

Carbon Nanotubes Synthesized Using Sugar Cane as a Precursor

Vanessa Romanovicz, Beatriz A. Berns, Stephen D. Carpenter, Deyse Carpenter

Abstract—This article deals with the carbon nanotubes (CNT) synthesized from a novel precursor, sugar cane and Anodic Aluminum Oxide (AAO). The objective was to produce CNTs to be used as catalyst supports for Proton Exchange Membranes. The influence of temperature, inert gas flow rate and concentration of the precursor is presented. The CNTs prepared were characterized using TEM, XRD, Raman Spectroscopy, and the surface area determined by BET. The results show that it is possible to form CNT from sugar cane by pyrolysis and the CNTs are the type multi-walled carbon nanotubes. The MWCNTs are short and closed at the two ends with very small surface area of $S_{BET} = 3.691 \text{ m}^2/\text{g}$.

Keywords—Carbon nanotubes, sugar cane, fuel cell, catalyst support.

I. INTRODUCTION

CARBON NanoTubes (CNTs) are very important materials due their many properties; magnetic, optical, electrical and mechanical. They are versatile materials that have been used in different applications such as, electronic devices, catalyst supports, sensors, flat screen displays, gas storage, molecular sieves, polymer additives, high power capacitors, quantic resistor, structural composites, artificial muscle, etc. [1]. Within the last decade CNTs have been largely used in Fuel Cells (FC).

Amongst the various types of FCs the Polymer Electrolyte Membrane Fuel Cell (PEMFC) has received greatest attention because of its high efficiency and zero emission with merit to produce clean energy [2], [3]. The PEMFC, the Direct Methanol FC (DMFC) and the Direct Ethanol FC (DEFC) operate very similarly at relatively low temperatures using a Proton Exchange Membrane as the electrolyte sandwiched between the anode and cathode. The anode and the cathode support the catalysts during the electrochemical reactions and the base of this support is carbon. One of the problems related to the degradation of FC materials is carbon corrosion which causes instability of the cell. At the same time the carbon corrode the catalyst loses its mechanical support, electrical contact and the cell decreases performance as the surface area of the catalyst diminishes [2],[4]-[8].

The basic difference between the three FCs is the type of fuel, hydrogen, methanol and ethanol. While hydrogen fuel is more efficient and clean it does have difficult storage

problems to be resolved in contrast to alcohol fuels. It must be noted that methanol has a poisoning effect whereas ethanol less so.

Conventionally the raw material for CNT production is fossil based. Recently the literature has presented research using natural precursors to replace these fossil based materials with alternative renewable resources that are cheaper to produce large volumes of CNT. Some natural precursors for the synthesis are eucalyptus oil, camphor powder, coconut oil and palm tree [9], [10].

The CNT structure may be controlled during the synthesis using the appropriated parameters as catalyst composition, gas flux, temperature gradient, gas pressure, between others [11]-[14]. Some of the common techniques used to synthesize CNT are Laser Ablation, Arc discharge, Spray pyrolysis, and Chemical vapour deposition [11], [12], [15]-[18]. Many authors report that up to now the Chemical Vapor Deposition is the most suitable methodology to synthesize CNT, since it allows to control to some extent the diameter, length and the location they CNT grows. CVD synthesis requires, as other methodology, the use of a metal catalyst that sometimes is difficult to separate from the grown nano tubes and act as an impurity [19]. Pyrolysis is a common method to synthesize nanotubes, however it also uses catalyst.

Recently, the literature reported a new method to synthesize CNT by pyrolysis without the use of a catalyst [20]. The authors [20] synthesized the multi walled CNT type with a well developed tubular structure but poorly graphitized what leaves an open field to improve the methodology.

In this work the methodology chosen to synthesize the CNT is the pyrolysis and the template is the Anodic Aluminum Oxide (AAO). The precursor to CNT synthesis chosen is sugar cane juice and syrup as it is abundant, cheap and rich in carbon. Following the synthesis the CNTs are characterized to determine the dimensions, shape and if it is single or multi walled.

