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Conference Paper

Electrochemical Studies on Different Glassy Carbon Electrodes* II. Corrosion and Double Layer Characteristics

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The consequences of heat treatment in production of glassy carbon has been investigated by scanning electron microscopy, ESCA and electrochemical methods. Correlation has been found between the temperature of treatment and the physical appearance and electrochemical reactivity. Glassy carbon appears to be a small band gap semiconductor with isolated well type surface states produced by residues of the surface oxidation processes.

I — INTRODUCTION

In a previous publication¹ we have presented a detailed study of the influence of the heat treatment temperature (HTT) on the kinetic parameters of a range of redox reactions. The intention of this publication is to present the previous results in the context of a broader range of studies of the surface of glassy carbons subjected to electrochemical treatment.

This presentation is therefore in part the presentation of new results and in part a correlation of the results obtained in the earlier study with these new observations. In general for a material to be of use as an electrode, it should be stable in a range of solvents and over a wide range of polarizations and display a high overpotential for the HER and the oxygen evolution reaction. Glassy carbon now finds extensive applications in electroanalysis, electro-synthetic and as a surface for chemically modified electrodes^{2,4}.

Dunsch⁵ has recently reviewed many of these applications and also our current knowledge of its fundamental properties. He concluded that in addition to the many applications already found for the material, it might be considered as a substitute for expensive metal electrodes in a much wider range of applications and pointed out that its price, its chemical inertness in all but strong oxidizing media and its stability under electrochemical conditions were advantages that could lead to viable commercial exploitation. He concluded that its fundamental properties were still inadequately understood and further research was necessary.

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Glassy carbon is an artificially produced material, a fact that presents advantages and disadvantages⁶. It is obviously not possible to define an absolute glassy carbon surface state as is possible with Pt⁷ or Au. The advantage is that because it is prepared at different temperatures from a range of resins, we have available another parameter to vary systematically in any investigation. In this study we ask the questions, what is the influence of these parameters on surface stability and how do they influence a commonly measured parameter such as the capacity?

EXPERIMENTAL

The details of the preparation of surfaces and materials have already been presented in the earlier publication¹. Three sources of electrode materials were used, Tokai EB-3 (HTT 3000 C), SIGRI Elektrographit, West Germany (HTT 1000 C and 2400 C) and the Department of Materials Sciences, University of Wales (Swansea), (HTT range from 606 to 1200 C) where HTT is the heat treatment temperature for the preparation of the particular sample. The AC bridge used during the studies described in section IV was classical in design.

II — PRELIMINARY STUDIES OF SUPERFICIAL SURFACE STRUCTURE

In this section we shall describe some of the preliminary studies made using scanning electron microscopy (SEM) and XPS. We were interested in the level of chemical purity in the surface of a sample that had been polished and that gave apparently a reproducible and characteristic voltammogram as a test of a 'good' surface state. In addition we wanted to know the degree of macroscopic heterogeneity of the surfaces at different HTT. As alumina was used to polish the electrodes we expected to find Al in the surface by XPS even after prolonged cleaning procedures. The only element conclusively found was calcium. SEM gave us a better insight into the surface. Inspection of the Figures 1a, b, c, d for samples over the whole range of HTT, shows the decreased incidence of pitting of the surface as the HTT increases. Previous studies have shown that the density of the material is consistent with a structure containing about 30% voids in the higher HTT materials. At lower HTT it seems likely that the dispersion of these voids through the material is less homogeneous so that the type of holes that are shown in Figure 1a remain.

The HTT of the material is not the only factor that is important as a comparison of Figures 1b and 1c reveals. The HTT is similar for both materials but the degree of pitting is very different. This implies that both the starting material and/or the detailed preparation procedures also play an important rôle in the formation of these structural features. The calcium found by XPS in some of these pits may have its origin in one of these last two factors.

Apart from the obvious influence of the roughness factor which differs markedly between the surfaces in Figures 1b and 1c, there is, from the electrochemical results, little influence of these pits on the results described in the following sections.

In the following studies we have used exclusively the voltammetric characteristics to identify properly prepared surfaces. The preparation of this reproducible surface state frequently required stripping 30 000 atomic layers to reveal an unperturbed surface. The reason why such drastic procedures were necessary is not entirely clear but may result from some carry-over effect during the polishing process.

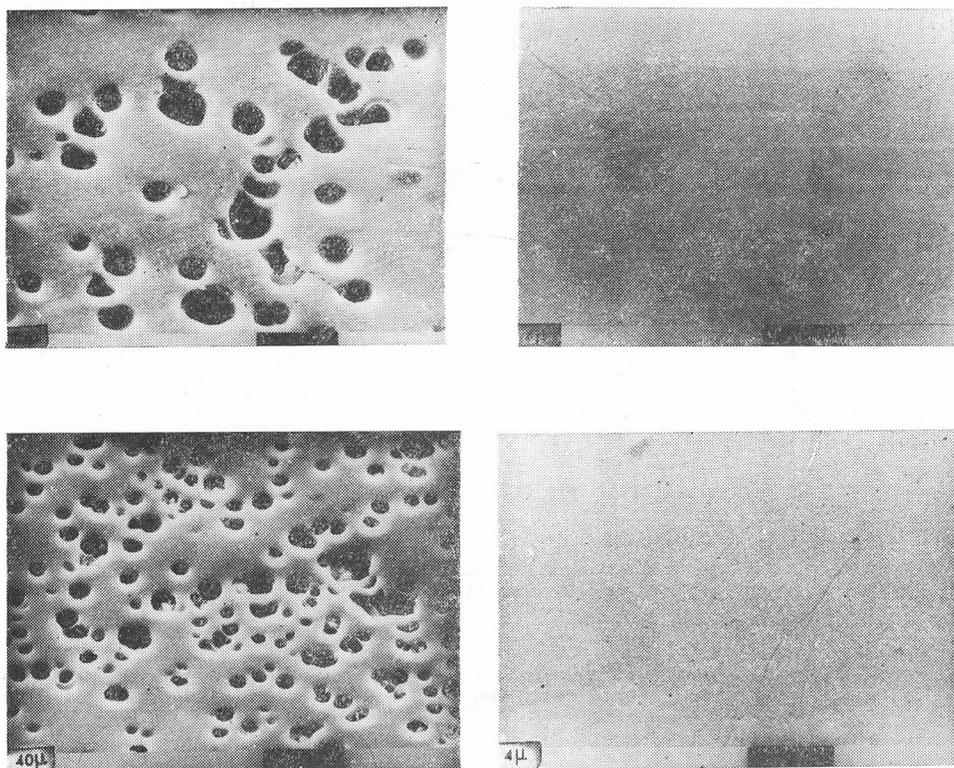


Figure 1. Scanning electron micrographs for a) Sw. 606, b) SIGRI 1000, c) Sw. 1000, d) Tokai 3000. Resolution indicated on each picture.

III — CHARACTERIZATION OF ELECTRODES UNDER EXTREMES OF POLARIZATION

The stability of glassy carbon electrodes is a factor of considerable importance to the prospective user of these electrode materials. In practice, the electrode should be mechanically stable under a wide range of polarization and should have high overvoltage characteristics for the production of hydrogen and oxygen. The usable potential range for these electrodes in the common mineral acids has been estimated by Zittel and Miller⁸ to be -0.8 to $+1.2$ V vs SCE. These authors suggest that in addition to the water decomposition reactions, the anions play a major rôle in the stability in nitric and hydrochloric acid solutions. Petak and Vydra⁹ reported that the surface undergoes a recrystallization process at high current densities and they consider that this is the principal factor limiting the use of these electrodes. We have carried out a further study of this behaviour in an attempt to relate the HTT and mechanical characteristics of the carbons to the electrochemical treatment of the electrode.

