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Carbon electrodes: Part 1. Hydrogen evolution in acidic solution

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The hydrogen evolution reaction has been studied using electrodes of vitreous carbon and graphite. The relative activity of the surfaces in promoting the hydrogen evolution reaction was found to be pyrolytic edge $\approx$ vitreous carbon $>$ pyrolytic face. Comparative measurements of the double-layer capacitances indicate that relative activity cannot be entirely explained in terms of relative surface areas. The activity of the surfaces was found to be very sensitive to electrode pretreatment. Kinetic parameters are presented for the hydrogen evolution reaction on these carbons.

Introduction

Carbon anodes have been used in many oxidations of organic materials [1, 2], but in relatively few cases have comparative studies of their performance been made [3]. Recently [4] it has been shown that different carbons do not behave identically in the oxidation of heptanoate anions, graphites producing products characteristic of carbonium ion intermediates whereas hard carbons gave substantial amounts of Kolbe products. It would seem therefore that, at least in reactions involving adsorbed intermediates, there exists a need to characterize clearly various carbons. Morcos and Yeager [5] have studied the reduction of oxygen on pyrolytic graphite face and edge orientations.

In this work we compare the activity of an isotropic carbon, vitreous carbon, with the activities of the two orientations of pyrolytic graphite in the hydrogen evolution reaction in acid solutions.

Experimental

(i) *Apparatus*

The electrolyte used in this study was molar perchloric acid, prepared from 'Aristar' (B.D.H.) grade perchloric acid and thrice distilled water. For the studies in 0·1 M and 0·01 M acid the overall ionic strength of the electrolyte was maintained by the addition of 'AnalaR' (B.D.H.) grade sodium perchlorate. The acidity of the electrolyte was determined by titration with standardized sodium hydroxide solution.

Pyrolytic graphite was obtained in the form of plate from Le Carbone Ltd., and was machined into discs. Vitreous carbon was obtained as rod from Vitreous Carbons Ltd. The electrodes were constructed by fixing a cylinder of the material on to a brass holder with a conducting cement (Johnson–Matthey). The whole was then encased in 'Flo-Tite' heat shrink p.t.f.e. tubing (Pope Scientific Inc., U.S.A.). The brass holder was bored to take a rotating shaft (Fig. 1).

The pyrolytic face electrode was prepared by removing a thin flake with a sharp razor blade. The pyrolytic edge electrode was prepared by cutting with a fine hacksaw and then slight polishing on fine emery paper to remove saw marks. The vitreous carbon was prepared by grinding with coarse emery paper, followed by polishing with fine emery paper and 'Gamma' grade alumina polishing powder (Griffin & George). All the electrodes were thoroughly washed in a jet of thrice-distilled water after preparation.

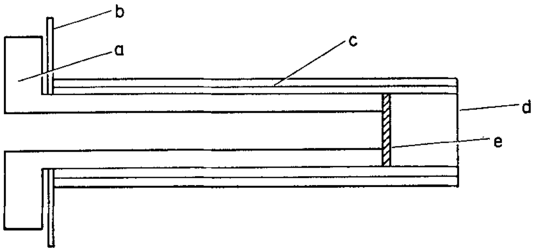

Fig. 1. Working electrode design (a) Brass holder, (b) p.t.f.e. collar, (c) 'Flo-Tite' tubing (double walled), (d) electrode material, (e) conducting cement).

The cell (Fig. 2) was a divided cell of 150 ml capacity in Pyrex glass. Incorporated in the design was a small gas-operated bubble pump which continuously filtered the electrolyte through a bed of activated carbon which had previously been demetallized by prolonged leaching with constant boiling hydrochloric acid. Deoxygenation was achieved by flushing with a stream of nitrogen. The cell was allowed to deoxygenate and filter for one hour after introducing the electrolyte before measurements were made.

