

Electrical Properties of Partial Carbonized Nanoporous Resin Based on Resorcinol-Formaldehyde

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Abstract: Organic xerogel compounds were prepared by sol-gel method from resorcinol-formaldehyde mixtures in acetone using picric acid as catalyst. The electrical properties of the obtained nanoporous carbon structures were explored by changing the pyrolysis temperature. In this study the electrical conductivity σ can be expressed as $\sigma = \sigma_0 \exp(-E_\sigma/kT)$, where E_σ depends on the carbonized temperature. The dc and ac conductivities of the obtained amorphous carbon have been investigated from 80 to 300 °C and in the frequency range between 40 and 10⁶ Hz for samples pyrolysed at different temperatures in the insulator-metal transition range. The temperature dependence of samples pyrolysed at low temperatures ($T_p=600-675$ °C) follows a Mott law, whereas samples pyrolysed at high temperature ($T_p=1000$ °C) show an Arrhenius dependence. Copyright © 2014 IFSA Publishing, S. L.

Keywords: Nanoporous Carbon, Resin, Resorcinol-Formaldehyde (RF), Electrical Properties, Variable range hopping (VRH).

1. Introduction

Sol-gel polymerizations have largely involved the hydrolysis and condensation of metal alkoxides to form inorganic aerogels or xerogels. Carbon xerogels were synthesized by polymerization of resorcinol with formaldehyde (RF), followed by pyrolysis at different temperatures under nitrogen atmosphere [1-4]. The electrical properties of carbon materials derived from organic precursors have been extensively studied over the years and have been shown to vary widely depending on the heat

treatment temperature (HTT) [5-9]. Later works [6, 10] described an electron hopping between localized states as the main mechanism for electric conduction for a sample treated at 700 °C. In this work, we present the results of the electrical conductivity properties for material treated in a nitrogen atmosphere at temperatures between 600-1000 °C. With the purpose of determining a mechanism of charge transport, the study of electrical conductivity has been made in the measurement temperature interval of 80 to 300 K for various mechanisms of conductivity, each characterized by a

particular type of temperature dependence. The ac conductivity measurements represent an experimental method to obtain information about the existence and location of these states. Several models have been proposed to interpret the frequency and temperature dependence of ac conductivity in amorphous materials [11, 12].

2. Experimental

The samples were synthesized using L. EL Mir et al. protocol [1-3]. The organic sol-gel polymerisation protocol presented in this study, involved a reaction between resorcinol and formaldehyde mixture in acetone using picric acid as a catalyst. The xerogel formation was obtained by a modified conventional fluid extraction where the precursor sol may be made at ambient temperature and pressure. The precursor solutions were prepared for cross-linking in acetone solution and the system was heated to ensure gel formation. In order to conserve the monolithicity and avoid shrinkage of the samples, some precautions were taken: the samples were prepared in small sizes of about 1.5×1.5×1 cm. After gelation the wet gel was put in a bigger ceramic vessel. Finally the obtained xerogel was transferred in an incubator and dried at 150 °C at small heating rate of about 10 °C/day. This method is quite successful in producing monolithic RF (Resorcinol formaldehyde) xerogels with little or no shrinkage at all during drying.

3. Results and Discussion

Fig. 1 displays the SEM micrographs of the xerogel and electrical conducting carbon (ECC) structures obtained at different pyrolysis temperatures, which exhibit significant differences in agglomeration particles.

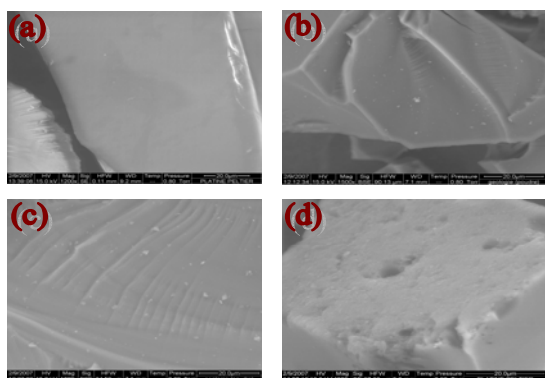


Fig. 1. SEM micrographs of (a): RF-150, (b): RF-575, (c): RF-675, (d): RF-1000.

