Characterization of reaction products and mechanisms in atmospheric pressure plasma deposition of carbon films from ethanol

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Abstract: Atmospheric pressure plasma deposition (APPD) of carbon films from a predominantly ethanol liquid phase was carried out under varying experimental conditions. A solid precipitate formed in the process was characterised by FT-IR and Raman spectroscopy. After each experiment the liquid phase was analysed for by-products by GC-MS. A number of compounds were found and mechanisms for their formation are proposed. These mechanisms involve the production of free radical species under the high energy plasma/discharge conditions of the process. The formation of groups of compounds was found to correlate with the voltage in the cell, but not with any other experimental parameter.

Introduction

The deposition of carbon films (especially diamond-like carbon) has gained increasing interest during the recent years. Extreme hardness, resistance to chemical attack, high intrinsic electrical resistivity, and high refractive index of the deposited material has made these films extremely useful in a variety of applications. Carbon films are generally amorphous and homogenous. They consist of a mixture of tetragonal (sp^3) and trigonal (sp^2) carbon-carbon bonds. The sp^3/sp^2 bonding ratio typically determines the microstructure and physical properties of the film and depends on the deposition technique used.

Many studies have been reported on the preparation of carbon films. Most methods are vapour deposition techniques. These include chemical vapour deposition,[1,2] microwave plasma decomposition of hydrocarbon gas,[3] ion beam,[4] pulsed laser,[5] sputtering[6] and oxy acetylene combustion.[7] Recently, Nabama,[8] Wang et al.,[9] Cao et al.,[10] Novikov and Dymont[11] and Roy et al.[12] reported the possibility of depositing carbon films, with diamond-like carbon properties, from organic liquids by electrochemical methods. The advantages of these methods over the other methods are the low deposition temperature and the more simple apparatus resulting from the fact that a vacuum is not required.

More recently, atmospheric pressure plasma deposition (APPD), has been developed, which combines galvanic processes and plasma-chemical phenomena. Unlike other plasma deposition techniques, the process occurs in liquid precursors and the plasma is confined to the cathode in a superheated vapour sheath surrounded by the liquid phase. This method, previously used in anodic configuration for the deposition of oxide films,[13,14] allows (in cathodic configuration) the production of a wide range of films, such as carbon, titanium and silicon.

The liquid phase plays an important role in the deposition and research has mainly been limited to alcohol or alcohol/water systems with a view to improving the sp^3/sp^2 ratio in order to get better film quality. This implies that a better understanding of the nature of the physicochemical process and the reaction mechanism leading to the formation of the carbon phase is needed.

In this work we investigated the atmospheric pressure plasma deposition (APPD) technique, for the deposition of carbon films from ethanol. The nature of the deposited film will be reported in a forthcoming publication. The nature of the solid and liquid by-products formed during the APPD process are reported in this paper. These products were characterised by Raman and infrared spectroscopy, and by scanning electron microscopy (SEM) and gas chromatography – mass spectrometry (GC-MS) analysis. Reaction mechanisms are postulated for the formation of the by-products and film growth.

Experimental

Materials

Previous workers in the field of deposition of carbon film have utilized a number of organic liquids in electrodeposition technique. The important properties of the electrolyte upon which the deposition of DLC film by an electrochemical route are believed to be the dielectric constant (ε) and dipole moment (σ). The strength of electric field able to be supported between the electrodes is limited by the dielectric constant while the basic ionic nature of the electrolyte depends on the dipole moment of the electrolyte. Thus, a favourable compromise between the two has to be made for efficient and effective electrolytic deposition of the film. A solution of ethanol ($\varepsilon \sim 24.55$; $\sigma \sim 1.69x\ 10^{-18}$ esu) and water ($\varepsilon \sim 80.37$; $\sigma \sim 1.87x\ 10^{-18}$ esu) thus seemed to be a good choice for the electrolyte. Adding a soluble salt will increase the conductivity of the solution, without significantly affecting the dielectric constant.

Analytical grade ethanol (99.5%) was used as a source of the deposited carbon film. The methanol and water contents were 0.1% and 0.2% respectively. Deionized water was used throughout the investigation. Reagent grade potassium chloride was added to increase the conductivity of the electrolyte used in the deposition process. Phosphate buffer (pH = 7) was used to control the pH of the solution.

