A DUAL WORKING ELECTRODE COULOMETRIC FLOW CELL

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A number of laboratory-scale coulometric flow cells have been described[1–3]. These have generally been employed for analytical purposes or for the electrochemical preparation of solutions for spectroscopic investigations. Flow cells incorporating two working electrodes, which can be used for carrying out two electrochemical steps on a flowing solution have also been devised[4–6]. The cell of Fujinaga *et al.*[4] employed two large beds of granular glassy carbon electrodes and was employed for the coulometric analysis of plutonium solutions; one electrode adjusted the oxidation state of the plutonium ions to a single known level and the second was used for the analysis itself. The cell of Braun *et al.*[5,6] was a voltammetric flow cell containing two closely spaced electrodes in a flow channel, and was similar in its applications to the rotating ring–disk electrode (RRDE). A species could be electrogenerated at one electrode and detected and collected at the second. While the RRDE or stationary electrodes with reversal techniques (*e.g.*, cyclic voltammetry) can be employed for elucidation of the mechanism of reaction for many electrochemical reaction schemes, there are some cases where additional analytical methods must be employed. Consider, for example, the reaction mechanism

$$O + ne \rightleftarrows R \xrightarrow{k} R' \tag{1}$$

where R and R′ are oxidized at nearly the same potential. Reversal or RRDE collection techniques are incapable of distinguishing between R and R′. Another case would be

$$O + ne \rightleftarrows R \underset{\searrow B}{\overset{\nearrow A}{}} \tag{2}$$

where, for example, neither A nor B are electroactive. The rate of disappearance of R could be determined electrochemically, but the fractional formation of A and B could not.

We describe here a dual electrode flow cell for studying electrode reactions. It is constructed of the thin porous electrodes separated by a thin insulated gap (Fig. 1). Solution flows first through one electrode (the generator electrode), maintained at a certain potential, E_g, then across the gap and to the second electrode (the detector electrode) maintained at a second potential, E_d. The flow rate is adjusted so that electrolysis at both electrodes is essentially complete ($>99\%$)

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and the transit time between electrodes across the insulator gap is known. The collection efficiency of the detector electrode can be measured, analogous to measurements at the RRDE, but also the collected effluent solution can be analyzed, at leisure, for starting material regenerated, products formed, etc. by electrochemical, spectroscopic or chromatographic techniques. The design differs from previous flow cells in its attempt at keeping the electrode thickness in the flow stream small while still maintaining high electrolytic conversion.

EXPERIMENTAL

Apparatus

    The dual electrode assembly is shown in Figs. 1 and 2. The circular porous working electrodes are porous silver disks 5 μm average pore diameter, available from Selas-Flotronics Co., Spring House, Pa. (Fig. 3). They are separated by a porous Teflon material (TRT/Kressilk, Elmsford, N.Y.), 200 μm thick, with a 0.2 cm^2 hole at the flow channel. The electrodes and separator were held in place between two O-ring joints (5 mm i.d.) (Ace Glass Co.). The leads to the working electrodes were thin platinum wires which pierce the O-rings. Two thin Teflon spacers with a 5 mm diameter hole held the contact wires, working electrodes and separator firmly in place. The joint assembly was held together by a Teflon clamp (not shown). The assembly could be taken apart quite easily for cleaning and replacement of the working electrodes.

    Each working electrode is provided with its own auxiliary (platinum) and reference (SCE) electrodes which are situated in individual compartments extending from the side of the flow channel and separated from it by either a fine glass frit or a filter paper plug as shown. The reference electrodes probe each working electrode very closely by means of glass capillaries connected to the reference
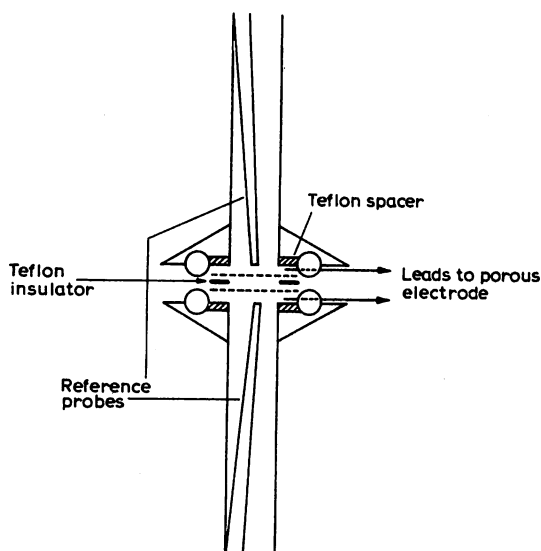

