1110 *Chem. Mater.* **1993,** *5,* 1110–1117

Synthesis, Characterization, and Electrochemical Activity of Halogen-Doped Glassy Carbon

Howard D. Hutton,[†] Wenhua Huang,[†] Daniel C. Alsmeyer,[†] Janet Kometani,[‡]
Richard L. McCreery,[*,†] Thomas X. Neenan,[*,‡] and Matthew R. Callstrom[*,†]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210,
and AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Received February 26, 1993. Revised Manuscript Received May 21, 1993

Chlorine- and fluorine-doped glassy carbon were synthesized via low-temperature thermal treatment of perhalogenated poly(1,3-butadiynylene-1,3-phenylene) oligomeric materials. The halogen-doped glassy carbon (DGC) materials were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy. Incorporation of the heteroatom dopants dramatically affected the densities, surface energies, and elastic moduli of the glassy carbon materials. The DGC materials exhibited low electrical resistivity, and their ability to function as efficient electrodes was investigated via voltammetry of the ferri/ferrocyanide couple. The halogen-doped electrodes exhibited electron-transfer rate constants for the $Fe(CN)_6^{3-/4-}$ redox system which were comparable to those of commonly used carbon electrodes.

Introduction

Glassy carbon (GC) has a unique combination of properties, including chemical and thermal inertness, hardness, impermeability to gases and liquids, and high electrical conductivity.[1] These properties result in the use of GC in a wide variety of applications, including medical implants,[1] high performance materials for the aerospace industry,[2] and as electrodes.[3] The surface modification of GC electrodes, via film deposition,[4–15] covalent bonding,[16–28] and chemisorption,[29–35] has greatly increased their selectivity in electrochemical reactions due to the modifier's ability to affect the interaction of molecules with the GC surface.[36,37] In practice, however, many surface-modified electrodes have limited applicability for electrocatalysis due to the mechanical instability of the films and the difficulty of regenerating the films in a convenient and reproducible fashion.[38,39] The homogeneous, rather than surface, modification of GC is highly desirable because of the expectation that an electrode modified at the atomic level would exhibit efficient catalysis, high stability, and comparatively simple renewability. However, the preparation of homogeneously doped GC via conventional thermolysis of polymers is impossible due to the high temperatures necessary for carbonization (1000–2500 °C) which results in a material with <0.5% of

---

[†] The Ohio State University.

[‡] AT&T Bell Laboratories.

(1) Jenkins, G. M.; Kawamura, K. *Polymeric Carbons—Carbon Fibre, Glass and Char*; University Press: Cambridge, 1976.

(2) Parmee, F. T. *Carbon Fibres* 1971, *38,* 154.

(3) Kinoshita, K. *Carbon: Electrochemical and Physicochemical Properties*; Wiley: New York, 1988.

(4) Albarelli, M. J.; White, J. H.; McMillan, M.; Bommarito, G. M.; Abruña, H. D. *ACS Symp. Ser.* **1988,** *378,* 216.

(5) Bartak, D. E.; Kazee, B.; Shimazu, K.; Kuwana, T. *Anal. Chem.* **1986,** *58,* 2756.

(6) Bettelheim, A.; White, B. A.; Raybuck, S. A.; Murray, R. W. *Inorg. Chem.* **1987,** *26,* 1009.

(7) Bettelheim, A. White, B. A.; Murray, R. W. *J. Electroanal. Chem.* **1987,** *217,* 271.

(8) Bettelheim, A.; Reed, R.; Hendricks, N. H.; Collman, J. P.; Murray, R. W. *J. Electroanal. Chem.* **1987,** *238,* 259.

(9) Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1984,** *106,* 59.

(10) Kao, W.-H.; Kuwana, T. *J. Am. Chem. Soc.* **1984,** *106,* 473.

(11) Kost, K. M.; Bartak, D. E.; Kazee, B.; Kuwana, T. *Anal. Chem.* **1988,** *60,* 2379.

(12) Kost, K. M.; Bartak, D. E.; Kazee, B.; Kuwana, T. *Anal. Chem.* **1990,** *62,* 151.

(13) Macor, K. A.; Spiro, T. G. *J. Electroanal. Chem.* **1984,** *163,* 223.

(14) Wan, G.-X.; Shigehara, K.; Tsuchida, E.; Anson, F. C. *J. Electroanal. Chem.* **1984,** *179,* 239.

(15) Weisshaar, D. E.; Kuwana, T. *J. Electroanal. Chem.* **1984,** *163,* 395.

(16) Lennox, J. C.; Murray, R. W. *J. Am. Chem. Soc.* **1978,** *100,* 3710.

(17) Lennox, J. C.; Murray, R. W. *J. Electroanal. Chem.* **1977,** *78,* 395.

(18) Lenhard, J. R.; Rocklin, R.; Abruña, H.; Willman, K.; Kuo, K.; Nowak, R.; Murray, R. W. *J. Am. Chem. Soc.* **1978,** *100,* 5213.

(19) Nowak, R.; Schultz, F. A.; Umaña, M.; Abruña, H.; Murray, R. W. *J. Electroanal. Chem.* **1978,** *94,* 219.

(20) Nowak, R. J.; Schultz, F. A.; Umaña, M.; Lam, R.; W., M. R. *Anal. Chem.* **1980,** *52,* 315.

(21) Oyama, N.; Brown, A. P.; Anson, F. C. *J. Electroanal. Chem.* **1978,** *87,* 435.

(22) Oyama, N.; Anson, F. C. *J. Am. Chem. Soc.* **1979,** *101,* 739.

(23) Oyama, N.; Anson, F. C. *J. Electrochem. Soc.* **1980,** *127,* 247.

(24) Watkins, B. F.; Behling, J. R.; Kariv, E.; Miller, L. L. *J. Am. Chem. Soc.* **1975,** *97,* 3549.

(25) Willman, K. W.; Rocklin, R. D.; Nowak, R.; Kuo, K.-N.; Schultz, F. A.; Murray, R. W. *J. Am. Chem. Soc.* **1980,** *102,* 7629.

(26) White, B. A.; Murray, R. W. *J. Electroanal. Chem.* **1985,** *189,* 345.

(27) Yacynych, A. M.; Kuwana, T. *Anal. Chem.* **1978,** *50,* 640.

(28) Rocklin, R. D.; Murray, R. W. *J. Electroanal. Chem.* **1979,** *100,* 271.

(29) Collman, J. P.; Marrocco, M.; Denisevich, P.; Koval, C.; Anson, F. C. *J. Electroanal. Chem.* **1979,** *101,* 117.

(30) Collman, J. P.; Bencosme, C. S.; Durand, R. R., Jr.; Kreh, R. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983,** *105,* 2699.

(31) Collman, J. P.; Bencosme, C. S.; Barnes, C. E.; Miller, B. D. *J. Am. Chem. Soc.* **1983,** *105,* 2704.

(32) Collman, J. P.; Anson, F. C.; Barnes, C. E.; Bencosme, C. S.; Geiger, T.; Evitt, E. R.; Kreh, R. P.; Meier, K.; Pettman, R. B. *J. Am. Chem. Soc.* **1983,** *105,* 2694.

