# MODELING THE CARBONIZATION PROCESS USING AC AND DC CONDUCTIVITY METHODS

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## Abstract

This study is focused on the analysis of both AC and DC conductivity changes during conversion of microcrystalline cellulose to carbons over the temperature range from 250°C to 1000°C. Microcrystalline cellulose is highly refined cellulose with all the inorganic impurities removed. By using this material as a model, we can gain a better understanding of the structure and property changes that occur at different stages of carbonization. Our studies have illustrated that microcrystalline cellulose carbons prepared at various carbonization temperatures showed four distinct regions of electrical conductivity with respect to increases in heat treatment temperature i.e. the degree of carbonization: (I) decrease in conductivity is noted due to the loss of dipole polar groups; (II) linear response to an AC field was observed due to carbon cluster nucleation and growth; (III) non-linear frequency AC response is noted due to electron hopping; and (IV) DC conductivity was observed due to percolation. This research has shown that by using highly pure carbon precursors such as microcrystalline cellulose and by carefully controlling the carbonization parameters, a more comprehensive and definitive description can be made for the decomposition and carbonization mechanisms of hydrocarbon and carbohydrate carbon precursors.

## Introduction

Electrical properties of carbon materials have been studied extensively over the years and have been shown to vary widely depending on the nature of the precursor and the heat treatment temperature (HTT). Microcrystalline cellulose is a basic component of wood that has been highly refined to remove all the inorganic ash. By using this high purity precursor material, it is believed that more definitive observations could be made on the thermal decomposition and carbonization mechanisms of organic compounds as they are converted to non-graphitizing carbons. This study focuses on measuring changes in AC and DC electrical conductivity of microcrystalline cellulose during its transformation into carbon over the temperature range from 250°C to 1000°C.

Studies have shown that electrical resistivity of soft carbons increase nine orders of magnitude as HTT varies from 600°C to 900°C, resulting in a non-metal to metal transition (Mrozowski 1952). In an attempt to describe such observations, a band model for semi-conductors was proposed in which resistivity was a function of an energy gap. Later work (Giuntini and Jullien 1978, Guintini and Zanchetta 1979) described electron hopping as the main mechanism for electric conduction for samples heat treated to 600°C. For samples heat treated to 650°C, electrical conductivity was described as being the result of transport between localized states near the Fermi level.

Two main theories, Anderson-Mott model and Cohen-Jortner transition, were proposed to explain the nonmetal-metal transition observed in carbon materials (Delhaes and Carmona 1981). Both theories involve the presence of localized and extended states which depend highly on the degree of randomness. Anderson-Mott model was proposed for carbon as it involves an increase of randomness competing with localized states. As randomness decreases as a function of increasing HTT, the number of localized states increases and a connection of such localized states increases electrical conductivity. However, the Anderson-Mott model has been challenged as it applies only to homogeneous solids. Cohen-Jortner transition assumes long-range fluctuations of properties and a more continuous transition from non-metal to metal. This latter model proposes the existence of metallic sites in a non-metallic and random medium. A connection between such metallic sites in an inhomogeneous regime gives rise to the electrical conductivity change observed in carbon.

More recent studies (Kercher and Nagle 2002) showed a change of DC electrical conductivity of carbonized medium-density fiberboard heat treated to temperatures of 600°C and above. A percolation model based on the nucleation and growth of high conducting sites embedded within a dielectric was used to explain the varying conductivities. AC studies (Sugimoto and Norimoto, 2004, 2005) of carbonized wood materials heat treated to temperatures lower than 600°C showed frequency dependent conductivity values. Dipole polarization and Maxwell-Wagner interfacial polarization were used to explain such

results.  Furthermore, a heterogeneous structure exhibiting interfacial polarization that seems to occur at the interface of isolated conductive regions was described to support both percolation and interfacial polarization (Kercher and Nagle 2004).

This study was undertaken to fully characterize the electrical property changes that take place during the carbonization process which involve both compositional and structural changes.  By using a high purity precursor material, more definitive observations can be made regarding the conversion processes that take place during carbonization.

## Materials and Methods

### Sample Preparation

Avicel microcrystalline cellulose powder was mechanically pressed and compacted into 2 inch diameter disks at 10 Tons.  Pressed disk samples were placed on graphite sheets to ensure uniform temperature distribution during heating.  Samples were then heat treated in an inconel-lined retort furnace to final HTTs under constant argon flow following heating schedule:

100°C /hr to 250°C
3 hr dwell
5°C /hr to 275°C
2 hr dwell
5°C /hr to 325°C
2 hr dwell
50°C /hr to 450°C
1 hr dwell
100°C /hr to final HTT
12 hr dwell
100°C /hr to 25°C

Samples for electrical conductivity studies have final HTT temperatures of 250°C, 300°C, 350°C, 400°C, 450°C, 500°C, 550°C, 600°C, 650°C, 700°C, 750°C, 800°C, 900°C and 1000°C.

