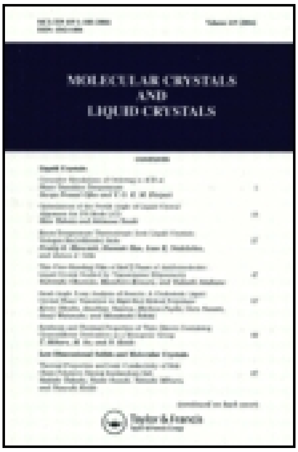

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A Simple Way to Obtain Glassy Polymeric Carbon and Its Use as Electrode for Analytical Purposes

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A Simple Way to Obtain Glassy Polymeric Carbon and Its Use as Electrode for Analytical Purposes

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The present work describes the production of glassy polymeric carbon from phenol formaldehyde resins by using different heating rates for each step of pyrolysis. The final product is a suitable material that can be used as electrode for monitoring charge transfer reactions or as supporting electrode for electroactive polymers. The obtained material was characterized by powder X-ray diffraction, infrared spectroscopy and the electrochemical properties were investigated by cyclic voltammetric technique.

Keywords glassy polymeric carbon; cyclic voltammetry; electrode

I. INTRODUCTION

Glassy Polymeric Carbon (GPC) produced from thermosetting resins is a material that combines some of the properties of glass with physical and chemical properties of carbon. Moreover, because of its chemical inertness, biocompatibility and electrical properties, GPC has been used in fields such as biology, ceramics and battery technology [1,2]. Another promising application using its electrical properties is acting as solid electrodes for monitoring charge transfer reactions or as supporting electrode for electroactive polymers [3,4]. In order to produce this material based on GPC we used cross-linked resin precursor such as Resol submitted to controlled thermal treatment. The precursor material was polymerized to 200^{0}C, and carbonized in inert environment to 1000^{0}C at very low temperature rates to avoid changing the shape or disruption from the volatile products of the carbonization [1,2]. The present work was performed in order to investigate the potential use as electrode of GPC prepared at relatively low temperature. The material was electrochemically characterize and its stability in different media was evaluated by cyclic voltammetry. Its surface characteristics were also investigated.

II. MATERIALS AND EXPERIMENTAL DETAILS

All chemicals used were reagent grade and were used without previous treatment. Water was purified by a Millipore Milli-Q System. For the production of glassy polymeric carbon electrode, a commercial phenol formaldehyde resin was supplied by Alba Química (Cascophen Al 5309). The resin was poured into a glass tube mold (4.0 mm *x* 30 mm), subsequently was cured in an oven at 60°C for 72 hours in air. Then the mold was disassembled and the cross-linked polymer was pyrolised in a tubular furnace to 1000°C in a nitrogen atmosphere at the following heating rates: 19°C/h (from 25°C to 130°C), 10°C/h (130°C to 230°C), 3°C/h (230°C to 600°C), 22,5°C/h (600°C to 1000°C), followed by 2 h at 1000°C.

The GPC cylinder electrode was polished using alumina (< 0.05 μm) and an electrical contact was made using cooper wire and silver paste. In order to understand the electrochemical properties of GPC, cyclic voltammetry experiments were carried out with a Ecochemie Autolab PGSTAT 20 potentiostat/galvanostat interfaced to a PC computer. The conventional three-electrode arrangement was used, consisting of working electrode (GPC), a platinum wire auxiliary electrode and a reference electrode of either saturated calomelane electrode (SCE) or reversible hydrogen electrode (RHE) in a glass tube. The infrared spectra were recorded from 4000 cm^{-1} to 400 cm^{-1} on a Spectrum RX FTIR System spectrometer, with the samples dispersed in KBr and pressed into pellets. The X-ray diffraction data were recorded on SIEMENS D5005 diffractometer using a graphite monochromador and CuK$_\alpha$ emission lines (1.541 Å, 40 kV, 40 mA).