(33) Danilova, N.; Radyyushkina, K.; Shembel, E. Ksenzhek, O.; Merenkova, P.; Tarasevitch, M. *Elektrokhimiya* **1990,** *26,* 894.

(34) Elliott, C. M.; Marrese, C. A. *J. Electroanal. Chem.* **1981,** *119,* 395.

(35) Bettelheim, A.; Chan, R. J. H.; Kuwana, T. *J. Electroanal. Chem.* **1979,** *99,* 391.

(36) Murray, R. W. *Acc. Chem. Res.* **1980,** *13,* 135.

(37) Faulkner, L. R. Chemical Microstructures on Electrodes. *Chem. Eng. News* **1984,** *Feb 27,* 28.

(38) Shaw, B. R. In *History of Electrochemistry*; ACS Symp. Ser.; American Chemcial Society: Washington D.C., 1989; Vol. 390, p 318.

(39) Pocard, N. L.; Alsmeyer, D. C.; McCreery, R. L.; Neenan, T. X.; Callstrom, M. R. *J. Mater. Chem.* **1992,** *2,* 771.

0897-4756/93/2805-1110$04.00/0

any element other than carbon regardless of the precursor.[3,40]

We have recently discovered a novel synthesis of glassy carbon which requires relatively low (~600 °C) thermal treatment for its preparation.[41–43] This low-temperature synthesis allows, for the first time, the preparation of homogeneously doped glassy carbon (DGC) materials. The synthesis of DGC materials involves the preparation of diacetylenic oligomeric or polymeric precursors, molding of the powder to form a disk, or alternatively, casting a film from solution, followed by thermal treatment to form glassy carbon. The key development to our success was the recognition that the thermal transformation of these highly unsaturated macromolecules could be carried out at relatively low temperatures allowing the production of glassy carbons containing substantial (>20 wt %) levels of heteroatoms.

We have pursued the preparation of heteroatom-doped glassy carbon in an effort directed toward controlling the interaction of small molecules with carbon surfaces with the ultimate goal of controlling the electrocatalytic behavior of these surfaces. We describe here the synthesis of chlorine-doped GC (Cl-GC6), fluorine-doped GC (F-GC6), and glassy carbon (GC6) from perchlorinated and perfluorinated poly(1,3-butadiynylene-1,3-phenylene) (the nomenclature GC6 signifies glassy carbon prepared at 600 °C). We also assess the effect of these dopants in glassy carbon by examination of the physical properties of these materials, including their electrical resistivities, densities, elastic moduli, thermal stabilities, and surface energies as compared to conventional GC prepared at temperatures of 1000–2500 °C. We also report that these materials function as efficient electrodes for the benchmark $Fe(CN)_6^{3-/4-}$ redox system, and exhibit unusually low voltammetric background currents.

Experimental Section

All NMR spectra were obtained on Bruker AC-200 or AC-250 spectrometers. IR spectra were recorded with a Perkin-Elmer 1600 FTIR spectrometer. XPS spectra were obtained with a Physical Electronics 550 ESCA/Auger spectrometer using a Mg anode (Mg Kα, 300 W, 15 kV). Mass spectroscopic analyses were carried out by the Ohio State University Chemical Instrument Center on a VG 70-250S mass spectrometer. Raman spectra were obtained with a Spex 1403 double monochrometer, a RCA 31034A photomultiplier, and a 514.5-nm laser with ca. 50 mW at the sample. Scanning electron micrographs were obtained on a Hitachi Model S-510 instrument. Contact angle measurements were obtained with a Cahn DCA-322 dynamic contact angle analyzer. All contact angles were measured at 25 °C and were the result of no less than 3 measurements/sample. DSC and TGA analyses were obtained on a Perkin-Elmer 7 Series thermal analysis system. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. 1,2,3,5-Tetrafluorobenzene, pentafluorobenzene, phenylacetylene, pentachlorobenzene, diisopropylamine, tetramethylethylenediamine (TMEDA), pyridine, copper(II) acetate monohydrate, copper(I) iodide, and palladium(II) chloride were used as received from Aldrich. 1,2,3,5-Tetrachlorobenzene (Lancaster) and (trimethylsilyl)acetylene (Farchan) were used as received. Silica gel (230–420 mesh) was obtained from Brinkman. Solutions of 1 mM $K_4Fe(CN)_6$ (Mallinckrodt) were prepared in 1 M KCl in purified ("Nanopure" from Barnstead) water.

1,2,3,5-Tetrachloro-4,6-diiodobenzene (5). To a cooled solution of concentrated sulfuric acid (250 mL) was added periodic acid (15.0 g, 66 mmol). To this clear solution was added, in portions, potassium iodide (32.8 g, 200 mmol). An exothermic reaction took place with the evolution of iodine vapor. 1,2,3,5-Tetrachlorobenzene (**3**, 2.49 g, 11.8 mmol) was added dropwise and the reaction mixture was heated at 70 °C for 2 h. The solution was poured onto ice (100 g) and extracted with diethyl ether (3 × 100 mL). The combined ethereal solutions were washed with 10% sodium thiosulfate solution until the organic layer was colorless and dried ($MgSO_4$). The solution was filtered and the solvent was removed in vacuo leaving a yellow solid. Recrystallization from benzene:ethanol (1:1) gave **5** (4.37 g, 80%) as white needles: mp 200–201 °C; ^{13}C NMR (62.9 MHz, C_6D_6) δ 155.3, 140.2, 138.5, 98.3 ppm; HRMS calcd for $C_6Cl_4I_2$ 465.6844, found 465.6839.

1,2,3,5-Tetrachloro-4,6-diethynylbenzene (7). To a solution of 1,2,3,5-tetrachloro-4,6-diiodobenzene (**5**, 1.22 g, 2.62 mmol) in diisopropylamine (200 mL) were added bis(triphenylphosphine)-palladium(II) dichloride (37 mg, 0.05 mmol) and copper(II) acetate monohydrate (12 mg, 0.06 mmol). The solution was degassed via a rapid stream of argon and (trimethylsilyl)acetylene (0.56 g, 5.7 mmol) was added dropwise over a period of 15 min. The reaction mixture was stirred at room temperature for 2 h and then heated to reflux. During reflux the solution turned dark brown with the formation of a heavy precipitate. The solution was heated until gas chromatographic analysis indicated the disappearance of starting material (12 h). The reaction mixture was cooled to room temperature and filtered to remove salts. The filtrate was concentrated in vacuo and the oily residue was taken up in dichloromethane. The solution was washed with an aqueous 5% HCl solution (2 × 100 mL), water (2 × 100 mL) and brine (1 × 100 mL). The combined organic layers were dried ($MgSO_4$) and the solvent removed in vacuo yielding the crude product as a yellow powder. The solid was dissolved in a minimum amount of *n*-pentane and chromatographed over silica gel. Elution with *n*-pentane yielded 1,2,3,5-tetrachloro-4,6-bis[(trimethylsilyl)ethynyl]benzene (713 mg, 67%) as white needles: mp 93–94 °C; IR (KBr) 2961, 2899, 2161, 1409, 1384, 1366, 1340, 1251, 849 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.29 (s) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 138.6, 137.1, 131.6, 122.7, 109.3, 97.0, 0.23 ppm. Anal. Calcd for $C_{16}H_{18}Cl_4Si_2$: C, 47.29; H, 4.47; Cl, 34.45. Found: C, 47.14; H, 4.45; Cl, 34.29. To a solution of the 1,2,3,5-tetrachloro-4,6-bis[(trimethylsilyl)ethynyl]benzene (683 mg, 1.60 mmol) prepared above, in degassed methanol (50 mL), was added potassium hydroxide (31 mg, 0.55 mmol) in water (1 mL). The solution was stirred at room temperature until gas chromatographic analysis indicated the reaction was complete (0.5 h). The reaction mixture was diluted with an equal volume of water, and extracted with *n*-pentane (5 × 100 mL). The combined organic layers were dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a yellow solid. The solid was dissolved in a minimum amount of *n*-pentane and chromatographed over silica gel. Elution with *n*-pentane yielded **7** (300 mg, 72%) as white needles: mp 190–200 °C; IR (KBr) 3307, 2116, 1364, 1263 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.77 (s) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 138.4, 137.1, 131.4, 122.5, 89.6, 76.6 ppm; HRMS calcd for $C_{10}H_2Cl_4$ 261.8911, found 261.8920.