It is clear that carbon microparticles aggregate, which means that heat treatment improves the network structure density that was also observed at macroscopic dimension. For RF-1000 (Resorcinol formaldehyde pyrolysed at 1000 °C) carbon sample,

a highly porous microstructure, was observed in the SEM.

Natural logarithm of σ versus $1000 T^{-1}$ is plotted in Fig. 2 for the resorcinol-formaldehyde carbonized between 600 and 1000 °C. The electrical conductivity σ can be expressed as follow:

$$\sigma = \sigma_0 \exp\left(-\frac{E_\sigma}{KT}\right), \quad (1)$$

where k is the Boltzmann constant. T is the absolute temperature. σ_0 and E_σ are found to be a function of the carbonized temperature. The logarithm of the activation energy E_σ was plotted versus the reciprocal of the carbonizing temperature T_p in Fig. 3. As T_p increases from 600 to 675 °C, the energy gap E_{gap} (E_σ) decreases from 200 to 10 meV as the degree of percolation of conductive carbon clusters increases. kT must surpass the energy gap E_{gap} to observe dc conduction. At low pyrolysis temperatures, E_{gap} is superior to kT , the d.c conductivity is properly described by a Mott law indicating a transport mechanism via variable range hopping.

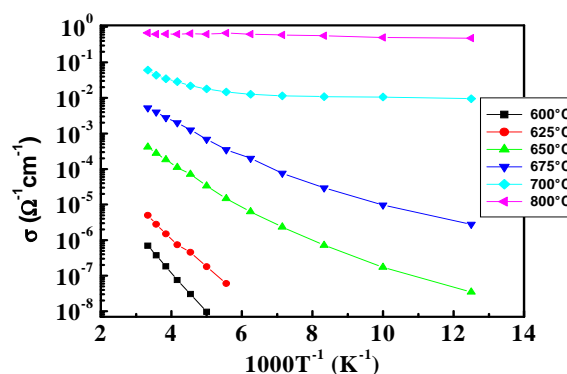


Fig. 2. Variation of dc conductivity in logarithmic scale versus measurement temperature ($1000/T$) for samples pyrolysed at different temperatures in transition range.

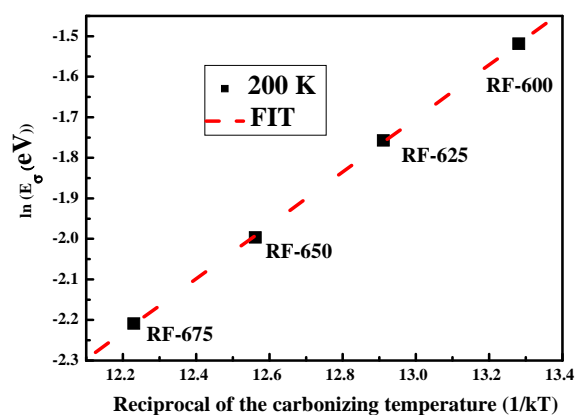


Fig. 3. E_σ was plotted versus the reciprocal of the carbonizing temperature T_p . These parameters are evaluated at the temperature of 200 K.

At higher pyrolysis temperatures, E_{gap} is lower to kT , E_{σ} is the activation energy for the carbonization including many processes. The temperature dependence of samples pyrolysed at low temperatures ($T_p=600\text{--}675\text{ }^{\circ}\text{C}$) follows a Mott law, whereas samples pyrolysed at high temperature ($T_p=700\text{--}1000\text{ }^{\circ}\text{C}$) show an Arrhenius dependence.

Ac electrical conductivities and the exponent s of the carbonized microcrystalline materials are summarized in Fig. 4. and Fig. 5.

