21. Yamashita, H., Ohtsuka, Y., Yoshida, S. and Tomita, A., *Energy Fuels*, 1989, **3**, 686.
22. Yamashita H. and Tomita, A., *Ind. Eng. Chem. Res.*, 1993, **23**, 409.
23. McKee, D.W., in *Chemistry and Physics of Carbon*, vol. 16, ed P. L. Walker, Jr. and P. A. Thrower, Dekker, New York, 1981, pp. 1-118.
24. Baker, R.T.K., NATO SCI Series E, *Applied Science*, 1986, **105**, 231.
25. Hüttinger, K.J., Alder J. and Hermann, G., in *Carbon and Coal Gasification*, NATO ASI Series, ed. J. L. Figuereido and J. A. Moulijn, Martinus Nijheff, Dordrecht, Netherlands, 1986, p.213.
26. Yamashita, H., Yoshida S. and Tomita, A., *Energy Fuels*, 1991, **5**, 52.

Electrochemical behavior of flexible graphite

C. A. Frysz
Wilson Greatbatch Ltd., 10,000 Wehrle Drive
Clarence, NY 14031, U.S.A.

D. D. L. Chung
Composite Materials Research Laboratory, Furnas Hall
State University of New York at Buffalo
Buffalo, NY 14260-4400, U.S.A.

(Received 12 November 1996; accepted in revised form 14 March 1997)

Key Words - A. exfoliated graphite, D. electrochemical properties.

Flexible graphite refers to exfoliated graphite flakes which have been compressed without a binder, so that they mechanically interlock and shear, forming a flexible sheet that resembles a piece of paper that can be cut easily (e.g. with scissors). Flexible graphite is used mainly for gaskets for fluid sealing [1-5]. This paper provides the first study of the electrochemical behavior of this material, as the flexibility, ease of shaping and unusual microstructure, compared to other forms of carbon, suggest possible attraction for its use as an electrode material in batteries, for electrolysis, or in sensors. In the case of batteries, flow cell developers concentrate efforts on developing low-cost, solid carbon and graphite electrodes. The current technology utilizes carbon polymer composite structures, glassy carbon or dense graphite. These materials limit electrode design in that they are not very flexible, and especially in the case of glassy carbon are difficult to shape. Regarding electrolysis, platinum is commonly the electrode material of choice. However, it is very expensive. Therefore, practical electrodes which are corrosion resistant, low in cost and electrocatalytically active are desired. Carbon and graphite satisfy these requirements. Flexible graphite offers the advantage of shapeability. Finally, carbon and graphite electrodes are characteristically used as sensors for detecting organic and inorganic species in solution. Typically selected are glassy carbon, which is hard, brittle and poses some problem when it comes to forming or shaping, and polymer coated or polymer bound graphites, which are often limited to use in aqueous media given the incompatibility of the coating or binding media with organic or inorganic electrolytes. Like the previous cases cited, flexible graphite offers easy forming and shaping, and, because flexible graphite is uncoated and devoid of binders, it provides excellent chemical compatibility in all electrolytes as well as thermal stability.

Two thicknesses of flexible graphite (Grade GTB) were supplied in the form of a sheet by EGC Enterprises Inc., Mentor, Ohio. The sheet thickness of one sample measured 0.38 mm, whereas that of the second measured 3.75 mm. Electrochemical testing was performed by cyclic voltammetry (CV), using the method and setup described in [6]. A saturated calomel electrode served as the reference and a platinum wire as the auxiliary electrode. Three working electrodes were fabricated and separately tested. The working electrode comprising the thinner flexible graphite was fabricated by cutting a rectangular sheet sample, 6 mm x 10 mm, piercing the end of the rectangular sheet sample with a copper wire, coating the connection with conductive carbon paint and inserting the assembly into a glass tube. The free end of the flexible graphite sheet sample was fixed at 5 mm from the edge of the glass tube. The total exposed electrode surface area (which comprised predominantly the area in the plane of the sheet, i.e., the basal plane of graphite, yielding a basal-to-edge surface area ratio of 10) was 66 mm^2. Two electrodes using the thicker flexible graphite sheet were fabricated in the same manner as the thinner electrode. One electrode was 11 mm wide (a basal-to-edge surface area ratio of 1.5, and an exposed surface area of 190 mm^2), whereas the second was 4 mm wide (a basal to edge surface area ratio of 0.75, and an exposed surface area of 90 mm^2). In every case, the glass tube was filled with polyester and the polyester cured, leaving the extending flexible graphite exposed and uncontaminated for CV testing. The CV current densities were calculated by dividing the measured current by the area of the exposed electrode surface area.

