as nucleation points for high yield carbon nanotube growth in molten carbonates.^{9,10} The addition of Zn, such as occurs in a coating on galvanized steel, further lowers the activation energy for CNT formation.¹⁰⁻¹³ In this process, the production of carbon, such as CNTs, by electrolysis in lithium carbonate occurs simultaneously with the production of oxygen and dissolved lithium oxide:

Li₂CO₃ consumed by electrolysis is continuously replenished by reaction of this excess Li₂O, formed as a product in the eqn (1) electrolysis reaction, with CO₂ from the air (or CO₂ available in higher concentration from stack emissions):

net reaction (combining eqns (1) and (2)):

As illustrated in Fig. 1, the synthesis splits atmospheric or smokestack CO_2 , dissolved in a molten carbonate by electrolysis. The carbon footprint of the energy cost to produce the CNTs from CO_2 is insignificant when nuclear or solar, wind or hydro renewable energy is used to drive the electrolysis, and is only a small fraction of the electricity generated when natural gas is used to drive the electrolysis.¹⁴

During the electrolysis, oxygen is evolved at a nickel anode, and with control of low levels of transition metal additives, uniform carbon nanotubes are produced at high yield at a steel cathode. Carbon isotope labeling was used to track CO_2 as the building blocks of the CNFs.¹¹ Solid core CNFs were formed with C-13 isotope CO_2 ,⁴¹ whereas more valuable carbon nanotube, CNT, morphologies were formed with inexpensive, natural isotope CO_2 .¹¹ This electrolytic synthesis provides a facile route for the transformation of this greenhouse gas into a wide range of high-value CNT commodities, and this wide range of valuable products formed at low energy provides an important economic incentive to drive climate mitigation by carbon dioxide removal. The utility of CNTs will vary widely with the physical properties (morphology, uniformity, conductivity, etc.).

Figure 1 High yield electrolytic synthesis of carbon nanostructures from dissolved air or smoke stack concentrations of CO₂ in molten lithium carbonate. (D) During CO₂ electrolysis, transition metal deposition controls nucleation of the carbon nanostructure. (E) edge-on high magnification SEM view of synthesized CNT and (F) extended SEM view of synthesized CNTs. ~~E~~-Bottom: C2CNTs (CO₂ to CNTs) provide high conductivity and superior structural and conductive materials for a range of applications including lightweight jets, strengthened bridges, wind turbines, and electric vehicle body components and batteries. Modified from reference 12. Cell illustration S. Licht.

This research article focuses on a highly favored route to the synthesis of controlled nanostructures at high rate, high yield, and low cost by molten carbonate electrolysis. Synthetic components (steel cathode, nickel anode and inorganic carbonate electrolyte) are readily available and advantages include (1) that production is limited only by the cost of electrons (electricity) providing a substantial cost reduction compared to conventional CVD and polymer spinning syntheses and that (2) the only reactant is CO₂ - transforming this greenhouse gas into a stable, valuable product and providing an economic incentive to remove anthropogenic CO₂ from flue gas or from the atmosphere. We show the wide, portfolio of carbon nanotubes that can be produced by controlling the electrolysis conditions in this one-pot synthesis. Examples of this large range of specific morphologies is summarized in Fig. 2, as well as the enhanced electronic conductivities of CNTs that can be achieved through control of the electrolysis conditions in a one-pot molten carbonate synthesis. The top row of the figure presents TEM and SEM of carbon nanotubes synthesized from molten lithium carbonate. CO₂ is electrolytically split at high yield to oxygen gas at the anode, and carbon at the cathode, and Ni metal nucleation sites are evident as bright spots at the CNT terminals. In the middle-top SEM, CNTs prepared by extended duration electrolysis (ten hours, rather than 1 hour) are substantially thicker diameter. On the right top of the figure, electrolysis in C-13 isotope carbon salts (¹³CO₂ in Li₂¹³CO₃) form more solid core carbon nanofibers, rather than carbon nanotubes. In the left center row SEM, upon dissolution of lithium oxide, Li₂O, into (natural abundance isotope) Li₂CO₃, tangled, rather than straight, CNTs are formed by electrolysis. The tangled CNTs result from sp³ defects in the sp² graphene layered structures, as detected by Raman spectroscopy, and can lead to improved rechargeable battery storage capacity.¹² The middle and left of this row shows the SEM of CNTs grown at high yield by electrolysis in molten mixed carbonates, the right utilizes a less expensive electrolyte (50/50 wt% of Na₂CO₃

