



Negative differential resistance in nickel doped nano-carbon structures based on pyrogallol-formaldehyde xerogel

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Abstract

Nickel doped nano-carbon structures have been synthesized by sol-gel method. In our approach the xerogel formation was activated by picric acid as catalyst and electric properties were explored by changing the pyrolysis temperature. The obtained electrical conducting carbon (ECC) structures were characterized by various techniques, X-ray diffraction (XRD) and electrical analysis. I(V) characteristic of the ECC pyrolysed at 625 °C temperature range presents a negative differential resistance at room temperature were the behaviour depend on maximum of current applied to the sample. However, the dynamic conductance $G(\omega)$ of the sample pyrolysed at 700 °C shows a semi-conducting and metallic behaviours depending on measurement temperature.

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1. Introduction

Porous carbon structures, obtained after pyrolysis of some organic compounds, have been extensively studied for the past 20 years [1-5]. Containing a large surface area, porous carbon structures have been used in a wide variety of applications such as electrodes of supercapacitors, energy storage, gas sensors, advanced catalyst supports, chromatographic packing, and others [6-10]. However, no systematic study was investigated to illustrate electric behaviour in this material. In fact during carbonization, the physical properties, particularly the transport properties, undergo strong modification and depend on texture of the obtained material [11]. This evolution is experimentally related to a loss of heteroatoms, during the pyrolysis [12]. The process of carbonization appears as a solid phase nucleation. In fact, the loss of hydrogen promotes the production of bidimensional nanolayers [13]. However, although the number of publications on carbons is considerable, no totally satisfactory explanations on the evolution of their electronic properties in the range of carbonization are available. In fact, electrical properties in carbons depend strongly on structural and textural properties which are very close to the precursor, doping element, catalyst and elaboration protocol used.

We report in this paper, a low-cost preparation method of synthetic nickel doped porous electrical conducting carbon (ECC) structures based upon the gelation of pyrogallol–formaldehyde (PF:Ni) xerogel using picric acid as catalyst. The analysis of the obtained results revealed that, PF:Ni xerogel insulating phase was transformed progressively with pyrolysis temperature into ECC phase; this means that the percolation threshold observed in the obtained structure can be defined by thermal treatment process. The I(V) characteristic of the ECC pyrolysed at 625 °C temperature range presents a negative differential resistance at room temperature were the behaviour depend on maximum of current applied to the sample. The I(V) characteristic of the ECC pyrolysed at 625 °C temperature range presents a negative differential resistance at room temperature were the behaviour depend on maximum of current applied to the sample. In dc transport, the characteristic response time $\sigma(T)$ shows a linear $\ln \sigma$ versus $T^{-1/4}$ behaviour, closely related to variable range hopping (VRH) transport [14]. However, the dynamic conductance

$G(\omega)$ of the sample pyrolysed at 700 °C shows a semi-conducting and metallic behaviours depending on measurement temperature.

2. Experimental

2.1. Sample preparation

The synthesis of ECC structures has been done in three steps. In the first step, organic wet gels were prepared by mixing formaldehyde (F) with dissolved pyrogallol (P) in water (W) solution, using picric acid as a catalyst and nickel (Ni) as a doping element. In the second step, the obtained wet gels were dried in humid atmosphere at 50 °C for two weeks. To obtain a structured xerogel, the sample was transferred in an incubator and dried at 150 °C at a heating rate of 10 °C/day. The drying temperature was then maintained for two days. In the present study, the thermal treatment was carried out in a tubular furnace under nitrogen atmosphere. Each sample was put into a furnace and heated up to the desired pyrolysis temperature at a heating rate of 5 °C/min. A constant selected pyrolysis temperature was then maintained for 2 h and finally, the sample was cooled. The samples for electrical measurements were prepared by sculpting the ECC monolith on a parallelepiped shape and using silver paint on two parallel faces to assure ohmic contact.

2.2. Characterization techniques

The XRD patterns of ECC were carried out by a Bruker D5005 diffractometer, using Co K λ radiation ($\lambda = 1.78901 \text{ \AA}$). Electrical measurements in a temperature range of 80–300 K were carried out using a liquid nitrogen cryostat where the samples were kept under vacuum during the measurements. Current–voltage measurements were performed using a computer-controlled setup comprising a Keithley 220 current source and an Agilent 34401A multimeter. For ac measurements, an Agilent 4294A impedance analyser was used to collect impedance measurements over a wide frequency range. We employ a parallel mode to measure conductance G using an alternating signal with voltage amplitude of 50 mV.

