Applied Surface Science 466 (2019) 367–374

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

MWCNTs produced by electrolysis of molten carbonate: Characteristics of the cathodic products grown on galvanized steel and nickel chrome electrodes

S. Arcaro*, F.A. Berutti, A.K. Alves, C.P. Bergmann

Laboratory of Ceramic Materials, Engineering School, Federal University of Rio Grande do Sul - UFRGS. Osvaldo Aranha 99, Porto Alegre, RS 90035-190, Brazil

ARTICLE INFO

Keywords:
Multiwalled carbon nanotubes
Carbon dioxide
Electrolytic conversion CO_2

ABSTRACT

Electrolytic synthesis in molten salts has excellent possibilities for the production of various carbonaceous materials, nevertheless, a study of the synthesis conditions is necessary for that the carbon products obtained is in the carbon nanotube (CNT) structure. In this work, the possibility of production of MWCNTs (multi walled carbon nanotubes) by the electrolytic synthesis of molten salts has been shown. The product structure and morphology can be controlled by choosing the right electrolysis conditions (type of electrode, applied current and electrolysis time). The properties of the produced carbon-containing products were analyzed by XRD, TEM, HRTEM and Raman spectroscopy. A correlation of product properties with synthesis conditions and parameters has been made. When using steel and nickel chrome as cathode, the products have lower levels of defects and are partially filled with metal phase when 1 A and 4 h of electrolytic synthesis were used. The metal phase acts as a catalyst for the nanotubes generation in the electrolytic synthesis from molten salts. Even so, after electrolysis for 4 h, these products are 90% MWCNT. The MWCNT growth on the galvanized steel or nickel-chrome cathodes is similar to an average external diameter of 100–125 nm and internal diameter is 25–40 nm. However, when grown in nickel-chrome cathode, the nanotubes have better quality and smaller walls. No additional treatments are necessary.

1. Introduction

Recent studies report the capture and use of carbon dioxide (CO_2) due to the relationship between this gas and the global climate change. The concentration of CO_2 in the atmosphere is around 405 ppm (around 0.04% of the atmosphere). This is the highest concentration in history, and it continues to increase due to combustion of fossil fuels, deforestation, and massive industrialization [1–8].

There are different approaches to reduce CO_2 emissions, and despite the efforts, the high scale CO_2 capture methodologies continues to be a challenge in order to economically transform it into a stable and non-polluting product, providing an incentive to consume the atmospheric CO_2 and, possibly, mitigate the climate changes [9].

Studies [5,9–13] have shown a method of converting CO_2 to a useful product by reducing it to solid carbon via electrolysis in molten alkali metal carbonates. In the 1960 s [11,14–17], researchers established that carbon could be electro-deposited from molten salts containing carbonate and lithium ions (CO_3^{2-} and Li^+). It was subsequently proposed that this process could be utilized for the indirect conversion of CO_2 to solid carbon [18–22] through the electroreduction of CO_3^{2-} ions in the molten salt electrolyte to solid carbon and oxygen ions (reaction (1)). According to some authors [6,15,18,22,23] these oxygen ions can react with the CO_2 present in the atmosphere above the molten salt to regenerate the CO_3^{2-} ions (reaction (2).

$$CO_3^{2-} + 4e^- \rightarrow C + 3O^{2-} \qquad \text{(reaction 1)}$$

$$CO_2 + O^{2-} \rightarrow CO_3^{2-} \qquad \text{(reaction 2)}$$

More recently, carbon nanofibers (CNFs) or carbon nanotubes (CNTs) have been made from CO_2 under sufficient electrolysis conditions (suitable combinations of electrode materials, electrolyte, temperature and electrical current) [13,24–27]. These processes convert and store carbon in a compact and stable form and can provide an alternative to steel, aluminium, and cement industries whose productions are associated to massive CO_2 emissions [12,28]. Moreover, the CNTs can be synthesized at a 100-fold price reduction compared to conventional chemical vapor deposition (CVD) synthesis [9].