The counter electrode was a platinum plate of area 2 cm^2. The reference electrode was a palladium sphere of diameter 0·2 cm on a palladium wire which was sealed into glass. Before an experiment the sphere was cathodically charged with hydrogen in a molar solution of perchloric acid at a current of 200 mA. The potential of the Pd/H_2 electrode is given by Ratchford and Castellan [6] as +0·0504 V with respect to the standard hydrogen electrode. A check on the electrode used in this study showed that it maintained its potential with respect to a hydrogen electrode for >12 hours on one charge of hydrogen. This was a sufficient length of time for observations to be recorded.

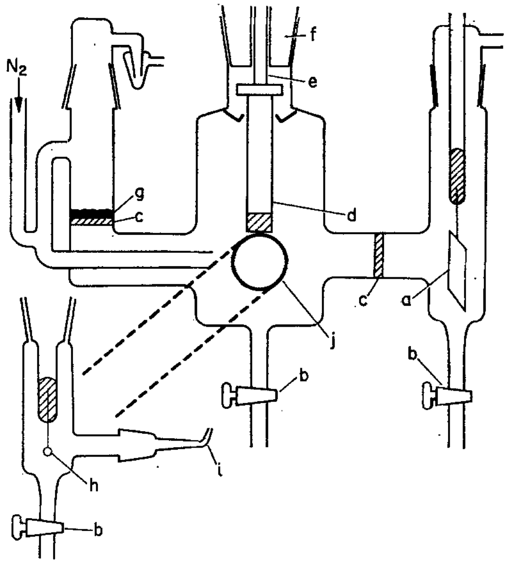

Fig. 2. The electrochemical cell (a) counter electrode, (b) taps, (c) sinters, (d) working electrode, (e) stainless steel shaft, (f) p.t.f.e. cone, (g) activated carbon, (h) reference electrode, (i) Luggin capillary, (j) B19 ground-glass joint).

The potentiostat and function generator are described elsewhere [7, 8]. Current decay curves were recorded on a TOA pen recorder. Voltammograms were photographed from a Tektronix type 503 oscilloscope. Electron micrographs were taken from a Cambridge Stereoscan Type 2A.

(ii) *Procedure*

Current-voltage curves over a range of several hundreds of millivolts were built up in 160 mV increments by a combined pulse-linear potential sweep technique. A pulse to the desired starting potential was used to trigger the sweep (Fig. 3). The reason for obtaining voltammograms in this fashion was the requirement to pass as few couloumbs as possible during a measurement in order to eliminate complications due to changes in the electrode surface.

The de-activation of the electrodes was studied by: (i) taking voltammograms using electrodes which had been cathodically pretreated, (ii) observing the current decay with time for an electrode (this procedure was used only for the pyrolytic face electrode) and (iii) recording

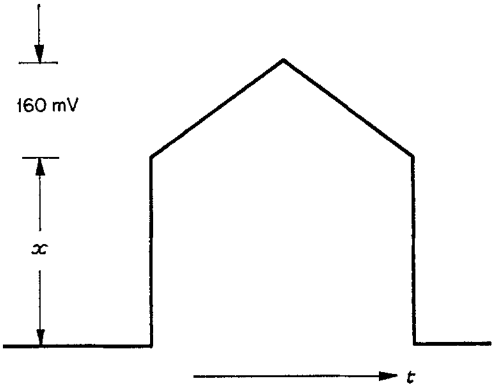

Fig. 3. Signal applied to potentiostat.

polarization curves at slow (0·1 mV sec^{-1}) scan rates.

Before and after polarization measurements the double-layer capacitances of the electrodes were measured as charging currents by linear potential sweeps at varying sweep rates in potential regions where no Faradaic currents were obtained.

Results

All potentials are quoted relative to Pd/H_2 in the working solution unless otherwise mentioned. No reversibility was detected in the potential sweep measurements, only cathodic currents being observed during anodic scans.

The current-voltage curves were plotted in the form log i *v.* E and extrapolated to the reversible hydrogen potential to obtain the apparent exchange current densities (i_0). Table 1 lists the measured parameters for both newly prepared electrodes and those which had been cathodically polarized at −0·8 V.

Table 1.