3. Results and discussion

The organic sol-gel protocol presented in this study, involved a reaction between pyrogallol and formaldehyde mixture in acetone using picric acid as a catalyst and nickel as a doping element. The precursor solutions were prepared for cross-linking in acetone solution and the system was heated to ensure gel formation. Finally the obtained wet gel was transferred in an incubator and dried at 150 °C at small heating rate of about 10 °C/ day. Figure 1 exhibits the XRD patterns of the extracted product as prepared in the second step and after heat treatment at 1000 °C in nitrogen atmosphere. The diffractogram XRD of this sample indicates the presence of three picks: the first around 30° correspond to the graphite (C) structure, the two other ones at around 52° and 61° correspond to the metallic nickel (Ni) phase. The average grain size G can be calculated using the Scherrer equation [15]:

$$G = \frac{0.9\lambda}{B \cos \theta_B} \quad (1)$$

where λ is the X-ray wavelength, θ_B is the maximum of the Bragg diffraction peak (in radians) and B is the line width at half maximum. After a correction for the instrumental broadening, the average value of the crystallites was found of about 9.7 nm for the graphite and 35 nm for the nickel.

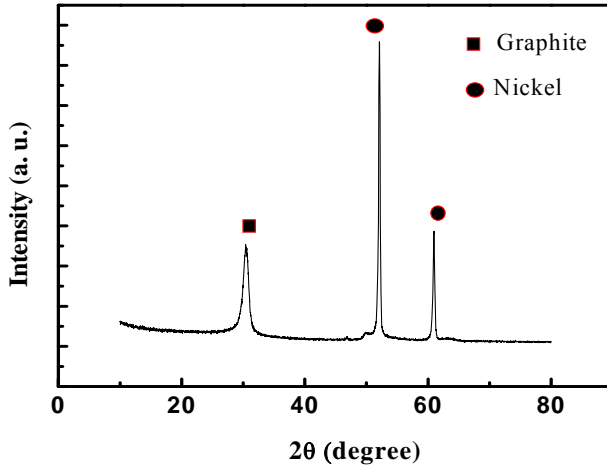


Fig. 1: XRD patterns of PF:Ni sample pyrolysed at 1000°C for 2 h in nitrogen atmosphere.

The dc room temperature bulk conductivity results as a function of the pyrolysis temperatures for undoped and nickel doped PF are plotted in Figure 2. The dc conductivity change markedly in transition range between 600 and 800 °C, and the effect of nickel as doping element is well illustrated.

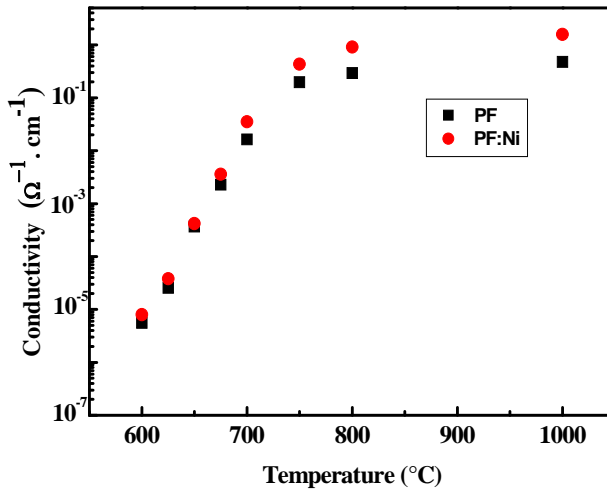


Fig. 2: The dc room temperature conductivity versus pyrolysis temperature.

In our previous work [16] we illustrated that the characteristic $I(V)$ of undoped PF treated at $675\text{ }^{\circ}\text{C}$ presents a negative differential resistance for the low measurement temperatures, and even when the sample was exposed to intensive current of about 100 mA the material doesn't change and conserve its initial behaviour.

Figure 3 presents the characteristic $I(V)$ of the PF:Ni sample treated at $625\text{ }^{\circ}\text{C}$. For the first time we illustrate the presence of negative differential resistance at ambient temperature and the path to go is not back the one. Indeed, the sample has a negative differential resistance in the first stage ((a): ascending current) and this behaviour doesn't exist anymore in second stage ((b): descendant current). This new observed phenomenon that is generated by the nickel can explain himself by the fact that when an important current (100 mA) was applied to the material, this last is going to change her behaviour completely and it becomes more conducting that precedent.