1,3-Diethynyl-2,4,5,6-tetrafluorobenzene (8). This procedure is a modified version of that published previously.[44] To a solution of 1,2,3,5-tetrafluoro-4,6-diiodobenzene (**6**, 10.0 g, 24.8 mmol) in diisopropylamine (300 mL) was added bis(triphenylphosphine)palladium(II) chloride (0.33 g, 0.47 mmol) and copper(I) iodide (0.10 g, 0.52 mmol). The solution was degassed via a rapid stream of argon, and (trimethylsilyl)acetylene (5.63 g, 57.5 mmol) was added dropwise over a period of 1 h at room temperature. The solution rapidly turned a dark green, and a heavy precipitate formed as the reaction mixture was heated to reflux. Heating and stirring were continued until gas chromato-

---

(40) Fitzer, K.; Mueller, K.; Schaefer, W. In *Chemistry and Physics of Carbon*; Walker Jr., P. L., Ed.; Dekker: New York, 1971; Vol. 7; p 237.

(41) Pocard, N. L.; Alsmeyer, D. C.; McCreery, R. L.; Neenan, T. X.; Callstrom, M. R. *J. Am. Chem. Soc.* **1992**, *114*, 769.

(42) Callstrom, M. R.; Neenan, T. X.; McCreery, R. L.; Alsmeyer, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 4954.

(43) Neenan, T. X.; Callstrom, M. R.; Bachman, B. J.; McCreery, R. L.; Alsmeyer, D. C. *Brit. Polym. J.* **1990**, *23*, 171.

(44) Neenan, T. X.; Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 2489.

graphic analysis indicated the reaction was complete (2 h). The solution was filtered, and the solid washed with dichloromethane (50 mL). The filtrate was concentrated in vacuo, dissolved in dichloromethane (250 mL), and washed with an equal volume of aqueous 5% HCl solution and water (twice). The organic layer was dried (Na_2SO_4), and the solvent removed under reduced pressure to give the crude product as a dark oil. The oil was dissolved in a minimum amount of hexanes and applied to a silica gel column packed in hexanes. Elution with hexanes yielded the desired product 1,2,3,5-tetrafluoro-4,6-bis[(trimethylsilyl)-ethynyl]benzene (3.93 g, 46%) as white needles: mp 56–57 °C (lit.[44] mp 55–57 °C); IR (KBr) 2981, 2926, 2083, 1505, 1263, 990 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.28 (s) ppm. To a solution of 1,2,3,5-tetrafluoro-4,6-bis[(trimethylsilyl)ethynyl]benzene (21.48 g, 62.81 mmol) prepared above, in degassed methanol (300 mL), was added potassium hydroxide (31 mg, 0.55 mmol) in water (1 mL). The solution was stirred at room temperature until gas chromatographic analysis indicated the reaction was complete (2 h). The reaction mixture was diluted with an equal volume of water, and extracted with *n*-pentane (5 × 100 mL). The combined organic layers were dried ($MgSO_4$), and the solvent removed under reduced pressure to yield a yellow oil. The oil was purified via bulb-to-bulb vacuum distillation to give **8** (8.74 g, 70%) as a clear liquid: bp 64–66 °C at 1.3 Torr (lit.[44] bp 55 °C at 1 Torr); IR (neat) 3307, 2130, 1480, 1263 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.50 (s) ppm.

Poly(1,3-butadiynylene-1,3-phenylene) (10). This procedure is a modified version of that published previously.[45,46] A solution of *o*-dichlorobenzene (75 mL), TMEDA (0.11 g, 0.95 mmol), copper(I) chloride (0.030 g, 0.30 mmol) and pyridine (2.5 mL) was stirred under oxygen at 65 °C. A solution of 1,3-diethynylbenzene (**2**, 2.10 g, 16.7 mmol) and phenylacetylene (**9**, 0.567 g, 5.56 mmol) in *o*-dichlorobenzene was added rapidly to the reaction flask. Heating and stirring under oxygen were continued for 2 h. The reaction was then stirred at room temperature under oxygen for an additional 3 h. The reaction mixture was poured into acidic methanol (2% HCl) to induce precipitation and a light yellow solid was collected. The solid was dissolved in THF (250 mL) and treated with tetramethylethylenediamine (TMEDA) to remove any residual copper in solution. The THF solution was poured into acidic methanol (2% HCl) to induce precipitation and a light yellow solid was collected by filtration (2.04 g, 76%): IR (KBr) 3050, 2200, 1578, 1463, 1377, 1084, 882, 780, 754, 679 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.7 (s), 7.3 (s) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 136.2, 133.8, 132.8, 129.7, 128.0, 122.8, 122.6, 121.5 ppm. Anal. Calcd for $C_{76}H_{34}$: C, 96.38; H, 3.62. Found: C, 96.14; H, 3.86.