The rate constant for electron transfer (k_s), the capacitance and the electrochemical area were calculated from the CV data, using the method in [6].

Fig. 1 displays the cyclic voltammogram obtained for the thinner flexible graphite with a basal-to-edge ratio of 10, while Figs. 2, 3 and 4 are for the thicker flexible graphite of ratios 15, 1.5 and 0.75 respectively. In each figure, the curve with the lowest positive peak current density is associated with the 20 mV/s scan, whereas the highest positive peak current density is associated with the 200 mV/s scan. The degree of electrochemical reversibility increased as the

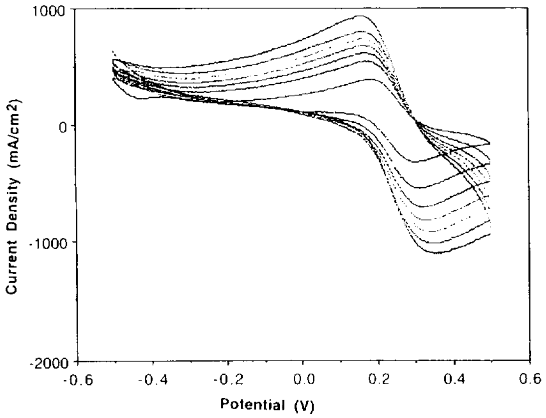

Fig. 1. Cyclic voltammetry results for thin flexible graphite with a basal-to-edge ratio of 10.

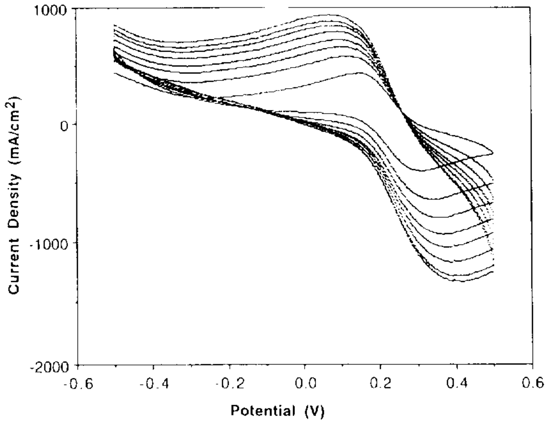

Fig. 2. Cyclic voltammetry results for thick flexible graphite with a basal-to-edge ratio of 15.

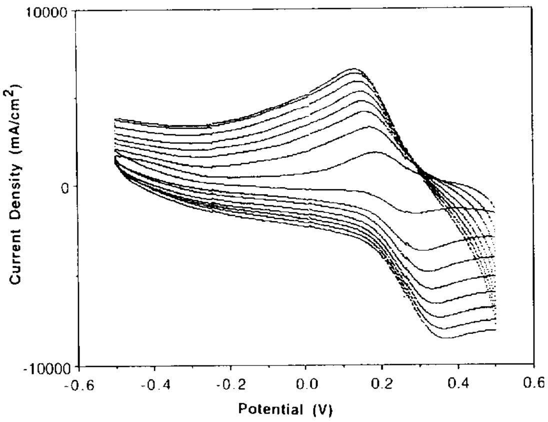

Fig. 3. Cyclic voltammetry results for thick flexible graphite with a basal-to-edge ratio of 1.5.