Electrode	i_0 (*A* cm^{-2})	*Tafel slope* V
Pyrolytic edge		
New	$8·8 \times 10^{-7}$	0·14
Pretreated	$4·7 \times 10^{-8}$	0·18
Vitreous carbon		
New	$6·8 \times 10^{-7}$	0·14
Pretreated	$6·4 \times 10^{-7}$	0·17
Pyrolytic face		
New	$5·8 \times 10^{-8}$	0·18
Pretreated	$4·9 \times 10^{-9}$	0·17

The parameters obtained from a linear potential sweep at 0·1 mV sec^{-1} were: (1) Edge, slope of 0·15 V, i_0 $2·29 \times 10^{-8}$ A cm^{-2}, (2) face, slope of 0·11 V, i_0 $2·61 \times 10^{-11}$ A cm^{-2}. Fig. 4, 5 and 6 show the relevant Tafel plots.

The figures show that the relative activities of the electrodes with respect to hydrogen evolution are pyrolytic edge ≈ vitreous carbon > pyrolytic face. There is also a decrease in activity when the electrode has been cathodically pretreated. This passivation of the electrodes was an extremely complex phenomenon, apparently involving several different processes which occurred at various rates. On switching a fresh electrode into the hydrogen evolution region the current fell immediately and continued to do so over a period of many minutes, commonly reaching less than 1% of the initial value. Partial reactivation resulted from scanning to more cathodic potentials; Fig. 7 shows the hysteresis observed at low scan rates. Switching to potentials positive to the region in which the H.E.R. took place also had the effect of reactivating the surface in subsequent cathodic measurements.

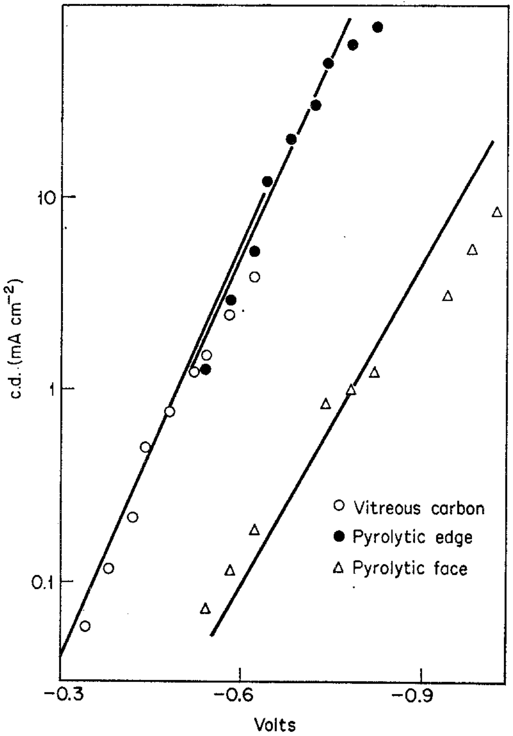

Fig. 4. Tafel plots for fresh electrode surface ($HClO_4$ 1·0 M, electrode rotation speed 150 rad sec^{-1}, sweep rate 1 V sec^{-1}). The points for each electrode are in groups of three, each group being obtained from a separate linear potential sweep of 0·16 V.

Fig. 8 shows a typical current decay curve for a pyrolytic face electrode upon being switched from +0·65 V to −0·5 V. Fig. 9 shows the reactivating effect of anodic polarization for different lengths of time. Fig. 10 shows the effect of anodic potential upon the reactivating process. Fig. 11 shows the decline in effectiveness of anodic reactivation with time, suggesting that an additional process of passivation is involved which cannot be reversed by anodic treatment.

