JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 495–500

Pyrolytically coated carbon cloth electrodes

E. SUTZKOVER, C. ZUR, M. ARIEL

Department of Chemistry, Technion IIT, Haifa, Israel

Received 20 July 1978

The performance of carbon cloth electrodes with a pyrolytic graphite coating deposited on their surface is reported. Cyclic voltammograms recorded with treated and untreated cloth, in the $-0{\cdot}9$ to $+0{\cdot}9$ V (versus Ag/AgCl) potential range, are compared. The extremely high residual currents observed on untreated cloth electrodes are absent after pretreatment; the latter maintain flat base lines even after repeated potential cycling. Optimum conditions for the pyrolytic process are recommended.

1. Introduction

Carbon electrodes, which have become increasingly popular both in electroanalysis and electrosynthesis, mainly as a result of their extensive potential range, may be modified in certain respects by a properly chosen pretreatment [1–3]. Compared to other carbon substrates, carbon cloths are inferior in mechanical strength and constancy of configuration under stress and exhibit a wide dispersion of pore dimensions. They are, therefore, hardly suitable for electroanalytical purposes. On the other hand, their large surface area, reasonable price and the ease with which they lend themselves to the construction of a variety of electrode assemblies point to their potential suitability for other electrochemical uses. To date these cloths are marketed for a variety of industrial applications, such as heating mantles, filtering media, supports in the plastics industry, etc. [4–5], where the chemical properties of the cloth surface, as determined by the presence and nature of surface groups, are of no particular significance.

Electrochemical results, on the other hand, are directly dependent on the nature of the electrode surface [6]. It was therefore decided to investigate the effect of exposing the cloth surface to amelioration and/or regeneration pretreatments on its performance as an electrode. The treatment of choice, dictated by the spatially complex structure of the cloth, was the formation of a pyrolytic graphite coating [7].

2. Experimental

2.1. *Reagents*

KCl (analytical reagent grade) was dissolved in iron-free de-ionized water to prepare the 0·5 M blank solution. 10^{-3} M $K_3Fe(CN)_6$ solution was prepared daily by dissolving the weighed ferricyanide in the appropriate volume of blank solution, the pH of which had been adjusted to 9 with KOH; it was stored in the dark. This procedure minimized the decomposition of ferricyanide or the formation of insoluble complexes [8]. He and CH_4 (99 vol%) gases were employed in the pyrolysis chamber.

2.2. *Electrodes and electrochemical cell*

The working electrodes were made of carbon or graphite cloth (TCM 216, and TGM 285, respectively, Le Carbon Lorraine). The performance of electrodes made of the untreated materials (specifications as detailed in a pamphlet issued by the manufacturers [5]) was compared to that of electrodes made of pyrolytically coated cloths. All potentials are referred to a Ag/AgCl reference electrode, immersed in the working solution; a Pt foil served as the auxiliary electrode.

The working electrodes (Fig. 1) were prepared by shielding 1 cm wide bands of the carbon cloth between two lightly clamped aluminium plates, wetting the overlapping edges with acetone and thoroughly saturating with two-component RTV

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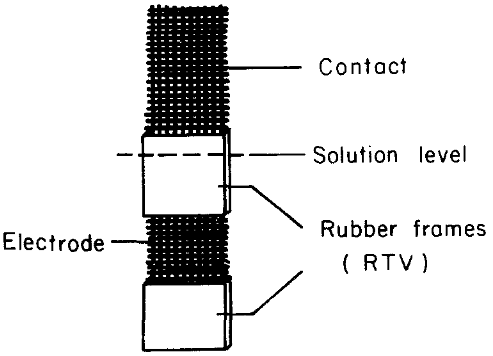

Fig. 1. Carbon cloth electrode.

silicone rubber (630 Dow Corning). The RTV rubber must saturate the exposed cloth completely to prevent subsequent penetration by solutions which would lead to unwanted 'memory' effects (i.e. carry-over from one experiment to the next).

2.3. *The pyrolysis system*

The object to be treated is introduced into a suitable container, filled with saturated hydrocarbon gas, and heated to a temperature sufficient for the formation of a layer of pyrolytic graphite on its surface. At 2100 ± 20° C a uniform coating is formed on various carbon substrates, its thickness depending on the duration of the deposition and on the composition of the gases inside the pyrolysis chamber. The scheme of the pyrolysis system is shown in Fig. 2. The cloth is placed between the copper clamps and fixed firmly, with uniform tension. Short, additional strips of cloth are put on both sides of the cloth, at the clamped edges, as protection against rupture by the applied pressure. The area to be coated is 50 mm x 60 mm. The base of the pyrolysis system is covered with an inverted 3 l stainless steel pot, with a small (ϕ = 10 mm) opening at its centre, through which the pyrolysis temperature may be measured. The CH_4/He gas mixture, in the desired ratio, enters the chamber through a gas inlet located at its base, at a rate monitored by an appropriate flowmeter. The high temperatures prevailing in the chamber gradually soften the copper clamps; these must, therefore, be hardened periodically.