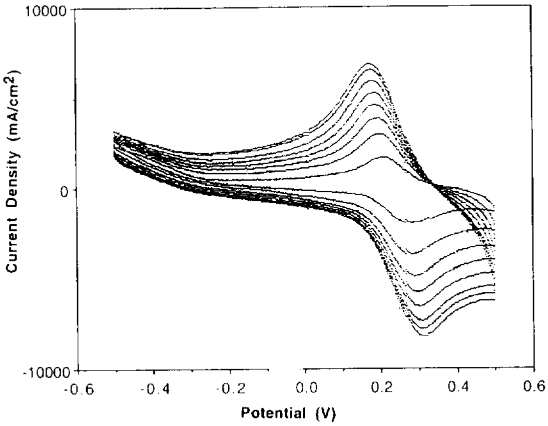

Fig. 4. Cyclic voltammetry results for thick flexible graphite with a basal-to-edge ratio of 0.75.

basal-to-edge ratio decreased. This is shown by the ratio of the anodic peak current density to the cathodic peak current density approaching 1 (Table 1). Irreversibility shifted to quasi-reversibility when the basal-to-edge ratio went below 15. The peak current densities also increased with decreasing basal-to-edge ratio. The electron transfer rate constant, k_s, for the thinner flexible graphite sample (basal-to-edge ratio of 10) was calculated to be 0.0031 cm/s (Table 2), twice that obtained for the thicker sample of ratio 1.5, but half that of the thicker sample of ratio 0.75. The difference in the k_s results between the thick and the thin samples may be attributed to differences in the amount of surface functional groups between the two samples, as the residual intercalate concentration may differ between them [7]. Comparison of the thicker sample k_s results, however, indicates an increase in electron transfer rate with a decrease in the basal-to-edge ratio, i.e., with an increase in edge plane sites. A similar effect was observed with electrochemical area, A (Table 2), which increased with decreasing ratio (thick flexible graphite samples). The capacitance, C, of the samples evaluated

Table 1 Cyclic voltammetry results obtained at a potential scan rate of 200 mV/s

Carbon type	Anodic peak current density I_a (mA/cm^2) (± 25)	Cathodic peak current density I_c (mA/cm^2) (± 25)	I_a/I_c (±0.2)	Peak separation ΔE (mV) (± 10)
Flexible graphite[a] (basal/edge ratio of 10)	1100	504	2.2	206
Flexible graphite[b] (basal/edge ratio of 15)	1032	115	8.9	338
Flexible graphite[b] (basal/edge ratio of 1.5)	4761	2321	2.1	236
Flexible graphite[b] (basal/edge ratio of 0.75)	6285	3231	1.9	138
Carbon paste[c]	975	704	1.4	222
Glassy carbon[c]	1213	1040	1.2	122

[a]Thickness = 0.015 in. (0.38 mm); [b]Thickness = 0.150 in. (3.81 mm); [c]From [7].

Table 2 Electrochemical behavior

Carbon type	k_s (cm/s) ± 0.0002	Capacitance† (μF/cm^2), ± 0.05	Electrochemical area* (cm^2) ± 5
Flexible graphite[a] (basal/edge ratio of 10)	0.0031	1.16	96
Flexible graphite[b] (basal/edge ratio of 15)	irreversible	2.09	28
Flexible graphite[b] (basal/edge ratio of 1.5)	0.0014	1.92	40
Flexible graphite[b] (basal/edge ratio of 0.75)	0.0071	3.10	105
Carbon paste[c]	0.0023	2.43	27
Glassy carbon[c]	0.0090	1.56	17

[a]Thickness = 0.015 in. (0.38 mm); [b]Thickness = 0.150 in. (3.81 mm); [c]From [7].
†Calculated using outer planar area; *Geometric area = exposed electrode area

essentially increased with a decreasing ratio, i.e., with decreasing basal plane area, as the difference between C values of 2.09 and 1.92 μF/cm^2 in Table 2 is small.