mixed with Li_2CO_3), and the middle uses a denser electrolyte (20/80 wt% of BaCO_3 mixed with Li_2CO_3). On the bottom row are new CNTs from this study; the left & middle show that high electrical conductivity CNTs are grown from boronated electrolytes and (right) thin walled CNTs are grown from calcinated (calcium cation containing) electrolytes.

Figure 2 Portfolio of CNT and CNF morphologies synthesized at high yield from carbon dioxide in molten carbonate under various electrolysis conditions. Top row: carbon nanotubes are electrosynthesized in molten lithium carbonate during short (2nd from left) or long duration electrolyses and right: solid core carbon nanofibers are grown from ^{13}C isotope. Middle row, left: tangled, rather than straight carbon nanotubes are grown from lithium carbonate containing dissolved oxide; a high yield of carbon nanotubes can also be

grown by electrolysis from mixed (middle) Ba/Li or (right) Na/Li electrolyses^{10,17,40}. Bottom row, left & middle: high electrical conductivity CNTs are grown from boronated electrolytes and (right) thin walled CNTs are grown from calcinated electrolytes.

In 1999, Wei and co-workers demonstrated that boron doping of bulk arc synthesized CNTs can improve their room temperature electrical conductivity by an order of magnitude²⁷, which has been subsequently confirmed for both arc and CVD synthesized carbon nanotubes.^{9,25,26,28-29}

RESULTS AND DISCUSSIONS

In prior studies we have introduced a straightforward, high yield electrosynthesis of carbon nanotubes from molten carbonates. We delineated the effects on that synthesis of the (i) nucleation agent (such as nickel, cobalt, and iron transition metals) and (ii) electrosynthesis current density, (iii) electrosynthesis charge (total current density passed, on CNT size and purity), (iv) temperature, (v) ready electrolysis scalability, (vi) alkali cation comparing lithium to lithium/sodium or alkali eutectic carbonate electrolytes, vii) electrolyte density comparing the low density lithium carbonate electrolyte to a high density lithium/barium carbonate (higher electrolyte density opens pathways to the free floating extraction of electrogenerated CNTs), (viii) ¹²C versus ¹³C carbon isotope (resulting in hollow versus filled CNTs), and (ix) higher oxide concentration on the CNT morphology (which adds sp³ defects and tangles the CNTs).¹⁰⁻¹⁶ A major advantage of the electrochemical synthesis of CNTs is the ease of control of the nanostructure by systematic variation of the electrolysis parameters. In this study we include the new additional substantial effects of doping (focusing on boron doping, but including phosphorous, nitrogen and sulfur doping) which is readily accomplished through electrolyte additives, the

influence of magnesium and calcium carbonate electrolytes, and a straightforward removal (thermal treatment) of less structured carbons from the electrosynthesized CNTs.

One-pot synthesis of doped, highly conductive CNTs

Figure 3 The liquid component of the binary $\text{Li}_2\text{O} : \text{B}_2\text{O}_3$ (wt%) system.³⁹

Pure B_2O_3 (mp 450 °C, white, melts clear) and the melt is a glass insulator. However when molten B_2O_3 contains with dissolved Li_2O (mp 1438 °C, white, melts clear) it becomes an electrochemical conductive liquid, which we have previously explored as a molten air battery electrolyte⁴⁹. The binary system of B_2O_3 and Li_2O presents a complex phase diagram with an extensive homogenous liquid phase above 767 °C in Fig. 3 as we have previously reviewed in that molten air battery reference. We observe here that the combined salt of boron and lithium oxides, lithium metaborate, LiBO_2 (mp 849 °C, white) is highly soluble in Li_2CO_3 (dissolves clear), retains a high electrochemical conductivity, and is a successful additive for the one-pot synthesis of boron-doped highly conductive CNTs.