The first series of experiments concerned the influence of the scan reversal limits on the cyclic voltammogram.

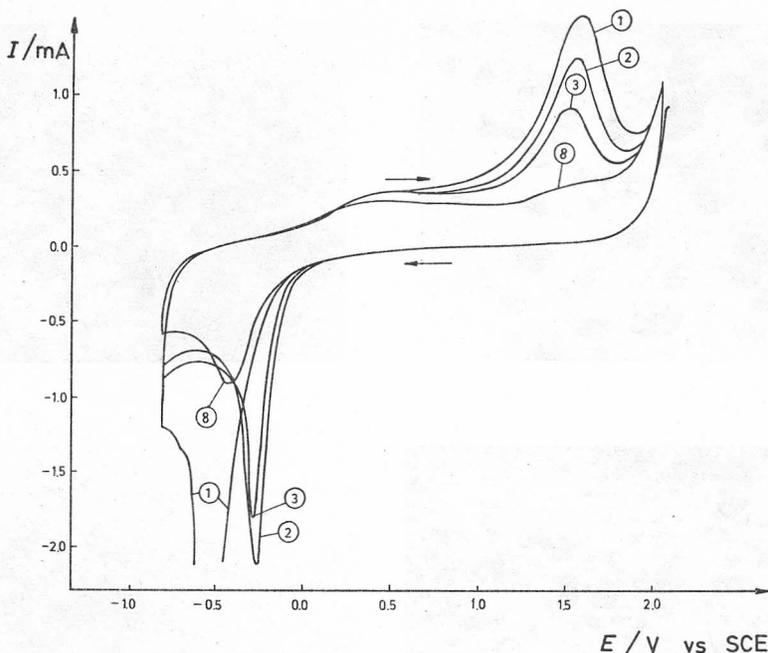


Figure 2. Glassy carbon electrode, Sw. 1093, freshly polished then preoxidized in the working solution for 20 s prior to initiating sweep sequence. Solution was 1.0 M HClO_4 , sweep rate 262 mV s^{-1} . The arrows indicate direction of cycling and the numbers are the cycle number in the sequence

A typical large amplitude voltammogram is shown in Figure 2. This shows the relaxation of the surface to a steady state after 20 s electrolysis at the positive reversal potential. The observed redox process is rather irreversible. Two important features should be noted; the progressive decrease with cycling of the oxidation peak height and the dependence of this peak potential on cycle number which can be contrasted with the behaviour of the reduction peaks. This latter feature decreases in size with cycle number but at the same time the potential of the peak shifts first in a positive direction (cycle 1 to cycle 2) and then on all succeeding cycles in a negative direction. This is a general feature of all oxidizable glassy carbon surfaces under these measurement conditions. As these characteristic peaks are absent in the steady state, the relaxation towards this steady state involves the removal or blocking of these redox surface sites if this behaviour is directly related to the phenomena described in the previous publication.¹ The active surface state can be immediately regenerated if the positive potential limit is increased at the same sweep rate. If this limit is increased slowly, a directly related growth in both the oxidation and reduction peak is observed. The potential of the reduction peak becomes more negative during this procedure which is similar to the behaviour observed on Pt^{10} . When the positive reversal potential exceeds 2.2 V, oxygen evolution occurs and prolonged cycling at this amplitude increases greatly the size of the redox peaks.

If the preelectrolysis potential is altered to 100 mV positive of the oxidation peak the characteristics in Figure 2 do not appear. We can compare our results

with those obtained by Laser and Ariel using the RRDE technique¹¹. They showed that on a polished glassy carbon electrode oxygen evolution started at about 1.0 V vs SCE (c. f. Figure 2). Our voltammetric curves are very similar over the same scanning range but whereas their scan was always terminated at 1.3 V vs SCE, we extended the scan to more positive potentials. In order to find out the extent to which the features in this positive potential region are controlled by solution processes, we studied the voltammetric behaviour at a rotating glassy carbon disc electrode. The characteristics in Figure 2 were independent of rotation rate supporting our hypothesis that these characteristics are related only to surface processes. In the presence of oxygen in the solution, a wave which is influenced by rotation speed occurred at -0.3 V. This corresponded to O_2 reduction and disappeared when the solution was thoroughly deoxygenated.

If the cathodic reversal potential is decreased to the HER potential the structure of the voltammogram in Figure 2 immediately disappears, irrespective of the positive reversal potential.

Cyclic voltammograms quite similar to those in Figure 2 were observed in 0.1 M $HClO_4$ and 0.5 M H_2SO_4 . In 0.15 M NaOH and 0.01 M $HClO_4$ in 90% ethanol water mixtures the voltammogram was also similar, but the development of the features was slower. This behaviour is not observed on natural graphite where the kinetics of formation of the electrochemically generated graphite oxide become more reversible as the non-aqueous content of the solution increases¹².

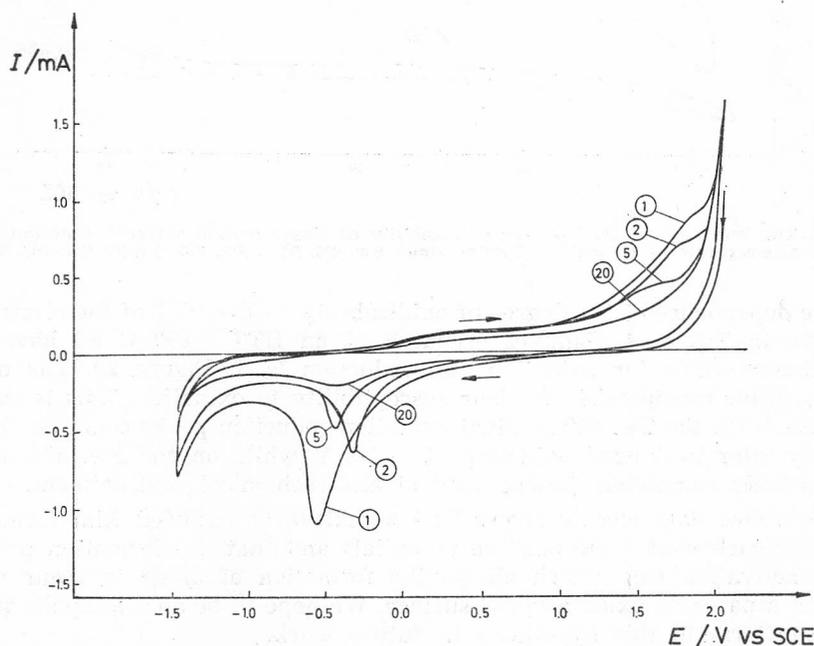


Figure 3. Glassy carbon electrode, SIGRI 2400 freshly polished then preoxidized in the working solution for 20 s prior to initiating sweep sequence. Solution was 0.5 M K_2SO_4 , sweep rate 344 $mV s^{-1}$. The arrows indicate sweep direction and the numbers are the cycle number in the sequence.