Fig. 1. Close-up view of the dual working electrodes and "O-ring" joint portion of the assembly.
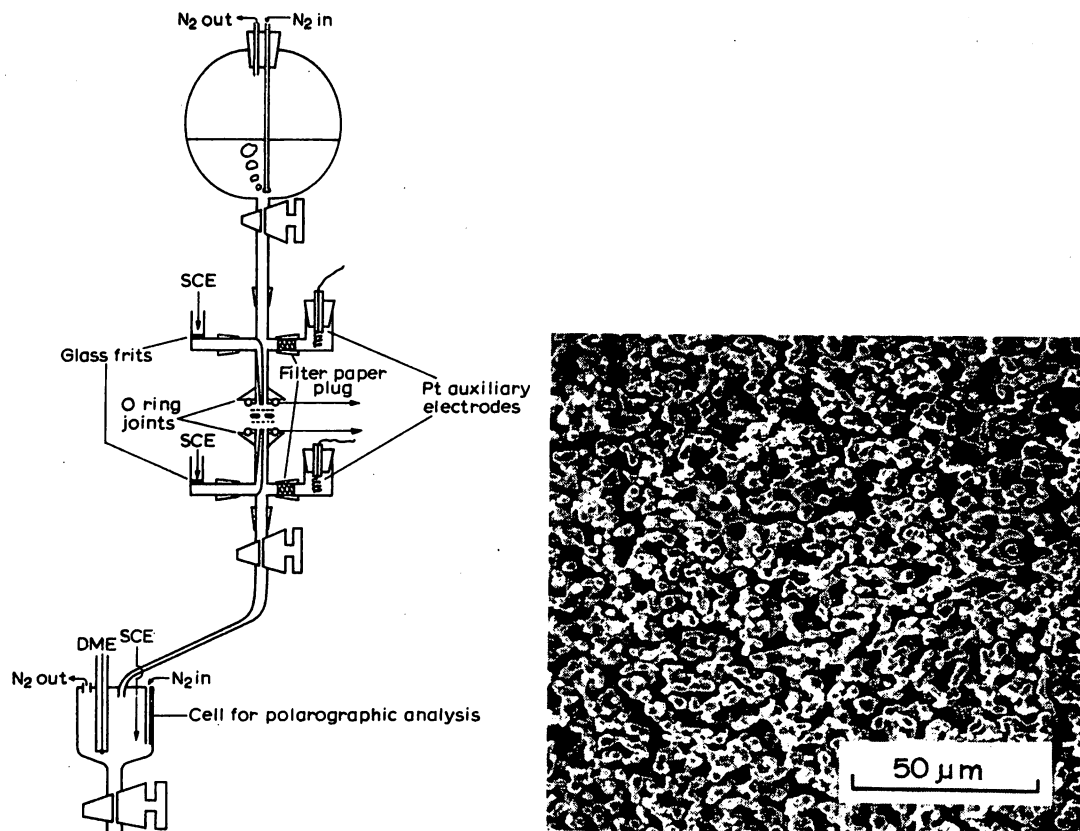
Fig. 2. Diagram of the complete dual working electrode flow cell assembly. Solution flows by gravity from the upper solution reservoir to the lower analysis cell. For greater clarity the "O-ring" joint portion of the cell is in an exploded form.

Fig. 3. Scanning electron microscope photograph of porous silver electrode material.

compartments as shown. The cell assembly is connected, by means of standard taper joints, to the solution reservoir and to an outlet tube. The solution flows under gravitational force from the reservoir and the flow rate is adjusted by means of one or both stopcocks. For testing the cell, analysis of the effluent solution was accomplished using d.c. polarography with the solution flowing directly into the polarographic cell. Nitrogen was used in the reservoir and polarographic cell for deaeration.

Two completely separate control circuits must be used with this cell and only one of the working electrodes can be grounded; a similar six electrode system is required in the cell of Braun et al.[5,6]. In test experiments with one working electrode, the potential was controlled with either a Wenking Model 61RH or a Princeton Applied Research (PAR) Model 173 potentiostat. In two electrode experiments, the detector electrode potential was adjusted under solution flow with a simple battery–potentiometer combination with the potential measured vs. the reference electrode with a Digitec Model 204 voltmeter and the current measured

with a Heath Model IM 102 digital multimeter, while the generator electrode was controlled with a potentiostat. Polarographic analyses of the effluent solutions were performed using either a Sargent Model XV polarograph and a simple dropping mercury assembly, or a PAR Model 170 instrument with a PAR Model 172 drop timer.

