Journal of CO_2 Utilization 18 (2017) 378–389

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Co-production of cement and carbon nanotubes with a carbon negative footprint

Stuart Licht

Department of Chemistry, George Washington University, Washington, D.C. 20052, USA

ARTICLE INFO

Article history:
Received 11 September 2016
Received in revised form 30 December 2016
Accepted 16 February 2017
Available online 19 March 2017

Keywords:
Cement
Carbon nanotube
Calcination
Greenhouse gas
Carbon dioxide

ABSTRACT

C2CNT (CO_2 to carbon nanotube) cement plants are introduced and analyzed with a significant economic incentive to eliminate current plant CO_2 greenhouse gas emissions. The exhaust from partial and full oxy-fuel cement plant configurations are coupled to the inlet of a C2CNT chamber in which CO_2 is transformed by electrolysis in a molten carbonate electrolyte into CNTs at a steel cathode and pure oxygen at a nickel anode that is looped back in improving cement line energy efficiency and production rate. A partial oxy-fuel process looping O_2 back through the plant calcinator has been compared to a full process in which it enters through the plant kiln. The first provides easier retrofit; the second maximizes efficiency by minimizing N_2 throughput. Providing an economic impetus to carbon dioxide removal, per ton CO_2 avoided the C2CNT cement plant consumes $50 electricity, emits no CO_2, and produces $100 cement and ~$60,000 of CNTs.

1. Introduction

Climate change is causing species extinction, harming the planet and humanity [1]. Cement production accounts for the largest global emissions of the global warming greenhouse gas carbon dioxide of any manufacturing process, generating 5–6% of the global anthropogenic emissions of this greenhouse gas. Humans consumes over 1 ton of concrete per person per year. 3×10^{12} kg of cement annually, and the cement industry releases 9 kg of CO_2 for each 10 kg of cement produced; emitting 36 Gt globally annually Sales et al., Hills et al. [2,3]. In this study we propose and explore the conversion of cement plant carbon dioxide emissions to carbon nanotubes as an incentivized pathway to transform and eliminate CO_2 emissions from cement plants. Recently we've demonstrated a novel chemistry for the efficient, low cost, high yield transformation of CO_2 to carbon nanotubes [4–10], that builds on our CO_2 splitting and CO_2 elimination studies [11–18]. In this process, voltage is applied to split CO_2 in an electrolysis chamber between a nickel anode and a galvanized steel cathode into pure oxygen gas and a solid carbon product. This is a low energy, high efficiency process when conducted in molten carbonate electrolytes, and provides a reaction pathway to transform the greenhouse gas into a high value commodity. CO_2 is bubbled into the carbonate, dissolves to form more carbonate as described in equation 1, and during electrolysis, oxygen is evolved at the anode, while a thick solid carbon builds at the cathode (Fig. 1). The carbonate electrolyte is not consumed and the net reaction is CO_2 splitting into carbon and O_2, for example using Li_2CO_3 as the electrolyte:

$$\text{Dissolution: } CO_2(\text{gas}) + Li_2O(\text{soluble}) \rightarrow Li_2CO_3(\text{molten}) \quad (1)$$

$$\text{Electrolysis: } Li_2CO_3(\text{molten}) \rightarrow C(\text{CNT}) + Li_2O\ (\text{soluble}) + O_2(\text{gas})$$

$$\text{Net: } CO_2(\text{gas}) \rightarrow C(\text{CNT}) + O_2(\text{gas})$$

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 [19,20], capacitors [21], Li-ion batteries [5], nanoelectronics [22], and catalysts [23] to the principal component of lightweight, high strength building materials due to their characteristic superior strength, electrical and thermal conductivity, flexibility and durability.

2. The C2CNT process

Under appropriate molten carbonate electrolysis conditions, and in accord with the net Eq. (1), CO_2 gas is converted to CNFs or their hollow form carbon nanotubes (CNTs). From their respective

E-mail address: slicht@gwu.edu (S. Licht).

