

SURFACE OXIDE STRUCTURES ON POROUS CARBON

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INTRODUCTION

Carbon surfaces are covered with chemisorbed oxygen species which have a profound influence on surface properties. The structure of these oxides has been the subject of a great deal of research for a long period of time. In order to facilitate investigations, it is usual to deliberately increase the oxide concentration by some oxidative procedure involving air, oxygen or aqueous solutions of oxidants such as nitric acid or hydrogen peroxide(1). These procedures are difficult to control so that incremental oxidation of the carbon surface cannot readily be carried out. In this work anodic oxidation of a porous carbon is described and the structure, or structures, of the oxides formed described in terms of the results of temperature programmed desorption experiments, acidic oxide concentration determinations and the measurement of the enthalpy of reaction with aqueous sodium hydroxide.

EXPERIMENTAL

The apparatus used for anodic oxidation is shown in Fig.[1].

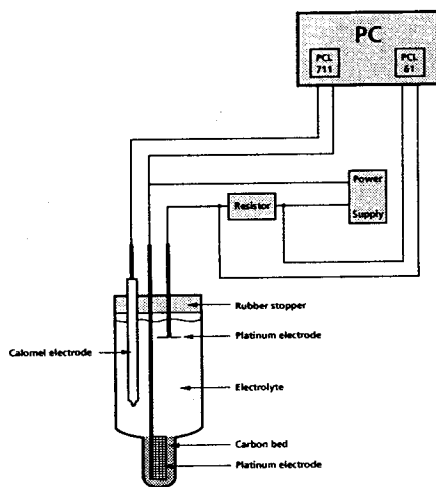


Fig. 1

The total charge passed and the potential of the carbon anode with respect to the calomel electrode was registered on a PC. Only small amounts of gas were observed to form at the anode during a run. Following the oxidation the carbon samples were washed with copious amounts water and then washed further by

soxhlet extraction for a period of at least two weeks. All samples were air dried at 110°C. Acidic oxides were measured by the conventional depletion technique carried out over a range of base concentration and the "reaction isotherm" obtained, analysed by application of the Langmuir equation. Both aqueous NaOH and NaOH/NaCl solutions were used(2). Enthalpy of neutralization data were obtained using a flow calorimeter(3). The temperature programmed desorption procedures has been described earlier(4).

RESULTS AND DISCUSSION

Fig.[2] shows the relationship between the total mill- equivalents of charge passed and the total millequivalents of oxygen desorbed as carbon dioxide and carbon monoxide at 900°C.

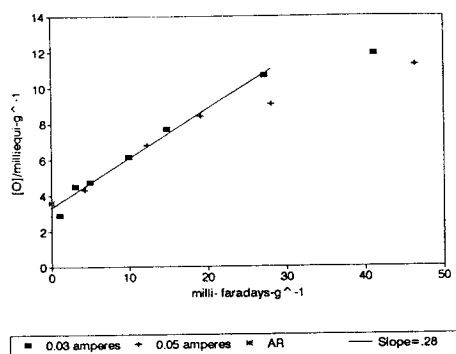


Fig. 2

A yield of about 30% is obtained initially, for both current levels used, but it is seen to decrease at higher charges. The decrease is larger at the higher operating current.

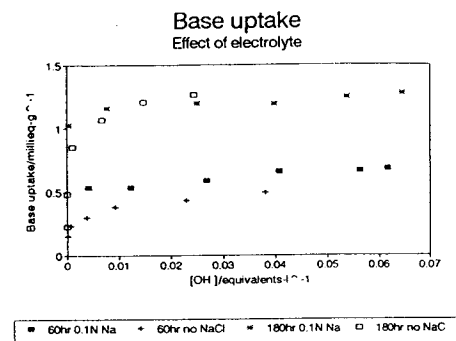


Fig. 3

Fig.[3] illustrates the results obtained by the NaOH depletion technique for a slightly anodically oxidized sample and one that had been oxidized to a higher degree.

The base uptake for slightly oxidized sample is seen to depend strongly on the presence of an inert electrolyte. This effect has been reported earlier(2). Provisionally, this finding can be ascribed to the formation of oxide groups within the smaller pores of the carbon which can only be reached, by the base reactant, if the width of the electrical double layer is markedly diminished. For chemically oxidized carbons the electrolyte effect is not so pronounced. In Fig.(4) the relationship between the surface concentration of acidic groups, obtained from base depletion in NaOH/NaCl, and the amount of CO₂ desorbed from the surface at 900° C is shown.

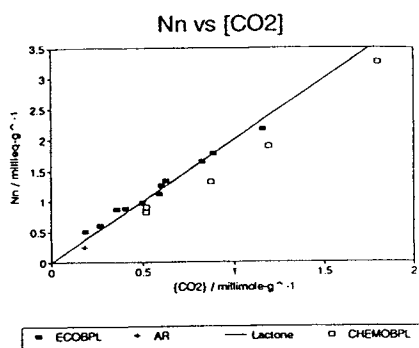
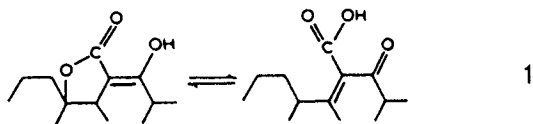


Fig. 4

Included in the figure are similar data for chemically oxidized BPL(5). The figure suggests that the electrochemical oxidation produces structures of the f-lactone type(6), such as;



which on hydrolysis produces two equivalents of acid but gives only one mole of CO₂ on thermal desorption. By way of contrast the chemically oxidized material appears to produce less than two equivalents of acid per mole of CO₂. This observation may be explained by assuming that some of the keto form of 1, for which the ratio of equivalents of acid to moles of CO₂ desorbed is unity, is also present. Similarly, the presence of simple γ lactones could account for the observation. Finally, the calorimetric experiments indicate that the enthalpy of neutralization of the surface oxides with 0.1N NaOH is constant within the experimental error for both the electrochemical and chemical oxidized carbons and does not depend on the extent of oxidation, Fig. (5)

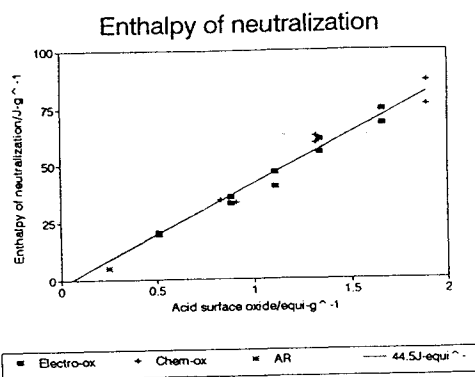


Fig. 5

This enthalpy value, -44.5 ± 2 k-joules/equiv, results in the value of $+11$ k-joules/equiv. for the enthalpy of dissociation for the acidic surface groups. Since non aromatic and aromatic carboxylic acid enthalpy of dissociation values are either only slightly positive or negative, this result indicates that the amount of free carboxylic structure on the surface is very small. Values of the enthalpy of ionization for phenols, on the other hand, are generally quite positive(7). Therefore, the present observations support the lactonic structures proposed in that hydrolysis and ionization of such structures should display an enthalpy change which is some sort of sum of the dissociation enthalpy for a carboxylic acid and a phenol structure.

CONCLUSION

Support for the presence of lactonic structures of the surface of carbon is found by three independent measurements of surface properties.

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