

CHARACTERIZATION OF FLUORINATED GRAPHITE*

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*Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp.

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Volume 40, No. 3
Preprints of Papers Presented at the
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August 20-25, 1995

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THE CHARACTERIZATION OF FLUORINATED GRAPHITE

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Keywords: Fluorine, X-ray photoelectron spectroscopy, atomic force microscopy

INTRODUCTION

The characterization of solid fossil fuels by chemical and spectroscopic methods requires extensive modelling in less complex systems for chemical proof of principle and technique development. In previous work coal was fluorinated with dilute, elemental fluorine under conditions that were expected to lead to materials that contain only fluoromethine moieties. The solid state, cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectra of the fluorinated coal are complex, indicating more chemical modification than originally anticipated.

Our goal in the coal derivatization was to sequentially increase the severity of the fluorination and observe by ^{19}F and ^{13}C NMR the type and concentration of fluorine functional groups created in the coal milieu. This requires the ability to discriminate between C, CF, CF_2 , and CF_3 moieties in the coal matrix. The task can be accomplished by implementing the spectral editing technique of Wu and Zilm¹ which distinguishes different kinds of carbon resonances, especially CH and CH_2 resonances. These experiments utilize cross polarization (CP) and polarization inversion (PI) to effect the discrimination. Our version of this experiment is a triple resonance experiment that incorporates ^{19}F - ^{13}C CP, PI, and simultaneous ^1H and ^{19}F dipolar decoupling.

In order to evaluate the elemental fluorine chemistry in a matrix simpler than coal, fluorinated graphite was prepared. X-ray photoelectron spectroscopy (XPS) was used to characterize the surface species, i.e., count CF, CF_2 and CF_3 species. These well-characterized samples are the models we will use to test the NMR editing experiments. The XPS and atomic force microscopy (AFM) data on the first fluorinated graphites we have prepared are reported in this paper.

EXPERIMENTAL

Fluorination of Graphite. Highly oriented pyrolytic graphite (HOPG), 0.7 g, was ground in a ceramic mortar and placed in a 19 mm quartz tube. The tube was placed in an oven and the powder was dried in a flow of nitrogen ($2\text{--}3\text{ cm}^3/\text{min}$) at 250°C for 2 h. The flow of nitrogen was replaced by pure fluorine ($2\text{ cm}^3/\text{min}$) over 30 min and fluorination was continued for an additional 20 h at $250\text{--}260^\circ\text{C}$. At the end of the fluorination the fluorine gas stream was replaced with nitrogen and the sample was cooled. The nitrogen purge was continued for 2 h at room temperature. The sample was then transferred to a glass vial under nitrogen and flushed for an additional 2 min to displace traces of air and moisture. The visual appearance of the sample did not change significantly during the fluorination.

A second sample of HOPG, a single platelet with dimensions of $0.4 \times 0.8 \times 0.05\text{ mm}$, was subjected to the fluorination under similar conditions for 21 h. The isolated platelet was stored under nitrogen in a glass vial. No change in the visual appearance of the sample was found and the weight loss of the sample during the fluorination was less than 0.1%.

Atomic Force Microscopy (AFM). The atomic force microscope used in this investigation was a Digital Instruments Inc., Nanoscope II which uses a Si_3N_4 tip attached to cantilever to scan the surface. Tip motion is monitored by light deflected from the cantilever.

X-ray Photoelectron Spectroscopy (XPS). The XPS data were acquired on a Kratos Ltd. spectrometer. The energy analysis chamber is a Kratos Axis system designed for general purpose XPS using a small spot lens. In this instrument the standard orientation of the detector is orthogonal to the sample surface. The data reported in Table 1, are from experiments performed in this configuration. The spectrum of the HOPG platelet was also recorded after tilting the platelet 35° from its normal orientation to the detector. The x-ray source used in this work was an Al K α monochromator (15 kV, 60 ma maximum). A UV flood lamp was used to charge

neutralize the fluorinated HOPG powder sample. The pass energy of the HOPG platelet was 20 eV. The pass energy of the HOPG powder was 40 eV. The instrument was calibrated to Au 4f at 84.0 eV. The graphitic component of the C 1s peak was observed at 284.5 eV for the conductive HOPG platelet, as expected. The graphitic component of the powdered, nonconductive HOPG was assigned this same value.