A typical voltammogram for neutral media is shown in Figure 3. There is the expected displacement of the HER to more negative potentials and in this case the surface reduction process and the HER are separated by nearly 1 V. With the positive limit the same as in Figure 2 the potential of the reduction peak retains the same dependence on cycle number. The oxidation peaks are much smaller and less well defined and this process is less easily carried out in this media. In contrast, the potentials of the reduction peaks seem to be independent of this change of solution.

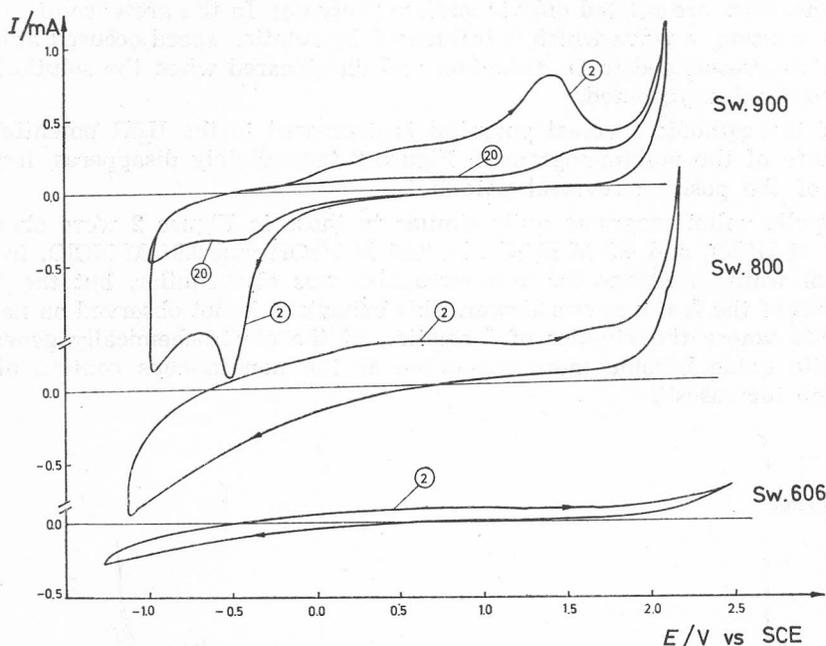


Figure 4. The influence of HTT on the oxidizability of glassy carbon surfaces. Solution 1.0 M HClO_4 at a sweep rate of 344 mV s^{-1} . Cycling times Sw. 900, 20 s; Sw. 800, 2 min; Sw. 606, 5 min.

The dependence of the degree of oxidizability on the HTT of the electrodes is shown in Figure 4. Samples prepared at an $\text{HTT} > 800 \text{ C}$ all have the same characteristic for oxidation and reduction (c. f. Figure 2.). The other samples differ considerably in their susceptibility to oxidation. This is shown in Figure 4. On the Sw. 800 residual oxidation-reduction peaks could be observed only after prolonged oxidation at $> 2.2 \text{ V}$ while on the Sw. 606, these features were completely independent of electrochemical pretreatment.

The above data clearly shows that a multilayer oxidized film forms on the glassy carbon at large positive potentials and that the formation process has an activation step which allows the formation of oxide to occur more easily on a partially oxide covered surface. We hope to be able to apply quantitative criteria to this hypothesis in future work.

The mechanical stability of the electrode under electrolysis at extreme positive potentials has already been investigated by Dodson and Jennings¹³. In their galvanostatic tests with a current density of 20 mA cm^{-2} , the electrode

was found to flake. These flakes disintegrate suddenly when heated below red heat. Chemically oxidized graphite behaves in the same way and the authors concluded that the surface of glassy carbon under these conditions may be similar to that of graphite. This may be a result of the surface recrystallization process suggested by Petak and Vydra⁹. We have frequently observed instability in the surface of our glassy carbon electrodes. Pulsing the electrode to very high positive potentials, prolonged oxygen evolution or the passage of high currents all seem to induce mechanical instability in the electrode surface. A micrograph of the peeled surface is shown in Figure 5.

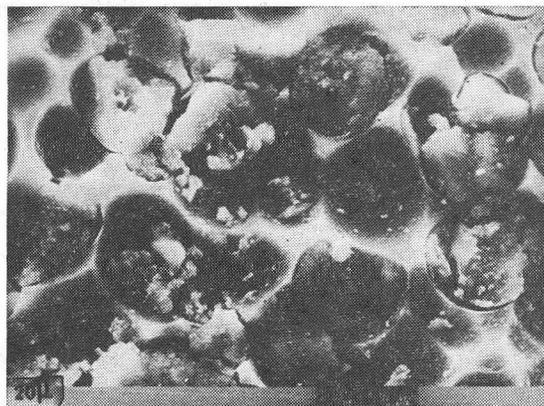


Figure 5. Scanning electron micrograph of Sw. 900 after extended electrolysis in 1 M HClO_4 at +2.2 V.

The surface, before electrochemical destruction, was prepared in the usual way. The resulting surface shows a characteristic network of crystallites and there is strong evidence for an inhomogeneous splitting process for the surface flakes. The extent of propagation of this perturbed structure into the bulk of the glassy carbon was also shown by the extensive polishing that was necessary to recreate a characteristically clean and well polished surface. The detailed mechanism of these processes is unclear.

IV — DOUBLE LAYER STUDIES AS A PROBE OF THE SURFACE STRUCTURE

In contrast to the extreme polarization conditions employed in the studies in the previous section, in the next two sections we are concerned with the behaviour of the electrodes under less extreme conditions, where the positive potential limit of sweep never exceeds +1.5 V.

Capacity measurements on carbon are not simple. Even with the basal plane of pyrolytic graphite, the semiconducting properties and the extreme sensitivity of the surface to polarization complicate the measurement. There are only a few reports of capacity measurements on glassy carbon electrodes. Zittel and Miller reported a value of $200 \mu\text{F cm}^{-2}$ calculated from their voltammetric curves⁸. Randin and Yeager attempted bridge measurements of the capacity in acidic, neutral and alkaline media and found a large capacity increase at low frequencies¹⁴.

A priori, the capacity of a semiconducting electrode can be expected to have a high frequency limit due to its space charge capacity^{6,15}. The measurements of Randin and Yeager confirm this prediction¹⁴. The deviations at lower frequency may be due to surface states but may also be due to non-irreversible faradaic processes. Both pyrolytic graphite and glassy carbon electrodes have a leakage current over their whole range of polarization and at no potential can they be called ideally polarizable. We have employed two experimental techniques to measure capacities, calculations on the basis of voltammetric curves and the AC bridge technique.

a) Capacities Calculated from Linear Sweep Voltammograms

Two types of experiment were performed.

