

Electrochemical properties of graphite fibre/epoxy composite electrodes

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The electrochemical behaviour of two types of carbon fibre/epoxy composite electrodes was studied and compared to that of glassy carbon. Background currents are low over a range of about 2.1 V, allowing the study of electrochemical reactions from about -0.6 V to $+1.50$ V versus rHe in aqueous solutions.

Oxygen evolution studies over a wide pH range in buffered solutions yield exchange current densities in the range of $2-70 \mu\text{A cm}^{-2}$, with a minimum in neutral solutions. The Tafel slopes are high, in the range of $0.3-0.4$ V in acid and neutral solutions, rising further in alkaline solutions.

The limiting current density for the oxidation of I^- ions was equal, within experimental error, to that found for glassy carbon, although about half the surface consists of inactive epoxy matrix material. Such behaviour is consistent with recent theoretical calculations for a partially inactive electrode surface, as long as the Nernst diffusion layer is comparable with or larger than the gaps between electroactive areas on the surface.

1. Introduction

Composite materials based on graphite or carbon fibres in a nonconducting matrix such as epoxy or nylon are finding ever increasing applications as structural elements, mainly where a high strength to weight ratio is essential. The conductivity of such composites depends on the weight per cent loading with fibre and on the method of preparation. In particular, when the fibres are orientated parallel to each other, relatively high conductivity will be attained in the direction of orientation and very little perpendicular to it. In composites containing randomly oriented (usually short) fibres, the conductivity is essentially isotropic.

The specific resistance of carbon fibre composite electrodes can be as low as $1-5 \text{ ohm cm}$, permitting their use as electrodes in a wide range of electrochemical applications. When properly polished, they present a very smooth surface, which is more resistant to abrasion than high density graphite. Such electrodes are stable under alternating voltage conditions in the presence of chloride ions, where all metals would fail, as long as heavy gas evolution is avoided.

In a recent publication [1], the use of graphite fibre/epoxy electrodes for electrochemical disinfection under alternating voltage conditions was demonstrated. The use of different types of composite electrodes for this purpose, their relative service life and modes of failure were studied [2]

In view of the above, and possibly other applications of carbon fibre composite electrodes, it is of interest to determine their fundamental electrochemical properties. In this paper, studies on two types of composite electrodes are reported: randomly oriented and highly oriented. Both have a nominal loading of 60 wt% graphite. In the latter, the exposed area is perpendicular to the axis of orientation of the fibres. A glassy carbon electrode was also studied under identical conditions, for the purpose of comparison.

Three types of experiments were performed: (1) the background currents were measured in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ from hydrogen and oxygen evolution, (2) the kinetics of oxygen evolution were studied as a function of pH, (3) the limiting current for the oxidation of iodide in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was measured for each electrode and the results were compared.

2. Experimental procedure

2.1. *The cell and electrodes*

A three-compartment cell was employed. A graphite rod counter electrode and a saturated calomel reference electrode were separated from the working electrode with glass frits. The working electrodes had the standard rotating disc electrode configuration. The surface area of the two graphite fibre composite electrodes was 0.466 cm^2 and that of the glassy carbon was 0.264 cm^2 .

Special care must be taken in making good electrical contact with the back of the composite electrodes. In previous work [1], where relatively large currents were passed (up to 20 mA cm^{-2}), the back of the electrode was plated with a layer of nickel. In the present work, a thin layer of gold was vapour deposited on the back of the electrode. A piece of carbon felt was placed between the electrode and a copper disc, which made contact with the external circuit through a spring. Uniform contact with the back of the electrode is particularly important for highly oriented fibre composites, since any part left without contact will leave a similar part of the surface of the electrode inactive.

2.2. *Instrumentation*

A Pine Company rotating disc assembly was used. Potentials were controlled with an Elron model CHP-1 potentiostat and measured with an El-Hama Ind. digital pH meter, model PBS 730. Currents were recorded on a Telrad model 712 strip-chart recorder.

2.3. *Solutions*

All solutions were prepared with triple-distilled water. Buffer solutions were prepared by standard methods [3] and adjusted to the desired pH value by adding acid or base as required. Na_2SO_4 was added to make the ionic strength approximately unity in all solutions.

