

# CHANGES IN ELECTROCHEMICAL BEHAVIOR OF POLYMERIC CARBON INDUCED BY VARYING HEAT-TREATMENT

H. Maleki, C.M.A. Brett\* and G.M. Jenkins

Center for Irradiation of Materials, Alabama A&M University, USA  
and the University of Coimbra\*, Portugal.

## INTRODUCTION

Glassy polymeric carbon [1] is particularly attractive as an electrode material because of its thermal stability, biocompatibility, large potential range and robustness [2]. It is now available commercially but little has been published on the effect of heat-treatment on electrochemical behavior.

Electrodes are made by carbonizing various resin precursors. The product starts conducting above 500°C to form a semiconductor with a band gap which decreases with the firing temperature, approaching zero at 3000°C. The conductivity increases by many orders of magnitude as indicated in Figure 1, in step with changes in the Raman structure. According to our basic model [1] for the carbonization of phenolic resin, neighboring resin chains coalesce to form defective ribbon-like graphene molecules and the number of delocalized electrons increase with the extent of ribbon formation. Carbonization is complete at 1200°C. The material can then be heated up to 3000°C with no phase change and without any large further alteration in most physical properties. Defects are removed progressively with rise in temperature with the production and movement of vacancies and so electrical conductivity does significantly rise; transmission electron microscopy and diffraction show that sub-crystalline order increases.

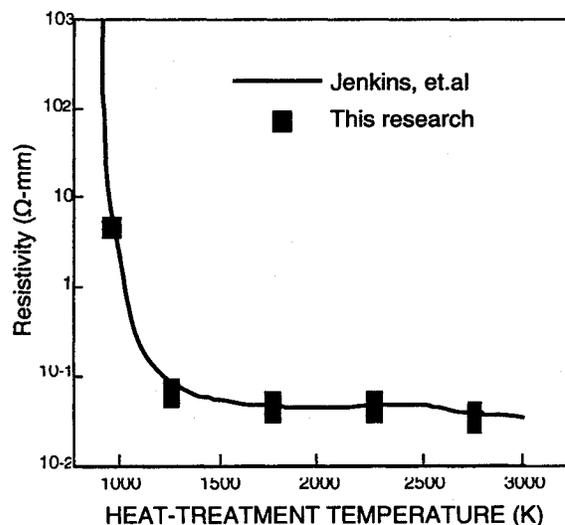
## SAMPLE PREPARATION

In Huntsville, disc samples were made from a resol supplied by Georgia-Pacific and normally used in producing resin hollowware by spraying on hot rotating mandrels. In this case, the discs were made by molding cylinders and slicing in a diamond saw. Heat-treatments at representative stages of

pyrolysis were chosen between 500°C and 3000°C.

In Coimbra, these discs of glassy carbon of diameter 6 mm were made into electrodes by attaching a copper wire to the rear face with silver epoxy, sealing the assembly in glass tubes of internal diameter 6 mm with regular epoxy resin to expose one face which was polished to obtain a flat circular surface. Initial polishing was effected with 600x abrasive paper followed by a diamond sprayed polishing cloth using successively smaller particle size down to 1 mm until a mirror-like finish was obtained. Between experiments, polishing with 1 mm diamond sprayed cloth was repeated.

Electrochemical tests were first conducted on standardized potassium sulfate and sulfuric acid aqueous solutions, using cyclic voltammetry, in order to examine the potential between hydrogen and oxygen evolution and probe the existence of any other peaks which might occur.



## RESULTS AND DISCUSSIONS

In the case of potassium sulfate electrolyte, the hydrogen evolution potential versus a saturated calomel electrode (SCE) was found to become more negative with increasing heat-treatment temperature: -1.3V for 650°C, -1.6V for 1000°C and -2.0V for 2500°C. Greater hysteresis in the cathodic part of the voltammetric curves was encountered for low firing temperatures. Conversely, the oxygen evolution potential vs. SCE remained at about +2.0V, with a slight tendency to become less positive with increasing firing temperature. Small voltammetric peaks of height up to 20 mm for reduction and oxidation of surface species were found at -0.5V and +1.5V, respectively. Immersion in electrolyte over a period of hours rendered the reduction peak of surface groups at -0.5V more pronounced. Results obtained in sulfuric acid electrolyte were similar except that hydrogen evolved more easily, as would be expected. These electrochemical measurements correlate well with the amount of residual hydrogen in the carbonized resin. The small change in hydrogen evolution potential contrasts markedly with the enormous changes in electrical conductivity on firing below 1000°C.

The oxidation of potassium ferricyanide (1 mM in 0.4 M K<sub>2</sub>SO<sub>4</sub>) was examined as a test redox species. No significant difference was found in electrochemical behavior between samples pyrolysed at different temperatures. This may be so because oxidation occurs in the range 0.1-0.5V versus SCE (with a half wave potential of 0.22V), which is a region in the voltammetric profile of the electrolyte when there is no oxidation or reduction of surface-bound species. It should be noted with respect to electrode kinetics that:

the electrode kinetics are variable and initially show lack of reproducibility, as determined by cyclic voltammetry, square wave voltammetry and electrochemical impedance. It appears that the more oxidized the surface, the faster the electrode kinetics. leaving a freshly prepared polished

electrode in electrolyte (or electrolyte plus redox couple) for a few hours enhances the electrode kinetics. If the electrode is left in air for the same period the kinetics becomes slower. This suggests that the amount of oxygen may be constant, while the type of chemical bond involved is changing.

Surfaces were examined by scanning electron microscopy and by electron probe microanalysis (EPMA), which was aimed at probing the state of oxidation of the surface before and after polishing, and possible adsorption of electrolyte or redox species. Although there is evidence of surface porosity in freshly prepared unpolished samples, this disappears on polishing in every case. EPMA elemental analysis detects carbon and oxygen only, independently of electrode history. The oxygen signal is largest on unpolished samples, although it decreases significantly for firings above 2000°C. After polishing the electrodes, the oxygen signal is much smaller and only increases slowly with time.

These electrochemical measurements demonstrate clearly the effect of fabrication temperature on voltammetric response. The effect is currently being analyzed further.

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## REFERENCES

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