SHORT COMMUNICATION

Graphite felt as an electrode for thin–layer electrochemistry

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1. Introduction

Thin layer electrochemistry has been extensively studied as an electroanalytical tool since 1963 [1]. Among the important features typifying this method are the low current densities involved, which allow highly irreversible reactions to be studied, the easily attainable steady state conditions, the high sensitivity and the extremely small volumes that can be used.

Several thin layer electrochemical cells were designed throughout the years. As reviewed by Hubbard and Anson [2], the most important are the capillary wire electrode, the micrometer electrode, chamber electrodes, electrodes made from flat glass plates coated with metal films and the mercury pool electrode.

Most of the cells mentioned above are rather sophisticated and require elaborate methods, both in their construction and use. A simplified approach to the design of a thin layer cell was presented by Yoshimura *et al.* [3] with the introduction of a porous filter paper as a separator between a mercury and a platinum working and auxiliary electrodes respectively.

In the present paper we introduce a new concept for the design of thin layer electrochemical cells. In this cell, the working electrode is made of graphite cloth or felt separated from the tested bulk solution by a porous electrically inert material. The graphite felt used in the present work as a working electrode has a specific surface area of approximately $1\,m^2\,g^{-1}$ (as determined by the BET method) and a void volume of approximately 90% of the total volume. It is composed of conductive fibres, $10\,\mu m$ in diameter.

From these specifications, an average thickness of $10–50\,\mu m$ can be estimated for the solution layer attached to each individual fibre. This is also the average spacing between the fibres as can be observed by SEM. Each fibre and its solution layer essentially forms a thin layer cell element. If the electrode is properly isolated from the bulk solution so that diffusion of ions to it is negligible, it should function as a well defined thin layer cell.

The use of fibrous conductive matrices provides a fast and convenient way for constructing thin layer electrochemical cells: they are easily replaceable when necessary and no special adjustments are required.

2. Experimental details

The experimental setup is shown schematically in Fig. 1. Graphite felt, RVG-2000 (Le Carbon Lorrein, France) was used as a working electrode. A disc of this material, 4 mm thick and 10 mm in diameter, was lightly pressed by a glass rod between two 3 mm thick sintered glass discs and mounted in a glass tube which was dipped in the solution. A gold wire served as a current collector.

The void volume of the working electrode strongly depends on the pressure applied to it. Since this factor determines the amount of the electroactive species entrapped within the electrode, it is important to apply the same pressure upon replacing the electrode in order to guarantee good reproducibility. In the present case this was done by keeping the two frit glasses 3.5 ± 0.01 mm apart. This distance provided a pressure which assures good contact between the gold current collector and the felt and yet allows free solution flow through the later. Once this distance is set and remains unchanged throughout the runs, peak currents reproducible in the $\pm 2\%$ range are acquired. It should be noted that a single electrode should serve for many runs provided it is treated properly (i.e.,
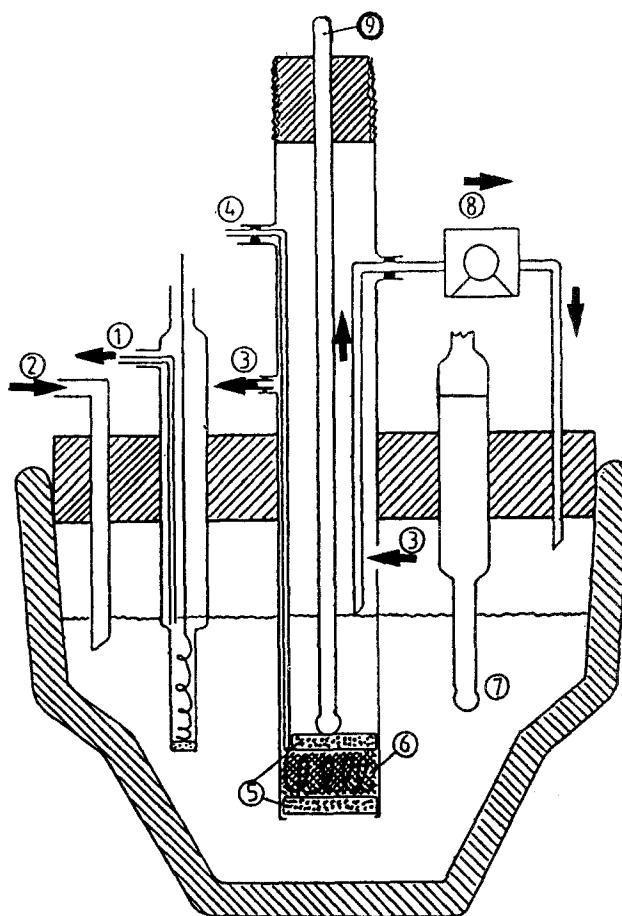

Fig. 1. The electrochemical cell: 1 — Auxiliary electrode; 2 — Argon inlet; 3 — Argon outlet; 4 — Gold wire; 5 — Sintered glass; 6 — Working electrode (graphite felt); 7 — Reference electrode; 8 — Peristaltic pump; 9 — Glass rod.

contamination is avoided by regular treatment with acid or exposing to high anodic potentials).

Since the electrode is bulky and was partially separated from the bulk solution by the sintered glass discs, provisions were made to circulate the solution through it and to face it with a fresh solution whenever required. This was done by pumping the solution from the rear side of the electrode by a mini peristaltic pump and returning it to the main vessel as shown in Fig. 1.

The relatively thick sintered glass discs supporting the graphite felt provide an efficient protection from diffusion of electroactive species into and from the solution entrapped within the felt during a single experiment. This can be figured out as follows: According to Einstein's expression, $X^2 = 2Dt$ (where X is the diffusion distance and D the diffusion coefficient), the characteristic diffusion time, t, through a glass disc is 100 min whereas a typical voltage sweep takes about 10–20 min.