Flow rates were determined by measuring the volume of solution collected in a graduated cylinder during a standard time interval, determined with an electric stop clock. All reported currents have been corrected by subtracting the background current observed at the same flow rate for solutions not containing the electroactive species.

Chemicals

Reagent grade chemicals were used in the preparation of all solutions. Nitrogen used for deaeration was passed over heated copper wire before introduction into the cell. The water for preparation of solutions was deionized water. It was also necessary to filter the aqueous solutions through a Flotronics glass fiber millipore filter (PF-10) or a porous silver disk filter before introduction into the flow cell. Failure to do a prefiltration led to gradual clogging of the porous disk working electrodes and changes in flow rate with time. N,N-dimethylformamide (DMF) and the organic compounds were purified as described elsewhere[7]. The prefiltration step was unnecessary with the DMF solutions.

RESULTS AND DISCUSSION

Principles

Although a number of treatments of flow through a porous electrode have appeared (see, for example, ref. 1), the rather complex nature of the electrode material (see scanning electron microscope photograph, Fig. 3) and the desire to use it mainly under coulometric conditions (that is, a high degree of conversion on flow through the electrode) suggest that only a simple approximate treatment is merited. We assume that electroactive material in a pore must diffuse radially to the walls of the pore to be electrolyzed, while moving through the pore in the flow stream. The average time, t, necessary for a species with diffusion coefficient, D, to diffuse a distance, l, is

$$t \approx l^2/2D \tag{3}$$

The rate of movement down the pore is v/a, where v is the flow rate of solution in $cm^3 \, s^{-1}$ and a is the total cross sectional area of the pores (cm^2). Thus, an element of solution moves a distance, x, down the pore in a time

$$t = ax/v \tag{4}$$

so that for a high conversion efficiency in a porous electrode, material must diffuse a distance equal to the radius of the pore, r, in a time, t, given by eqn. (4) with x equal to L, the thickness of the porous electrode, or

$$r^2/2D = aL/v \approx t \tag{5}$$

Thus, high conversion efficiency will be obtained as long as

$$v \leqslant 2aLD/r^2 \tag{6}$$

For the porous silver disk electrodes, $L = 50$ μm, $r = 2.5$ μm (for 5 μm pore), and $a \approx 0.1$ cm^2 (assuming a pore area of half the surface area); eqns. (5) and (6), with a D of 5×10^{-6} cm^2 s^{-1}, lead to a maximum flow velocity of about 0.1 cm^3 s^{-1} (6 cm^3 min^{-1}) and a residence time in the electrode of about 5 ms. At this flow rate, solution crosses the interelectrode gap of 200 μm in about 40 ms. More porous electrode materials, such as platinum gauze (e.g., 80 mesh) or gold micromesh could also be employed as electrode materials, but these required longer residence times (either thicker electrodes or slower flow rates) to attain high conversion.

By Faraday's law, the current, i, can be related to v and concentration, c, by the equation

$$i = nFcvf_c \tag{7}$$

where f_c is the conversion efficiency, which depends upon v, electrode dimensions and conformation, etc.; for total conversion on passage through the electrode, $f_c = 1$.

Single electrode experiments

To test the conversion efficiency as a function of flow rate, experiments were performed with electrolysis occurring at only one working electrode by comparing the measured current to that calculated from the known values of v and c. The f_c value was also determined by polarographic analysis of the effluent solution at different flow rates. A typical graph of reduction current vs. flow rate for a solution containing 1 mM copper((II) sulfate, 1 M ammonium chloride and 1 M ammonia with the silver electrode maintained at potentials on the limiting current plateau for the reduction of Cu(II) to Cu(I) is shown in Fig. 4. The dotted line shows the predicted current for $f_c = 1$ using eqn. (7). In this experiment conversions greater than 99% occur for flow rates up to 0.5 ml min^{-1}. The actual flow rate limit for high conversion depended strongly upon the particular silver disk electrode employed. Changing from one disk to another in the same lot would give very different current and efficiency behavior. For example, consider efficiencies determined for a solution containing 1 mM iron(III) and 0.25 M potassium oxalate at various flow rates by reduction of the Fe(III) to Fe(II) at a silver disk electrode maintained at -0.45 V vs. SCE and analysis of the effluent solution by d.c. polarography for Fe(III) and Fe(II) (Fig. 5). For this electrode greater than 99% conversion occurred for flow rates up to 3 ml min^{-1}. Under conditions of $f_c > 0.99$, the measured and calculated (eqn. (7)) currents were in close agreement with each other. For example, for flow rates of 0.22, 0.32, and 2.04 ml min^{-1}, experimental currents of 0.40, 0.59, and 3.69 mA, were measured, compared to calculated values of 0.40, 0.59, and 3.70 mA, respectively.