RESULTS AND DISCUSSION

Figure 1 compares the AFM image of the surface of a platelet of HOPG prior to fluorination (a) with the surface after fluorination (b). The images depict a 250 x 250 nm surface area (note the expanded z scale). At the resolution used for these measurements the graphite surface is flat. The surface after fluorination exhibits random rutted or channeled features with dimensions on the order of tens of nm. Features are etched into the surface to a depth of ca 1 nm. Since the XPS results discussed below are compatible with the surface functionality being CF_x moieties, the surface features shown in Fig. 1b likely represent fluorination of the surface with loss of surface carbon extending to a depth equal to several graphite layers.

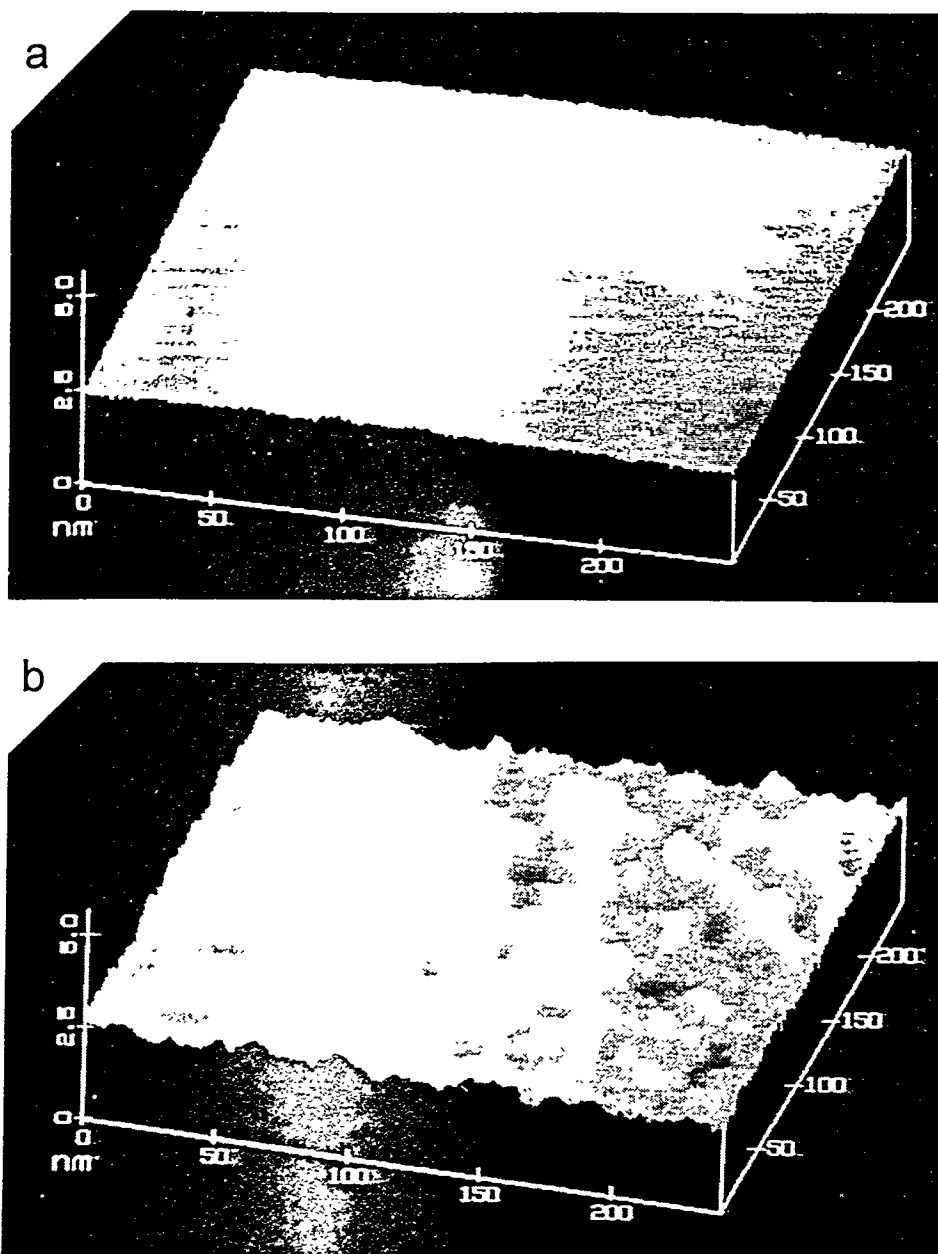


Figure 1. Atomic Force Microscopy Images of a: HOPG and b: Fluorinated HOPG

Two fluorinated samples were analyzed by XPS: the first is the sample of HOPG used for the AFM measurements shown in Fig. 1b; the second was a fluorinated graphite powder described in the experimental. Qualitative XPS survey scans showed only carbon, fluorine and oxygen on both surfaces. Figures 2 and 3 show the C 1s, F 1s and O 1s spectra of the platelet and powder sample, respectively. The powder had to be charge neutralized, which may account for some of the increase in peak width. Each spectrum has been band fitted, showing the different components which comprise the spectrum. Table 1. lists the atomic concentrations, peak position and width of each component.

Table 1. XPS Data for Fluorinated Platelet and Powdered HOPG

| Platelet HOPG | | | |
|---------------|-------------------|----------------|-----------------|
| XPS Peak | Binding Energy eV | Peak Width, eV | Atomic Conc., % |
| C 1s 1 | 284.5 | 0.6 | 49.8 |
| C 1s 2 | 285.7 | 1.42 | 6.7 |