Pentachloroethynylbenzene (11). To a solution of pentachloroiodobenzene (1.22 g, 3.2 mmol) in diisopropylamine (200 mL) were added bis(triphenylphosphine)palladium(II) dichloride (0.15 g, 0.21 mmol) and copper(II) acetate monohydrate (0.05 g, 0.25 mmol). The solution was degassed via a rapid stream of argon and trimethylsilylacetylene (1.19 g, 12.0 mmol) was added dropwise over a period of 15 min. The reaction mixture was stirred at room temperature for 2 h and then heated to reflux. During reflux, the solution turned dark brown with the formation of a heavy precipitate. The solution was heated until gas chromatographic analysis indicated the disappearance of starting material (12 h). The reaction mixture was cooled to room temperature and filtered to remove salts. The filtrate was concentrated in vacuo, and the oily residue was dissolved in dichloromethane. The solution was washed with an aqueous 5% HCl solution (2 × 100 mL), water (2 × 100 mL), and brine (1 × 100 mL). The combined organic layers were dried ($MgSO_4$) and the solvent removed in vacuo yielding the crude product as a yellow powder. The solid was dissolved in a minimum amount of *n*-pentane and chromatographed over silica gel. Elution with *n*-pentane gave the product pentachloro[(trimethylsilyl)ethynyl]-benzene (0.76 g, 68%) as white needles: mp 81–82 °C; IR (KBr) 2960, 2908, 2160, 1345, 1246 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.30 (s) ppm; ^{13}C NMR (50.323 MHz, $CDCl_3$) δ 144.9, 134.8, 133.2, 124, 109.4, 92.7, 0.30 ppm. Anal. Calcd for $C_{11}H_9Cl_5Si$: C, 38.38; H, 2.64; Cl, 50.84. Found: C, 38.87; H, 2.34; Cl, 51.44. To a solution of the pentachloro[(trimethylsilyl)ethynyl]benzene (120 mg, 0.348 mmol) prepared above, in degassed methanol (50 mL), was added potassium hydroxide (31 mg, 0.55 mmol) in water (1 mL). The solution was stirred at room temperature until gas chromatographic analysis indicated the reaction was complete (0.5 h). The reaction mixture was diluted with an equal volume of water and extracted with *n*-pentane (5 × 100 mL). The combined organic layers were dried ($MgSO_4$) and the solvent removed under reduced pressure to yield a yellow solid. The solid was dissolved in a minimum amount of *n*-pentane and chromatographed over silica gel. Elution with *n*-pentane yielded **11** (65 mg, 69%) as white needles: mp 179–181 °C; IR (KBr) 3307, 2100, 1350, 1315 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.80 (s) ppm; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 144.5, 136.0, 131.5, 123.2, 108.2, 97.1 ppm; HRMS calcd for C_8HCl_5: 271.8521, found 271.8531. Anal. Calcd for C_8HCl_5: C, 35.31; H, 0.37. Found: C, 35.37; H, 0.40.

Ethynylpentafluorobenzene (12). This procedure is a modified version of that published previously.[44] To a solution of pentafluoroiodobenzene (8.80 g, 29.9 mmol) in diisopropylamine (300 mL) was added bis(triphenylphosphine)palladium(II) chloride (0.46 g, 0.65 mmol) and copper(I) iodide (0.13 g, 0.65 mmol). The solution was degassed via rapid stream of argon, and (trimethylsilyl)acetylene (3.55 g, 36 mmol) was added dropwise over a period of 1 h at room temperature. The solution rapidly turned a dark green, and a heavy precipitate formed as the reaction mixture was heated to reflux. Heating and stirring were continued until gas chromatographic analysis indicated the reaction was complete (2 h). The solution was filtered and washed with dichloromethane. The filtrate was concentrated in vacuo, and the residue was dissolved in dichloromethane (250 mL) and washed with an equal volume of aqueous 5% HCl solution and water (twice). The organic layer was dried (Na_2SO_4), and the solvent removed under reduced pressure to give the crude product as a dark oil. The oil was dissolved in a minimum amount of hexanes, and applied to a silica gel column (150 g) packed in hexanes. Elution with hexanes yielded the desired product pentafluoro[(trimethylsilyl)ethynyl]benzene (5.23 g, 66%) as a clear liquid: bp 95–98 °C at 13 Torr (lit.[44] bp 97 °C at 13 Torr); IR (neat) 2980, 2923, 2080, 1505, 990 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.14 ppm. To a solution of the pentafluoro[(trimethylsilyl)ethynyl]benzene (1.20 g, 4.55 mmol) prepared above, in degassed methanol (50 mL) was added potassium hydroxide (31 mg, 0.55 mmol) in water (1 mL). The solution was stirred at room temperature until gas chromatographic analysis indicated the reaction was complete (2 h). The reaction mixture was diluted with an equal volume of water, and extracted with *n*-pentane (5 × 100 mL). The combined organic layers were dried ($MgSO_4$), and the solvent removed under reduced pressure to yield a yellow oil. The oil was purified via bulb-to-bulb vacuum distillation to give the desired product (**12**, 732 mg, 84%) as a clear liquid: bp 129–131 °C (lit.[44] bp 65–67 °C at 1 Torr); IR (neat) 3310, 2135, 1480, 990 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.55 ppm.

Poly(1,3-butadiynylenetetrachloro-1,3-phenylene) (13). The preparation of **13** was accomplished analogously to that described for the preparation of **10** from **7** and **11** in an 74% yield: IR (KBr) 2116, 1363, 1263, 783, 762, 657, 638 cm^{-1}; ^{13}C NMR (62.9 MHz, C_7D_8) δ 143.9, 138.0, 137.1, 136.0, 127.2, 125.8, 98.6, 84.6 ppm.[47]

Poly(1,3-butadiynylenetetrafluoro-1,3-phenylene) (14). The preparation of **14** was accomplished analogously to that described for the preparation of **10** from **8** and **12** in an 89% yield: IR (KBr) 2172, 1620, 1479, 1434, 1124, 1093, 965, 742, 694 cm^{-1}; ^{13}C NMR (62.9 MHz, C_7D_8) δ 167.2, 155.0, 150.1, 137.7, 132.6, 97.1, 83.2, 68.0 ppm. Anal. Calcd for $C_{76}F_{34}$: C, 58.56. Found: C, 58.32.

General Procedure for the Preparation of the Highly Cross-Linked Solids GC6, Cl-GC6, and F-GC6. Powdered oligomer (**10**, **13**, or **14**, 200 mg) was added to 1-cm-diameter circular die and pressure (6800 bars) was applied. The die was heated to 330 °C for 1 h (heating rate 20 °C/min) and allowed

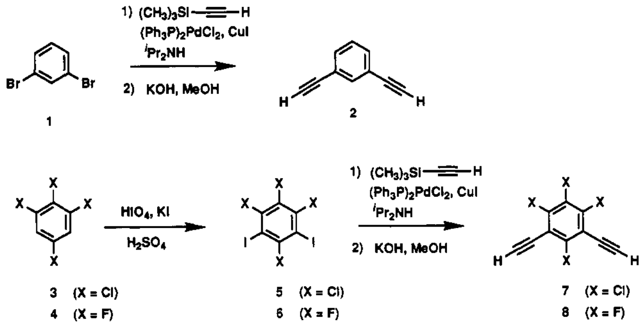
---

(45) Hay, A. S. U.S. Patent 3,300,456, 1967.

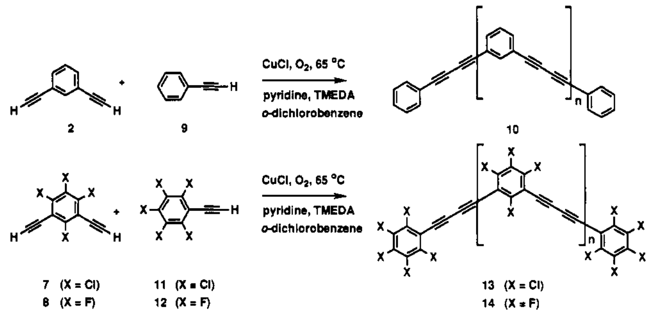
(46) Hay, A. S.; White, D. M. *Macromol. Synth.* **1979**, *7*, 11.