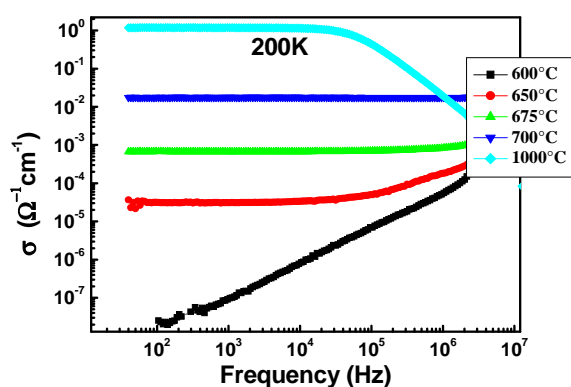


Fig. 4. Electrical conductivity measurements vs. frequency near the percolation threshold, HTT 600, 650, 675, 700 and 1000°C.

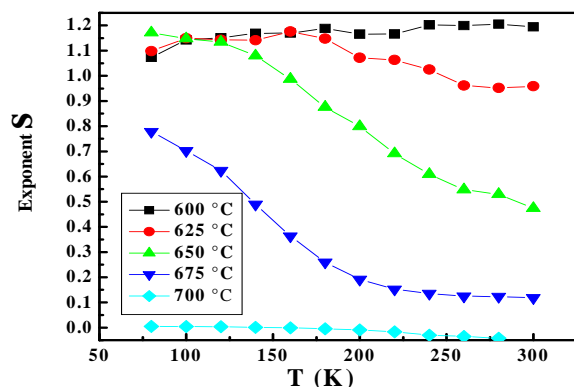


Fig. 5. Temperature dependence of exponent s near the percolation threshold, HTT 600, 650, 675 and 700 °C.

Four distinct regions of electrical conductivity can be identified. These regions can be correlated with the microstructural changes that take place during carbonization. In region I (600 °C), the ac conductivity starts to increase with heat treatment temperature due to the formation and growth of conducting carbon clusters. The electrical conductivity of this region increases with increase in frequency of applied electric field. As indicated by Sugimoto and Norimoto [13, 14], at this HTT range, the hydrocarbon is not fully depolymerized and still possesses high concentrations of hydroxyl and carboxyl functional groups that dominate the overall electrical conductivity in this region. These organic

groups have dipole moments that respond to an applied ac field and such dipole interaction increases with frequency.

In region I, the frequency dependence of the ac conductivity obeys the universal power law [15]:

$$\sigma(\omega, T) = \sigma_{dc}(T) + A(T)\omega^{s(T, \omega)}, \quad (2)$$

where the angular frequency exponent has a value equal to that of unity 1. The value of the exponent close to one indicates that the observed ac conductivity is due to phonon-assisted hops between spatially distinct sites similarly to the dc contribution, and not to the photon absorption for which exponent $s = 2$ is usually found.

In region II (650–675 °C), The frequency dependence of the ac conductivity obeys the power law (2), where the angular frequency exponent s has a value less than unity 1, in this region, a further increase of ac conductivity with increasing of heat treatment temperature is observed. In addition, the ac conductivity demonstrates a non-linear frequency dependency due to electron hopping, interfacial polarization, and onset of a percolation threshold. In region III (700 °C), a frequency independent conductivity (dc conductivity) is observed and continues to increase with heat treatment due to the growth and further percolation of carbon clusters. Finally in region IV (700–1000 °C), the dc conductivity reaches a plateau with increasing heat treatment temperature as the system reaches a fully percolated state. When the frequency is increased the conductivity does not change until a critical frequency (ω_0) occurs. After this critical frequency the conductivity increases slowly but nonlinearly, so there is for each temperature a critical frequency ω_0 beyond which a power law is followed. Kilbride et al., [16] proposed an experimental definition of the critical frequency given by the following formula:

$$\sigma(\omega_0) = 1.1\sigma_{dc}, \quad (3)$$

Butcher and coworkers developed a so-called “extended pair approximation” (EPA) [17] in which the effect on the relaxation rate for a given pair of sites of all the other sites in the network is taken into account in an averaged way. This effect was neglected in pair approximation where the hopping or tunneling was restricted to a pair of potential wells. In terms of microscopic theory, the exciting field changes the relative environment of a pair of centers and causes transition between them governed by the intrinsic relaxation time τ of the pair. The resultant loss is dominated by pairs having relaxation times τ around $\frac{1}{\omega_0}$. So in the limit of high frequency,

transitions are taking place mostly from those sites for which relaxation times are very small i.e. only from neighbouring sites. In region IV, At high

temperatures and high frequencies, the conductivity increases with the frequency characterizes a metallic behaviour.