2.4. *Sequence of measurements*

The working electrode was removed from solution and polished on a polishing wheel with alumina

powder of 1 micron grain-size, 0.3 micron and 0.05 micron, before the measurement of each current–potential plot. The electrode was then washed with distilled water, cleaned in an ultrasonic cleaner for 5 min and finally inspected under a low power optical microscope to detect any major faults on the surface.

Between different solutions the cell was rinsed in distilled water, then in triple-distilled water and finally baked in an oven at 500°C for 30 min to remove impurities which may have been adsorbed on the glass. In measurements of oxygen evolution kinetics, oxygen was bubbled through the solution before the experiment and above it during the experiment. In measurements of the background current and of the oxidation of iodide, purified nitrogen was used instead.

Current–potential measurements were made point by point. The potential was applied and the current was recorded until a steady value was reached.

3. Results and discussion

3.1. *Background current*

The background current, measured at steady state (1600 rpm) on a randomly orientated graphite fibre composite electrode in 1.0 mol dm^{-3} sulphuric acid, is shown in Fig. 1. The 'window' on the potential scale, between hydrogen evolution on the negative end and oxygen evolution on the positive end, is close to 2.1 V, making the study of other electrochemical reactions in this region possible. The small residual currents observed are probably due to reduction of oxygen (when measurements are started in the oxygen evolution region) and oxidation of hydrogen (when measurements are started in the hydrogen evolution region).

It should be noted that the overpotential for hydrogen evolution is roughly the same as for oxygen evolution on this type of electrode, unlike the behaviour observed for most metals.

3.2. *Oxygen evolution kinetics*

The oxygen evolution reaction was studied over a wide pH range, from 0.1 to 13.3, in buffered solutions. Figures 2a and b show Tafel plots

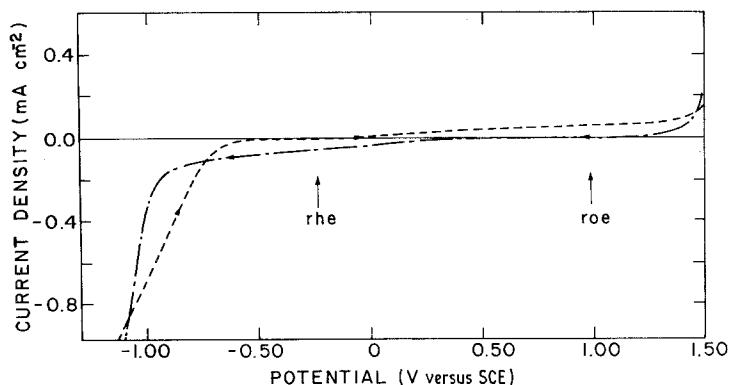


Fig. 1. Steady-state background current density on a randomly orientated graphite fibre/epoxy composite electrode, in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ (1600 rpm).

obtained at pH 0.30 and 11.6, respectively, on highly orientated fibre composite electrodes. The linear portion of the curve extends typically over 0.2–0.4 V, but this represents only one decade or less in current density. The Tafel slopes were high in all measurements, ranging mostly from 0.3–0.4 V decade⁻¹. A clear dependence on pH could not be determined, although it seems that the Tafel slope is independent of pH in acid and neutral solutions and tends to rise to higher values in alkaline solutions. In Fig. 3 the slopes obtained in two independent sets of measurements are shown, as a function of pH. The high values observed for the Tafel slope are probably associated with organic impurities (originating from the epoxy matrix material) which block part of the graphite fibres or form a thin film over it. In view of the large scatter of results for the Tafel slopes

in different solutions (cf., Fig. 3) a detailed theoretical discussion is not warranted.

The values of the exchange current density i_0 are plotted as a function of pH in Fig. 4 for the same two sets of measurements. Each point in the last two figures represents the average of 2–5 independent experiments. The electrodes were carefully polished before each experiment to enhance the reproducibility, which is inherently poor for graphite fibre composite electrodes.