(47) Repeated elemental analyses of this material failed due to incomplete combustion.

Scheme I



Scheme II



to cool slowly to room temperature. The dark disk produced was placed in a quartz tube and heated to 600 °C (rate 1 °C/min) under dynamic vacuum (0.005 Torr) and held at 600 °C for 6 h. After cooling to room temperature, the glassy carbon disk was removed from the quartz tube.

General Procedure for the Preparation of GC6 Films on Conventional Glassy Carbon. A 1.5-cm-diameter glassy carbon disk (Atomergic GC25) was washed with acetone and distilled water and then sonicated in distilled water for 5 min. The disk was dried in a vacuum oven (65 °C, 0.15 mmHg) and then affixed to a photoresist spinner. A saturated solution of the oligomer in toluene (5 mL) was added dropwise to the glassy carbon disk (rotating at a rate of 200 rpm) until the disk was completely covered with the solution. Spinning was continued at a constant rate until evaporation of the toluene was complete (5 min). This procedure provided reproducible, homogeneous films with thicknesses in the range 2–5 μm. The thin film on glassy carbon was placed in a quartz tube which was inserted into a furnace such that one portion of the tube extended outside the furnace for connection to a diffusion vacuum pump. The vessel was evacuated (10^{-6} mmHg) and then heated at a rate of 1 °C/min to 600 °C. Thermal treatment at 600 °C was continued for 6 h. The sample was then cooled to room temperature at a rate of ~10 °C/min and removed from the tube as a dark, highly reflective film on the glassy carbon substrate.

General Procedure for Voltammetry. Cyclic voltammetry was performed with a triangle wave generator and personal computer as described elsewhere.[48] The active electrode area was determined by a Teflon washer and equalled approximately 0.1 cm^2, with each electrode area determined by chronoamperometry of $Fe(CN)_6^{3-/4-}$. All voltammetry was performed on thin film electrodes immediately after removal from the vacuum curing apparatus. Solutions were degassed with argon before use and an argon stream was maintained over the solution during voltammetric measurements. All potentials are reported vs the normal hydrogen electrode (NHE).

Results and Discussion

1. Synthesis. The syntheses of the required 1,3-aryldiacetylene compounds are illustrated in Scheme I.[49] 1,3-Dibromobenzene (**1**) was converted to 1,3-bis[(trimethylsilyl)ethynyl]benzene by reaction with trimethylsilylacetylene using palladium and copper catalysis in diisopropylamine.[50,51] The trimethylsilyl protecting groups were removed in quantitative yield by treatment with a catalytic quantity of potassium hydroxide in aqueous methanol to give 1,3-diethynylbenzene (**2**). Iodination of 1,2,3,5-tetrachlorobenzene (**3**) or 1,2,3,5-tetrafluorobenzene (**4**) with potassium iodide and periodic acid in concentrated sulfuric acid gave an 80% of 1,2,3,5-tetrachloro-4,6-diiodobenzene (**5**) and an 87% yield of 1,2,3,5-tetrafluoro-4,6-diiodobenzene (**6**).[52] Selective reaction of the more reactive aryliodides with (trimethylsilyl)acetylene, mediated by palladium and copper catalysis, followed by removal of the trimethylsilyl groups with potassium hydroxide in methanol, gave 72% and 70% yields of 1,2,3,5-tetrachloro-4,6-diethynylbenzene (**7**) and 1,3-diethynyl-2,4,5,6-tetrafluorobenzene (**8**), respectively.

Oligomerization of **2** with phenylacetylene (**9**) under oxidative coupling reaction conditions, using dioxygen and 2 mol % of cuprous chloride in o-dichlorobenzene at 65 °C, gave a homogeneous solution of poly(1,3-butadiynylene 1,3-phenylene) (**10**, Scheme II).[53,54] Similarly, oxidative coupling of **7** with pentachloroethynylbenzene (**11**) or **8** with ethynylpentafluorobenzene (**12**)[44] gave poly(1,3-butadiynylenetetrachloro-1,3-phenylene) (**13**) and poly(1,3-butadiynylenetetrafluoro-1,3-phenylene) (**14**), respectively. A 3:1 molar ratio of the diethynyl aromatic to monoethynyl aromatic was used in all cases to limit the molecular weight and maintain solubility of the oligomeric materials. If the oxidative coupling reaction was carried out using less than ~30 mol % of the monoethynyl aromatic molecule, precipitation of the polydiacetylene occurred during the reaction and the resulting materials were typically insoluble in conventional organic solvents. The reaction solutions containing soluble oligomers (**10**, **13**, and **14**) were added separately to 5% hydrochloric acid methanolic solutions, which resulted in their precipitation from solution, and the solids were collected by filtration. These materials (**10**, **13**, and **14**) were treated with tetramethylethylenediamine in tetrahydrofuran to remove copper salts, followed by addition of the tetrahydrofuran solution to a 5% hydrochloric acid methanol solution to precipitate the oligomeric materials as light yellow powders. This methodology allows the removal of residual copper salts to a level below the detection limits of an X-ray photoelectron spectrometer (~0.1 atom %).

The oligomeric materials were molded into disks in a 1-cm die under pressure (6800 bar), thermally treated to 330 °C over a 3 h period, allowed to cool, and then removed from the die. Further thermal treatment to a final temperature of 600 °C (ramp rate of 1 °C/min, 6 h at final temperature) was carried out under a blanket of high-purity argon or under dynamic vacuum (0.005 Torr) in a quartz vessel to give the black, shiny carbon solids GC6, Cl-GC6, and F-GC6 (Scheme III). The GC figure in Scheme III represents the highly cross-linked, sp^2-hy-

---

(48) Allred, C. D.; McCreery, R. L. *Anal. Chem.* **1992**, *64*, 444.

(49) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M. *Macromolecules* **1988**, *21*, 3525.

(50) Takahashi, S.; Kuromaya, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

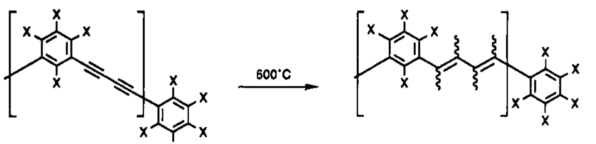
(51) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

(52) Mattern, D. L. *J. Org. Chem.* **1983**, *48*, 4772.

(53) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275.

(54) Dawson, D. J.; Fleming, W. W.; Lyerla, J. R.; Economy, J. In *Reactive Oligomers*; Harris, F. W., Spinelli, H. J., Eds.; ACS Monograph; American Chemical Society: Washington D.C., 1982; Vol. 282; p 63.