Efficiency studies for aprotic solvents were carried out with solutions of diethyl fumarate (DEF) in DMF solutions containing 0.1 M tetra-n-butyl-ammonium fluoroborate, since we were interested in using this cell to study the isomerization of diethyl maleate to DEF[7]. Typical results of experimental current vs.
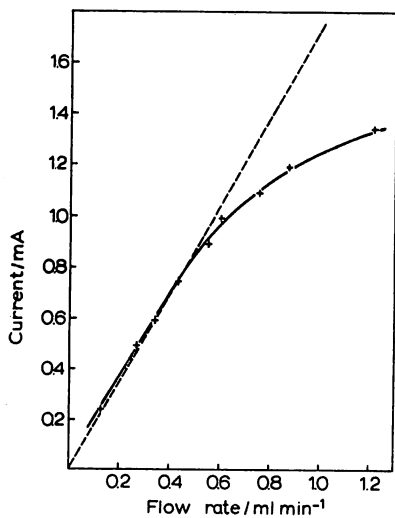
Fig. 4. Current as a function of flow rate for reduction of 1 mM Cu(II) in 1 M NH$_3$–1 M NH$_4$Cl at a single porous silver disk electrode. Dotted line represents calculated values for 100% efficiency of reduction.
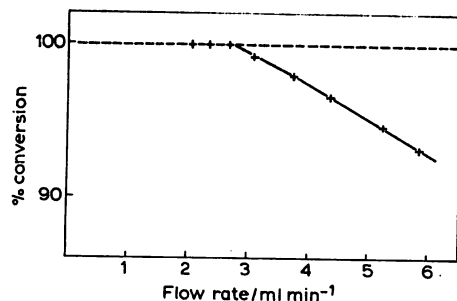
Fig. 5. Efficiency of reduction of 1 mM iron(III) in a 0.25 M potassium oxalate solution, based on effluent analysis, at a single porous disk electrode.
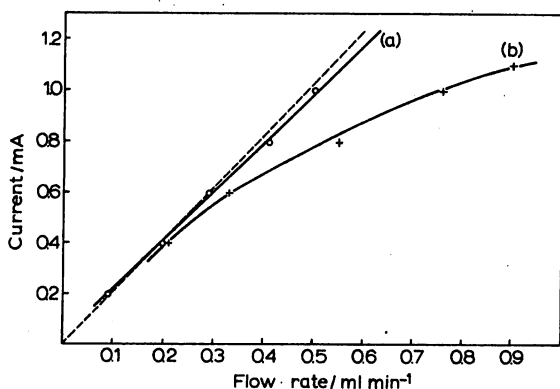

Fig. 6. Current as function of flow rate for the reduction of 1.4 mM diethyl fumarate in DMF–0.1 M tetra-n-butylammonium tetrafluoroborate. (a) First results with values taken from high to low flow rates. (b) Results taken after experiments in (a), showing effect of polymerization. Dotted line represents calculated values for 100% efficiency of reduction.

flow rate are shown in Fig. 6. While the results are generally in agreement with those in aqueous solutions, the polymerization side-reactions of the anion radical[8] cause film formation on the working electrode and change of efficiency with time. In Fig. 6, the five experimental points in curve (a) were taken quickly from high to low flow rates and agree quite well with the calculated ($f_c = 1$) line. During this experiment, however, a visible amount of yellow polymer appeared to be building up on the working electrode, and experimental points taken later

(curve b) show a significant decrease in conversion efficiency, especially at the higher flow rates.