The methodology of electrolysis of carbonates to convert CO_2 into CNTs is simple and scale-up is possible and is ongoing. CNTs are valuable making CO_2 into a desired feedstock, rather than only a greenhouse gas pollutant, which is a promising development to mitigate this greenhouse gas emission and climate change. To study the possibility to create more electrically conductive CNTs with this pathway, we simply added LiBO_2 in the electrolyte to investigate the possible formation of B-doped CNTs. With, or without, the addition of LiBO_2 , long, uniform, straight CNTs are formed during the electrolysis at high yield of over 90% (based on the current applied and the four electron per tetravalent carbon reduction in eqn (1)).

Typical SEM of the washed, boron doped product is shown in Fig. 3. At higher levels of added LiBO_2 (> 10% by mass), the level of non-uniform impurities in the CNT product

increases (not shown). Specifically, with < 10% by mass of LiBO_2 plus 50g Li_2CO_3 electrolyte, very good quality, straight carbon nanotubes are formed in the system of 1.5 g, 3 g, or 5 g of LiBO_2 respectively. However, there was still ~10% amorphous carbon nanoparticles in the product as estimated from the SEM. With the 5 g addition of LiBO_2 , the diameter distribution of the CNTs (200 to 500 nm) is somewhat larger than observed when no LiBO_2 is added. When 8 g of LiBO_2 (> 10%) was added, the diameter of the CNTs was quite widely distributed in the range from 150 nm to 1.5 μm , indicating more LiBO_2 induced heterogeneity. The high level of LiBO_2 may alter the macro-environment of reduction at the cathode, and/or the deposition of boron onto some nickel nuclei can form NiB instead of pure Ni resulting in a more heterogeneous growth patterns with less nanostructure. At 17 wt% added LiBO_2 to the Li_2CO_3 electrolyte, particles, rather than nanotubes, became the dominant product. Other (non-electrolytic) CNT syntheses concur that a high-level of boron-doping changes the CNT product into a less ordered morphology³¹ due to the formation of B_xC_y domains/defects and/or an accumulation of boron into clusters.

Figure 3 SEM images at low (left, 20 μm bar scale) and high (right, 10 μm bar scale) magnification of B-doped CNTs formed by electrolysis in 5g LiBO_2 and 50 g Li_2CO_3 at 770°C.

Figure 4 Raman spectra of B-doped CNTs, from bottom to top, the LiBO_2 addition is 1.5g, 3g, 5g and 8g.

To identify whether the obtained CNTs are B-doped CNTs, or a mixture of boron element plus pure CNTs, Raman spectra were recorded using an incident laser of 532 nm and are presented in Fig. 4. In our conventional (boron-free) electrosynthesized CNTs from a pure lithium carbonate electrolyte, the G band, which is related to graphite in-plane mode of E_{2g} symmetry, is observed at 1575 cm^{-1} . However, for the samples with LiBO_2 added, the G band shifts to higher wave numbers. The upshift indicates that hole carriers have been transferred from boron to the MWNTs. The charge transfer shortens the C–C bond increasing the force constant, and thus enhances the lattice frequency of the MWNTs. In other words, the shifts of the G band to the higher frequency is considered to be caused by the deformation of the graphitic structure with an increasing boron concentration.^{32,33} As seen in Fig. 4, when either 1.5g, 3g, 5g or 8g of LiBO_2 has been added to electrolyte prior to the electrosynthesis, subsequent to the synthesis the G band of the product shifts to 1583,