If, instead of considering i_0 values, the current

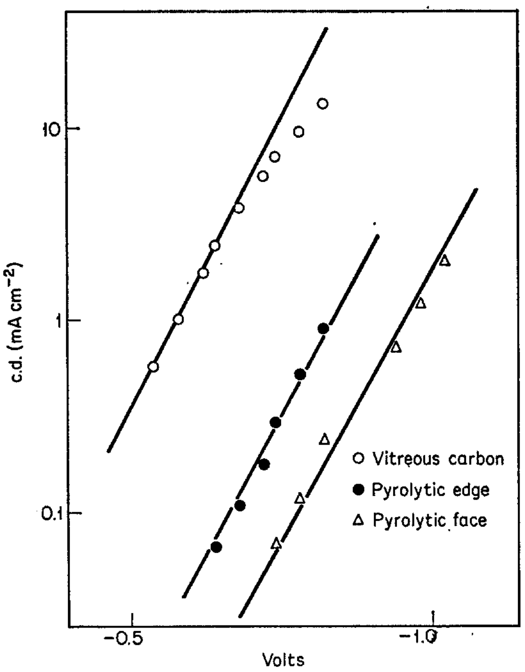

Fig. 5. Tafel plots for cathodically polarized surface ($HClO_4$ 1·0 M, electrode rotation speed 150 rad sec^{-1}, sweep rate 1 V sec^{-1}). The points for each electrode are in groups of three, each group being obtained from a separate linear potential sweep of 0·16 V.

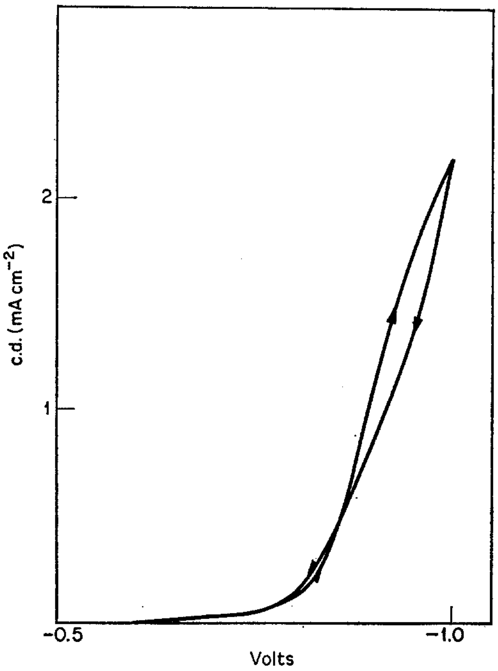

Fig. 7. Polarization curve for pyrolytic face electrode with slow linear potential sweep ($HClO_4$ 1·0 M, electrode rotation speed 150 rad sec^{-1}, sweep rate 0·1 mV sec^{-1}).

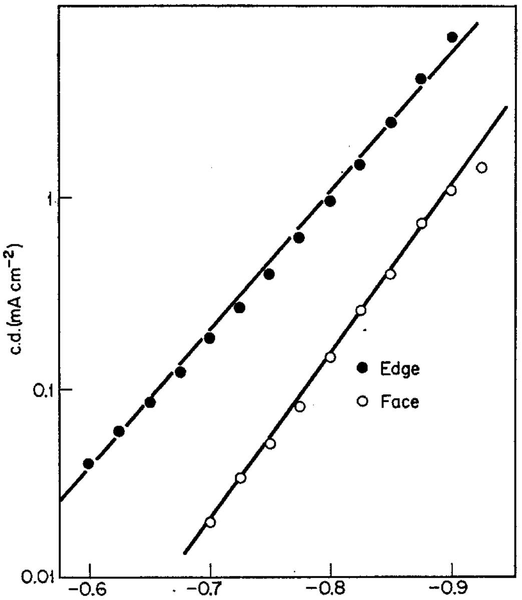

Fig. 6. Tafel plots for slow linear potential sweeps ($HClO_4$ 1·0 M, electrode rotation speed 150 rad sec^{-1}, sweep rate 0·1 mV sec^{-1}). The Tafel plot was made from the cathodic polarization curve only.

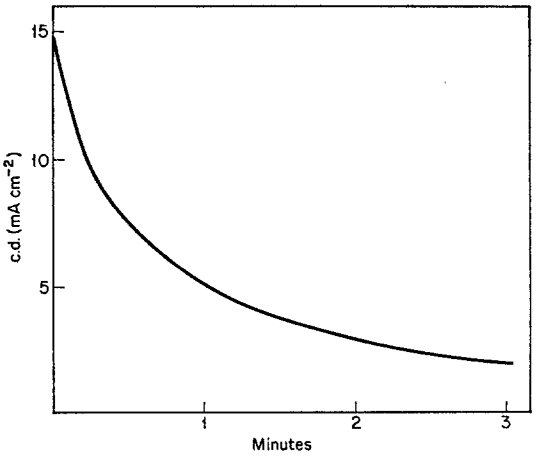

Fig. 8. Current density-time decay curve ($HClO_4$ 1·0 M, electrode rotation speed 150 rad sec^{-1}, pyrolytic face electrode). The electrode was switched to −0·5 V after anodic treatment at +0·65 V.