Thanks to their extraordinary mechanical, electrical, and thermal

---

* Corresponding author.
E-mail address: sabrinarcaro@yahoo.com.br (S. Arcaro).

https://doi.org/10.1016/j.apsusc.2018.10.055
Received 4 April 2018; Received in revised form 7 September 2018; Accepted 5 October 2018
Available online 06 October 2018
0169-4332/ © 2018 Elsevier B.V. All rights reserved.

properties, carbon nanotubes (CNTs) have been at the forefront of research for more than 20 years [29-31]. The main methods of producing CNTs include chemical vapor deposition (using organo-metallic reagents), arc discharge synthesis, and polymer pulling/carbonization synthesis. However, these methods of production, although quite traditional are expensive. Therefore, the applications of carbon nanotubes have been limited so far by the high cost of their synthesis. For comparison purposes, CNFs or CNTs synthesized by contemporary CVD and polymer technologies for composites require 30–100 times higher energy compared to aluminum production [27]. In addition, it is important to highlight that unlike any other method of CNT synthesis, the electrolytic synthesis uses CO_2 as main reactant.

Commonly, the process of CNT growth relies on the decomposition of a carbon-containing precursor on the surface of a metal catalyst. The most widely used catalysts are Fe, Ni, Co, Mo, as well as their oxides and alloys and also spinels [32–35]. However, it is accepted that iron nanoparticles are the most suited catalyst for CNT growth. On the other hand, the growth of carbon nanostructures from electrochemical techniques remains a new idea, and very recent studies [23,34] show for the first time, the formation of carbon nanofibers or large-diameter CNTs (> 100 nm) obtained using Ni or Ir anode and steel cathode. In these systems, it is presumed that the Ni erosion of is the origin of the metal catalyst particles. There are no clear route exists to control the formation of a surface-bound catalyst for CNT growth [9,13,25,36]. Other study shows the ability to capture CO_2 and electrochemically convert into CNTs using atomic layer deposition (ALD) to produce a passive alumina coating on the Ni anode surface to inhibit mass transfer and isolate Fe as a primary catalyst species at the cathode where CNTs are grown [3].

In this study, for the first time to our knowledge, the influence of the type of the electrodes (nickel-chrome and galvanized steel), the applied current, time of electrolysis and the atmosphere of reaction (atmospheric air or argon) were analyzed to evaluated the characteristics of the carbon products obtained (CNT, amorphous carbon or carbon ribbons).

2. Materials and methods

The electrochemical reaction was performed in a tubular mullite furnace that is 50 mm in diameter and 500 mm in length. It was positioned vertically inside a programmable muffle furnace. The lid of the reactor provides feedthrough for the two electrodes and the thermocouple. Inside the tube, an alumina crucible was filled with 40 g of Li_2CO_3 (purity 99.0%), to act as the electrolyte when melted. The processes were carried out at 770 °C, which is a slightly higher temperature that the melting point of Li_2CO_3. Firstly, the carbonate was left at this temperature for 6 h to ensure that the molten was homogeneous and all moisture had been removed.

Galvanized steel and nickel-chrome rods were employed as electrodes. They each have an area of 1 cm^2 and were positioned at 5 cm depth in the molten carbonate, separated by 1 cm from one another. In a first arrangement, galvanized steel was the cathode and nickel-chromium was the anode. In the second, the inverse, galvanized steel was the anode and nickel-chromium was the cathode. The electrolysis was performed using a constant current (0.5, 1, or 2 A). A controllable power supply was used to control the applied current. The electrolysis was made in atmospheric air up to 4 h. A test was made using argon flow as reaction atmosphere, using 1 A and 2 h of electrolysis.

Fig. 1 shows the schematic illustration of electrolysis set-up including the different cathodes and anodes utilized in this study.

After the reaction, the cathode, covered with carbon products, was removed from the carbonate bath and subsequently washed in acetic acid solution to remove the excess of electrolyte and other possible impurities (oxides). The carbonaceous products were washed with water and ethyl alcohol to remove residual acetic acid and oven dried for 12 h at 80 °C.