A platinum wire separated by a frit glass was used as a counter electrode. In order to minimize interference of the counter electrode reaction products with the reactions occurring on the working electrode, the solution level in the counter electrode compartment was kept slightly below that in the cell by pumping it through a thin Teflon tube connected to a vacuum line.

Linear sweep voltammetry was applied using an Opal (Israel), Model 30-50, potentiostat and a PAR, Model 175, universal programmer. In a typical experiment the solution was circulated for several minutes through the working electrode at a flow rate of $2\,\mathrm{ml\,min^{-1}}$ under open circuit conditions to ensure a complete replacement of the solution encased within the internal electrode volume. Then the pumping was stopped and the potentiostatic linear voltage sweep was commenced.

3. Results and discussion

In order to test the effectiveness of the graphite felt as a thin layer cell we used the reversible redox reactions
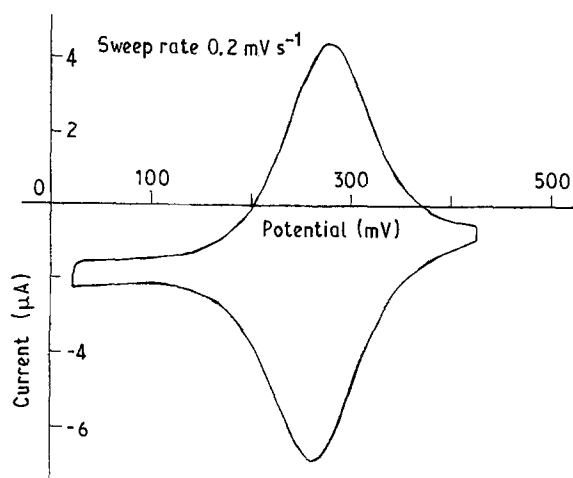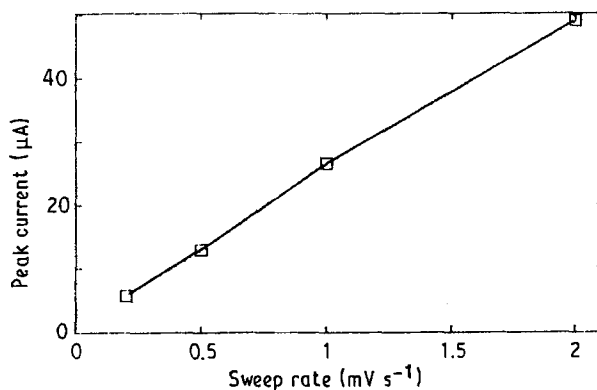

Fig. 3. Peak current as a function of the sweep rate for the couple ferro–ferri cyanide.

of the couple ferro–ferri cyanide. Figure 2 shows that a typical voltammogram taken with 10^{-4} M ferricyanide in 1 M $NaClO_4$ follows the well known dual bell shape pattern. In Fig. 3 the peak current is given as a function of the sweep rate. The curve up to $1\,\mathrm{mV\,s^{-1}}$ follows a straight line with a slope of $0.02626\,\mathrm{A\,V^{-1}\,s^{-1}}$. The theoretical slope for a reversible reaction can be calculated from the expression,

$$I_\mathrm{p} = \frac{n^2 F^2 V C^0}{4RT} \ (r)$$

as given by Hubbard and Anson [2]. In this equation, I_p is the peak current, n the number of electrons taking part in the reaction; r, the sweep rate; V, the void volume of the felt electrode; C^0, the bulk concentration; F, the Faraday number and R and T are the gas constant and the absolute temperature respectively. The calculated slope is 0.02816 which is in good agreement with the experimental figure given above.

Figure 4 shows the dependence of the difference between the cathodic and the anodic peak potentials on the sweep rate. It is evident that up to $1\,\mathrm{mV\,s^{-1}}$ difference is constant (11–15 mV) and increases significantly as the sweep rate increases. Although theory predicts a complete overlap of the two potentials for a reversible reaction, most of the thin layer cells proposed in the past, as well as the present one, show a difference even at very low sweep rates [4]. This difference can be eliminated by placing the reference elec-

Fig. 2. A typical thin layer voltammogram for the couple ferro–ferri cyanide.
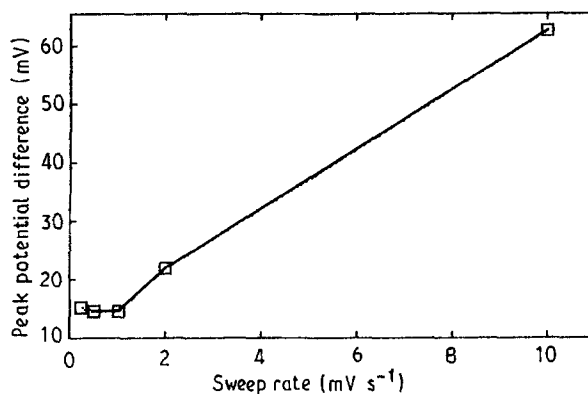

Fig. 4. The difference between the cathodic and anodic peak potentials as a function of the sweep rate.

trode as close as possible to the working electrode, a requirement which is not easily achieved with many of the thin layer cells.

As an additional support for the effectiveness of the graphite felt as a thin layer cell it should be noted that the integral charge calculated from the area under each peak is within $\pm 5\%$, in agreement with the charge equivalent contained in the solution entrapped within the electrode void volume. This proves that the electrode is indeed well isolated from the bulk solution during the voltage sweep.

References

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[2]   A. T. Hubbard and F. C. Anson, in 'Electroanalytical Chemistry', Vol. 4, edited by A. J. Bard, Marcel Dekker, New York (1970) p. 129.

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