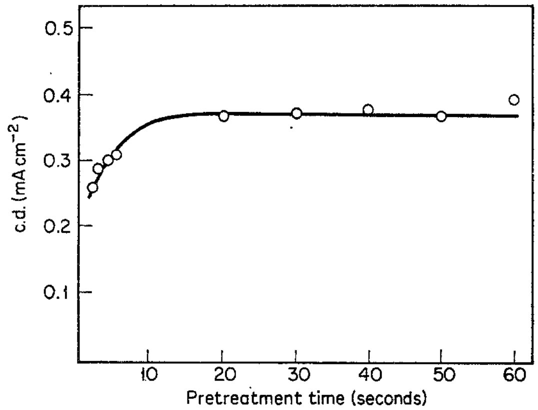

Fig. 9. Initial current density obtained upon switching from 0·00 V to $-0{\cdot}5$ V after different pretreatment times ($HClO_4$ 1·0 M, electrode rotation speed 150 rad sec $^{-1}$, pyrolytic face electrode).

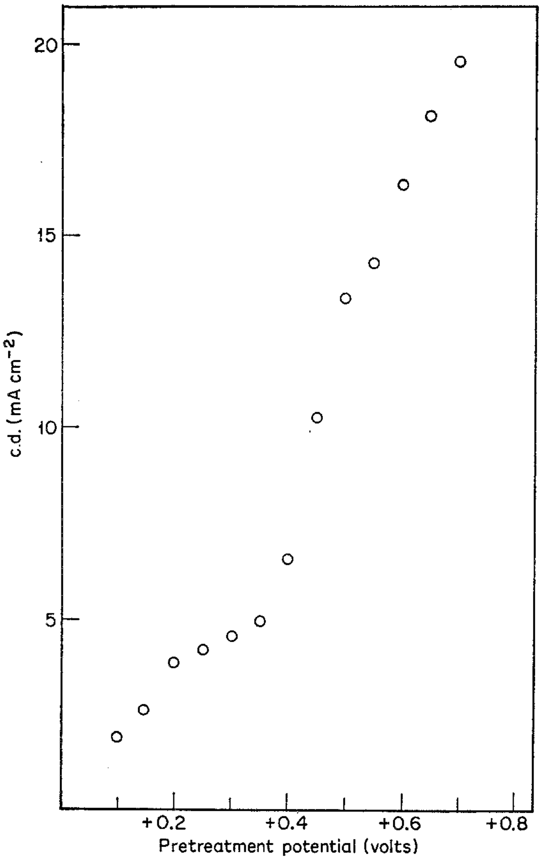

Fig. 10. The effect of anodic pretreatment potential upon the initial current density obtained on switching to $-0{\cdot}5$ V. The points were taken with the pretreatment potential becoming progressively more anodic ($HClO_4$ 1·0 M, electrode rotation speed 150 rad sec^{-1}, pyrolytic face electrode, pretreatment time 10 seconds).