The pyrolytic coating process proceeds in five steps:

(a) He gas is streamed through the chamber at the rate of 2 l min^{-1} for 15 min, to ensure an inert

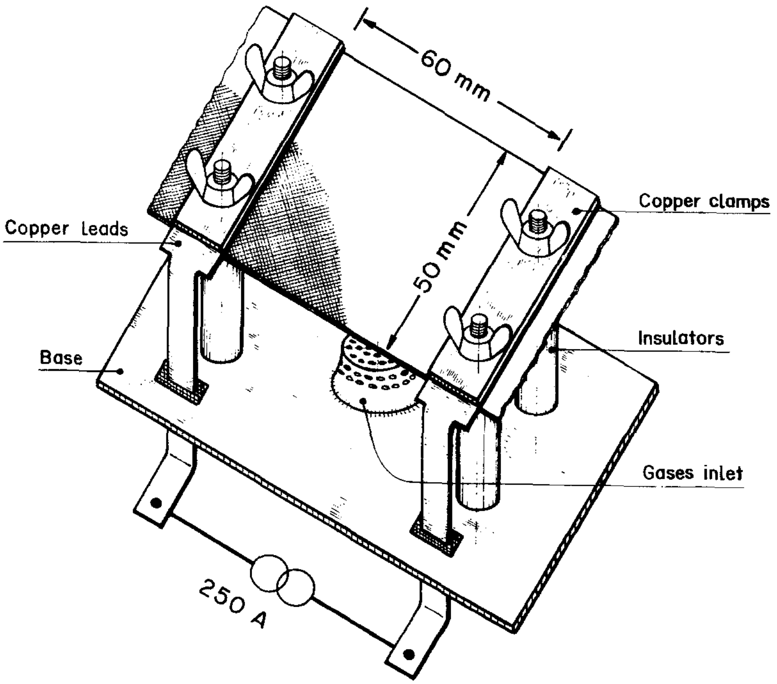

Fig. 2. Schematic outline of pyrolysis system.

atmosphere and prevent subsequent oxidation of the cloth.

(b) The electric current is switched on for a moment to heat the cloth sufficiently to remove any moisture from it.

(c) The CH_4/He mixture is streamed through the chamber at $3\,l\,min^{-1}$, for 5 min.

(d) The electrical current is switched on for 15 s.

(e) The cloth is allowed to cool to room temperature, with He again streaming through the chamber.

CH_4/He ratios of 0·07, 0·2 and 0·5 were tested in step (c), above; in experiments designed to study the influence of the thermal treatment exclusively, pure He gas was used.

The pyrolysis temperature was determined by scanning the radiation of the incandescent cloth, through the opening on top of the pyrolysis chamber, with a pyrometer (the Pyrometer Instrument Co, Inc., Bergerfield, NY). The observed temperature variations are ascribed, in the main, to the varying composition of the pyrolysis gas mixture and the slight variations in tension in the clamped cloth. The thickness of the coating is limited by stresses between successive graphite layers formed and between the graphite and the substrate.

2.4. *Electrochemical apparatus and methodology*

Cyclic voltammetry was the method chosen to monitor the changes incurred in the electrochemical performance of the cloths as a result of the pyrolytic coating. Voltammograms recorded under identical conditions were compared. All measurements were made with a three-electrode set-up, using a home built potentiostat (50 mA/ 50 V) capable of compensating iR-drops by positive feedback, and a triangular wave generator. The voltammograms were recorded on a Yokogawa 3078 X–Y recorder. Small potential differences were measured with a Null-Mikrovoltmeter, Knick, Berlin.

3. Results and discussion

The mechanical properties of carbon cloth are significantly improved by pyrolytic coating, which adds 5–10% weight to the cloth, depending on the duration of the deposition. (In contrast, carbon cloth subjected only to the thermal treatment loses about 5% of its original weight.) With the added weight, the mechanical strength also increases: woven cloth strips which had been coated and then subjected to moments of $15\,g\,cm^{-1}$, bent to a 45° angle versus the supporting surface and did not break up to moments of $30\,g\,cm^{-1}$. Untreated cloth does not break, but immediately bends to the maximum angle under the force exerted by its own weight. This 'stiffening' effect is anisotropic; the results given above relate to the direction in which the cloth is stretched in the pyrolysis system but in that normal to it they are a little lower.