Two electrode experiments

The efficiency of collection of a second, detector, electrode following complete conversion at the generator electrode, was tested using the Fe(III)–potassium oxalate system. Current–potential curves for both electrodes with a flow rate of 0.72 ml min^{-1} are shown in Fig. 7; the upper curve is a plot of generator electrode current (i_g) vs. E_g and the lower curve is a plot of detector electrode current (i_d) vs. E_d for E_g maintained at -0.45 V vs. SCE. These curves are similar to disk and ring voltammograms found with the RRDE, except here the collection efficiency of the detector electrode approaches 100%. A graph of i_g, for $E_g = -0.45$ V, and i_d, for $E_d = +0.27$ V, at different flow rates for this same system is shown in Fig. 8. Note the equality of i_d and i_g even at flow rates where the conversion efficiency at the generator electrode falls below 100%.
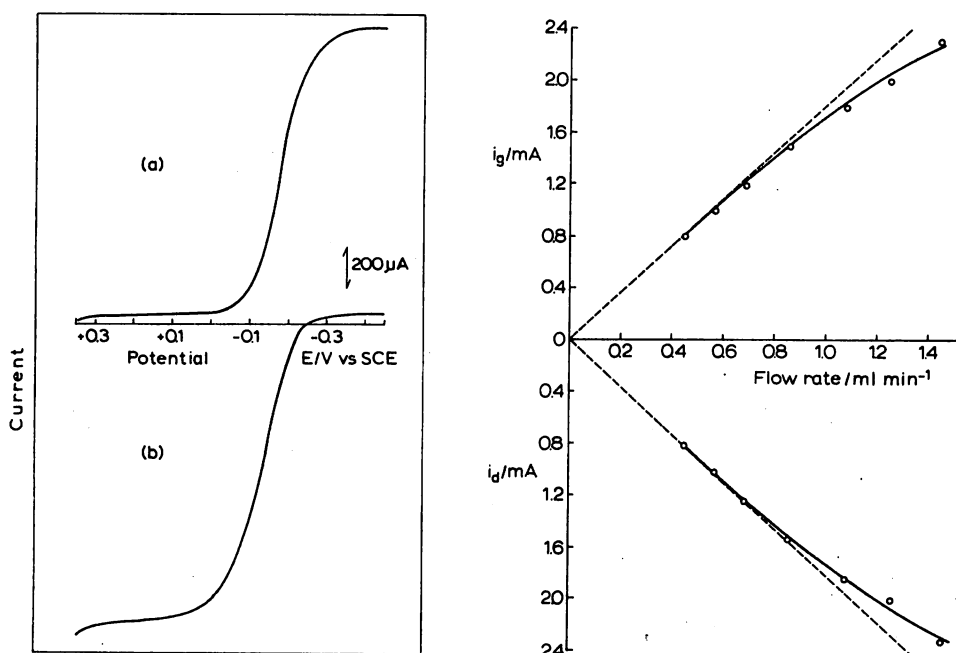
Fig. 7. Dual working electrode flow cell experiment for 1 mM iron(III)–0.25 M oxalate system. (a) i_g vs. E_g, (b) i_d vs. E_d with $E_g = -0.45$ V vs. SCE.

Fig. 8. i_g and i_d for dual working electrode flow cell for 1 mM iron(III)–0.25 M oxalate system, with $E_g = -0.45$ V (reduction Fe(III)→Fe(II)) and $E_d = +0.27$ V (oxidation Fe(II)→Fe(III)), as a function of flow rate.

The dual electrode system has also been used for studies with DMF solutions of DEF and diethylmaleate (DEM)[7]. These studies involved reduction of either DEF or DEM at the generator electrode, reoxidation of the products at the indicator electrode, and analysis of the effluent solution for products and starting material.

The results showed unambiguously that the radical anion of DEM isomerizes to that of DEF and also undergoes dimerization in a time which is short compared to the transit time between the electrodes. Full details are given elsewhere[7].

In addition to the obvious kinetic measurement applications of the dual electrode flow cell, which generally will require a more reproducible system for quantitative masurements, one can envisage preparative applications such as a two-step electrolysis of a flow stream, with a programmed time delay between the two steps or perhaps the addition of a second reagent stream between the two electrodes. Other electrode materials certainly merit investigation; these include silver disk electrodes of smaller pore sizes (utilizing flow under high pressure), gold micromesh electrodes[9], and other forms of woven wire cloth electrodes.

ACKNOWLEDGMENT

SUMMARY

A flow cell comprising two thin, closely-spaced, porous silver disk electrodes as generator and indicator electrodes is described. The range of maximum flow rates for greater than 99% conversion at the generator electrode was investigated using aqueous and DMF solutions and shown to be about 0.5 to 3 ml min^{-1}. At these flow rates the efficiency of collection of electrogenerated product at the indicator electrode approaches 100%. Applications of such a dual-electrode flow system are described.

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