Experimental test facility

The basic process of APPD is the electrolysis of a solvent at high voltage. In our test facility, we used a direct current power supply (Bertran 105-02R) with a maximum voltage of 2000 V and a maximum power output of 1kW. The electrodes can be cylindrical or flat. The test facility was composed of two electrodes separated by a distance of 20 mm. The anode was composed of iron, aluminium or graphite, with a surface area in solution of 5 cm^2. The film was deposited on the copper, aluminium or titanium cathodes. The surface area in contact with the solution was 1 cm^2. The surface area of the cathode was thus much lower than that of the anode. Hence, the current density is concentrated around the cathode, leading to the formation of a vapour sheath around the cathode by boiling of the solution[15]. A glow discharge is then initiated by the high electric field in the gas sheath around this electrode. This glow discharge is necessary for the deposition of the film and induces a large number of chemical reactions. A jacketed glass reactor was used for the process, allowing cooling of the system to control the temperature between 30 and 80°C. A sampling system was installed in the reaction chamber to collect liquid during the process enabling study of the temporal evolution of the electrolyte composition. The liquid was analysed using GC-MS. The precipitate formed during the process was separated from the solution and then analysed by FT-IR and Raman spectroscopy. Figures 2 and 3 illustrate the design of the test facility.

Film deposition

Carbon films were deposited at 76ºC using different combinations of anode and cathode materials as described above.

In order to create glow discharge conditions for the deposition, a DC current with an applied voltage in excess of 800 V was used. The current density was kept in the range 320-430 mA/cm^2 with a ramp rate a wide range of 81-1000 V/s. The treatment was carried out for 3600 seconds. The electrolyte consisted of absolute ethanol (90%), deionized water (10%) and 5 gm KCl. The pH of the solution was kept neutral throughout the deposition process using phosphate buffer of pH = 7.

GC-MS analysis

Liquid aliquots were collected during the process for GC-MS chromatographic analysis. A Fisons 8000 gas chromatograph interfaced to an MD800 mass detector was used. The chromatographic parameters are shown in

Table 1: (Tables at end of document)

Spectroscopic measurements

Raman (633nm excitation) and infrared spectroscopic analyses of the solid precipitate formed during the process were carried out using a Renishaw 1000 Raman microprobe spectrometer (Renishaw plc, Wotton-under-Edge, UK) and a Nicolet NEXUS 870 FT-IR spectrometer (Thermo-Nicolet, Madison, WI), respectively.

Results and discussion

Table 2 summarises the experimental parameters for a number of APPD experiments showing variations in the cathode and anode materials, the voltage, the treatment time and the ramp rate. Also shown in this Table is a list of the most common compounds found in the liquid phase together with an indication of whether their presence was detected after a particular experiment. A black precipitate was formed during the glow discharge step of the electrodeposition process.

Spectroscopic analysis of precipitate

The precipitate was filtered, dried and subjected to FT-IR analysis. Fig. 3 shows a spectrum obtained from a precipitate formed in an experiment where an aluminium anode was used. Clearly, there can be seen a broad band at 3375 cm^{-1}, together with bands at 1634 cm^{-1}, 1515 cm^{-1}, 1406 cm^{-1} and 1094 cm^{-1}. The weakness of the C-H stretching bands around 3000 cm^{-1} indicates that the precipitate is predominantly inorganic in nature. The band at 3375 cm^{-1} can be assigned to the OH stretching mode of hydroxide and occluded water, while that at 1634 cm^{-1} can be assigned to the bending mode of the water. Bands around 1000 cm^{-1} can be assigned to O-H bending and deformation modes of inorganic hydroxide. The nature of the hydroxide depends on the anode material. When an iron anode was used the hydroxide was mostly likely to be ferric hydroxide (Fe(OH)$_3$), while an aluminium anode would give aluminium hydroxide (Al(OH)$_3$). The presence of these elements in the precipitates was supported by SEM-EDS results. When a graphite anode was used no hydroxide was detected in the precipitate.

The Raman spectrum of the same precipitate (Fig.4) using 633nm excitation, showed two broad bands at 1607 cm^{-1} and 1325 cm^{-1} which are characteristic of carbon. The two bands can be correlated, respectively, to the two well known vibrational modes of graphite, the G-band which derives from the crystalline graphite, and the D-band which derives from more disordered carbon.[16-19] The positions of these bands in the precipitate are shifted somewhat from the positions typically found for crystalline graphite, which are about 1580 and 1370 cm^{-1}, respectively. The peak shifts indicate that the carbon in the precipitate is more disordered than crystalline graphite, and may be nanoparticulate in nature.[19] The fact that the intensity of the 1325 cm^{-1} D-band is similar to that of the G-band also indicates a relatively disordered carbon.

The above data seems to indicate that the precipitate is a mixed material containing inorganic hydroxides derived from the anode, where a metallic anode was used, together with finely-divided disordered carbon.