The electrical properties, i.e. the frequency-dependent complex conductivity, of a metal are governed by the relaxation time τ , the characteristic time scale of the current response. Following the Drude model [18], the conductivity is given by:

$$\sigma(\omega) = \frac{\sigma_{dc}}{1 - i\omega\tau} = \sigma_{dc} \frac{1 + i\omega\tau}{1 + \omega^2\tau^2}, \quad (4)$$

with σ_{dc} is the dc conductivity and τ the scattering time. The frequency dependence of the ac conductivity obeys the Drude law:

$$\sigma(\omega, T) = \frac{\sigma_{dc}}{1 + \omega^2\tau^2} = \frac{Ne^2\tau}{m} \frac{1}{1 + \omega^2\tau^2}, \quad (5)$$

This simple classical Drude model provides is a very good explanation of dc and ac conductivity in metals. The real part of the conductivity, equals the dc conductivity at zero frequency and follows a $\frac{1}{\omega^2}$ behaviour at high frequencies.

Fig. 6 shows the variations of the relaxation time versus heat-treatment temperature.

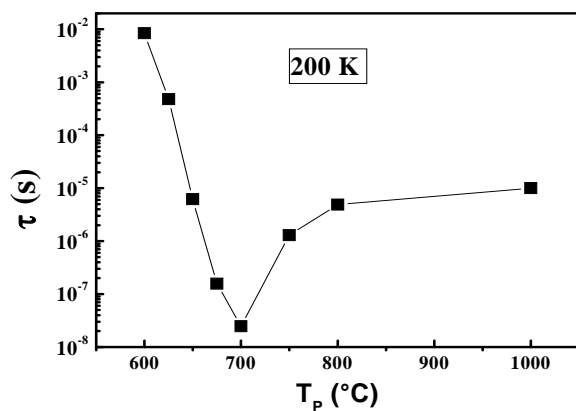


Fig. 6. The relaxation time as a function of heat-treatment temperature at 200 K.

The relaxation time decreases with increasing pyrolysis temperature, in 700 °C presents a minimum. This temperature dependency is interpreted in terms of structural transformations in the amorphous carbon networks. The relaxation time exhibits a minimum at the phase transition point between insulator and metal. For the high temperatures the approach of the metallic state is accompanied by the successive suppression of the hopping contribution at low frequencies and, which finally become a strong Drude contribution in the fully metallic state. The experimental results on

frequency and temperature dependence of ac conduction in amorphous carbon were analyzed in the framework of available microscopic models [19].

3. Conclusion

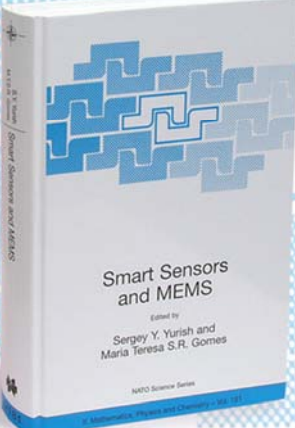
Electrical conductor carbon structures have been synthesized by a new protocol of sol-gel method combined with a furnace firing in nitrogen atmosphere. The analysis of the obtained results revealed that, the polymeric insulating phase was transformed progressively with pyrolysis temperature into carbon conducting phase, this means the formation of long continuous conducting path for charge carriers to move inside the structure with thermal treatment and the samples exhibited tangible percolation behaviour where the percolation threshold can be determined by pyrolysis temperature. The band gap depends on the carbonized temperature. When the carbonized temperature is higher, the band gap between the impurity level and the conduction band is smaller. At low pyrolysis temperatures, the d.c and ac conductivities are properly described by a Mott law indicating a transport mechanism via variable range hopping.

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