1587, 1589, 1600 cm⁻¹, respectively. According to the linear relations between G-band shift and boron-doping level in the study of Ishii et al³² the boron content was estimated from ~0.7 at% to ~2 at%. Moreover, the D to G ratio, that is the ratio of intensity between the D-band, which is associated with disordered carbon and amorphous carbon, and the graphitic G-band, increases with the increase of added LiBO₂. This indicates that an increasing number of defects were generated with the increase of B-doping level. The B-doping was observed to create B_xC_y domains, e.g. BC₃ at low doping level³⁴, or B₄C, B₁₃C₂ domains at high doping level³⁵, and thus increase the defects of CNTs. Each of these features in the spectra indicate that the resulting samples are boron-doped CNTs, rather a mixture of boron element and pure CNTs. It should be noted that the boron-content in B-CNTs differs substantially from the B/C ratio in the electrolyte. For example, 8g of LiBO₂ added to the 50g of Li₂CO₃ is a B/C=31 at% in the electrolyte, but only resulted in ~2% of B obtained in the CNT sample product. There is no indication that (other than the improved conductivity that will be shown) the excess LiBO₂ in the electrolyte is harmful and this large difference between the percentage of boron added to the electrolyte and the percentage of boron in the product appears to be related to the voltage of reduction of lithium metaborate into boron-element, which as presented in Fig. 5, is ~2.015V at 770°C (1043K) according to the thermodynamic calculations of eqn (5) from the entropy and enthalpies of the individual species. This is higher than the reduction of carbonate to carbon, which is < 1.6V¹⁶, and during simultaneous deposition at the cathode (depending on kinetics) will tend to favor the formation of carbon over boron at the cathode.

Figure 5 The thermodynamic potential for the reduction of lithium metaborate to boron as a function of temperature as calculated from the entropy and enthalpies of the individual species.

Boron-doping is well known for the production of metallic CNTs and enhancing the conductivity of CNTs³⁶. To investigate the boron dopant effect on molten carbonate synthesized CNTs on the conductivity, we measured this property using samples synthesized with increasing level of dopant. As a comparison, the conductivity of amorphous carbon nanoparticles, straight CNTs, and tangled CNTs electrosynthesized from Li_2CO_3 melts were also measured and the data is included in Table 1. The 9 wt % LiBO_2 electrolyte synthesized CNTs exhibit one order of magnitude conductivity higher than straight CNTs (formed in pure Li_2CO_3), and 30 fold higher than amorphous carbon nanoparticles or our electrosynthesized tangled CNTs (we have shown that added oxide, such as 4m Li_2O (10.7 wt%) in the Li_2CO_3 electrolyte adds defects and results in tangled CNTs). Among samples with the added B-dopant, the conductivity first rose from an addition of 1.5g of LiBO_2 to the synthesis electrolyte, until a maximum for 5g LiBO_2 and then decreased at higher concentrations of added LiBO_2 . The boron doping enhanced the

conductivity but an excess of added boron (> 10 wt% LiBO₂ in the electrolyte) decreased the quality (less CNTs, more nanoparticles), Hence, there is an observed conductivity maximum with increased LiBO₂ addition.

Table 1 Electrical conductivity of carbons.

Sample	Conductivity (Ohm ⁻¹ m ⁻¹)
Amorphous Carbon	3.8×10 ³
Straight pure Li ₂ CO ₃ CNTs	11.5×10 ³
Tangled 10.7wt% Li ₂ O in Li ₂ CO ₃ CNTs	4.2×10 ³
2.9wt% LiBO ₂ in Li ₂ CO ₃ CNTs	29×10 ³
5.7wt% LiBO ₂ in Li ₂ CO ₃ CNTs	96×10 ³
9.1wt% LiBO ₂ in Li ₂ CO ₃ CNTs	118×10 ³
13.8wt% LiBO ₂ in Li ₂ CO ₃ CNTs	49×10 ³
16.7wt% LiBO ₂ in Li ₂ CO ₃ CNTs	8.5×10 ³

A successful and direct pathway for the one-pot electro synthesis of boron doped carbon nanotubes from carbon dioxide via the addition of a soluble lithiated dopant to the molten carbonate electrolyte has been introduced here. This suggests a similar pathway and opportunity for the synthesis of other doped carbon nanotubes, such as nitrogen, phosphorous or sulfur doped nanotubes. Different dopants inserted into the CNT at different concentrations change both the physical and chemical properties of the CNTs.³⁷⁻³⁹ Sulfur-doped carbons have a range of potential applications, including heterogeneous catalysis, sorption, and energy conversion and storage. However, to date few approaches have been developed to intrinsically blend sulfur into the carbon matrix.⁴⁰ N-doped carbons

have a range of potential applications, including O₂ oxidation & reduction, fuel cell catalysts, supercapacitors, and sensors.⁴¹⁻⁴⁵ Similarly, P-doping of carbons can greatly affect their properties and applications including reduced elongation fracturing, as aerobic oxidation catalysts, batteries and ultra sensitive sensors.⁴⁶⁻⁴⁹