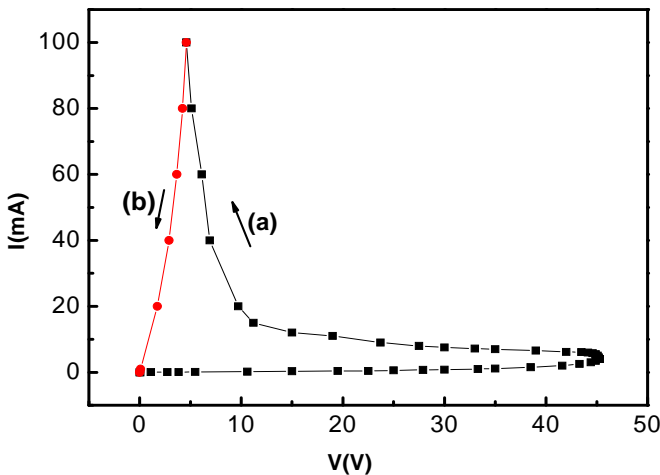


Fig. 3: $I(V)$ characteristic of the PF:Ni treated at 625°C with a current maximal of 100 mA at room temperature; (a): ascending current and (b): descendant current.

Figure 4 shown the $I(V)$ characteristic of identical sample at the last one but in this study the sample was exposed at different controlled currents. It is clear from this study that we can control the electric properties of the material by the maximum current applied to

the sample i.e. the characteristic can be fixed by the maximum of current observed by the sample.

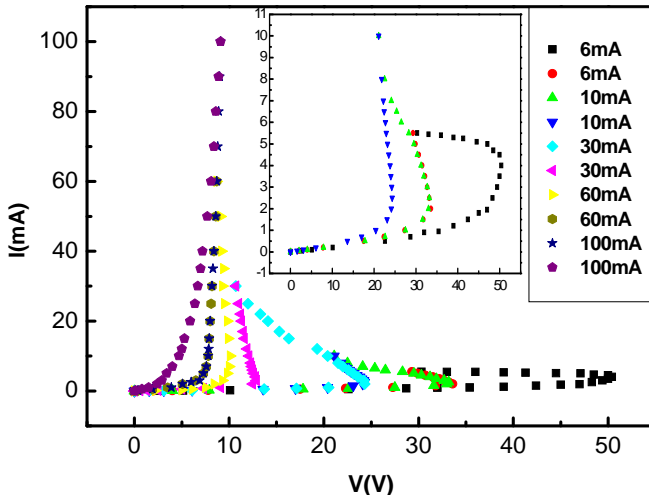


Fig. 4: Evolution of the characteristic I(V) for the PF:Ni treated at 625°C using different controlling maximal currents; ascending and descendant current behaviours.

The ac conductance of the PF:Ni prepared at 700 °C (Figure 5), presents a semi-conducting behaviour at low frequency (40 Hz) this is confirmed by the coefficient of resistance of temperature $TCR < 0$ (Figure 6.a), and for the high frequencies (2 MHz), our material has two different behaviours; semiconductor for $T < 140$ K and metal for $T > 140$ K ($TCR > 0$) (Figure 6.b). Where the TCR is given by relation (2) [17]:

$$TCR = \frac{R_T - R_{300}}{R_{300} (T - 300)} \cdot 10^6 \left(ppm. K^{-1} \right) \quad (2)$$

Where R_{300} is the resistance at room temperature and R_T is the resistance at measurement temperature (T).