Scheme III



10 (X=H)
13 (X=Cl)
14 (X=F)

GC6
Cl-GC6 (X=Cl)
F-GC6 (X=F)

Table I. Thermal Analysis of Materials GC6, Cl-GC6, and F-GC6

	differential scanning calorimetry[a]			thermal gravimetric analysis[b]			
				nitrogen		air	
sample	T_{onset} (°C)	T_{max} (°C)	cure energy (cal/g)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)
GC6	102	125	−121	735	(13.5%)[c]	682	759
Cl-GC6	230	262	− 39	470	778	413	825
F-GC6	211	226	−107	663	(45.9%)[c]	563	653

[a] Calorimetry was performed on oligomeric precursors. The ramp rate was 5 °C/min. [b] The heating rate was 10 °C/min. $T_{10\%}$ is the temperature at which 10% of the initial mass of the sample is lost, and $T_{50\%}$ is the temperature corresponding to loss of 50% of the samples mass. [c] For these cases $T_{50\%}$ exceeded the upper limit temperature of the thermal analyzer (950 °C). The values reported are percent weight lost at 950 °C.

bridized nature of glassy carbon.[40] The mnemonic for these glassy carbon materials describes the dopant atom, which in these cases include fluorine and chlorine, and the temperature, 600 °C, for the formation of glassy carbon signified by GC6. Comparison materials denoted GC10 and GC25 are commercially prepared GC prepared at 1000 and 2500 °C, respectively. An alternative to the preparation of disks of these materials is the preparation of coatings of doped glassy carbon on various substrates. Thin films of **10**, **13**, or **14** were cast on a conventional glassy carbon substrate (GC25) from toluene solution and thermally treated at 600 °C (ramp rate of 1 °C/min, 6 h at final temperature) under a dynamic vacuum (1×10^{-6} Torr) in a quartz vessel. These materials gave thin, continuous films of GC6, Cl-GC6, and F-GC6 which were ideal for electrochemical studies (see below).

2. Characterization of Heteroatom-Doped Glassy Carbon. The cross-linking reaction of the oligomeric materials was examined by differential scanning calorimetry. These materials exhibited a cure onset temperature of ~100 °C for **10** and ~220 °C for the chlorine (**13**) and fluorine (**14**) oligomeric materials (Table I). On a molar basis, the cure energies were quite similar with values of 115, 104, and 166 kcal/mol for **10**, **13**, and **14**, respectively, indicating that the halogen dopants do not substantially interfere with the formation of a highly cross-linked carbon lattice. The thermal stabilities of GC6, Cl-GC6, and F-GC6 were examined by thermal gravimetric analysis. The three materials possessed a similarly high thermal stability (Table I). Under an air atmosphere, the halogen doped solids were slightly less resistant to decomposition than GC6 as evidenced by losses of 10% of their mass 120 °C lower for F-GC6 and 260 °C lower for Cl-GC6. Under a nitrogen atmosphere, the Cl-GC6 material exhibited the lowest thermal stability of the GC materials with a loss of 10% of its mass 260 °C below GC6 and a loss of 50% of its mass at 778 °C. Both F-GC6 and GC6 exhibited excellent thermal stability under a nitrogen atmosphere although F-GC6 lost 10% of its mass 70 °C lower than GC6 and a greater portion of its mass at the upper limit (950 °C) of the thermal analyzer.

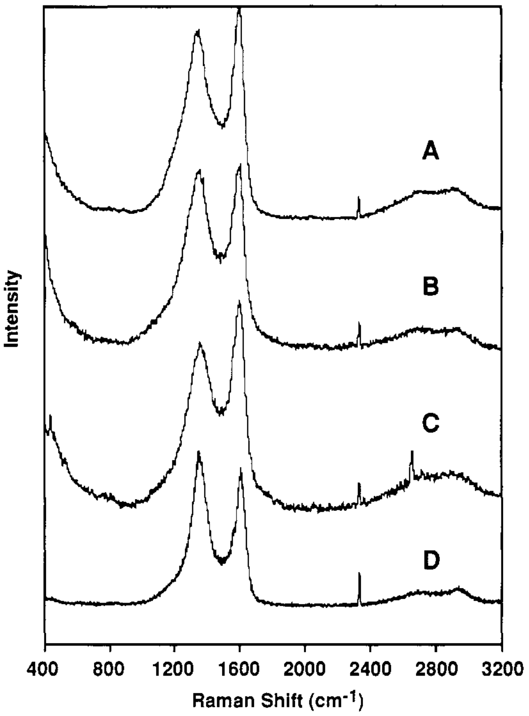


Figure 1. Raman spectra of (A) GC6, (B) Cl-GC6, (C) F-GC6, and (D) GC10.

Raman spectroscopy was employed to determine the microcrystalline structure of the heteroatom doped GC materials. Raman analyses of GC6, Cl-GC6, F-GC6, and conventional glassy carbon (GC10, Atomergic) found bands at approximately 1580 and 1360 cm^{-1} which are characteristic of a sp^2-hybridized lattice (Figure 1).[55–62] The spectra of the heteroatom doped materials are quite similar to conventionally prepared GC, indicating that the heteroatom dopants did not affect the formation of the sp^2–hybridized carbon lattice. The variation in the 1360/1580 intensity ratios is due to a small variation in microcrystallite size of the GC lattices. To determine the fate of the halogens in the glassy carbon matrix, the materials were also examined by X-ray photoelectron spectroscopy. Examination of the XPS spectrum of Cl-GC6 found the oxygen (1s) electron at 532.6 eV and the chlorine (2p) electron at 201.1eV (Figure 2A). These values are relative to the carbon (1s) electron used as an internal reference at 284.6 eV. Similarly, examination of the F-GC6 spectrum finds the carbon and oxygen peaks as well as the fluorine (1s) electron at 686.5 eV (Figure 2B). Comparison of the peak areas for the halogens to the peak area of the C(1s) electron in Figures 2A and 2B found that the Cl-GC6 material contains ~20 wt % chlorine and the F-GC6 material contains ~15 wt % fluorine.

The formation of a highly cross-linked graphitic lattice, as indicated by the Raman spectra, suggests that the

---

(55) Bowling, R. J.; Packard, R. T.; McCreery, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 1217.
(56) Dresselhaus, M. S.; Dresselhaus, G. *Adv. Phys.* **1981**, *30*, 290.
(57) Wang, Y.; Alsmeyer, D. C.; McCreery, R. L. *Chem. Mater.* **1990**, *2*, 557.
(58) Nemanich, R. J.; Lucovsky, G.; Solin, S. A. *Mat. Sci. Eng.* **1977**, *31*, 157.
(59) Nemanich, R. J.; Solin, S. A. *Phys. Rev. B* **1979**, *20*, 362.
(60) Tuinstra, R.; Koenig, J. L. *J. Chem. Phys.* **1970**, *53*, 1126.
(61) Vidano, R. P.; Fishbach, D. B. *J. Am. Chem. Soc.* **1978**, *61*, 13.
(62) Vidano, R. P.; Fischbach, D. B.; Willis, L. J.; Loewhr, T. M. *Solid State Commun.* 1981, *39*, 341.