B and N have been the most studied carbon dopants due to their proximity in size (and atomic number) to C.³⁸⁻³⁹ In our initial attempts to produce N, P and S doped electrosynthesized CNTs the dopant source were the common polyatomic anions metaphosphate, nitrate, and sulfate with lithium as the cation (LiPO₃, LiNO₃ or Li₂SO₄), and we have observed here that each of these salts are soluble in molten lithium carbonate. Compared to the 3e⁻ reduction needed to form elemental boron as a dopant from lithium metaborate in eqn 5, LiPO₃ and LiNO₃ would respectively require a 5e⁻ reduction to form elemental P or N, and Li₂SO₄ requires a 6e⁻ reduction to form S. Whereas B, P and N are less electronegative than carbon, sulfur is more electronegative. Hence, as a rough estimate (based on electronegativities and without attempting to predict competing kinetic phenomena) carbon may be easier to form by electrolysis from the oxide, than B, P or N, making the latter oxides good candidates for simultaneous reduction to elemental dopants during CNT electrosynthesis, whereas S may be a thermodynamically preferred reduction product to CNTs, which could inhibit CNT formation in a sulfate containing electrolyte..

We report here preliminary results of attempts to simultaneously electrosynthesize and P, N or S dope CNTs in molten lithium carbonates. In each case 1 mol % of either LiPO₃, LiNO₃ or Li₂SO₄ was added to 50 g of 770°C lithium carbonate, and a 0.82 A electrolysis was conducted for 1.5 hour. As seen on the left side of Figure 6, high quality (low non-CNT carbon content) CNTs were formed with the LiPO₃ additive. Increasing the mole % of the LiPO₃ caused SEM observed increased tangling of the CNTs (not shown). As seen on the right side of the figure, CNTs were also formed with the LiNO₃ additive, but contained a high

level (~60%) of non-CNT carbon content). In accord with the electronegativity analysis, there was no observed carbon (CNT or otherwise) product formed at the cathode during the equivalent Li_2SO_4 in Li_2CO_3 electrolysis. In future studies, the P and N CNT molten carbon electrosyntheses will be optimized, the extent of P or N doping gauged, and applications of P or N doped electrosynthesized CNTs will be explored and reported, while the S CNT process will be modified into a two-step process in which CNTs are first electrosynthesized in the sulfur-free molten carbonate electrolyte, and subsequently a sulfur salt is added to the electrolyte, and the electrolysis is then continued in an attempt to dope the CNT product.

Figure 6 SEM of CNTs formed by electrolysis in Li_2CO_3 with 1 mol % of either (left) LiPO_3 (wt%) or right LiNO_3 at 770°C .

Influence of magnesium carbonate and calcium carbonate in the electrolyte towards the morphology of CNTs.

Interestingly, we observed that while the aqueous solubility of calcium oxide is high and calcium carbonate is nearly insoluble in water, the opposite solubility trend occurs in

molten lithium carbonate as a solvent.⁵⁰ The solubilities of either lithium oxide, Li₂O, or barium oxide, is high (> 6 molal) in Li₂CO₃ at 750°C, whereas CaO is nearly insoluble.⁵⁰ Normally, CaCO₃ does not melt, decomposing to CaO and CO₂ at ~850°C in the conventional limestone to lime production process. However, at lower temperatures we found that CaCO₃ is highly soluble in Li₂CO₃. CaCO₃ dissolved to over 6 molal in Li₂CO₃ at 750°C, and can provide an enriched source of Ca²⁺ cations prior to electrolysis. When these soluble Ca²⁺ cations are in the electrolyte, the insolubility of CaO when generated during the electrolysis (equation 6) provides an opportunity to substantially modify the interfacial environment at the electrolyte/cathode interface during the carbonate electrolysis.