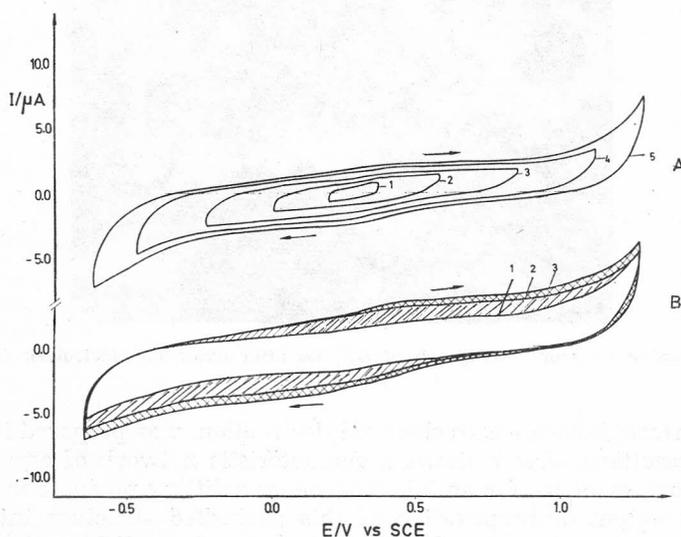


Figure 6. Cyclic voltammograms for Tokai 3000 in 0.5 M H_2SO_4 at a sweep rate of 190 mV s^{-1} . Steady state voltammograms are recorded.

(A): the five different amplitudes at the same sweep rate.

(B): (1) is the initial sweep voltammogram, (2) was recorded after 15 minutes and (3) was recorded after 30 minutes.

The first is illustrated by the voltammogram in Figure 6A. The amplitude of the voltammetric sweep was varied systematically in the direction indicated at constant sweep rate. The amplitude was then systematically decreased back to its original amplitude. The first point to notice is the striking increase in current over the whole sweep range as the amplitude increases. This clearly illustrates the sensitivity of the faradaic processes at the surface to the sweep amplitude and the extent to which the system is non ideally polarizable⁶. Each curve was recorded after cycling for 2 mins. The increase in background current is considerably reduced if the freshly polished electrode is very rapidly swept with this amplitude program. The average capacities are: Figure 6A, A (1) = $37 \mu\text{F cm}^{-2}$ and A (5) = $164 \mu\text{F cm}^{-2}$. The relaxation of the surface is slow when the sweep amplitude is reduced and only relaxes to the proper curve if the number of cycles swept at the largest amplitude is restricted. This

shows the irreversibility of the changes that occur at the surface in the region of $\geq +1.2$ V.

The second type of experiment is illustrated in Figure 6B. The amplitude was now set as for Figure 6A(5), and the freshly polished electrode was cycled continuously. The voltammogram was then recorded at 15 minute intervals. The capacities slowly tend to a limiting value for given sweep amplitude, in this case about $250 \mu\text{F cm}^{-2}$. These values of capacity do not depend to any discernable extent on the solution conditions as experiments with HClO_4 , K_2SO_4 and 50 and 90% ethanolic solutions yielded similar values.

b) Capacity Measurements Using the AC Technique

The initial aim of these measurements was to obtain capacity values approaching the low frequency limiting value on these electrodes. This required careful polishing of the electrode and precise control of the potential at the entry of the electrode into the solution. The capacity of the electrode was then measured as a function of frequency in 50 mV steps with a rest time of 3—5 minutes at each point. The capacity-potential curves for 0.5 M H_2SO_4 are shown in Figure 7. These are similar in shape to those obtained earlier by Randin and Yeager¹⁴ although the actual values are very different. The capacity on the negative sweep is always higher than that on the positive sweep and the peak at 0.3 V is considerably broadened. The hysteresis in the curves is increased if the electrode is held at its positive reversal potential for 20 mins. before starting the measurement sweep and in this case the peak at 0.3 V on the positive going sweep is already broadened with respect to the same sweep on the freshly polished electrode. After preoxidation of the surface, the values of the capacity increase by more than an order of magnitude. The problem of the slow relaxation of the capacity is also illustrated in this figure by the inclusion of data measured 60 mins. after the end of the measurement cycle. The relaxation time depends markedly on the electrode potential and the direction of the sweep. In acidic solutions, the first half of the positive sweep relaxes quickly but the second half requires at least 5 mins. equilibration time. For the negative going sweep the converse is generally true.

These measurements are sensitive not only to the electrochemical conditions but also to the surface preparation procedures. If the preparation is carefully performed the results are reproducible within a few percent as can be seen for two very different electrodes in Figure 8. The qualitative and quantitative characteristics of the capacity potential curve were independent both of the source of the material and of its HTT when the surface had been correctly polished. This is only true when allowance is made for the roughness factors on the different electrode.

If the curves in Figures 7 and 8 are compared, their similarity is striking. There is apparently little or no influence of the anion in the positive potential region, $E < 0.6$ V.

In order to investigate further the influence of the electrolyte on the surface and possibly to estimate the point of zero charge for this material, a series of capacities were measured at decreased electrolyte concentrations. The results are shown in Figure 9.

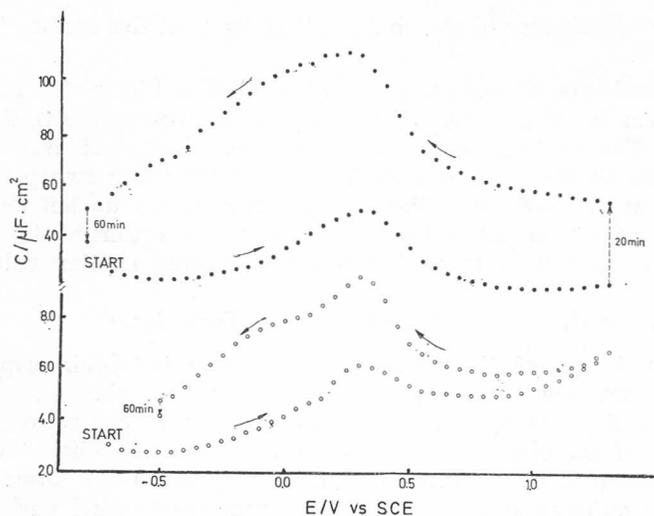


Figure 7. Capacity-potential curves for Tokai 3000 in 0.5 M H_2SO_4 at 2000 Hz. Details of the measurements are given in the text. Electrode freshly polished(o); Electrode oxidised(o).

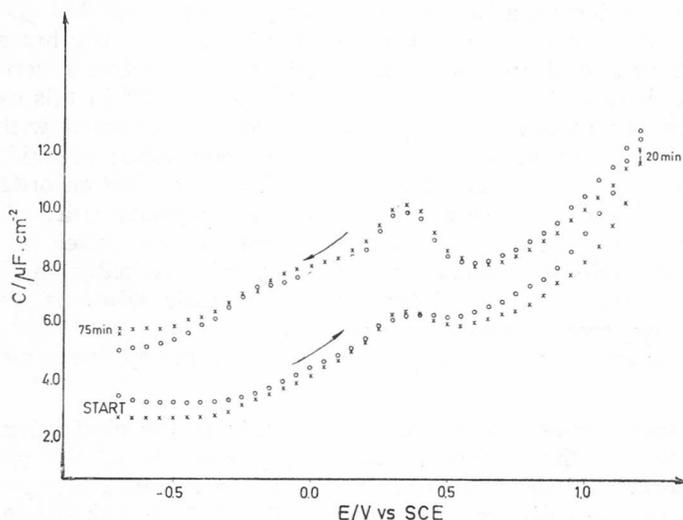


Figure 8. Comparison of capacity-potential curves for two samples of glassy carbon, (X) Tokai 3000, (O) SIGRI 2400 in 1 M HClO_4 at 2000 Hz. Direction of cycling is shown by arrows.

The hysteresis characteristic becomes more complicated at lower concentrations and the overall value of the capacity decreases as the electrolyte

concentration decreases, but even in 2 mM solutions there is no sign of the expected diffuse layer minimum. This might be expected to decrease the capacity at this concentration by some 15% over a potential span of about 150–200 mV.