| C 1s 3 | 287.0 | 2.03 | 4.4 |
| C 1s 4 | 289.8 | 1.55 | 13.0 |
| C 1s 5 | 291.8 | 1.70 | 5.0 |
| C 1s 6 | 294.1 | 2.49 | 2.6 |
| F 1s 1 | 688.6 | 1.50 | 15.7 |
| O 1s 1 | 532.1 | 2.28 | 0.9 |
| O 1s 2 | 535.1 | 1.45 | 2.0 |
| Powdered HOPG | | | |
| C 1s 1 | 284.5 | 2.17 | 33.2 |
| C 1s 2 | 285.7 | 1.93 | 0.6 |
| C 1s 3 | 287.0 | 1.48 | 3.5 |
| C 1s 4 | 289.2 | 2.37 | 24.4 |
| C 1s 5 | 292.0 | 2.30 | 1.8 |
| C 1s 6 | 293.9 | 2.65 | 0.2 |
| F 1s 1 | 686.1 | 3.05 | 5.5 |
| F 1s 2 | 688.1 | 2.49 | 24.6 |
| O 1s 1 | 532.9 | 3.95 | 5.2 |
| O 1s 2 | 534.8 | 1.51 | 0.9 |

The C 1s peak at 284.5 eV is from pure graphite. Bonding an electronegative atom to carbon shifts the C 1s peak to higher binding energy. The second major carbon peak at 289 eV represents CF and a shift at approximately 292 eV represents CF₂. The C 1s peak at 294 eV is attributed to CF₃.² The CF₂ moiety has an F 1s peak at ca 690 eV; the CF F 1s peak shifts to approximately 689 eV. The assignments of chemical shifts to bonding type indicated here are from XPS data bases.³

The spectra indicate that the surface of both materials has been fluorinated. The dominant peak in the carbon spectrum for both samples is at 284.5 eV and is due to graphitic carbon. The majority of the fluorine is in the form of CF. Both the C 1s and the F 1s peaks corresponding to CF are approximately equal in both samples, supporting these assignments. There are minor components in the C 1s spectrum which indicate CF₂ and CF₃. The XPS analysis was repeated for the platelet sample of fluorinated HOPG after tilting the platelet 35°. This orientation biases the sensitivity of the analysis to the surface layer relative to the underlayers. An increase in the F 1s and the C 1s of the CF component relative to the graphitic C 1s peak is observed, showing fluorine to be concentrated on the surface.