A minimum in the plot of $\log i_0$ versus pH has been observed by Vielstich and co-workers for hydrogen evolution [4] and for oxygen evolution [5] on metals. It is also well known in fuel cell research [5], that catalysis of the oxygen evolution/reduction reaction is poorest in neutral solutions, as observed here.

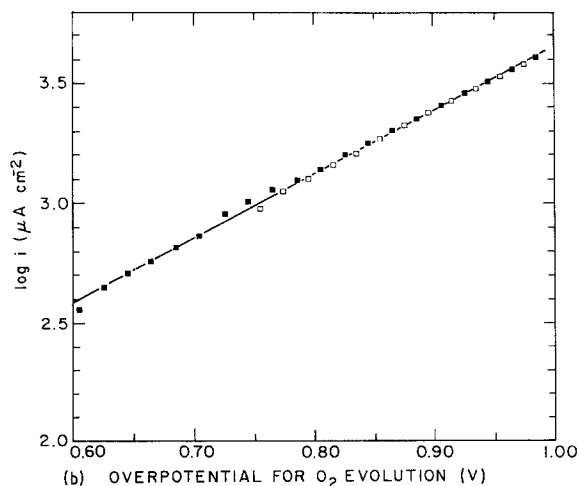
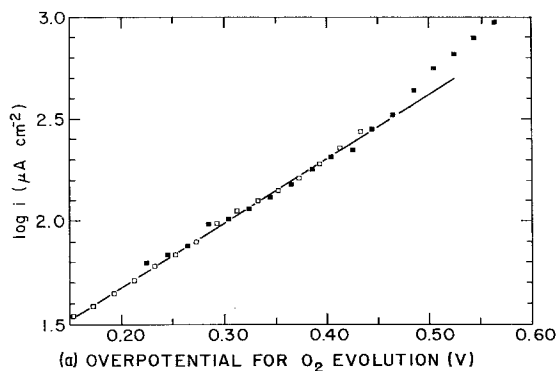


Fig. 2. Tafel plots for oxygen evolution on a highly orientated graphite fibre/epoxy composite electrode. (a) pH = 0.30, $b = 318 \text{ mV decade}^{-1}$, $i_0 = 11.2 \mu\text{A cm}^{-2}$. (b) pH = 11.6, $b = 388 \text{ mV decade}^{-1}$, $i_0 = 12.0 \mu\text{A cm}^{-2}$. Different points indicate two sets of independent measurements.

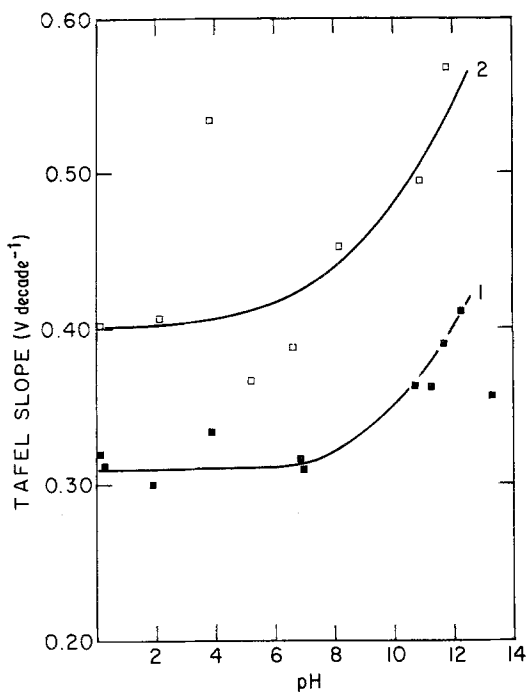


Fig. 3. Tafel slopes for oxygen evolution on highly orientated graphite fibre/epoxy composite electrodes as a function of pH. Different points correspond to two sets of measurements.

3.3. Oxidation of iodide

Oxidation of iodide ions in dilute solution ($0.4\text{--}1.0\text{ mmol dm}^{-3}$) was studied on three types of electrodes. The supporting electrolyte was 1.0 mol dm^{-3} sulphuric acid.