### AC Measurements

AC conductivity measurements were conducted using a HP4194A Impedance/Gain Analyzer.  Samples for AC measurements included those that were heat treated at final temperatures of 250°C to 650°C.  Parallel conductance was recorded as function of frequency (ranging from 1000Hz to 1MHz) at room temperature.
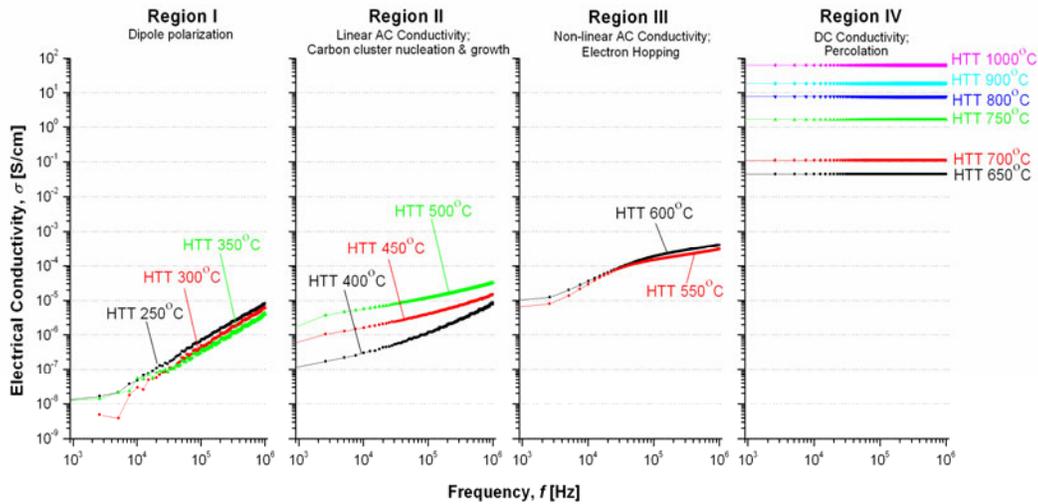
### DC Measurements

DC conductivity measurements were conducted using a four-point probe apparatus.  The standard procedure for measuring electrical resistivity as described by ASTM C 611-98 (ASTM 2003) was closely followed.  Samples were machined to fit specimen dimensions and to reduce errors from surface imperfections. A Lodestart 8300 variable power supply was used as the current source and two HP 34401A multimeters were used for current and voltage measurements. Two contacts spaced at a known distance were used to record the voltage drop through the sample while current was applied.  Voltage drops were recorded for both directions of current flow and its average value was used to calculate resistivity.  Resistivity, $\rho$, for each sample was then calculated using the following relation:

$$\rho = \frac{V_P A}{DI}$$

[1]

where $V_p$ is the average potential drop across the probes; $D$ is the distance between the probes; $A$ is the contact area of the sample; and I is the current applied through the sample.  Electrical conductivity, $\sigma$, for each sample was then calculated as the inverse of resistivity, $\rho$.

# Results and Discussion

The results from electrical conductivity measurements have provided new insight into the carbonization processes of cellulose materials. Figure 1 shows that the conversion of microcrystalline cellulose to carbon can be divided into four distinctly different electrical conductivity regions with each region exhibiting different atomistic electrical transport mechanisms. These four regions consist of [I] the thermal-driven loss of polar groups attached to the cellulose molecule at temperatures below 350°C; [II] nucleation of highly conductive carbon clusters from 400°C to 500°C that exhibit interfacial polarization along with a linear AC conductivity frequency response; [III] the growth of the carbon clusters and these clusters moving closer to each other with increasing HTT temperature resulting in a non-linear AC conductivity towards frequency in the temperature range of 550°C to 600°C; and [IV] at 650 °C, DC conductivity is observed as the cluster start to percolate.



**Figure 1.** Electrical conductivity measurements for microcrystalline cellulose derived carbon monoliths for various heat treatment temperatures (HTTs).

### Region I: Cellulose Depolymerization/Loss of Polar Groups [250°C – 350°C]

For cellulose samples heat treated to temperatures in the 250°C to 350°C range, the AC conductivity decreases with an increase in HTT. The decrease of electrical conductivity with an increase in HTT is explained by the loss of polar groups. The volatile polar groups such as hydroxyl and carboxyl in cellulose and partially carbonized cellulose can rotate in the presence of an AC field and produce dipole polarization that gives the material AC electrical conductivity. Electrical studies on wood based carbons (Sugimoto and Norimoto 2004, 2005) as well as on the chemical degradation of cellulose (Fitzer et al 1971) indicated that a hydrocarbon precursor was not completely de-polymerized until a HTT of 350°C was reached. Our results are in agreement with these studies and suggest that as HTT increases, the volatile groups that were previously responsible for dipole polarization, are gradually driven off as the precursor is decomposed. This results in the observed decrease in AC conductivity as the HTT temperature is increased from 250°C to 350°C.