The fluorinated HOPG platelet has a 2.6:1 ratio of $\text{CF}:\text{CF}_2$. The ratio in the powder is 13.6:1. The platelet has more comparable concentrations of CF_2 and CF functional groups (desirable in an NMR test sample) but a low absolute concentration of all CF species that may make the NMR analysis difficult. The XPS correlation between the fluorinated platelet and powder reveals the same qualitative chemistry occurs in both materials. Attempts to increase the CF_2 component in the powder are in progress.

ACKNOWLEDGEMENTS

This research was sponsored by the Division of Chemical Sciences and the Division of Material Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

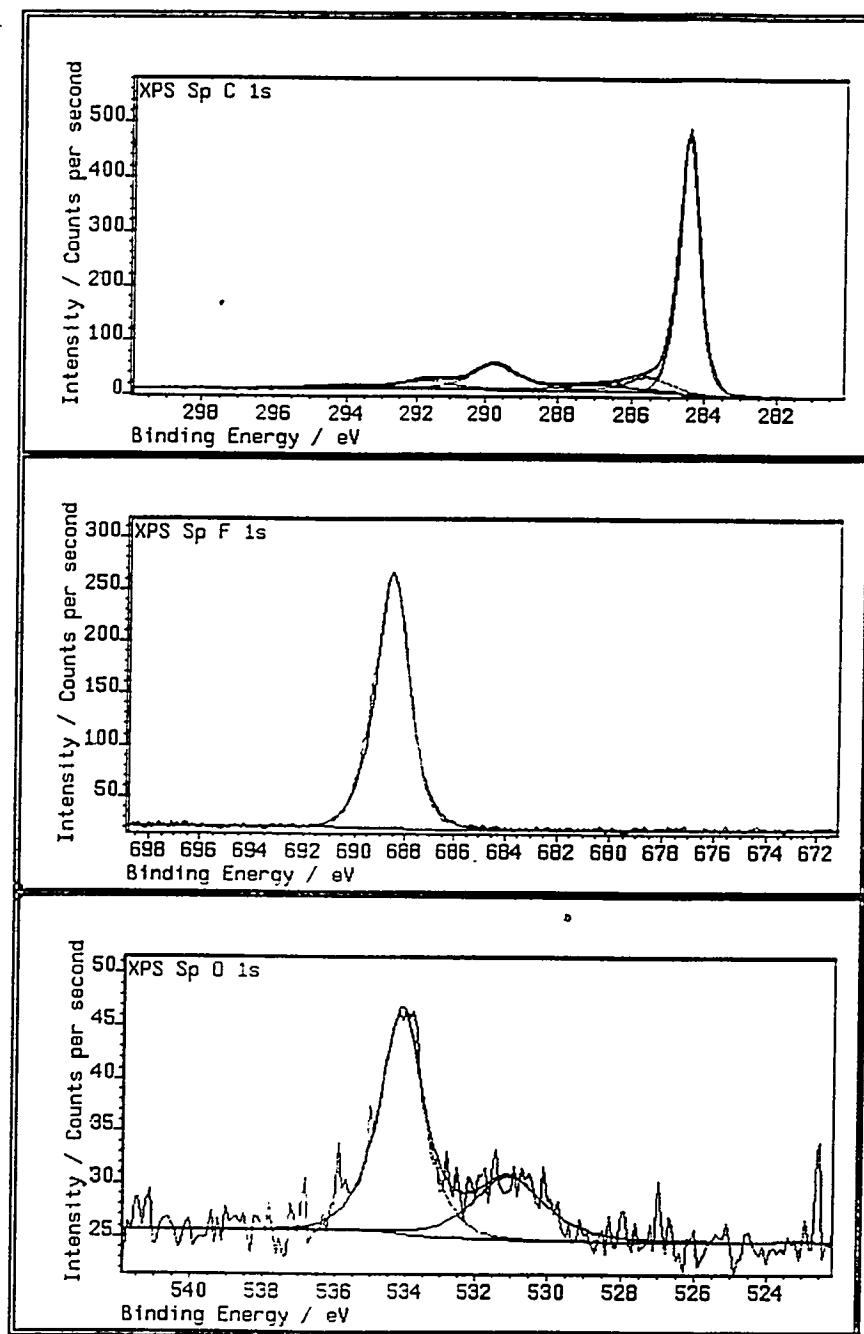


Figure 2. Carbon, Fluorine, and Oxygen X-ray Photoelectron Spectra of a Fluorinated HOPG Platelet.