The disappearance of the peaks in Figure 9 as the concentration decreases is consistent with the changes in voltammetric curves for the same systems.

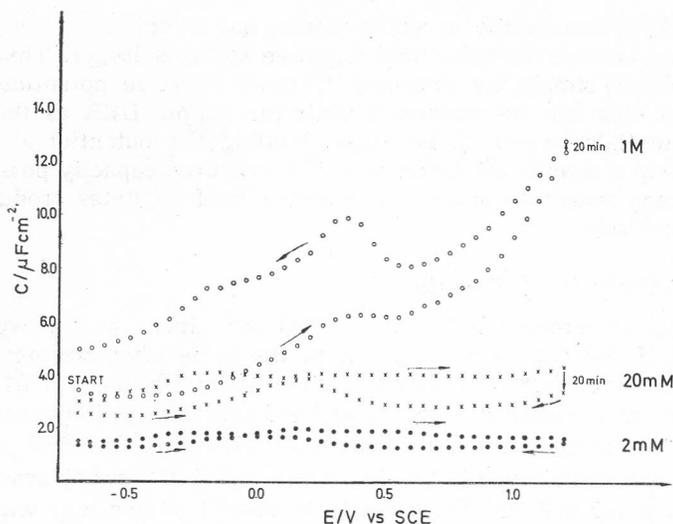


Figure 9. Capacity-potential curves for Tokai 3000 at 2000 Hz as a function of the electrolyte (HClO_4) concentration.

The curves in this figure were all obtained on freshly polished electrodes. If, however, the electrode is preoxidized fully before making the capacity measurements under the conditions of Figure 9, the capacities at all concentrations are much larger and the characteristic peak in the capacity-potential function reappears.

The measurements discussed so far refer in general only to acidic media. Randin and Yeager¹⁴ reported capacity-potential curves for 0.9 M NaF but their curves differ completely from our results in 0.5 M K_2SO_4 shown in Figure 10.

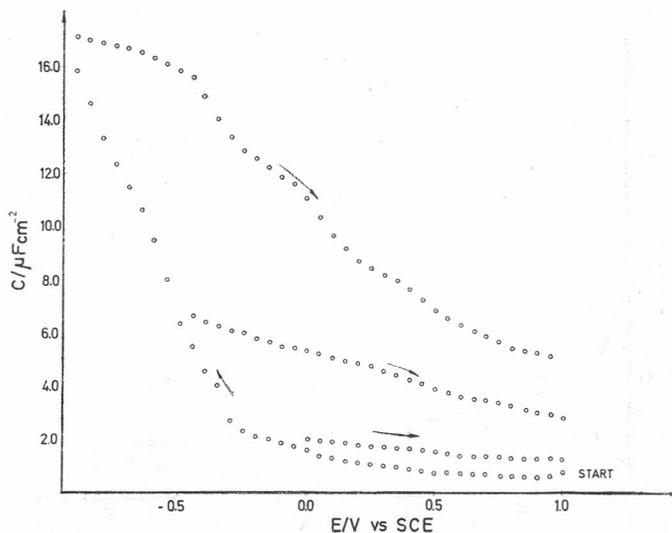


Figure 10. Influence of type of electrolyte on the capacity-potential function for Tokai 3000. Solution 0.5 M K_2SO_4 . Also shows the influence of the negative scan reversal potential on this relationship.

The peak, characteristic in acidic media, has completely disappeared and the hysteresis between positive and negative scans is larger. This hysteresis can be amplified simply by sweeping to more negative potentials. It seems unlikely that this can be associated with the simple HER as this does not occur at potentials > -1 V. However, holding the potential at a negative value results in a significant decrease in the measured capacity possibly suggesting that some reductive process is removing surface states produced during the oxidation cycle.

c) Further Analysis of Results

The large differences between the AC and linear sweep capacities are unimportant if the data are compared at the same effective measuring frequency. This comparison was carried out by extrapolating the AC capacities as a function of frequency to the effective linear sweep frequency. In order to carry out the comparison under conditions where the electrical perturbation of the electrode was similar in the two cases, the linear sweep scan amplitude was limited to 100 mV and the capacity measured in this way was compared with the AC capacity over the whole potential range.

As indicated in the introduction and elsewhere, the chemical nature of the glassy carbon surface is ill defined. As the capacities themselves do not seem particularly diagnostic of the surface process and the many changes that occur even under very mild polarization, it is pertinent to ask whether more information of a quantitative nature may be obtained from the frequency dependence of the capacity. We have already discussed the expected characteristics for such a system and a typical curve for a freshly polished electrode is shown in Figure 11. The high frequency limiting value can be seen to be approached in this plot.

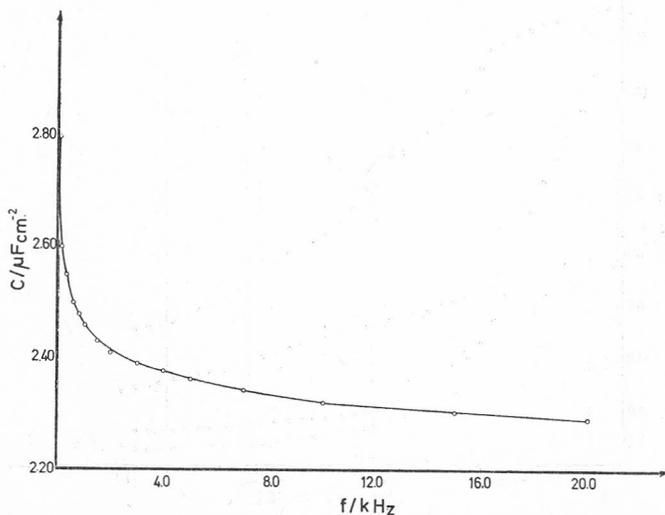


Figure 11. Frequency dispersion of freshly polished SIGRI 2400 electrode at 0.8 V vs SCE in 0.5 M K_2SO_4 .

From the observations made above, it is clear that the principal contribution to the observed capacity derives from phenomena in the surface of the glassy carbon. If the basic value of the space charge capacity in the glassy carbon surface is low, the normal values of capacity in the solution in series would have little influence of the observed values. If we consider the surface of the carbon, its capacity can be considered to comprise at least this space charge capacity. The deviations observed at low frequency all imply that the capacitive contribution leading to these changes should shunt the space charge capacity. The only alternative explanation of this change of the capacity is related to a faradaic impedance at the surface. Attempts to describe these data using Cole-Cole plots gave unreasonable plots and this solution was rejected. We therefore tried to analyse the observed behaviour using the shunting concept. The space charge is thin in glassy carbons and it is not unreasonable to imagine that there are residual or electrochemically produced species that are capable of bypassing this layer. It is interesting to try to analyse this contribution using a simple parallel circuit concept in which there are resistive and capacitive components in parallel with the space charge