CNTs are grown in this unusual high CaO environment. CaO can both intermingle with the CNTs during formation, and excess CaO can precipitate to the bottom of the electrolysis chamber (due to the higher density of CaO than that of the Li/Ca carbonate mix electrolyte).

In our experiments, CaCO₃ was purposely added into the electrolyte to study the formation of insoluble CaO towards the carbon nanostructure. As shown in the SEM image in Figure 7, the introduction of CaCO₃ (10g) results in the formation of some thinner-walled CNTs. However as seen in this figure, in this higher CaO rich interfacial environment, the CNT content of the carbon product is ~15% and the main product was amorphous carbon. Compared to the ~250nm wall thickness of conventional CNTs in Fig. 2, the wall thickness of the Ca-electrosynthesized CNTs is ~50nm in Fig. 7. A better yield of thin-walled CNTs is obtained by the co-introduction of LiBO₂ and CaCO₃, since boron at low level doping has been shown to promote CNT growth in other modes of CNT syntheses.⁵⁴

Figure 7 SEM of CNTs formed by electrolysis in Li_2CO_3 with 16.7 wt% CaCO_3 at 770°C.

Figure 8 SEM of CNTs formed by electrolysis in Li_2CO_3 with 5.0 wt% LiBO_2 and 11.7 wt% CaCO_3 at 770°C.

As shown in Fig. 8, the addition of 3 g of LiBO₂ and 7 g of CaCO₃ to the 50g Li₂CO₃ electrolyte provided a higher yield (> 70%) chemical environment for the production of thin-walled CNTs.

Compared to calcium carbonate, magnesium carbonate is relatively easy to decompose at 350°C

The electrosynthetic effect of the addition of MgCO₃ to the electrolyte was also probed, This is equivalent to the introduction of MgO since the experiments were conducted at 770°C, and most MgCO₃ should decompose in accord with eqn (7). First, a precipitate was observed at the bottom of melt indicative of the low solubility of MgO in the Li₂CO₃ melt. Secondly, the addition of this 10 g MgCO₃ to 50 g Li₂CO₃, resulted in a cathode product composed of honeycomb like morphology of carbons interspersed with only a small amount of thin-walled CNTs. Even the addition of 3 g LiBO₂ (to 7g MgCO₃ and 50 g Li₂CO₃) resulted in only a ~ 35% CNTs interspersed within a product principally comprised of honeycomb morphology carbons as shown in Fig. 9. The formation of these honeycomb carbons may be due to colloidal suspensions of MgO in the molten salt, which surrounds and inhibits growth of the thin-carbon shells during the electrolysis. In this case, MgO particles serves as a sacrificial template similar to previous reports.⁵¹⁻⁵³ The difference between CaCO₃ and MgCO₃ addition is that CaO was simultaneously deposited along with carbon onto cathode during the electrolysis, while MgO was formed prior to electrolysis due to the lower temperature of MgCO₃ compared to CaCO₃, decomposition to the oxide and CO₂. This may be one reason for the better yield of the CNTs obtained with CaCO₃ addition.

Figure 9 SEM of CNTs formed by electrolysis in Li_2CO_3 with 5.0 wt% LiBO_2 and 11.7 wt% MgCO_3 at 770°C .

Variation of electrolysis potential with added LiBO_2 dissolved salts.

The addition of alkali earths, such as magnesium carbonate, increases the observed electrolysis potential. Interestingly, as shown in Fig. 10, the addition of Li_2BO_3 to these mixed alkali earth/lithium carbonates decreases the observed electrolysis potential. In each case at the lowest applied current of 0.05 A over a 5 cm^{-2} area the electrodes, a brief, initial plateau occurs at $\sim 0.5\text{V}$ during which we have observed a small dissolution of the anode occurs while the anode develops a stable nickel oxide layer, and subsequently the current plateaus at a higher current. This initial nickel release is important to develop a nickel concentration in the electrolyte, which allows deposition of the observed nickel nucleation sites on the anode. Subsequently carbon nanotube formation occurs and at an applied current of 0.4 A in these Li_2CO_3 molten electrolytes, required 1.5 V in the magnesium electrolyte, but only 1.3 V in the magnesium/boron mix electrolyte, and 1.2 and 1.5 V

respectively in the calcium/boron and barium/boron electrolytes. At higher currents the boron effect was even greater. At 0.82 A constant electrolysis, while the magnesium electrolyte requires an electrolysis potential of 2.1 V, the calcium/boron electrolyte required only 1.4 V. As expected and as seen in the figure, the required potential to drive electrolysis decreased with decreasing current density. Not shown in the figure is that added lithium oxide, higher temperature and higher anode to cathode relative surface areas (for example by texturing the anode or using a oversize anode), also decreased the electrolysis potential for any given applied current density.