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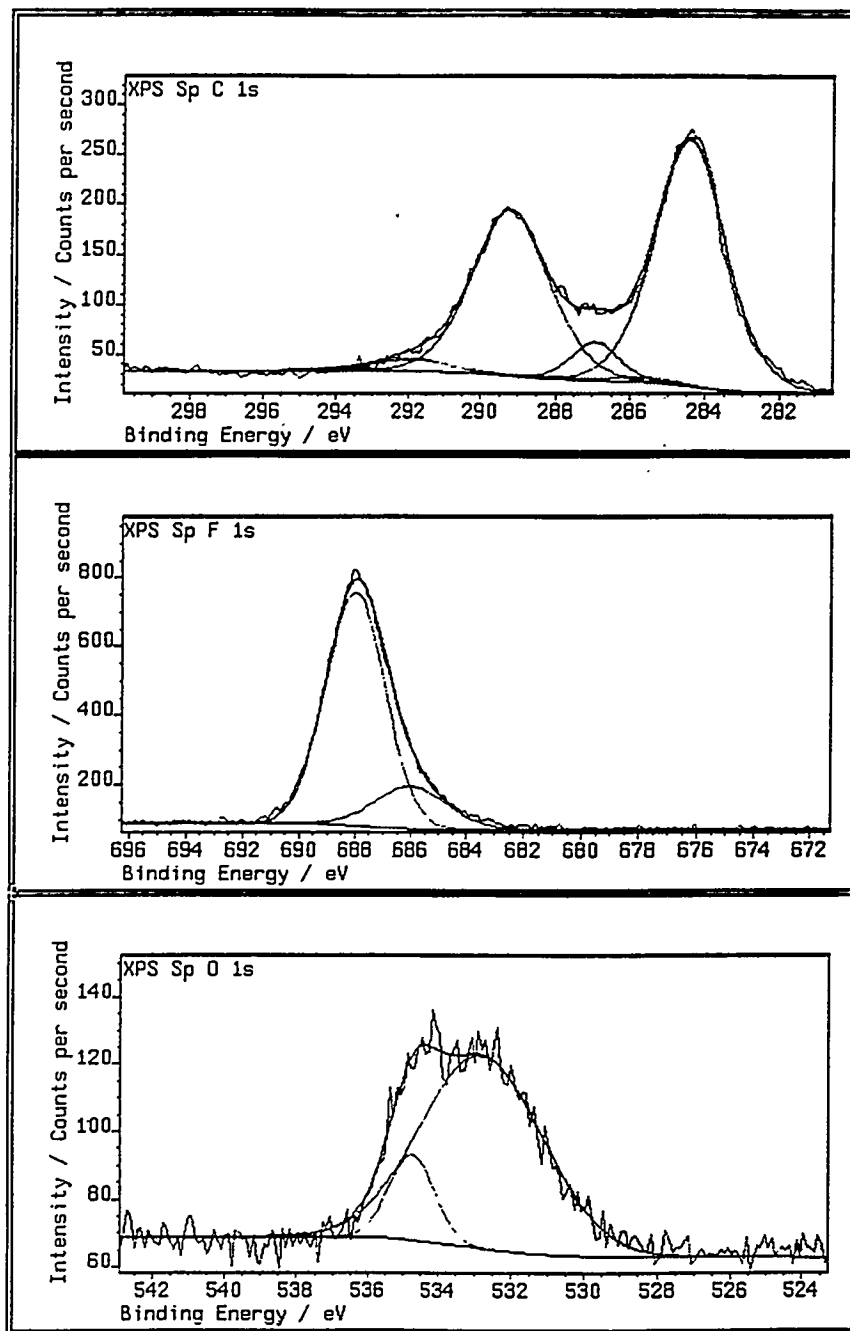


Figure 3. Carbon, Fluorine and Oxygen X-ray Photoelectron Spectra of a Fluorinated HOPG Powder.