*Region II: Nucleation of Carbon Clusters and their Growth [400°C – 500°C]*

At 400°C, the magnitude of electrical conductivity increases substantially. At this point, the polar volatile groups have essentially been driven off and the electrical conductivity is dominated by an interfacial polarization mechanism as described in a previous investigation (Sugimoto and Norimoto, 2004). However, Kercher and Nagle (2002, 2004) described these observations using a quasi-percolation theory where highly electrically conducting carbon clusters nucleate and grow until they begin to interact. Figure 3.1 (Region II) presents AC study results for electrical conductivity for samples with HTT of 400°C to 500°C. At 400°C, there is an increase in the AC conductivity associated with the onset of the homogeneous nucleation of the conducting nano-carbon clusters. Within the range of 400°C to 500°C, these conducting carbon clusters grow larger in size, thus resulting in the reduction of inter-particle distance accompanied by shrinkage of the carbon monolith. In this region, the AC conductivity response is essentially linear with increasing frequency.

*Region III: Clusters Interact Resulting in a Non-Linear AC Conductivity [550°C – 600°C]*

Samples heat treated from 550°C to 600°C exhibit further increases in conductivity, but a non-linear AC conductance is observed as the frequency is increased, which implies an electrical "switching" behavior for these materials. Electrical switching of amorphous carbon has been reported in the past for amorphous carbon thin films (Shimakawa and Miyake 1989, Egret et al 1997, Von Bardeleben et al 2003), but no references have been found for observing this effect in bulk amorphous carbons. This non-linear frequency response is believed to be due to the fact that the carbon clusters become sufficiently close to each other for electrons to be able to hop from one cluster to another as the frequency is increased. This leads to an increase of AC conductivity by approximately a factor of 15. These observations will be the subject of a separate publication where we will focus on the voltage and temperature response of these materials in this region.

Sugimoto and Norimoto (2004) observed similar results with carbonized wood specimens with HTTs of 500°C, 550°C, and 600°C, predicting that the increase in conductivity with frequency was due to interfacial polarization. Interfacial polarization is a result of the localized movement of free electrons and ions causing a dipole moment (Von Bardeleben et al 2003). Maxwell Wagner relaxation observed due to interfacial polarization is caused by a heterogeneous nature of the material (Sugimoto and Norimoto 2005). In this region, we predict that the conducting carbon clusters continue to grow within a dielectric matrix consisting of disordered carbon-hydrogen groups giving rise to interfacial polarization. As suggested by Giuntini et al (1978, 1979), localized migrations of charge carriers within the interfaces resulted from interfacial polarization indicate electrical conduction mechanisms at the Fermi level near an insulator-metal transition point. Giuntini described anthracene carbons heat treated to temperatures up to 600 °C as highly amorphous and its electrical conduction observed due to electron hopping between localized states. As HTT increases, conducting carbon clusters grow until these clusters are close enough where electron hopping and pre-quasi-percolation of two conducting sites, as predicted by Kercher and Nagle (2002, 2004), may occur.

*Region IV: Carbon Cluster Percolation - DC Conductivity [650°C – 1000°C]*

Samples heat-treated to 650°C and higher temperatures exhibited no frequency response indicating that percolation has taken place. Thus, samples heat-treated at temperatures higher than 650°C were measured using the four-point DC method. With further heat treatments to 1000°C, conductivity increased as inter-cluster distance was reduced due to continuous growth of these clusters and volume shrinkage.

## Conclusions

AC and DC electrical conductivity measurements have provided new insight on the decomposition and conversion of cellulose materials to carbon. Four distinct processes have been identified in the process of conversion of organics materials to hard carbons. In the first region with the HTT temperature ranging from 250°C to 400°C, a decrease of AC electrical conductivity was observed as a function of increasing HTT. This decrease was due to the loss of volatile polarizable dipole groups. In the second region, starting at 400°C, the AC electrical conductivity is observed to have a significant jump due to the homogenous nucleation of highly conducting carbon nano-clusters. Also observed is a linear response in the conductivity with increase in frequency due to the polarization of the localized free electrons. This linear response is believed to be due to the nano-clusters being sufficiently separated from each other that

they do not interact with each other. In region III starting at 550°C, the nano-clusters have grown in size and moved sufficiently close together that they start to interact with one another resulting in a non-linear response as the AC frequency is increased. In this region, electron hopping is believed to start occurring between conductive carbon clusters resulting over an order of magnitude increase in the AC conductivity. Above 610°C (region IV), DC conductivity is observed due to percolation effects.

## Acknowledgements

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