

ELECTROCHEMICAL BEHAVIOR OF FLEXIBLE GRAPHITE

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Introduction

Flexible graphite refers to exfoliated graphite flakes which have been compressed without a binder, so that the exfoliated flakes mechanically interlock and shear, forming a flexible sheet. It is used mainly for gaskets for fluid sealing [1]. This paper provides the first study of the electrochemical behavior of this material. 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. Platinum, however, 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 and inorganic electrolytes). Flexible graphite offers easy forming and shaping, and, because flexible graphite is uncoated and absent of binders, provides

excellent chemical compatibility in all electrolytes as well as thermal stability.

Experimental

Two thicknesses of flexible graphite (Grade GTB) were supplied in the form of sheets 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 Ref. 2. 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 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 mm². 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 mm²), whereas the second was 4 mm wide (a basal to edge surface area ratio of 0.75, and an exposed surface area of 90 mm²). 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 of Ref. 2.

Results and Discussion

The degree of electrochemical reversibility increases (as shown by the ratio of the anodic peak current density to the cathodic peak current density more approaching 1) as the basal-to-edge ratio decreased, with irreversibility shifting to quasi-reversibility when the basal-to-edge ratio went below 15. The peak current densities also increased with a 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, 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. Comparison of the thicker sample k_s results, however, indicate 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 , which increased with decreasing ratio (thick flexible graphite samples). The capacitance, C , of the samples evaluated essentially increased with a decreasing ratio, i.e., with decreasing basal plane area.

These results are compared to those similarly obtained for conventional carbon paste ($\Delta R = 222$ mV, $k_s = 0.0023$ cm/s, $C = 2.43$ $\mu\text{F}/\text{cm}^2$, and $A = 27$ cm^2) and glassy carbon ($\Delta E = 122$ mV, $k_s = 0.0090$ cm/s, $C = 1.56$ $\mu\text{F}/\text{cm}^2$, and $A = 17$ cm^2) [3]. 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 glassy carbon; glassy carbon most likely has a higher k_s value due to electrode surface preparation involving polishing using diamond powder and soft polishing cloth affixed to a rotating polishing wheel, then thorough rinsing 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.

Conclusions

Compared to carbon paste, flexible graphite is capable of offering better electron transfer rate, higher electromechanical area, and lower capacitance, without the need of a binder for flexibility. Flexible graphite is also easily cut into flat sheets. Flexible graphite, on the other hand, offers 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 glassy carbon or carbon paste.

References

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