Chromatographic analysis of liquid phase

Samples of the electroyte were collected for each experimental run. These were filtered and subjected to chromatographic analysis using GC-MS. The resulting chromatograms (Fig. 5) showed many peaks corresponding to by-products formed during the electrolysis. The MS detector identified these by-products and a list of the compounds found, together with their characteristic ion masses is given in Table 3[20].

Tables at end of document

It is also proposed that, when electrolysis of the solvent is carried out, local Joule heating occurs in the solvent, and then under suitable conditions of energy dissipation and glow discharge, a very shallow primary reaction zone containing high concentrations of radicals originating from the solvent can be formed adjacent to the cathode. Therefore, it can produce an extreme environment that is closely analogous to those brought about by plasma or ionising radiation. This is to say, some non-equilibrium reactions may occur, and some metastable products may be obtained.[21] As shown in Table 3, many reaction products are found in the electrolyte after the process. Mechanisms for the formation of the main by-products have been developed, and are shown in Scheme 1. These mechanisms rely on the presence of methyl radical, and on the formation of radical species from the ethanol by hydrogen abstraction from either the methyl or methylene moiety of the molecule. Oxidation reactions (ethanol to acetaldehyde to acetic acid; methanol to formaldehyde to formic acid) are also postulated. Not all intermediate compounds are detected by GC-MS. For example, neither formic acid nor acetic acid are detected but must be formed because both ethyl formate and ethyl acetate are present.

Visible sparks occur at the cathode and in the vapour sheath surrounding it during the APPD process, and it is assumed that these sparkes create highly reactive conditions in which different radicals can be formed, and that these radicals then lead to the formation of the reaction by-products. Methyl radicals are expected to be present in high concentration in the vicinity of substrate surface during electrolysis. Thus, the basic requirements for depositing carbon films are satisfied. The substrate surface would provide anchorage to the methyl radicals along with hydrogen ions, which would take part in breaking and making of sp^2 and sp^3 bonded carbon, respectively, to ensure the growth of carbon film.[22]

Effect of different experimental parameters on the liquid phase by-products

Methanol is always detected because it is a contaminant of the ethanol which is the major component of the liquid phase. A number of compounds were detected in all experiments. These were acetaldehyde, 2-propanol, ethyl acetate, ethyl formate and 1,1-diethoxyethane. A number of other compounds were only detected in those experiments performed at higher voltage, 920 V or greater. These componds included butadienyl acetylene, 1,2-ethanediol, 1,2-propanediol, 2,3-butanediol, and 1,3-butanediol. In our proposed mechanisms for these compounds (see Scheme 1) all require a hydrogen abstraction reaction from ethanol or methanol to form a radical species. Coupling reactions between the various possible radical species leads to this suite of similar compounds. The fact that butadienyl acetylene is part of this group supports our suggestion that it forms from 2,3-butanediol. It would seem therefore that the hydrogen abstraction reaction is more prevalent at higher voltage leading to increased concentration of hydroxy-containing radicals and hence a greater likelihood of radical coupling reactions to form diols.

Chloroform, which probably forms by reaction between methanol or formaldehyde and species derived from the chloride ion supplied by the KCl electrolyte, was detected in most of the low voltage experiments and never in the high voltage ones.

Further analysis of Table 2 shows that there is no clear correlation between the compounds formed and the other experimental parameters such as cathode or anode type, treatment time or ramp rate. From these experiments, the major determining factor for the formation of the various compounds in the liquid phase appears to be the applied voltage.

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Conclusions

The APPD process was applied to the deposition of carbon films from a predominantly ethanol liquid phase. The solid precipitate formed during the process could not be fully characterised by FT-IR and Raman spectroscopy, but was likely to be a mixed material consisting of an inorganic hydroxide derived from the metallic anode (when used) and finely-divided disordered graphitic carbon. The by-products formed in the liquid phase were analysed by GC-MS included more than 20 organic compounds, many containing hydroxy groups. Mechanisms for the formation of many of these compounds have been proposed involving radical species produced under the high energy plasma/discharge conditions of the process. The major factor for the production of the different organic by-products was the voltage. A number of compounds were formed under all experimental conditions, however a group of compounds which were diols, or diol derived, were only found under higher voltage conditions. Conversely, chloroform was only found in experiments carried out under low voltage conditions. The other experimental parameters such as cathode or anode type, treatment time or ramp rate did not appear to correlate with the compounds formed in the liquid phase.