http://dx.doi.org/10.1016/j.jcou.2017.02.011
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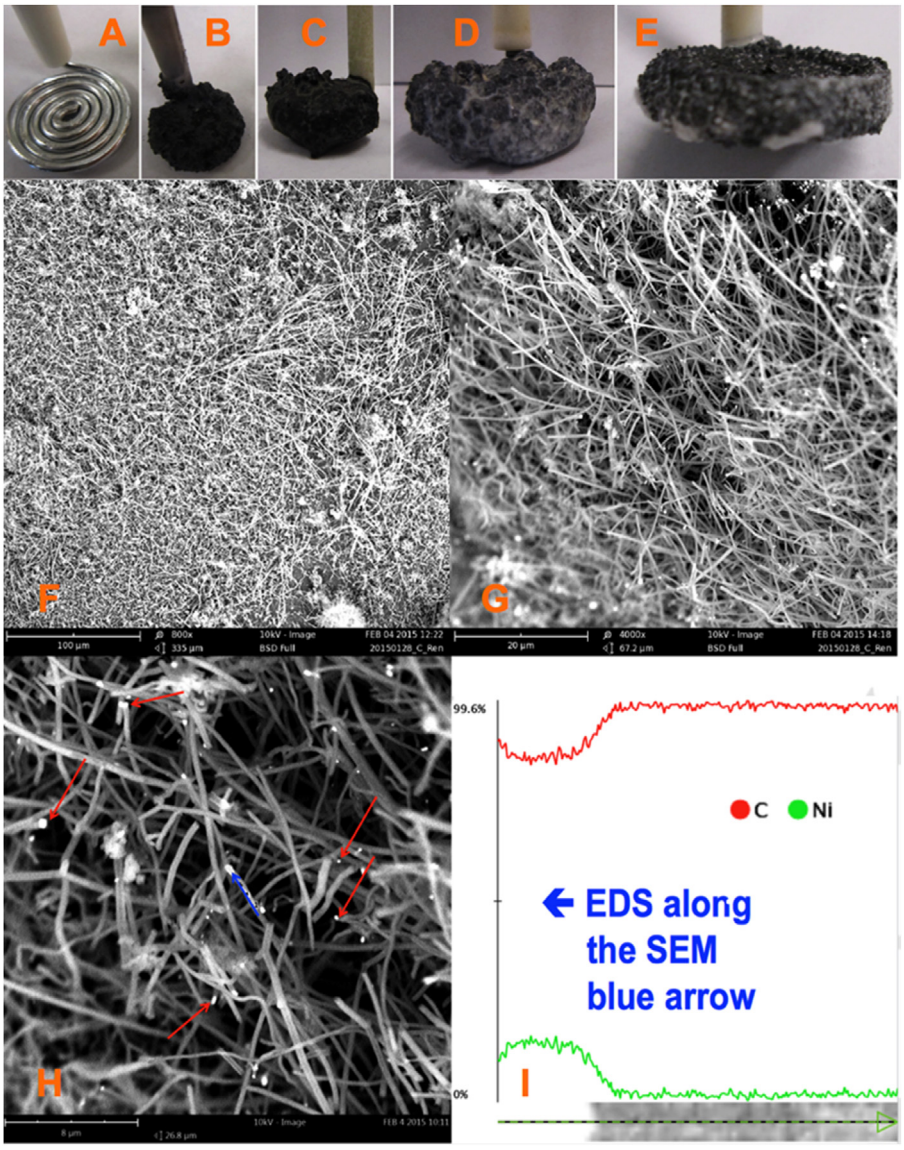

Fig. 1. CO_2 to carbon nanotubes formed at a coiled galvanized steel wire cathode with a nickel anode during 1 A constant current electrolysis in 750 °C molten Li_2CO_3 electrolyte. SEM F to H are shown at various magnifications of the product removed from the cooled, washed cathode. "A" shows the 10 cm^2 coiled wire cathode prior to electrolysis. The anode is the inner wall of a 20 ml Ni crucible with electrolyte. "B-E" exemplify typical maximum variation of cathodes after a long (4Ah) electrolysis in molten carbonate. Red arrows in SEM "H" indicate typical Ni nucleation sites. The blue arrow originates at one Ni site and moves along the CNF path. "I": EDS composition mapping along the 6 μ blue arrow path shown in SEM "H". (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

compositional mass, 1 ton of CNT is formed per 3.7 tons of CO_2 consumed, and provides a compact an means to remove, transform and store CO_2 from flue gas. Carbonate's higher concentration of active, reducible tetravalent carbon sites logarithmically decreases the electrolysis potential and can facilitate charge transfer at low electrolysis potentials. We observe that carbonate is readily split to carbon approaching 100% coulombic efficiency (coulombic efficiency is determined by comparing the moles of applied charge to the moles of product formed, where each mole of solid carbon product formed depends on four moles of electrons) [4–10].

As shown in Fig. 2, CO_2 directly from the atmosphere or from CO_2 emissions is electrolyzed to produce a variety of valuable carbon nanomaterials that have a range of uses. The morphology of the carbon product will vary whether natural abundance CO_2 is used in the synthesis, which produces (hollow) CNTs, or whether C^{13} is used, which produce (solid core) CNFs (Fig. 2B and C) [9]. High concentrations of lithium oxide can produce a tangled morphology (Fig. 2D), while no additional concentration of lithium oxide produces straight nanotubes (Fig. 2F). Fig. 2E shows cross-sections of the synthesized multiwalled carbon nanotubes, MWCNT. The use of naturally abundant CO_2, electrolysis current control, and the addition of small quantities of nickel to act as nucleating agents, leads to high yield of the particularly valuable CNTs. Due to their superior strength, conductivity, flexibility, and durability CNFs have a variety of applications including in nanoelectronics, in Li-ion batteries and as a principal component in the light-weighting of infrastructure construction materials, transportation (air, land, sea) vehicles, consumer electronics, wind turbine blades, and athletic equipment.

High current densities (>1 amp cm^{-2}) of carbon formation are sustained, and we observe similar sustained currents at carbon, inexpensive steel cathodes, or expensive platinum electrodes (each cathode effectively become a carbon electrode during the product deposition). XRD, SEM, TEM and Raman spectroscopy confirm that the product is carbon nanotubes, and EDS elemental spectroscopy as shown in Fig. 1 confirms that the CNT ends contain transition