In Fig. 5 a series of current/potential plots,

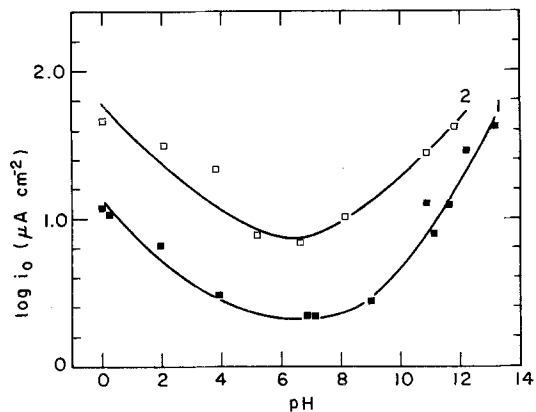


Fig. 4. The exchange current density for oxygen evolution on highly orientated graphite fibre/epoxy composite electrodes as a function of pH. Curves 1 and 2 correspond to the same curves in Fig. 3.

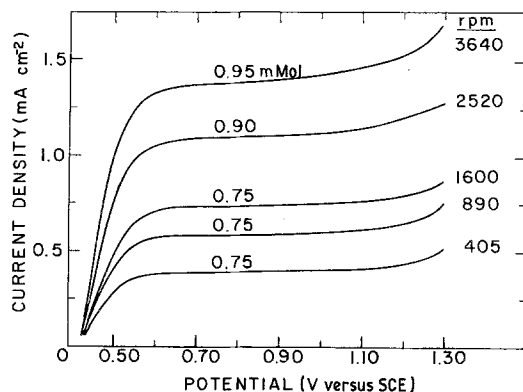


Fig. 5. Current-potential plots for oxidation of I^- in 1.0 mol dm^{-3} H_2SO_4 on randomly orientated graphite fibre/epoxy composite electrodes. Concentration of KI and angular velocity marked on each curve.

taken on a randomly orientated graphite fibre composite electrode are shown. The rotation rate and the concentration of KI are marked on each curve. The plateaus are flat and the half-wave potentials agree, within a few mV, with the calculated values, showing that the reaction occurs reversibly on this electrode.

A plot of the limiting current density i_L versus $(\text{rpm})^{1/2}$ is shown in Fig. 6 for 1.0 mmol dm^{-3} solutions of KI in 1.0 mol dm^{-3} H_2SO_4 . The slope of this line is of basic interest for studies on com-

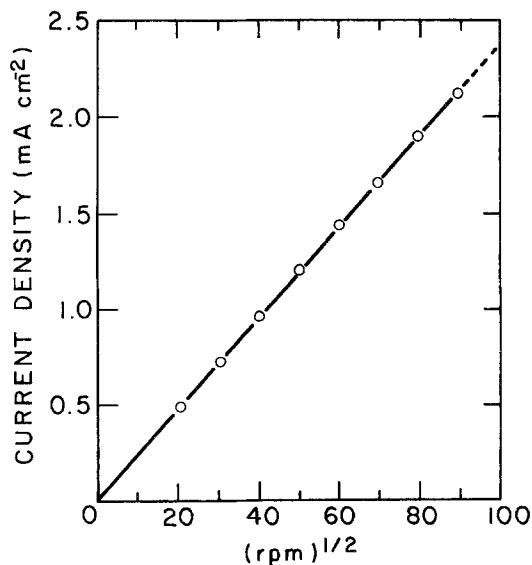


Fig. 6. Limiting current density for oxidation of 1.0 mmol dm^{-3} I^- in 1.0 mol dm^{-3} H_2SO_4 , plotted as a function of $(\text{rpm})^{1/2}$, for randomly orientated graphite fibre/epoxy composite.