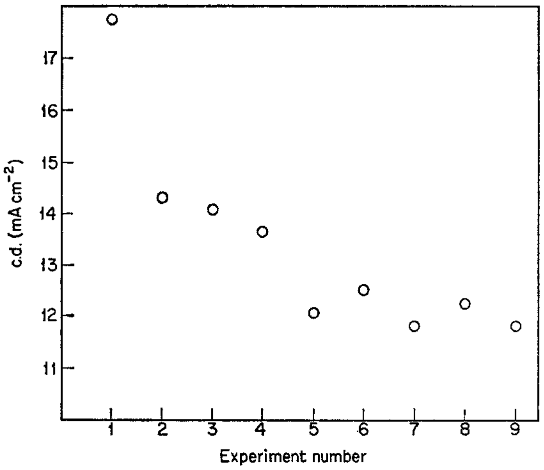

Fig. 11. The diminishing effect of successive anodic pretreatments at $+0{\cdot}65$ V upon the initial current density obtained upon switching to $-0{\cdot}5$ V. The current density was allowed to decay to 0·7 mA cm^{-2} between each experiment. ($HClO_4$ 1·0 M, electrode rotation speed 150 rad sec^{-1}, pyrolytic face electrode.)

densities obtained for the different electrodes at a constant potential are compared, the differences in activity are more clearly manifested. Table 2 shows the current densities obtained for the three electrodes at a chosen potential. These figures reinforce the conclusions drawn previously concerning the relative activities of the three electrodes and also confirm another trend shown in Table 1, i.e. that the passivating effect of cathodic treatment is much greater on the graphite electrodes than on the vitreous carbon electrode.

Table 2.

Electrode	*c.d. at $-0{\cdot}64$ V (mA cm^{-2})*
Pyrolytic edge	
New	12·7
Pretreated	0·06
Vitreous carbon	
New	4·71
Pretreated	3·01
Pyrolytic face	
New	0·27
Pretreated	0·03

To determine whether the relative activities of the electrodes could be explained in terms of surface area effects the double-layer capacitances of the electrodes were determined. The measurements obtained for pyrolytic edge and vitreous carbon were very sensitive to sweep rate; much more so than measurement on the pyrolytic face. The values given in Table 3 are the averages of measurements obtained at sweep rates of 0·3, 1·0 and 3·0 V sec^{-1}. Taking the capacitance values as a direct indication of the true surface areas of the electrodes the relative roughness factors for edge : vitreous : face are 12·8 : 7·5 : 1. The relative activities obtained from Table 2 are in the ratio 47·2 : 21·1 : 1.

Table 3.

Electrode	*Capacitance of new electrode $\mu F\ cm^{-2}$*	*Capacitance of pre-treated electrode $\mu F\ cm^{-2}$*
Pyrolytic edge	1397	629
Vitreous carbon	821	386
Pyrolytic face	109	45

An estimation of the order of the reaction with respect to hydrogen ion concentration was made by comparing current densities obtained at a chosen potential relative to the standard hydrogen electrode for the same electrodes in (a) 1·0 M perchloric acid, (b) 0·1 M perchloric acid/0·9 M sodium perchlorate. The results are shown in Table 4.

A measurement of the reaction order for the edge electrode was carried out to verify the unexpected result. The repetition indicated a reaction order of 2·40. In a further remeasurement using a 0·01 M perchloric acid solution the polarization waves were recorded at a rotation speed of 225 rad sec^{-1} and a scan rate of 0·3 V sec^{-1}. Results were plotted (Fig. 12) to test for first and second order behaviour. On the time scale of this measurement the order is clearly nearer to unity. The extrapolation of the first order plot to −0·68 V permitted comparison with the c.d. observed with 0·1 M electrolyte. At this potential the value of the reaction order was 1·5.

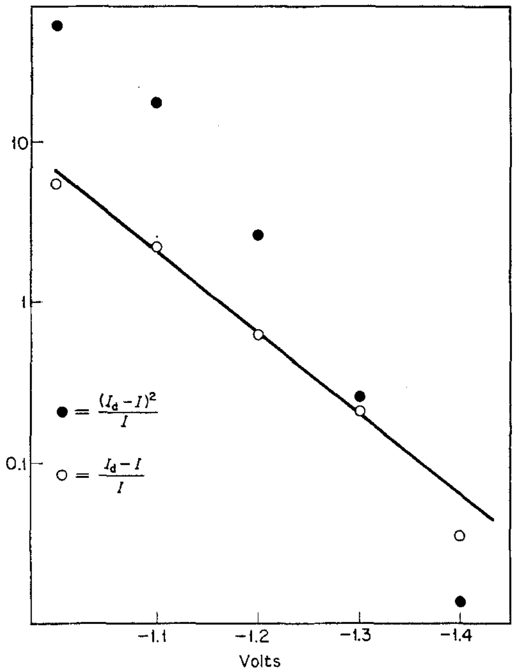

Fig. 12. Test plot for first and second order behaviour ($HClO_4$ 0·01 M $NaClO_4$ 0·99 M electrode rotation speed 225 rad sec^{-1}, sweep rate 0·3 V sec^{-1}, pyrolytic edge electrode area 0·44 cm^2).