II. PROCEDURE

The reagents used were chloroplatinic acid hexahydrate (Sigma Aldrich), filtered sugarcane juice, mesoporous alumina with pore diameter of 3.8nm (Aldrich), nitrogen gas, sodium hydroxide (Vetec), nitric acid (Synth), ethanol analytical grade (Lafan), acetone analytical grade (Synth) distilled water.

A. CNT Synthesis Method

The sugar cane used as precursor to the CNT synthesis came from SantaCatarina State, Brazil. The sugar cane was used as juice and syrup. The juice was vacuumed filtered

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twice as received to separate the coarse contaminants. Part of the sugar cane juice filtered in the previous procedure was used to prepare the syrup. The juice was put on a hot plate at 93°C during 9h until syrup consistency, after was left to cool down to room temperature. The juice and the syrup were kept in a refrigerator. The juice was qualitatively and quantitatively analyzed and the result is presented in Table I.

TABLE I
ELEMENTARY CHEMICAL ANALYSES OF SUGAR CANE JUICE (MG. KG⁻¹)

Components	(Mg.Kg)
Ca	93.55
Cl ⁻	17.26
Fe	2.53
P _{total}	184.67
Mg	158.80
K	474.89
Na	17.73
Reducing Carbohydrate	1.99
Non-reducing Carbohydrate	5.57

To prepare the CNT 20ml of juice was mixed to the AAO template and put in to a ceramic crucible that was taken to a tube furnace at 500°C, 550°C and 600°C, in an inert atmosphere of N₂, flux 30 and 40mL/min during 5h to carry out the pyrolysis.

Before to open the furnace it was switched off and left to cool down to room temperature to avoid the oxidation of the carbon produced. The CNTs formed were purified first by dissolution of the AAO. The CNTs were sonicated in NaOH 2M for 4h at 40°C [1]. Immediately after the sonication the material was rinsed in distilled water and vacuum filtered until the pH was neutral and then dried in an oven for 24h at 110°C [13].

The next step was to eliminate the amorphous carbon mixed to the CNTs. This was carried out under HNO₃ reflux for 5h, the material was rinsed in distilled water and vacuum filtered until the pH was neutral and then dried in an oven for 24h at 110°C [13]. The CNTs produced were characterized by TEM, XRD, Raman Spectroscopy and BET analysis.

III. RESULTS AND DISCUSSION

The samples 1, 2, 3 and 4 were taken to pyrolysis in the same conditions of precursor/template ratio, nitrogen flux, time of pyrolysis except by the temperature that was varied according to the Table II. The temperature is a key point to control CNTs diameter and wall thickness, according to the literature the higher the temperature the bigger the CNTs diameter [21], [11].

From the analysis of the results presented in Table II it was determined that there is a limiting temperature for the CNTs formation at the conditions of this work. The measurement of the internal and external diameters of the CNTs, independent of the precursor used, is dependant of the temperature as highest temperatures grown CNTs with bigger diameters [22]. The sample 3 produced with sugar cane juice presents CNTs with a much smaller external diameter than the samples 1 and 2 that were prepared with sugar cane syrup.

For the same temperature 500°C, samples 1 and 3 present very different values for the diameter of the CNTs, revealing that the precursor diluted or concentrated had an enormous effect in the diameter of the CNT.

Analyzing the wall thickness for samples 1 and 2 the CNTs synthesized are of multi walled type. According to the literature [20] thickness of the range 2 to 7nm are for single walled nano tubes and values above 7nm are related to multi walled. The CNTs formed in sample 3 were so small that was not possible to measure the thickness of the walls but because of the measurement of the external diameter and by analogy it would be classified as single walled nano tube.