III. RESULTS AND DISCUSSION

Well-defined carbon surfaces are difficult to prepare and formation of cracks can occur during the carbonization process [2,3]. A way to minimize these problems is controlling the thermal treatment. The rates of heating used in this work produced a compact, hard, electrically conducting material. During heating the following events occur: Up to 200°C the phenolic resin is cured by loss of volatile water molecules, solvent and phenol; from 200°C up to 300°C occurs precarbonization stage. from 300°C up to 800°C occurs the carbonization with the volatilization of organic fragments. It is important to note that this latter phase is critical, because gaseous products are formed and cracks can appear. Finally, the temperature is increased to 1000°C to accomplish complete carbonization and progressively close the pores and reduce the permeability, while the graphitic planes aggregate themselves to form the final structure of the GPC only consisted of long ribbon-like graphitic molecules of sp^2 carbon atoms arranged randomly in space [1].

The powder X-ray diffraction pattern of the GPC presents three broad peaks indicating that the product has a non-crystalline structure with short-range organization (Figure 1). The peaks at 24.5° and 44.3° can be ascribed to *002* and *100* reflections, respectively. The first peak is related to the distance between the graphite sheets and the resulting interlayer spacing (d = 3.65 Å) suggests that the layers are randomly stacked. The second one arises from the spacing between carbon atoms within a sheet (d = 2.05 Å) and both values are consistent with those of other polymeric carbons [1,4]. We also noted the presence of broad peak at 12.5° that could be attributed to the distance between two graphite sheets interleaved by another one (7.21 Å).

Infrared spectroscopy showed bands at 3446 cm^{-1} and at 1635 cm^{-1} which are attributed to OH stretching of water molecules that did not diffuse during the carbonization. Another band at 1031 cm^{-1} was attributed as CO stretching of CO_2 that had had a little shift to lower wavenumbers. Between 1500 and 1300 cm^{-1} could be observed many peaks from the aromatic rings that built up GPC.

The performed electrochemical studies showed that the electrode is stable when submitted to several successive redox cycles in sulfuric acid media (0.5 $mol.dm^{-3}$ and scan rate of 50 mVs^{-1}). We verified an increase of voltammetric charge indicating a hydration of active sites. Moreover, the capacitance value ($13.5 x 10^{-3} Fcm^{-2}$) suggests that the electrode has a higher active surface than other electrodes with 10^{-6} Fcm^{-2} of magnitude

[4]. This property will enable modify the electrode surface to obtain new properties such as electrocatalysis.

Assays using 0.05 mol.dm^{-3} potassium ferrocyanide ($K_4Fe(CN)_6$) aqueous solution with 1.0 mol.dm^{-3} KCl as supporting electrolyte, are shown in Figure 2. We verified that the reduction and oxidation peak potentials are influenced by scan rate. With its increase, the difference between the reduction and oxidation peak potentials (ΔEp) increases. At 200mVs^{-1} of scan rate, ΔEp value is approximately 120mV, comparable with the literature which reports values of 700mV for ΔEp at the same scan rate, for highly ordered pyrolytic graphite [4]. In addition, for low scan rate values, the ΔEp values indicated a reversible system. Comparing the performance with a platinum electrode with the same geometric area, we observed similar electrochemical behavior. However, GPC electrode has a higher current density, suggesting a higher active superficial area.

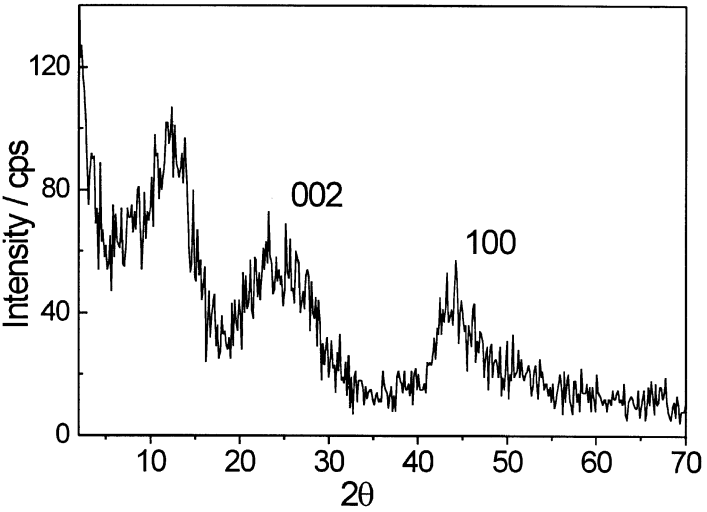

FIGURE 1: Powder X-ray diffraction pattern of polymeric glass-like carbon.