The materials obtained were evaluated regarding their structure with Raman spectroscopy (Renishaw inVia Spectrometer System, UK). The experiments were performed at room temperature from 0 to 3200 cm^{-1} using a 532 nm^{-1} laser excitation, 20 s exposure time, and 5% laser power. The crystallinity of the samples was evaluated by X-ray diffraction (XRD) (PHILIPS, X'Pert MPD) using 40 kV, 40 mA, and a Cu anode. Scanning and transmission electron microscopy (SEM and TEM) were used to characterize the morphology of the nanotubes. An SEM (EVO MA10, Carl Zeiss, Germany), TEM (Jeol JEM 1200ExII) and HRTEM (JEM 2010) were used for this characterization.

3. Results and discussion

The catalyzed growth of carbon nanotubes, in general, involves the saturation of a gaseous carbon precursor over metal particles [37], as it occurs when CVD techniques are used to obtain CNT. Recently, the growth of carbon nanotubes was demonstrated through CO_2 electrolysis in molten carbonates [5,9–13]. In this way, few studies [3] related to the growth mechanism of carbon nanotubes are reported and parameters such as size and catalyst composition remain incomprehensible without a clear understanding of how these components originate or evolve. Therefore, the focus of the present study is to verify the influence of the type of the electrode (galvanized steel or nickel-chrome) in the characteristics of obtained carbonaceous material.

It is accepted that the general process of electrolytic reduction of CO_2 to carbon via liquid carbonates electrolysis relies on the splitting of the molten Li_2CO_3 (melting point 723 °C) into carbon, which is then collected at the cathode. Authors have observed that carbon is deposited onto the cathode rather than lithium or lithium products [36,38]. Lithium carbonate (Li_2CO_3) has a lower standard reduction potential of carbon compared to the alkali metal, thus, Li_2CO_3 is one of the most efficient carbonates to be reduced to carbon [10]. Oxygen is generated at the anode and Li_2O is in the electrolyte (reaction (3)). Authors suggested that Li_2O then reacts with ambient CO_2 to regenerate the Li_2CO_3 electrolyte, thus the Li_2CO_3 consumed by electrolysis is continuously replenished (reaction (4)) using the CO_2 from the atmosphere [13–15,21,36,39].

$$Li_2CO_3 \rightarrow Li_2O + C + O_2 \qquad \text{(reaction 3)}$$

$$Li_2O + CO_2 \rightarrow Li_2CO_3 \qquad \text{(reaction 4)}$$

Previous works [9,13,27] have justified the argument of CO_2 capture by molten carbonate electrolyte using a 13C isotope experiment to track the CO_2 uptake and is transformed into carbon nanofibers and large diameter nanotubes.

In fact, it was observed in our experiments that the electrolyte (Li_2CO_3) can be used several times for electrolysis because it does not decompose into lithium oxide (Li_2O) or other compounds after concluding the electrolysis, as observed in Fig. 2(a) and (b), where, X-ray diffraction and Raman spectroscopy present the signals for commercial Li_2CO_3 (I) and the signals after electrolysis processes for 1 (II) and 4 h (III). However, an apparent increase in the crystallinity of Li_2CO_3 is observed in X-ray diffraction. This fact is probably associated to the effects of high temperatures (endured by the carbonate for extended periods). The most characteristic band on the Raman spectrum is the one of lithium carbonate at 1088 cm^{-1} due to symmetric stretching vibrations. Small bands at 154, 193, 1457, 742, and 704 cm^{-1} [40] are also present in the commercial Li_2CO_3 and after electrolysis for 1 and 4 h. The peaks and bands related to Li_2O were not identified in the analysis. This fact demonstrates that no significant structural change can be observed and that the electrolyte can be used repeatedly.

Raman spectra were collected to reveal the characteristics of the cathodic products, as-obtained (without washing) (Fig. 3(a)). The most intense bands were related to Li_2CO_3. This fact is expected because no purification treatment was performed. However, as shown in the inset in Fig. 3(a), broad and well-defined bands characteristic of

Download English Version:

https://daneshyari.com/en/article/11011492

Download Persian Version:

https://daneshyari.com/article/11011492

Daneshyari.com