TABLE II
CNTs SYNTHESIS CONDITIONS USED TO DETERMINE THE INFLUENCE OF TEMPERATURE

Sample No	Precursor	T (°C)	Presence of CNT	CNT internal diameter (nm)	CNT external diameter (nm)	CNT wall thickness
1	Syrup	500	y	30x77	66-99	64-12
2	Syrup	550	y	23-95	81-164	8-21
3	Sugar cane juice	500	y	xxx	11-15	xxx
4	Sugar cane juice	600	n	xxx	xxx	xxx

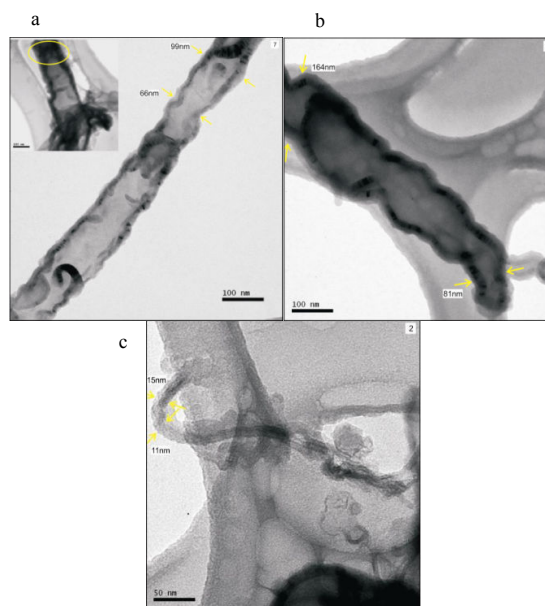


Fig. 1 TEM imaging of CNT synthesized at different temperatures of pyrolysis keeping constant all the other parameters (a) Sample 1 sugar cane syrup T=500 °C; (b) Sample 2 sugar cane syrup T=550 °C; (c) Sample 3 sugar cane juice T=500 °C

Fig. 1 presents the CNT formed from samples 1, 2, and 3 as the sample 4 did not form CNTs in the conditions presented in this work. It is observed that the CNTs morphology is similar showing closed ends and irregularities along the tubes with internal and external diameters different from the samples 1 and 2 that used the syrup as precursor. However, for the sample 3 produced from sugar cane juice the diameter of the CNTs are 6 to 10 times thinner than the other two and the

image shows more regularity along the tube than the CNTs from samples 1 and 2.

TABLE III
CNTs SYNTHESIS CONDITIONS USED TO DETERMINE THE INFLUENCE OF N₂ FLOW RATE

Sample No	Precursor	N ₂ flow (mL/min)	T (°C)	Time Pyrolysis (h)	Presence of CNT
3	Sugar cane juice	30	500	5	y
5	Sugarcane juice	40	500	5	n
1	Syrup	40	500	5	y

In order to understand further the synthesis of CNTs from sugar cane precursor the nitrogen flow was varied while the other parameters were kept constant. The synthesis of the CNTs has not been favored by the increasing of gas flow for the samples obtained with sugar cane juice precursor. However, it was observed formation of CNTs from the sugar cane Syrup at higher nitrogen flow. From these observations it is verified that there is an interaction between gas flow and carbohydrate concentration.

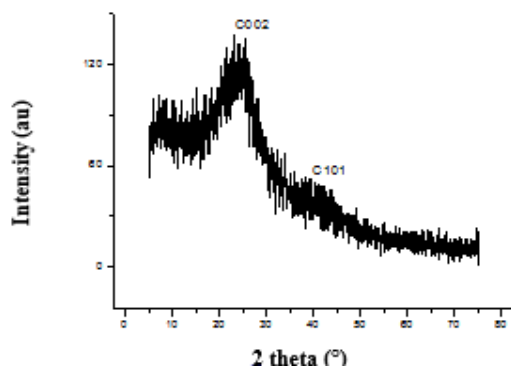


Fig.2 Diffraction pattern of CNT Synthesized by pyrolysis at 500°C, 40mL/min N₂ flow, for 5 hours, from sugar cane precursor. Diffractometer Philips X-Pert MPD, CuK_α radiation = 15.418nm