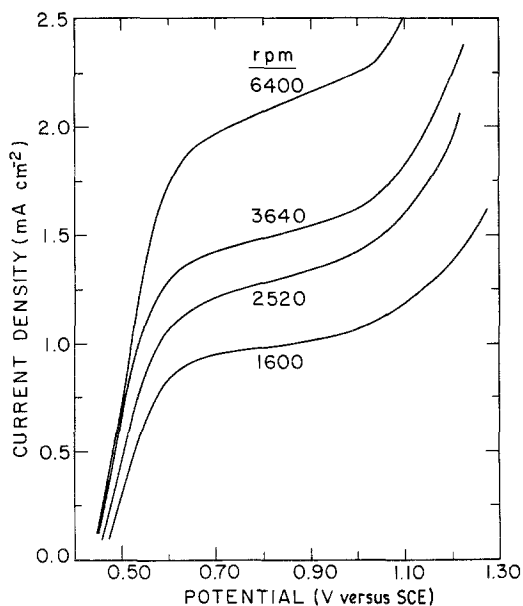


Fig. 7. Same as Fig. 5 but for highly orientated graphite fibre/epoxy composite electrode. Concentration of $\text{KI} = 1.0 \text{ mmol dm}^{-3}$.

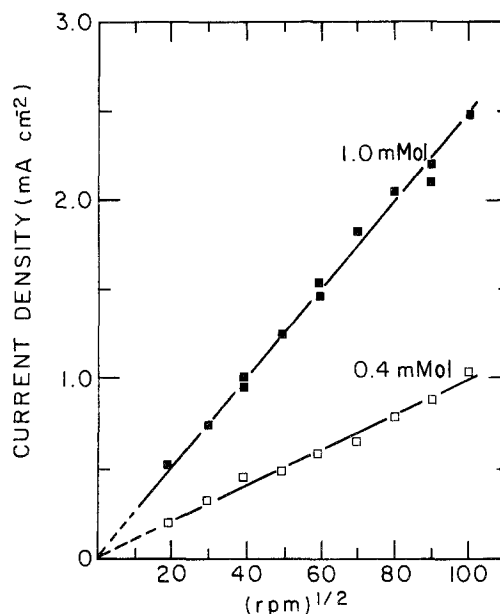


Fig. 8. Limiting current density for oxidation of I^- in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ on highly orientated graphite fibre/epoxy composite electrode, plotted as a function of $(\text{rpm})^{1/2}$ for two concentrations of KI.

posite electrodes. If we assume that the loading on the surface is equal to the bulk loading (a safe assumption for highly orientated composites but only approximately correct for randomly oriented fibre composites), only about half the surface would consist of conducting graphite fibres and therefore be electrochemically active*. One might therefore expect that the limiting current density would be only about half the value calculated, say, for a glassy carbon electrode. It was, however,

shown recently [6, 7] that mass transport to a partially blocked electrode would be equal to that of a fully active electrode if the diffusion layer thickness were of the same order of magnitude or larger than the average distance between active regions. This condition is fulfilled in the present experiments and the slope of $23.7 \mu\text{A cm}^{-2} (\text{rpm})^{-1/2}$ observed is close to the calculated value† of $25.7 \mu\text{A cm}^{-2} (\text{rpm})^{-1/2}$.

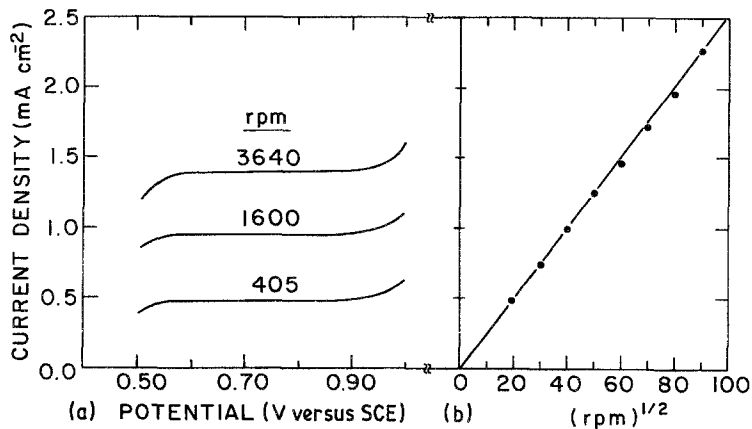


Fig. 9. Current-potential and limiting current versus $(\text{rpm})^{1/2}$ plots for the oxidation of I^- on glassy carbon. $1.0 \text{ mmol dm}^{-3} \text{ KI}$, $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$.

* In view of the difference in density between epoxy and graphite, a 60 wt% loading corresponds roughly to 45 vol%.