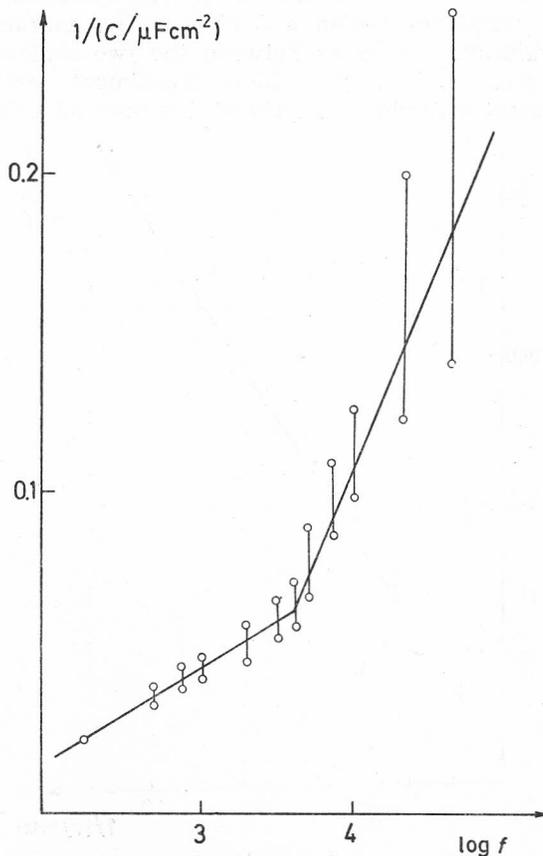


Figure 12. Plot of data in Figure 11 according to the parallel equivalent circuit model described in the text using Equation 2. Error bars are included. Slopes: $2.8 \times 10^{-2} \text{ cm}^2 \mu\text{F}$ (low frequency region), $0.128 \text{ cm}^2 \mu\text{F}$ (high frequency region).

capacity. The sites producing these effects will have a distribution of relaxation times and we can apply relationships used in amorphous dielectric theory^{16,17},

$$\tau = \tau_0 \exp (q/kt) \quad (1)$$

where τ is the relaxation time and q is a function of the energy well at a particular site. To calculate the dispersion of the impedance, a distribution function is also necessary for τ at these sites. If a flat function is assumed it can be shown that the following relationships result,

$$\frac{1}{C} = A_1 \log f + B \quad (2)$$

and

$$R = A_2/f \quad (3)$$

where f is the frequency of measurement.

Plots of the data for Figure 11 are shown in Figures 12 and 13. This type of fit was used by Clavilier¹⁸ to describe the formation of oxide films on Pt. The constant A_1 at low frequency agrees closely in magnitude with the values found earlier by various authors in the low frequency region but the values of A_1 in the high frequency region and of A_2 differ markedly from these earlier workers' values¹⁸. The break between the two regions occurs in the same frequency region for both plots. More experimental work is necessary before we can attempt a further analysis of this unusual behaviour.

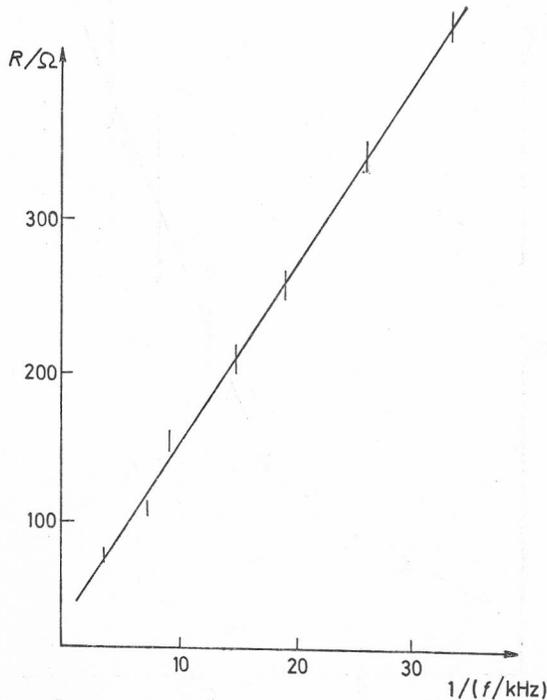


Figure 13. Plot of the low frequency resistive data for the measurements in Figure 11, derived from the simple parallel equivalent circuit model and plotted according to Equation 3. Plot for high frequency region not shown. Slopes: $15.7 \times 10^3 \Omega \text{ Hz}^{-1}$ (low frequency region), $9.7 \times 10^3 \Omega \text{ Hz}^{-1}$ (high frequency region).

V — THE KINETICS OF REDOX REACTIONS AS A PROBE OF SURFACE STRUCTURE

The studies described in the previous section were all concentrated on phenomena occurring in the region -0.5 to 1.3 V vs SCE and this section describes the use of the kinetics of 'simple' redox systems to probe more deeply the characteristics of the electrode in this same domain of polarization. The details of the techniques employed are described in detail elsewhere¹. Briefly, we employed cyclic voltammetry to study the kinetics and analysed the steady state voltammograms using the Nicolson and Shain theory¹⁹. The currents measured for the redox processes were always at least two orders of magnitude larger than the base line currents discussed in the previous sections so that base line corrections were not necessary. The aim of this investigation was to study the influence of the electrode material under differing degrees of oxidation on the redox process. It was quickly found that there were two classes of redox processes, those that were accelerated by the presence of the oxidized surface and those whose kinetic parameters were unaffected. In addition, the HTT of the electrode material seemed to be an important factor in the first class of reactions.

V.1 Reactions Proceeding Faster on an 'Oxidized' Surface.

To this group belong the $\text{Fe}^{2+}/\text{Fe}^{3+}$ (in both H_2SO_4 and HClO_4), the $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ and the quinone-hydroquinone couples.

On the freshly polished electrode surface, all these reactions have rather slow kinetics, much lower than the reported values on glassy carbon²⁰, platinum²¹ and gold^{22,23} in the literature. On glassy carbon freshly polished; ($\text{Fe}^{2+}/\text{Fe}^{3+} = 1.1 \times 10^{-5} \text{ cm s}^{-1}$, $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ and $\text{Q}/\text{H}_2\text{Q}$ are similar). The only interesting feature in these results is the oxidation reaction for $\text{Q}/\text{H}_2\text{Q}$ which is apparently much more reversible than its reduction step.

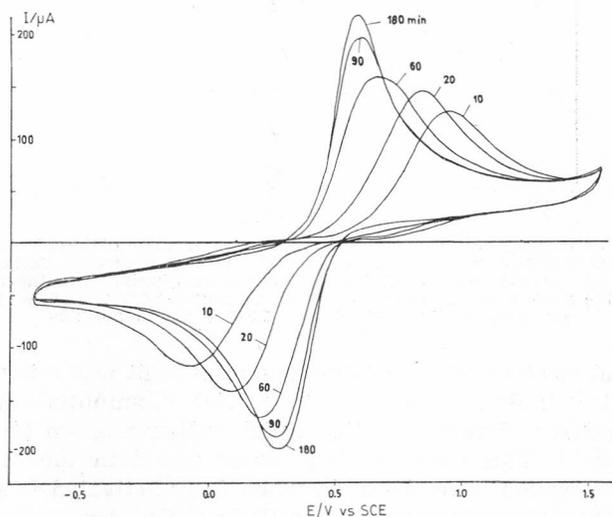


Figure 14. Effect of cycling on cyclic voltammograms for Fe^{2+} at freshly polished SIGRI 2400 electrode (sweep rate 224 mV s^{-1}). Voltammograms recorded after cycling for the time in minutes indicated on each curve.