The two peaks present in the spectrogram of the CNT obtained from sugar cane precursor at 2θ of 26° e 44° are characteristic from graphite layers of multi walled carbon nanotubes and correspond to the reflection planes of C(002) e C(101) and identifies the degree of graphitization of the CNT[23]-[27]. The interplanar distance of the (002) planes calculated by equation 1 for 2θ of 26° was 0.1759nm and for the planes (101) for 2θ of 44° the d-spacing calculated from Bragg's law was 0.110nm. These d-spacing values are distant from the characteristic values for graphite highly orientated and ordered.

$$n\lambda = 2d \sin \theta \quad (1)$$

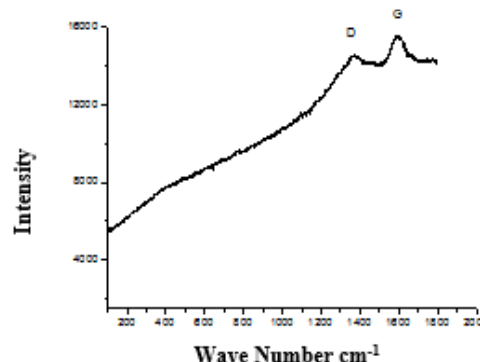


Fig. 3 Raman spectra of the NTCs synthesized by pyrolysis at 500°C, 40mL/min N₂ flow, for 5 hours, from sugar cane precursor

The result obtained from Raman Spectroscopy is very characteristic from carbon multi walled nano tubes (MWCNT). The Raman spectrum presents two peaks, the D-Band at 1380cm⁻¹ that is forbidden for ordered graphite, therefore its presence identifies disordered sp² carbon network or defects in its structure and the G-Band at 1580cm⁻¹ is a typical peak of the C-C bond of graphite[20], [28]. The ratio IG / ID bands from the Raman spectrum is 1.076 showing the MWCNT formed are not well graphitized. The Raman analysis converges with the values of external diameter measured for the MWCNT obtained from sugar cane syrup

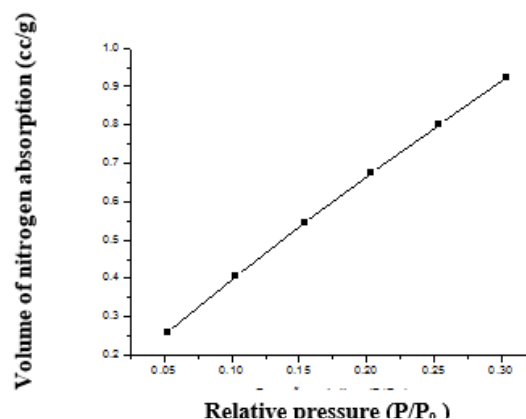


Fig. 4 Absorption/desorption Isotherm of N₂ at 77.35K for the MWCNT prepared from syrup am AAO template

Fig. 4 shows the sorption/ desorption Isotherms of N₂ at 77.35K MWCNT synthesized from sugar cane precursor and its shape is characteristic of macroporous (>50nm) material[13]. The isotherm shows a rapid increase of gas absorbed to low relative pressure because of the strong interaction of the active sites and the gas molecules. The first part of the curve is related to the first mono layer and is responsible for the information about the solid surface area. For this sample was determined a surface area of SBET= 3.691m²/g, small value of the surface area for the MWCNT in this work may be because the tubes are close in both ends.

IV. CONCLUSIONS

1. It is possible to synthesize CNT from sugar cane precursor and AAO template and they are the type multi walled CNT.
2. The surface area of the MWCNT obtained in this work was very small and the tubes were irregular in diameter, short in size and with the two ends closed.
3. The nitrogen flow, the temperature and the concentration of the precursor affect the MWCNT synthesis and the precursor in the form of syrup (concentrated) is more effective.

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