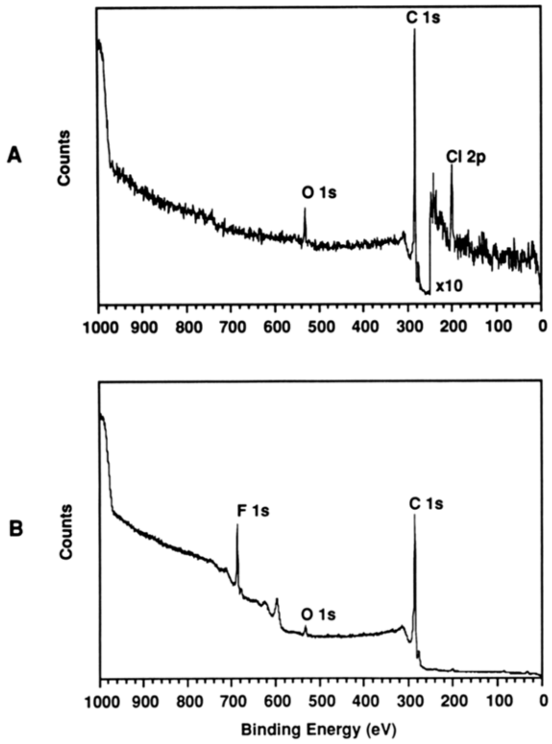


Figure 2. X-ray photoelectron spectra of (A) Cl-GC6 and (B) F-GC6.

heteroatom is not greatly perturbing the glassy carbon structure. Potentially, a portion of the heteroatom dopants could be contained in the lattice through formation of hypervalent bonds or in an ionic form. However, examination of the binding energies of the halogens by XPS does not lend support to this possibility. The binding energies for the Cl(2p) electron at 201.1 eV and the F(1s) electron at 686.5 eV are the expected values for a halogen bonded to carbon.[63–65] These findings are particularly intriguing considering that these halogen-doped materials contain >15 wt % of the halogens. Consideration of the Raman data together with the XPS data suggests that the most likely fate of the heteroatom in the carbon solid is that the halogen is bonded to carbon at the edge of the graphitic planes.

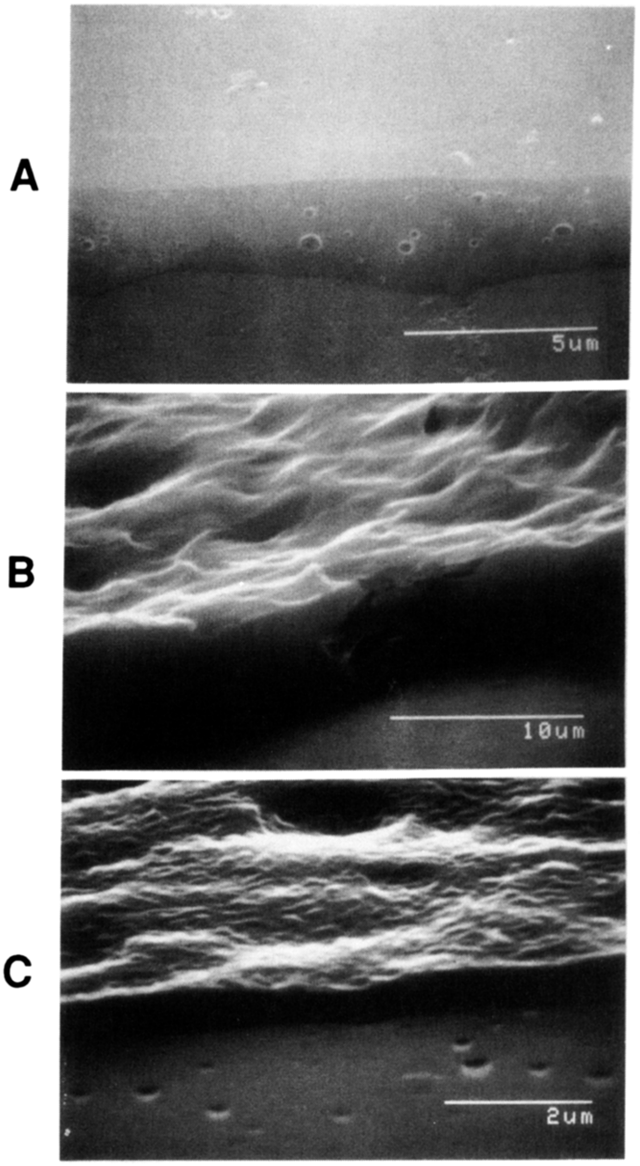


Figure 3. Scanning electron micrographs of (A) GC6, (B) Cl-GC6, and (C) F-GC6 thin films on GC25 (Atomergic) following thermal treatment to 600 °C.

Our interest in utilizing these materials for electrochemical applications prompted the preparation of films of GC6, Cl-GC6, and F-GC6 on a conventional glassy carbon substrate. The films were cast on GC25 (Atomergic) disks from saturated solutions of **10**, **13**, and **14** in toluene. The films were then thermally treated at 600 °C under a dynamic vacuum (1×10^{-6} Torr) as described above. Scanning electron microscopy was used to examine the surfaces of the films (Figure 3). Although the films were homogeneous and continuous, as prepared, they were thicker on the outer edges of the GC25 disks which resulted in fracture of the film leaving the sharp edges shown. Careful examination of the film substrate interface in Figure 3 clearly found that the GC6 materials form an intimate bond with the carbon substrate. The halogen-doped films were not as smooth as GC6. To obtain a direct assessment of the effect of halogen incorporation in glassy carbon, we investigated the surface energies of these materials.

The surfaces of solids are classified by categories of high and low energy with respect to wettability. The investigation of the surface energies of solid materials is important not only when considering electrochemistry, where the energetics of solid and liquid interfaces are critical to the efficiency of the process, but also in the preparation of composite materials where differences in the surface energies of materials ultimately affects the integrity of the resulting composites.[66] The contact angles of water, glycerol, ethylene glycol, and hexadecane on the GC materials were measured using the Wilhelmy plate technique.[67] The surface energies of our materials (Table II) were determined from the measured contact angles using an adaptation of the geometric multiliquid method

---

[63] Clark, D. T.; Kilcost, D.; Musgrave, W. K. R. *Chem. Commun.* **1971**, 516.

[64] Clark, D. T.; Kilcost, D.; Musgrave, W. K. R.; Adams, D. B. *J. Electron. Spectrosc.* **1975**, *6*, 117.

[65] Clark, D. T.; Feast, W. J.; Musgrave, W. K. R.; Ritchie, J. *J. Polym. Sci., Polym. Chem.* **1975**, *13*, 857.

[66] Donnet, J. B.; Bansal, R. C. *Carbon Fibres*; Marcel Dekker: New York, 1990.

[67] Johnson, R. E.; Dettre, R. H. *Surface and Colloid Science*; Wiley: New York, 1969; p 85.