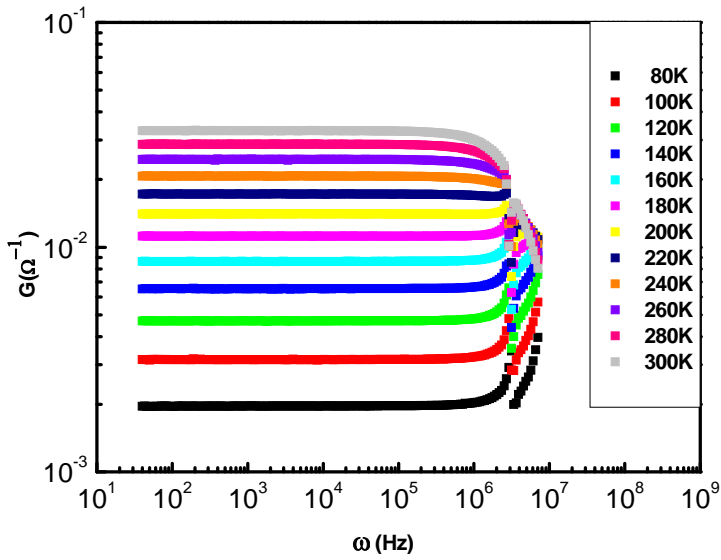
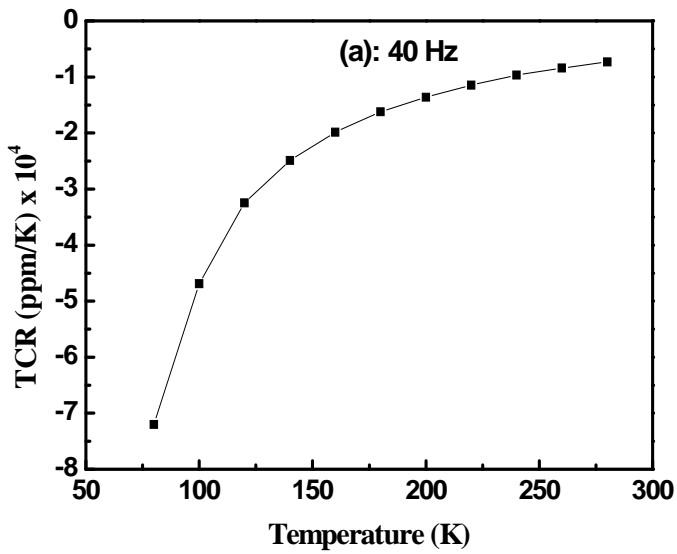


Fig. 5: Conductance versus frequency (log G via log ω) at various measurement temperatures of PF:Ni sample treated at 700°C.



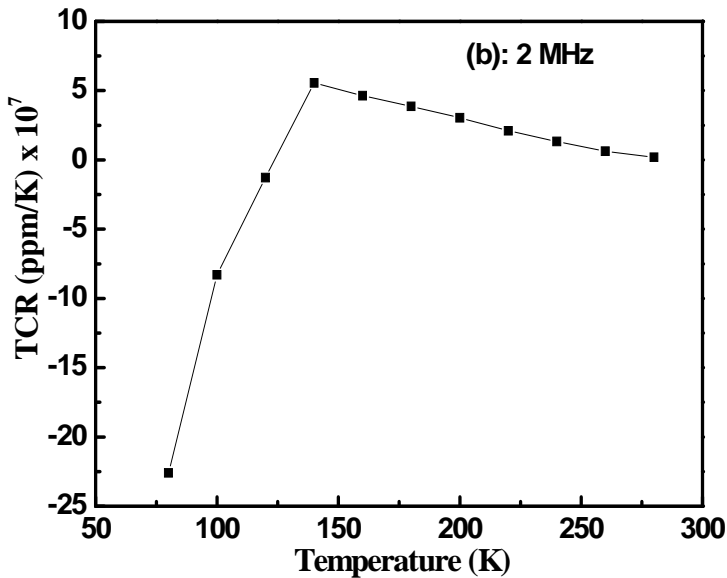


Fig. 6. Variation of TCR versus measurement temperature for the PF:Ni pyrolysed at 700 °C; (a): at low frequencies and (b): at high frequencies.

4. Conclusion

Electrically conductor carbon structures have been synthesized after pyrolysis under nitrogen atmosphere of an organic xerogel obtained by polymerisation of the pyrogallol and formaldehyde using nickel as a doped element in aqueous solution. The characteristic I(V) of the PF:Ni prepared at 625°C present a particular behaviour. In fact, the characteristic of the material is fixed by maximum of current applied to the sample (memory effect). And its ac conductance can be adjusted by 3D-GVRH conduction model. However PF:Ni prepared 700°C presents semiconductor and metallic behaviours depending on the measurement temperature. These results suppose the presence of different mechanisms of transport depending in study conditions. The non-linearity behaviour and the applications of this compounds will be the subject our future investigations.

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