If the electrode was cycled continuously for an extended period the rates of these reactions increased slightly. A more dramatic effect was found when the sweep amplitude was increased symmetrically to that shown in Figure 14. The rate constant k_c^\ominus increases slowly by more than two decades. This is similar to the behaviour reported by Taylor and Humffray²⁰ who pretreated their electrodes with chromic acid. A similar electrode activation was observed for $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ but the anodic reversal limit required the k_c^\ominus shows a 500-fold increase. $\text{Q}/\text{H}_2\text{Q}$ showed similar dramatic effects. It to activate the electrode in 90 minutes of cycling was only 1 V. For this reaction is reasonable to ask at what potential this electrode activations occur and how this potential is related to the studies in the previous sections. The reaction $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ was tested using an amplitude (I) -0.275 to $+0.690$ V cf. Figure 15. Cycling with amplitude (I) on a freshly polished electrode produced no change after 10 hours, voltammogram (2) Figure 15. In the next sequence the positive reversal potential was retained but the negative reversal potential was reset at -1.1 V (amplitude II). The freshly polished electrode was cycled for one hour with amplitude II. Voltammogram (3) shows the voltammogram at amplitude I after this treatment.

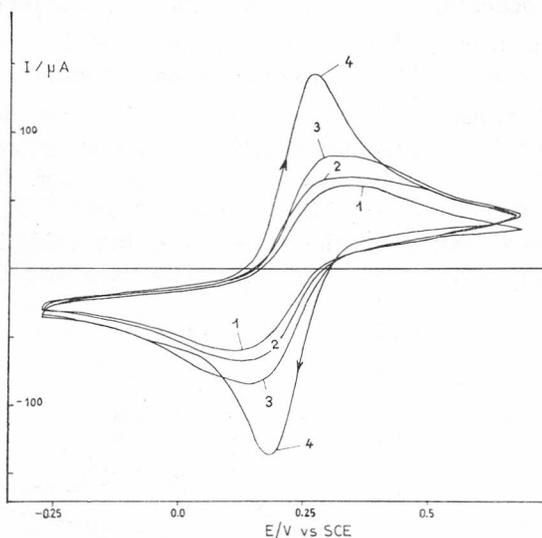


Figure 15. Effect of cycling various potential amplitudes and for different times on the cyclic voltammograms for $\text{Fe}(\text{CN})_6^{4-}/3-$ at a freshly polished Sw. 1093 electrode. Voltammograms recorded at a sweep rate of 96.5 mV s^{-1} . (1) immediately after dipping into the solution, (2) after cycling -0.275 to $+0.690$ V for 10 hours, (3) after cycling -1.090 to $+0.690$ V for 1 hour and (4) after cycling -0.275 to $+1.385$ V for 15 minutes.

In the final treatment the negative potential limit was retained, -0.275 V while the positive limit was increased to $+1.385$ V, amplitude III. This amplitude was cycled for 15 minutes after which voltammogram (4) was recorded using amplitude I. This confirms the results found in the capacity studies in the previous section. The electrode when fully activated is stable, i.e. the kinetics do not change when amplitude (I) is cycled for extended periods of time. Attempts to reduce the surface modifications with amplitude (II) are not successful if the electrode is fully activated. However at very negative

potentials, k_c^\ominus does decrease again, cf. section III. The activation is less successful if instead of cycling the electrode, it is simply electrolysed at the positive reversal potential in (III) or if the negative potential limit is increased. It can be shown that the activation process is independent of the redox couple cf. results in sections III and IV. The details of the methods employed to calculate the maximum attainable rate constants on the fully activated electrodes are described in detail elsewhere¹. Rate constants were measured on all the glassy carbon samples under these conditions and these maximum rate constants showed a good correlation with the energy of the band gap for different HTT temperatures, Figure 16.

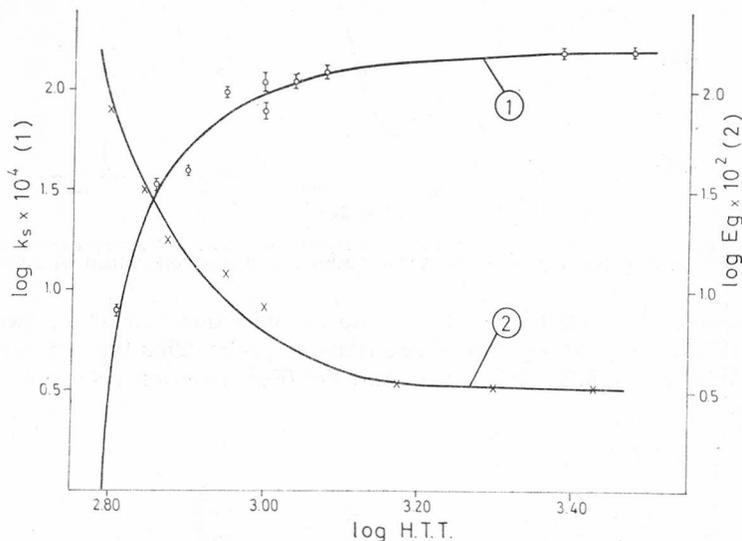


Figure 16. Dependence of (1) standard rate constant for $\text{Fe}(\text{CN})_6^{4-/3-}$ and (2) energy band gap (ref. 25) on HTT of glassy carbon electrodes.

The meaning of this correlation is not entirely clear as it has already been shown that the ease of oxidizability of the electrode also decreases with decreasing HTT.

The nature of the film can be further investigated by mechanically removing a part of the surface »oxide« film and remeasuring the kinetics on this partially cleaned surface. The increased peak separation, Figure 17, shows the direct relationship between the rate of the redox process and the »oxide« film. Reactivation can be simply achieved by reoxidation of the surface at $V \sim +1.3$ V.

We have already shown the mechanical destabilization effect of violent oxidation. However, although the film formed at these lower potentials can be stable, in some experiments it thickened and became poorly conductive. The kinetics were then retarded and the film became coloured, yellowish to blue in H_2SO_4 solutions. This might be consistent with known compounds formed between carbon and sulphate ions although no doubt a whole range of residues are formed under these conditions. The superficial appearance of the surface under SEM did not change but these films were found to form more readily on low HTT electrodes.

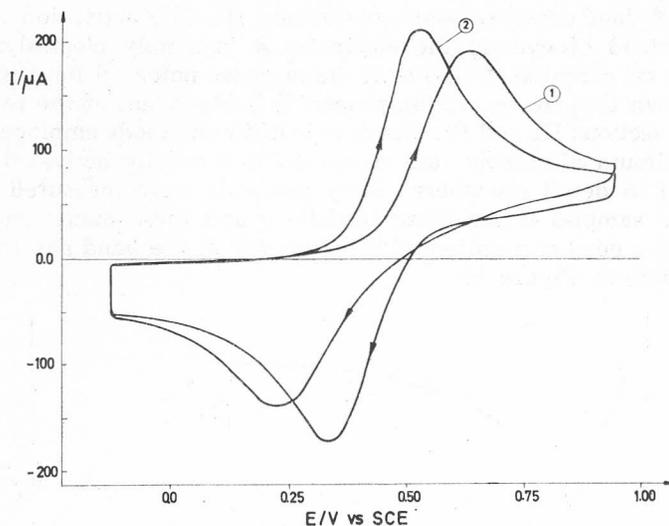


Figure 17. Cyclic voltammograms for Fe^{2+} in 0.5 M H_2SO_4 on SIGRI 2400 glassy carbon electrodes: 1) electrode activated by holding at + 1.385 V for 3 minutes, (2) electrode wiped with tissue paper.