Figure 10 The measured electrolysis potential as a function of constant applied current for various 770°C Li_2CO_3 electrolytes. In each case 5 cm² of anode sits horizontally above and faces 5 cm² of cathode. Each electrode is configured as a flat horizontal, coiled wire disc. The anode is coiled from 16 cm of 2 mm diameter wire, and the cathode from 31 cm of 1 mm galvanized steel wire.

Purification of CNTs.

The top of Figure 11 presents the cathode product subsequent to a typical electrolysis in a molten lithium carbonate electrolyte, but prior to any washing. In this study, each cathode is removed directly from the molten electrolyte, and prior to washing contains congealed electrolyte within the product. Here, electrolyte is evident on the left side of the SEM and carbon nanotubes on the right. This electrolyte is removed either with long term washing/sonicating with water or a rapid wash with concentrated HCl. In our syntheses, the obtained washed samples contain ~10% or less of amorphous carbons as seen in the lower portion of the figure. While, not high, this level of amorphous carbons could impact certain CNT applications being developed such as for nanoelectronics. In order to obtain CNTs with higher purity, a thermal treatment was carried out at certain temperature, e.g. 420°C for 1 hours. This purification increased the carbon content of the carbonate electrosynthesized product, as observed by SEM, to over 95% carbon nanotubes. However, further heating of the product at a higher temperature of 550°C for 2 hours, resulted in burn-off of all the remaining carbon as observed by SEM. Based on the weight loss, we calculate the metal content in as-synthesized CNTs is ~1 wt%, which via SEM and EDS⁶ is viewed as located on as nucleation sites for CNT growth. However, it should be noted that the useful, purifying burn-off temperature varied with different sample. For the thin-walled CNTs, all carbons, including CNTs and amorphous are burned off at 420°C.

Figure 11 Top: SEM of typical cathode product prior to washing. This specific example is subsequent to an extended (12 Ah) electrolysis. Subsequent to washing, the typical CNT products still contain a small fraction of amorphous carbons shown as circled in red in the Middle (lower magnification, 200 μ m scale) and Bottom (higher magnification magnification, 40 μ m scale).

CONCLUSIONS

CNTs formed from CO₂ as the reactant, can contribute to lower greenhouse gases, for example by consuming, rather than emitting CO₂, storing carbon in a compact, stable form, and by providing a stable, valuable, carbon composite material. Despite their superior mechanical, thermal and electronic properties, carbon nanotubes applications had been limited to date by the high cost of their conventional chemical vapor deposition synthesis. The CVD synthesized CNT cost is higher than for spun carbon fibers, and 2 to 3 orders of magnitude higher than that of conventional graphitic or amorphous carbons.¹⁴ Here, the facile, inexpensive synthesis of CNTs at high yield into a wide variety of uniform carbon nanotubes by electrolysis in molten carbonate at cost effective nickel and steel electrodes, provides an incentive to transform the greenhouse gas carbon dioxide into a useful, stable, valuable commodity.

METHODS

As illustrated in Fig. 2, this study focuses on the wide variety of controlled molten carbonate electrolyzer conditions that form carbon nanotubes with specific morphologies and properties. Lithium carbonate (Alfa Aesar, 99%) and oxides, such as lithium oxide (Alfa Aesar, 99.5%) as well as anhydrous lithium metaborate (LiBO₂, 99.9%, Alfa Aesar). barium

carbonate (Alfa Aesar, 99%), calcium carbonate (Alfa Aesar, 98%), and magnesium carbonate (Acros Organics, extra pure) are combined as various molten electrolytes, and are used here to demonstrate the first high conductivity, thin walled and purified CNTs formed by these high-yield molten carbonate electro-syntheses.