The stiffening of the cloth prevents its wrinkling or deformation by the streaming of solution through it. It also assures that the relative position of the threads in the cloth does not alter from experiment to experiment (thus ensuring constancy in electrode configuration).

Cyclic voltammograms, recorded with the blank solution in two potential ranges: (a) 0·0 to + 0·5 V and (b) − 0·9 to + 0·9 V versus the Ag/AgCl reference electrode, at electrodes made of untreated and treated cloth, were compared. Flat base lines were recorded in the narrow range with all electrodes (untreated and treated cloth).

Pyrolytic treatment affects the electrode surface. At the lowest CH_4/He ratio background currents are lowest, increasing gradually with increasing methane content.

After one single cyclic run (Fig. 3), untreated carbon cloth electrodes (curve a in Fig. 3) acquire very high residual currents, which cannot, subsequently, be removed. Thermally treated carbon cloth (curve b in Fig. 3) behaves similarly, although the residual currents are somewhat smaller. Pyrolytically coated electrodes (curve c in Fig. 3) remain unaffected. Residual currents remain low after repeated runs, extending beyond the potential limits of the system, where the medium becomes electroactive, resulting in high current densities. The 'narrowest' cyclic voltammograms (lowest residual currents) were recorded at carbon cloth electrodes which had been coated with the lowest methane content in the CH_4/He mixture (0·07 vol%); with rising CH_4 content the voltammograms broaden slightly.

The improved performance of pyrolytically

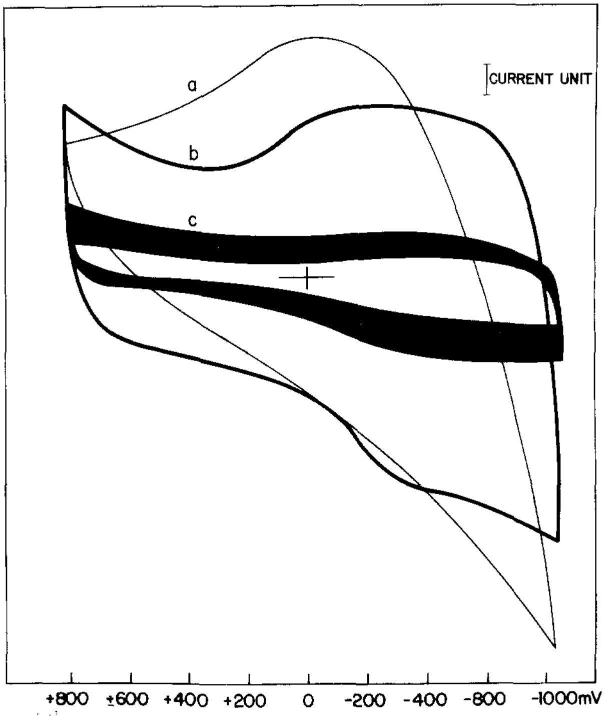

Fig. 3. Cyclic voltammetry of carbon screens, in 0·5 M KCl, pH 9, after different treatments: (a) untreated cloth; (b) thermally treated cloth; (c) range of variance of three pyrolytically coated screens. Recorder sensitivity (μA/current unit): (a) 1000; (b) 500; (c) 100.

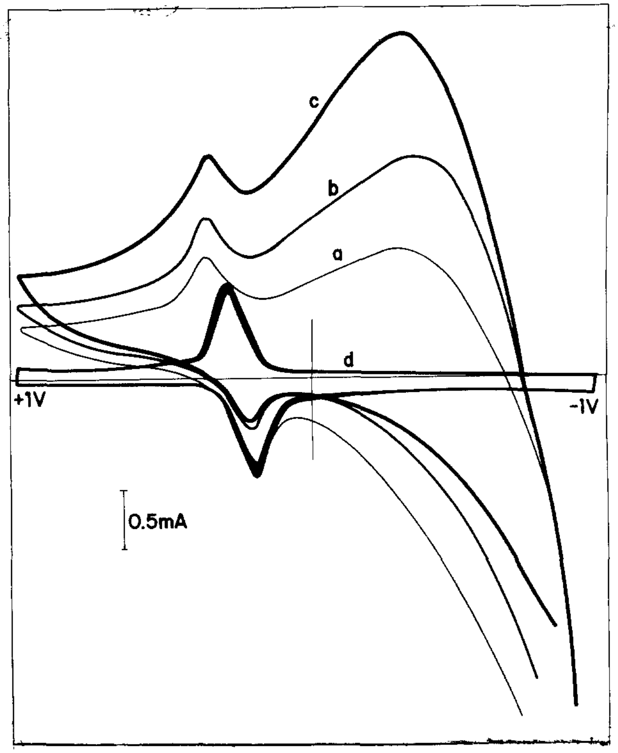

Fig. 4. Cyclic voltammetry in 10^{-3} M $K_3Fe(CN)_6$, 0·5 M KCl, pH 9 solution on: (a), (b), (c) untreated and: (d) treated carbon cloth.