These results are compared to those similarly obtained for conventional carbon paste shown in Tables 1 and 2 (ΔE = 222 mV, k_s = 0.0023 cm/s, C = 2.43 μF/cm^2, and A = 27 cm^2) and glassy carbon (ΔE = 122 mV, k_s = 0.0090 cm/s, C = 1.56 μF/cm^2, and A = 17 cm^2) [8]. The flexible graphite displays higher k_s compared to carbon paste in the case of the thin flexible graphite with high basal plane area, and the thick flexible graphite with a low basal plane area. In the case of the thin flexible graphite, the higher k_s may be due to different surface functional groups, whereas in the case of the thicker flexible graphite, to the increased number of edge sites. The k_s of both these flexible graphite samples is lower than that of glassy carbon, which most likely has a higher k_s value due to electrode surface preparation involving polishing using diamond powder and a soft polishing cloth affixed to a rotating polishing wheel, followed by a thorough rinse in deionized water. The capacitance, C, is lowest for the thin flexible graphite compared to carbon paste and glassy carbon, probably due to the surface functional group differences. The electrochemical area, A, is highest for the thick flexible graphite with ratio of 0.75, probably due to the contribution to electrochemical activity made by the edge sites. Compared to carbon paste therefore, flexible graphite is capable of offering better electron transfer rate, higher electrochemical area, and lower capacitance, without the need of a binder for flexibility. It is also easily cut into flat sheets. On the other hand it offers a lower electron transfer rate compared to glassy carbon, which is an electrode material that is very difficult to machine. The electron transfer rate, however, increases with increasing number of edge sites. Flexible graphite can display lower or higher capacitance compared to glassy carbon, depending on the ratio of basal to edge sites. Its electrochemical area is, in general, much higher than those of glassy carbon and carbon paste.

REFERENCES

1. Shane, J.H., Russell R.J. and Bochman, R.A., US Patent No. 3404061, 1968.
2. Huang, Z., *Runhua Yu Mifeng,* 1981, **6**, 28.
3. Shi L. and Fan, Y., *Runhua Yu Mifeng,* 1981, **27**, 17.
4. Flitney, R.K., *Tribology Int.* 1986, **19**, 181.
5. Chung, D.D.L., *J. Mater. Sci.* 1987, **22**, 4190.
6. Shui, X., Frysz, C.A. and Chung, D.D.L., *Carbon* 1995, **33**, 1681.
7. Kinoshita, K., *Carbon Electrochemical and Physicochemical Properties,* Wiley, New York, 1988, p. 297.
8. Frysz, C.A., Shui X. and Chung, D.D.L., *Carbon* (in press).

The effect of morphology on the properties of vapour-grown carbon fibres

F. W. J. Van Hattum[1], Ph. Serp[2], J. L. Figueiredo[2] and C. A. Bernardo[1]
[1] Departamento de Engenharia de Polímeros, Universidade do Minho, 4810 Guimarães, Portugal
[2] Laboratório de Catálise e Materiais, Faculdade de Engenharia, Universidade do Porto, 4099 Porto, Portugal

(Received 11 February 1997; accepted 4 March 1997)

KeyWords - A.carbon fibres, D.morphology, mechanical properties, surface properties.

Vapour Grown Carbon Fibres (VGCF) can be prepared via catalytic decomposition of a gaseous carbon source, such as methane or natural gas. Due to their potentially low cost, there has been a growing interest in the applications of these fibres, namely in polymer matrix composites [1-3]. This, in turn, has focused attention on their mechanical properties, as they control the overall properties of the composites. To determine the mechanical properties with sufficient accuracy it is necessary to know the geometrical characteristics of the fibres. The carbon fibres normally used in engineering applications have regular geometries, namely a circular cross-section, whose diameter does not vary significantly along the length. However, as a result of