Electrolyses are driven galvanostatically, at a constant current. The electrolysis is contained in a pure nickel 100 ml crucible (Alfa Aesar) or a pure alumina crucible (AdValue 99.6%). Electrolyses in the Ni crucible used the inner walls of the crucible as the anode. A wide variety of steel wires for coiled cathodes are effective, an economic form (used in this study) is national hardware V2568 18Ga' (diameter 0.04 inch). Following an initial low current (0.05 A for 10 minutes, 0.1 A for 10 minutes, 0.2 A for 5 minutes, and 0.4 A for 5 minutes) step to grow Ni nucleation sites on the cathode, CNTs or CNFs are grown on an immersed 10 cm² galvanized steel cathode at 0.8 to 1.00 A (constant, but depending on the experiment) for 1 hour. Observed electrolysis potentials are consistent with those we have recently reported for generic carbon deposition in a molten Li₃CO₃ electrolyte as a function of current density, and as previously reported, the potential decreases with addition of Li₂O to the electrolyte³. Nanostructures generated, are straight CNTs that are grown in electrolyte without added Li₂O, or tangled CNTs that are grown when Li₂O has been added to the electrolyte. During electrolysis, the carbon product accumulates at the cathode, which is subsequently removed and cooled. Subsequent to electrolysis the product remains on the cathode, but falls off with electrolyte when the cathode is extracted, cooled, and uncoiled. The product is washed with 11 M HCl, and separated from the washing solution by centrifugation.

The washed carbon product is analyzed by PHENOM Pro-X Energy Dispersive Spectroscopy (EDS) on the PHENOM Pro-X SEM or FEI Teneo LV SEM and by TEM with a JEM 2100 LaB6 TEM. Raman spectroscopy was measured with a LabRAM HR800 Raman

microscope (HORIBA) using 532.14nm wavelength incident laser light with a high resolution of 0.6 cm⁻¹.

For the synthesis investigations, the lithium carbonate mass is kept at 50 g and other electrolytic additions varied. For the boron-doped CNTs, various masses of lithium metaborate, LiBO₂, was added, including 1.5 g, 3 g, 5g, 8 g, and 10g of LiBO₂ with 50 g of Li₂CO₃. To investigate alkali earth cation effects on the morphology of the CNTs, different carbonates, such as MgCO₃, BaCO₃, or CaCO₃, were added into the electrolyte. The lithium carbonate mass is maintained at 50g and various masses of MgCO₃, BaCO₃ or CaCO₃ were added. After melting the electrolyte and increasing the temperature to 770°C, the cathode was immersed into the electrolyte, and a polarization pre-treatment (0.05 A/10min, 0.1 A/10min, 0.2 A/5min, and 0.4 A/5min) is conducted which we have found facilitates the formation of nickel CNT nucleation sites, and subsequently electrolysis is conducted at a constant current of ~0.9 A for 2 hours or more. The synthesis yield, $100\% \times C_{\text{experimental}} / C_{\text{theoretical}}$, is determined by the measured mass of washed carbon product removed from the cathode, $C_{\text{experimental}}$, and the theoretical mass, $C_{\text{theoretical}} = (Q/nF) \times (12.01 \text{ g C mol}^{-1})$ which is determined from Q, the time integrated charged passed during the electrolysis, F, the Faraday (96485 As mol⁻¹ e⁻), and the $n = 4 \text{ e}^{-} \text{ mol}^{-1}$ reduction of tetravalent carbon.

The electrical conductivities of samples that are removed subsequent to the electrolysis and washed were measured at room temperature. Each sample was placed in a hollow cylinder having ¼ inch inner diameter and was compressed in air between two brass pistons. 20mg of samples was used to measure the conductivity and the pressure was increased until 0.2MPa by compressing pistons. A digital vernier calliper was used to measure the height of the pellet. Conductivity was measured using AC impedance with Gamry interface 1000. Ohmic conductivity was measured as:

$$\sigma = L / RA \quad (8)$$

Where σ is electrical conductivity, L sample distance, A area of the piston surface, and R is resistivity.

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