The process of change of surface state by oxidation can be followed using the kinetics of one of this group of reactions as probe. This type of experiment is shown in Figure 18. In this figure the $\text{Fe}^{2+}/\text{Fe}^{3+}$ reaction occurs on the two

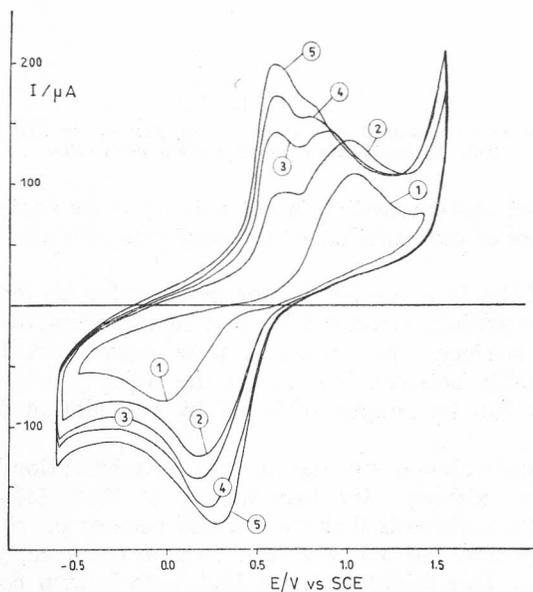


Figure 18. Cyclic voltammograms for Fe^{2+} in 0.5 M HClO_4 at a sweep rate of 215 mV s^{-1} illustrating the existence of two different kinds of surface on the Sw. 1093 electrode. Sweeps are presented as a function of cycling time, (1) at a freshly polished surface, (2) first cycle at the new amplitude after cycling amplitude for voltammogram (1) for 100 minutes, (3) after cycling amplitude (2) for 15 minutes, (4) and (5) after cycling respectively 15 and 30 minutes at the new amplitude.

types of surface. As the sweep cycles into the activation region, the peak for the rather irreversible oxidation is gradually replaced by a more negative peak characteristic of its fast oxidation. The 'oxide' film is apparently stable in air as the kinetics on activated surfaces stored out of solution were unchanged.

V.2 Reactions not Accelerated by Oxidation of the Electrode Surface

To this group belong the hexachlorirridate, ferrocene and nickelocene reactions. The rate constants are all large and except for the measurements on Sw. 606, k_c^\ominus varies only by a factor of 2 to 3 on different freshly polished electrode materials. If the surface is now oxidized by cycling into the oxidation region, the voltammograms in Figure 19 are found. Evidently the effect of oxidation is to block the electrode for the redox reaction while leaving the

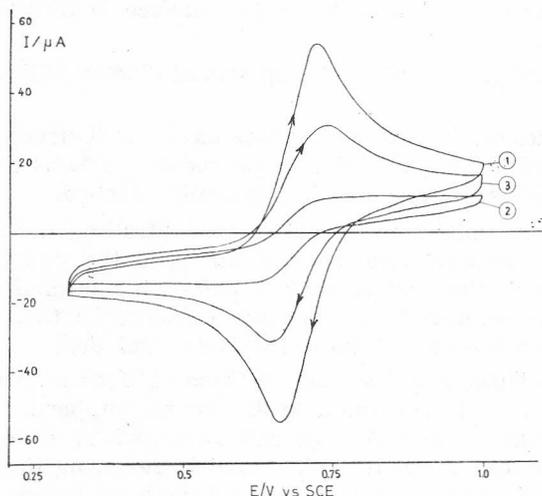


Figure 19. Effect of the anodic film on the cyclic voltammograms for IrCl_6^{2-} on Tokai 3000 in 1.0 M HClO_4 , (1) electrode freshly polished — initial cycle, (2) after cycling for +0.3 to +1.5 V for 5 minutes, (3) after (2) and electrode wiped with tissue paper.

kinetics of the reaction unaltered. This means that, unlike the previous group of reactions, there is little or no interaction of these redox couples with the oxidized or freshly polished surface. The average rate constants we measured agreed closely with those measured on a platinum electrode.

VI — GENERAL DISCUSSION

There are clearly a whole range of redox processes that can be electrochemically driven in the glassy carbon electrode surface, some reversibly and some irreversibly. The oxidation of the surface is not a 'simple' process like the oxidation of a metal surface and the surface 'film' that forms is both on and in the surface. This is clear for the colour changes observed and can be inferred from the capacity measurements. The types of residues that might be present in this surface layer have already been the subject of much speculation in the literature^{11,14,24} and until we can analyse the molecular state

of the surface in the presence of the solution, no unequivocal identification can be made. If the complexity of the starting material is considered, a resin or a complex cross linked material, the residues remaining, that influence the formation of the residues on the oxidized surface, will indeed be very dependent on the starting material, more so if the HTT is insufficiently high to induce the mobility in the solid phase necessary to form the homogeneous carbon structure. It is therefore imprudent to speculate on the meaning of the fits to the models presented in sections IV and V. In view the discussions already presented, neither of the quantitative fits is unreasonable but without the proper quantitative analysis of the initial and final surface states, any interpretation must remain qualitative.

The following general conclusions can be drawn:

- a) There is a direct relationship between the HTT and the physical form of the material,
- b) the electrochemical activity of the surface is directly related to the HTT of the sample,
- c) the material is a small band gap semiconductor with no range of ideal polarizability,
- d) the residues on the oxidized surface have a well structure at a molecular level as evidenced by the fact that some redox reactions are accelerated by these residues and some are simple physically blocked.

One factor that might be important in controlling the surface state if a comparison with metallic electrodes is made, is the possible generation of atomic hydrogen in the surface matrix before the normal HER potential is reached. Although we have found no direct evidence for the presence of atomic hydrogen, its presence cannot be definitively excluded.

Our final conclusions are similar to those of Dunsch⁵. There is a need for further research at a fundamental level into the properties of this material. Many of the results with redox systems reviewed by Dunsch can be rationalised using our results but it is clear that in resolving these inconsistencies, a number of other fundamental questions have been posed. Our fundamental research on this material is continuing.

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SAŽETAK

Elektrokemijska proučavanja elektroda od različitih staklastih grafita

L. Bjelica, R. Parsons i R. M. Reeves

S obzirom na to da površinu staklastog grafita nije moguće jednoznačno definirati, proučavani su materijali triju različitih proizvođača. Ti su materijali tijekom proizvodnje bili obrađivani na različitim temperaturama u području od 600 do 3 000 °C. Elektronskom mikroskopijom i spektroskopijom proučavana je struktura površine elektroda, koje su tada ispitivane elektrokemijskim tehnikama cikličke voltametrije, kapaciteta dvosloja, te mjerenjem kinetike tipičnih redoks-reakcija.

Utvrđeno je da termička predobradba uvjetuje i fizički oblik materijala i njegovo elektrokemijsko ponašanje. Staklasti grafit ponaša se poput poluvodiča s uskim zabranjenim pojasom, a oksidirana površina pokazuje niz dubokih stanja. Ta površinska stanja posljedica su oksidacijskih procesa, a utječu na kinetiku elektrokemijskih reakcija ubrzavajući neke od njih, blokirajući druge.

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