Table. 4

Electrode	*c.d. in 1 M[H^+] mA cm^{-2}*	*c.d. in 0·1 M [H^+] mA cm^{-2}*	*Reaction order*	*Tafel slope in 0·1 M[H^+] V*
Pyrolytic edge (1)	4·13	0.04	2·04	0·20
Vitreous carbon(2)	1·29	0·117	1·04	0·25
Pyrolytic face(3)	0·69	0·69	1·06	0·16

(1) Measured at −0·55 V w.r.t. S.H.E.
(2) Measured at −0.47 V w.r.t. S.H.E.
(3) Measured at −0·70 V w.r.t. S.H.E.

S.H.E. = abbr. for standard Hydrogen Electrode.

Discussion

The order of activities of the three electrodes with respect to hydrogen evolution was observed to be pyrolytic edge $\approx$ vitreous carbon $>$ pyrolytic face. Comparison of the current densities obtained at a set potential with the relative roughness factors from Table 3 indicate that to some extent the relative activities could be explained in terms of surface area effects, but not entirely. These findings are similar to those of Morcos and Yeager [5], who reported that the pyrolytic edge electrode was more active than the face electrode in promoting the reduction of oxygen.

The results may not fully demonstrate the difference in activities between graphite planes and edges; the less active 'plane' surfaces undoubtedly, as indicated by the value of the roughness factor and by the electron micrograph (Fig. 13), contain many edges which could conceivably provide all the active centres. Likewise the large roughness factor of the nominal edge orientation arises from the exposure of planes; thus normalization of the activities on the basis of double-layer capacitance measurements may be misleading if the relative activities of idealized planes and edges are of interest.

It is possible here only to speculate upon the origins of the deactivation phenomena which were observed to occur at three electrodes during hydrogen evolution. The absence of oxidation currents on the anodic sweep indicate that surface coverage by hydrogen atoms is small. Deactivation by the physisorption of organic species occurring either as impurities or as products of the reduction of the carbon surfaces is believed to be unlikely as reactivation of the surface was not immediate and complete upon switching to extremes of potential at which the materials would be expected to desorb. Blocking of sites by deposition of trace metal impurities is rejected as a major cause for similar reasons.

Surface area may be reduced by the formation of hydrogen gas in pores and crevices in the electrode and smoothing through the mechanical removal of broken planes by hydrogen bubbles is to be expected on the edge orientation. Indeed the double-layer capacitance measurements before and after hydrogen evolution support this view.

A further mechanism of deactivation might be postulated in terms of the hydrogenation of active sites which may occur when pairs of neighbouring sites are simultaneously occupied by hydrogen atoms, an event which may be sufficiently infrequent to give the saturation effect the half-life of several minutes observed experimentally in the current-time decay curves.

The most unexpected result was the reaction order of approximately two for the hydrogen ion in the H.E.R. on the graphite edges whereas that found with vitreous carbon and pyrolytic faces was unity. This result would appear to disprove the view that reactivity of the nominal face surfaces derives from the edges exposed. Moreover it is necessary to postulate that the number of active sites on the edge orientation varies with the hydrogen ion concentration. This interpretation is supported by the observation that rapidly changing the hydrogen ion concentration at the electrode surface (by varying the potential when 0·01 M solutions were used) leads to a reaction order of near unity. Presumably the variation in surface activity with pH occurs more slowly and is 'frozen' by the measurement techniques. The change in the graphite edge with variation in pH may be attributable to the removal or modification of the numerous acidic or basic surface groups always present on carbons [9].

Acknowledgement

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