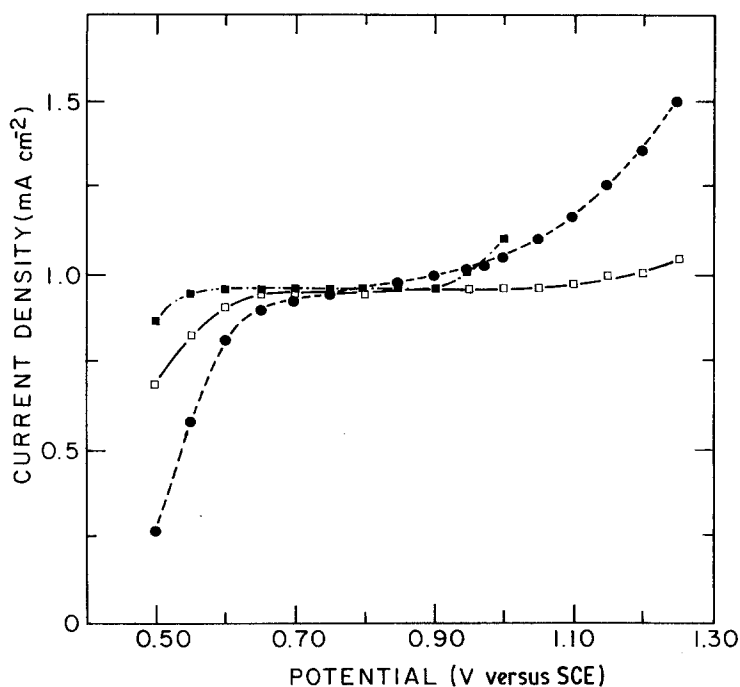


Fig. 10. Comparison of current-potential plots for the oxidation of 1.0 mmol dm^{-3} KI in 1.0 mol dm^{-3} H_2SO_4 at 1600 rpm on three types of electrodes. ■■■, glassy carbon. □□□, randomly orientated graphite fibre/epoxy composite. ●●●, highly orientated graphite fibre/epoxy composite.

A similar set of curves is shown in Fig. 7 for a highly orientated fibre composite electrode. The half-wave potential in these curves is about 50–60 mV more anodic than that calculated, showing a degree of irreversibility. The plateau is not flat and the current at 800 mV (SCE) was taken in order to obtain Fig. 8, which also contains data for a more dilute solution of $0.40 \text{ mmol dm}^{-3}$ KI. The measured slopes in Fig. 8 are 97% of the value calculated[†]. While this is somewhat arbitrary (by the choice of potential at which the limiting current is measured) it shows that the electrode acts, under the present experimental conditions, as though its whole surface were active.

Figures 9a and b show data taken on a glassy carbon electrode. The current-potential curves exhibit flat plateau regions, as for randomly orientated fibre composite electrodes, and the slope of i_L versus $(\text{rpm})^{1/2}$ is 97% of the calculated slope.

The behaviour of the three types of electrodes is compared in Fig. 10, showing the superior characteristics of the randomly orientated graphite

[†] The diffusion coefficient of I^- in 1.0 mol dm^{-3} sulphuric acid was taken as $1.52 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ based on earlier measurements [8].

fibre epoxy composite electrode for electrochemical measurement.

Acknowledgement

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References

- [1] G. E. Stoner, G. Cahen Jr., M. Sachiani and E. Gileadi, *J. Bioelectrochem. and Bioenerget.* 9 000 (1982).
- [2] G. Stafford, PhD Dissertation, University of Virginia (1981).
- [3] 'Handbook of Chemistry and Physics' 56th Edition, Chemical Rubber Company (1975/76) p. D-133.
- [4] W. Vielstich, 'Fuel Cells', Wiley-Interscience, New York (1965) p. 53.
- [5] *Idem, ibid.* p. 129.
- [6] T. Gueshi, K. Tokuda and H. Matsuda, *J. Electroanal. Chem.* 89 247 (1978).
- [7] H. Reller, E. Kirowa-Eisner and E. Gileadi, *J. Electroanal. Chem.* in press.
- [8] T. Bejerano and E. Gileadi, *J. Electroanal. Chem.* 82 209 (1977).