coated carbon cloth electrodes becomes evident on the addition of an electroactive substance [$K_3Fe(CN)_6$] to the blank solution. On the untreated cloth current peaks related to the $K_3Fe(CN)_6$ are superimposed on a large residual background, making their evaluation impossible (Fig. 4, a–c); on the treated cloth, a well-shaped cyclic voltammogram is obtained (Fig. 4d).

The peak heights recorded (i.e. the electrochemical surface areas of) at the electrodes seem to be virtually unaffected by the treatment (Fig. 4). This supports the assumption that the main effect of the pyrolytic treatment is the removal of electroactive surface groups, with the concommittant decrease in the originally high background currents.

Since the pyrolytic treatment results in the deposition of a graphite layer on the carbon cloth and in view of an earlier study conducted in this laboratory [9], graphite cloth (TGM 285) was subjected to the same treatment and its behaviour studied. As expected, voltammograms recorded on untreated and treated graphite cloth were virtually identical with those obtained with treated carbon cloth electrodes.

The 'equalizing' effect of the pyrolytic treatment is shown in Figs. 5a and b showing the result of superimposing ten cyclic voltammograms, recorded at ten different graphite and ten different pyrolytically coated carbon screens, respectively. It may be noted that the cloth electrodes behave in a way resembling a thin layer cell because most of the reactant volume is imprisoned between the strands in narrow channels. The smaller currents recorded at the carbon cloth electrodes are due to the difference in the thickness of the strands used in weaving the original cloth: that of the graphite cloth is thicker, thus providing a larger electrochemical surface for the same 1 cm^2 electrode area. (The number of strands per unit area is the same for both kinds of cloth; the void space remaining in between is smaller in the case of the heavier graphite cloth.)

Attempts at achieving good 'wetting' showed treated carbon cloth to be superior to graphite cloth; the latter suffers an approximate 10% weight loss during the rinsing with organic solvents. The use of graphite cloth for electrode assemblies designed for use in organic solvent systems is therefore inadvisable.

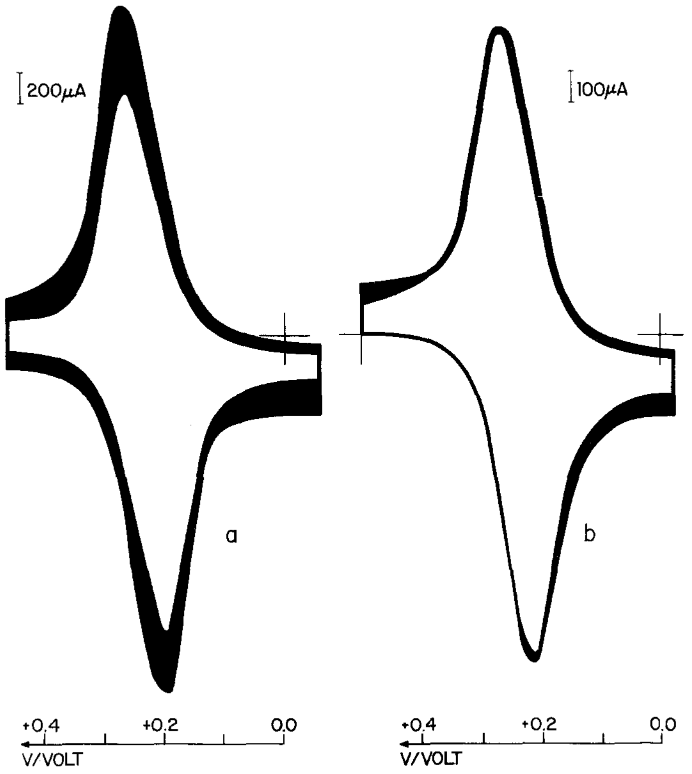

Fig. 5. Cyclic voltammetry of ten graphite (a) and ten carbon (b) screens, all after pyrolytic treatment, in 10^{-3} M $K_3Fe(CN)_6$, 0·5 M KCl, pH 9 solution.

The improved mechanical and electrochemical properties of the pyrolytically coated cloth triggered further research, investigating its performance as an electrode in flow through cells. Results of this work will be reported forthwith [10].

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