Table II. Density (ρ), Young's Modulus (E),[a] Shear Modulus (S),[a] Conductivity (σ), and Surface Energies of GC6, Cl-GC6, F-GC6, and GC Prepared by Conventional Methods at 2500 °C (GC25)

		surface energy						
sample	synth temp (°C)	dispersive (dyn/cm)	polar (dyn/cm)	total[c] (dyn/cm)	ρ (g/cm^3)	E (MN/m^2)	S (MN/m^2)	σ (S/cm)
GC25[b]	2500	29.0	4.5	33.5	1.46	29100	12350	100
GC6	600	26.0	5.3	31.3	1.50	28500	10800	0.7
Cl-GC6	600	24.5	5.4	29.9	1.35	7270	2860	0.1
F-GC6	600	26.0	1.3	27.3	1.22	19100	8050	0.2

[a] The modulus measurements were determined by an ultrasonic method previously described.[45] Uncertainty in the measurement is <5%. [b] Atomergic glassy carbon. [c] Uncertainty in total surface energies are ±0.1 dyn/cm.

developed by Kaeble.[68] Because surface preparation has a tremendous effect on the wettability of materials,[69,70] the materials were polished repetitively until no changes in the contact angles were found to ensure that the differences in measured surface energies were due to differences in the surface composition of doped and nondoped samples and not due to sample preparation.[71] It is important to note that the changes in the contact angles of a given sample between repetitive polishings were approximately 2 orders of magnitude smaller than the differences between samples of different composition. As Table II illustrates, the incorporation of fluorine into GC noticeably decreased the surface energy of the material relative to GC. This is not surprising in view that many materials containing fluorine, including Teflon and graphite fluorides, have low surface energies.[72] The incorporation of chlorine into GC also resulted in a slightly lower surface energy relative to GC. The values obtained for commercial GC25 and GC6 (33.5 and 31.3 dyn/cm) were in agreement with literature values (32–35 dyn/cm) for conventionally prepared GC.[73]

The densities, elastic moduli and conductivities of GC6, Cl-GC6, F-GC6, and GC25 are also contained in Table II. The densities and elastic moduli of GC6 are remarkably similar to conventional GC prepared at 2500 °C. However, the incorporation of halogens into the glassy carbon matrix dramatically affects the densities and elastic moduli of the carbon solids. Since a high degree of cross-linking occurs upon heating to 600 °C, an increase in modulus and density was expected. This increase was observed for GC6, but substantially lower densities were found for the halogen-doped materials. The loss of a portion of the halogen dopants upon heating could account for the decreased densities of these materials. As we are particularly interested in the use of these materials for electrochemistry, we examined the resistivity of the solids in response to their thermal treatment. The materials GC6, Cl-GC6, and F-GC6 were electrically insulating upon heating to 330 °C. However, treatment at 600 °C for 6 h resulted in materials with electrical conductivities of ~1 S/cm (Table II). These conductivities for the heteroatom-doped GC are quite high considering the high level of heteroatom incorporation in these solids. Their conductivities are sufficient to result in minimal ohmic potential error in electrochemical experiments, particularly for thin-film electrodes.

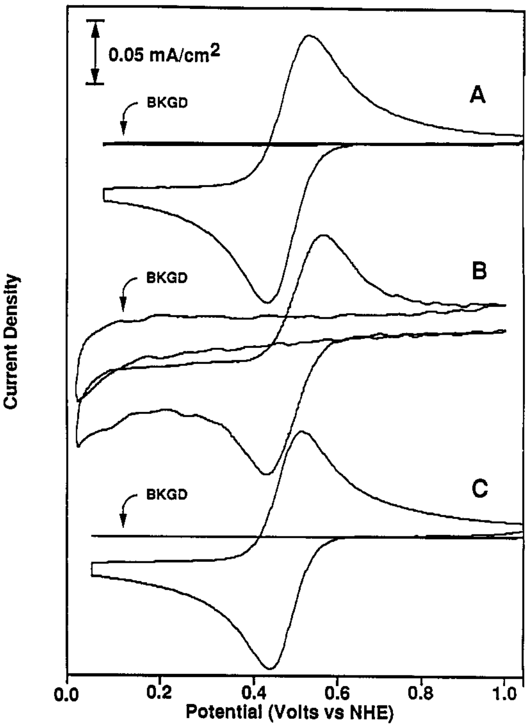


Figure 4. Cyclic voltammograms of 1 mM ferrocyanide in 1 M potassium chloride and backgrounds in 1 M potassium chloride on (A) GC6, (B) Cl-GC6, (C) F-GC6 thin films. Scan rates were 10 mV/s.

The applicability of the halogen-doped materials to electrochemical charge transfer was assessed with cyclic voltammetry (CV) using thin-film electrodes immediately after thermal treatment in a 10^{-6} mmHg vacuum. Figure 4 shows CV's for 1 mM $Fe(CN)_6^{3-/4-}$ in 1 M KCl, plus background CV's obtained in 1 M KCl. The low, flat background currents observed for the F-GC6 material implies a low porosity surface relatively free of oxides. Although the Cl-GC6 background was higher, this difference did not occur reliably. On the basis of the background currents observed, the F-GC6, Cl-GC6, and GC6 materials exhibited capacitances of 8, 400, and 30 μF/cm^2, respectively. The F-GC6 capacitance was consistently lower than the 30–70 μF/cm^2 typical of GC electrodes.[74] The electron-transfer rate constant calculated from the difference in peak potentials[74] averaged $(5.2 \pm 1.5) \times 10^{-3}$ cm/s for five different electrodes. The Cl-GC6 surface exhibited comparable and slightly lower rate constants of 1.0×10^{-3} cm/s. These rate constants are similar to those for many GC and graphite electrodes which have rate constants ranging from 0.001 to 0.01 cm/s.[75] However, they are not as high as those observed for activated GC surface which can be as high as 0.8 cm/s.[75,76]

---

(68) Kaeble, D. H. *J. Adhesion* **1970**, *2*, 66.
(69) Donnet, J. B. *Carbon* **1986**, 762.
(70) Schrader, M. E. *J. Phys. Chem.* **1975**, *79*, 2508.
(71) Polishing was accomplished using 1.0-, 0.3-, and 0.05-μm alumina paste sequentially, followed by sonicating in nanopure water for 5 min.
(72) Watanabe, N.; Nakajima, T.; Ohsawa, N. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2029.
(73) Donnet, J. B. *Bienn. Conf. Carbon* **1981**, *15*, 267.
(74) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.
(75) McCreery, R. L. *Electroanal. Chem.* **1991**, *17*, 221.
(76) Rice, R. J.; Pontikos, N.; McCreery, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 4617.

Thus, halide doping into the GC has minimal effects on electron-transfer kinetics to GC, at least for the conditions employed here. The lower rates observed for the GC6 materials may be due in part to residual surface impurities from the curing atmosphere.

The Cl-GC6 and F-GC6 materials contain a high level of chlorine and fluorine dopants in a glassy carbon matrix. These materials are markedly different from conventional GC in both their physical properties and their surface energies. Significantly, these halogen doped GC materials allow a degree of control over the hydrophobicity of the surface of carbon materials by the homogeneous, rather than surface, modification of glassy carbon. These GC6 materials exhibit low voltammetric background currents and reasonably efficient electron transfer rates. We are continuing to explore the use of these materials in various electrocatalytic systems.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9007132) for their financial support of this work and to the Center for Materials Research of the Ohio State University for partial support of this effort. We are also grateful to Mr. Roy Tucker and Ms. Clare McDonald for their valuable assistance in obtaining the XPS and SEM data, respectively.