Acknowledgement

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Figure Captions
1.   Schematic diagram of test facility, 1: Cathode support, 2: Anode,
       3: Jacketed glass vessel, 4: Water inlet, 5: Teflon shield, 6: Solution addition,
       7: Thermometer, 8:Solution sampling system, 9: Gas exhaust, 10: Treated
       Cathode
2.   A photograph of the test facility.
3.   FT-IR Spectrum of a representative solid precipitate.
4.   Raman Spectrum of a representative solid precipitate.
5.   Typical GC-MS chromatograms of a representative liquid sample: (a) retention time $0 - 2$
       min; (b) retention time $3 - 20$ min.

Table 1. Chromatographic parameters used in the analysis of liquid aliquots

Parameter	Details
Column:	**BP 624 Cyanopropylphenyldimethylpolysiloxane capillary column: 30m x 0.32 mm ID, film thickness 1.8 μm. SGE (Melbourne, Australia)**
Injection volume:	**1 μL (split mode)**
Oven temp:	**35 ºC (hold for 5 min.)**
	165 at 15 ºC/min (hold for 3 min.)
	180 ºC at 10ºC/min (hold for 2 min.)
Carrier gas:	**He**
Linear velocity:	**50 cm/sec. Set at 50 ºC**
Detector:	**MSD at 250 ºC**
Ionization mode:	**EI**
Mode:	**scan (scan time 0.9 sec), range 500**
Split ratio:	**80:1**

Table 2. Correlation between the electrical parameters, nature of electrodes and formed by-products

EXPERIMENTAL PARAMETERS {Electrolyte composition: Ethanol (100%) + buffer (10ml) + KCl (5g)}									
Cathode type	Al	Al	Al	Al	Cu	Cu	Cu	Cu	Al
Anode type	Al	Al	Al	C	C	C	C	C	C
Voltage	920	950	800	850	810	950	950	810	810
Treatment time	5400	3600	3600	3600	3600	1800	3600	3600	3600
Ramp rate	920	950	800	850	850	950	950	810	810
Average power in the discharge (W)	306	366	255	263	288	386	383	204	277
BY-PRODUCTS (• = present)									
Methanol	•	•	•	•	•	•	•	•	•
Acetaldehyde	•	•	•	•	•	•	•	•	•
1,3-Butadiene	•	•			•	•	•	•	
2-Propanol	•	•	•	•	•	•	•	•	•
Ethyl acetate	•	•	•	•	•	•	•	•	•
Chloroform				•	•			•	•
Butadienyl acetylene	•	•				•	•		
Ethyl formate	•	•	•	•	•	•	•	•	•
1,1-Diethoxyethane	•	•	•	•	•	•	•	•	•
Methoxy acetaldehyde	•	•				•	•		
1,2-Ethanediol	•	•				•	•		
1,2-Propanediol	•	•				•	•		
2,3-Butanediol	•	•				•	•		
1,3-Butanediol	•	•				•	•		
Phenylethyne	•	•					•		
Benzocyclobutane	•	•							
2,2-Diethoxy ethanol				•	•	•	•	•	•
1,3-Propanediol							•	•	
Methyl phenyl acetylene	•	•	•				•		
Hydroxy acetaldehyde								•	

Table 3. GC-MS Characterization of by-products formed during APPD process

By-product	Retention time (R_t/min)	Characteristic Ions (m/z)
Methanol	0.892	33,32,31,29,28,15,14
Formaldehyde	1.042	31,30,29,28
Acetaldehyde	1.375	45,44,43,29,26,25
1,3-Butadiene	1.709	51,50,49,48,37,36,25,24,13
2-Propanol	2.992	60,59,46,45,43,39,29
1-Propanol	4.626	60,59,43,42,41,31,29
Ethyl acetate	5.159	88,73,70,61,45,43,31,29
Chloroform	5.576	87,85,83,82,48,47,35
2-Butanol	5.773	74,73,60,59,57,46,45,41,31,29
Butadienyl acetylene	6.559	79,78,77,74,63,52,51,50,39,38,28
Ethyl formate	7.659	76,75,63,47,29
1,1-Diethoxy ethane	8.126	104,103,75,73,61,47,45,43,31,29,28
Methoxy acetaldehyde	9.143	59,56,46,45,44,31,29,28
Ethanediol	10.743	45,44,43,33,31,29
1,2-Propanediol	10.993	76,75,61,57,46,45,43,31,29
2,3-Butanediol	11.266	75,72,57,47,45,43.31,29,28
1,3-Butanediol	11.426	75,72,57,55,45,43,29,28
2,2-Diethoxy ethanol	12.309	104,103,89,61,47,31,29,28
1,3-Propanediol	14.010	59,58,57,45,43,31,28,28,27
Hydroxy acetaldehyde	14.343	61,60,43,42,41,33,32,31, 29,28