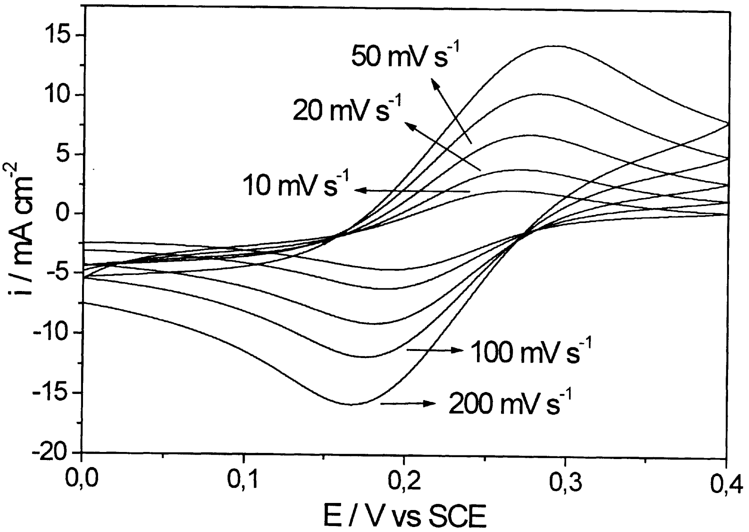

FIGURE 2: Cyclic voltammograms in KCl 1.0 mol.dm^{-3} with $[Fe(CN)_6]^{2-}$ 0.05 mol.dml^{-3} at different scan rates (E = potential, V = volts).

To further investigate the electrode performance, we synthesized electrochemically onto the GPC electrode surface an intrinsic conductive polymer (poly-o-toluidine) from a 0.5 mol.dm-3 o-toluidine solution in sulfuric acid media (0.5 mol.dm^{-3}) with a scan rate of 50 mVs^{-1}. We verified that the first redox cycle presents an anodic peak (oxidation of dimers and trimers as well as formation of oligomers) and after successive oxidation-reduction cycles (from 0.0V to 1.2 V *vs*. RHE, the reversible hydrogen electrode) an increase of the intensity of the redox peaks observed was attributed to electrochemical behavior of the polymer [5]. In comparison with the experiment performed with platinum electrode, we noted that the total redox charge is lower, evidence that GPC electrode has a high active surface in agreement with the previous results.

IV. CONCLUSIONS

We have investigated the production of glassy polymeric carbon from phenol formaldehyde resins by using different heating rates for each step of pyrolysis in nitrogen atmosphere up to 1000°C. The difference between anodic and catodic potentials of $[Fe(CN)_6]^{3-/2-}$ redox pair was lower than those reported in literature, suggesting use of GPC electrode for monitoring charge transfer reactions or as supporting electrode for electroactive polymeric species. In addition, our electrodes present a highly electrochemically active surface, as demonstrated by cyclic voltammetric experiments, making possible their utilization in electrocatalysis. It is important to note that glassy polymeric carbon is stable in acid media, mechanically resistant and is both easy to produce and inexpensive.

ACKNOWLEDGMENT

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REFERENCES

[1] G.M. Jenkins and K. Kawamura, *Polymeric Carbon-Carbon Fiber, Glass and Char*, Cambridge University. Press, 1976.

[2] H. Maleki, L.R. Holland, G.M. Jenkins, R.L. Zimmerman and W. Porter, *J. Mater. Res.*, **11**, 2368 (1996).

[3] H. Maleki, C.D. Cojocaru, C.M.A. Brett, G.M. Jenkins and J.R. Selman, *J. Electrochem. Soc*, **145** (3), 721 (1998).

[4] R.L. McCreery, *Electroanalytical Chemistry*, ed. A.J. Bard, Dekker, New York, Vol. 17, 1991, p. 374.

[5] E.M. Andrade, F.V. Molina, M.I. Florit and D. Posadas, J. *Electroanal. Chem.*, **415**, 153 (1996).