
NEW HIGHLY EFFICIENT COULOMETRIC CELL WITH HOMOGENEOUS POTENTIAL DISTRIBUTION ON THE WORKING ELECTRODE

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A highly efficient coulometric cell was designed and constructed, ensuring a constant potential over the whole surface of the working electrode and suitable for very rapid electrolysis. It consists of concentric cylindrical Teflon parts; also the working and auxiliary electrodes are cylindrical and concentric. Electrolysis can be carried out under anaerobic conditions. Functioning of the cell was tested on the oxidation of hexacyanoferrate(II) and chlorpromazine and reduction of hexacyanoferrate(III). The new cell is suitable for routine quantitative analyses and in studying the mechanism and kinetics of moderately rapid chemical reactions.

Coulometry with controlled potential of the working electrode is suitable not only for the determination of various electroactive substances but also for the study of the mechanism and kinetics of electrochemical reactions^{1,2}. In our opinion, the method could be more widely used if some experimental difficulties were overcome, related to the reproducibility of measurements and conditioned by the construction of the reliably working coulometric cell. It is essential in this respect that the potential distribution over the surface of the working electrode be uniform; this depends on the cell geometry.

Another condition for reliable analysis is that the time of electrolysis be as short as possible. This helps to eliminate interfering effects (residual charge or parasitic chemical reactions) increasing with time, and enables one to repeat the electrolysis several times within an acceptable time interval. Thus, the results can be treated statistically and the influence of random errors suppressed.

Last but not least, the form of the cell should be as simple as possible to prevent hydrodynamic complications, which could produce fluctuations of the measured current, adversely affecting the reproducibility of measurements of the current–time or charge–time dependences.

Analysis of Conditions for Optimum Course of Coulometric Measurements

Potential distribution on the surface of the working electrode depends on the

distribution of current density at the surface^{3,4}. Its uniform distribution can be achieved by placing the auxiliary electrode symmetrically with respect to the working electrode, their surfaces being parallel to each other, *i.e.* in our case they are concentric cylinders. Any deviation from symmetry would cause inhomogeneous electric field between the electrodes, *i.e.* nonuniform distribution of current density on their surfaces, and accordingly nonuniform polarization of the working electrode. The differences between polarization at various points on the surface may reach several hundreds of mV in solutions of low conductivity⁴, resulting in systematic errors in controlled-potential coulometry. Thus, parasitic reactions, *e.g.* decomposition of the supporting electrolyte may proceed on a portion of the electrode surface, which makes selective electrolysis impossible: the difference between half-wave potentials of two components may be lower than the difference in polarization between two regions of the working electrode surface⁴.

The time of electrolysis can be minimized in two ways: either by increasing the rate of stirring or by increasing the ratio of the surface area of the working electrode to the volume of the electrolysed solution. A very intense stirring increases the rate of the mass transport, but at the same time bubbles are formed by turbulence of the solution. This causes fluctuations of the current, an undesirable phenomenon in predictive coulometry* and in studying the kinetics and mechanism of chemical reactions, where the instantaneous current is important. The stirring rate can therefore be increased only to a certain limit.

The ratio of the surface area of the working electrode (A) to the volume of the electrolysed solution (V) is limited by the condition that the volume of the diffusion layer be negligible against that of the solution. In the proposed coulometric cell, for example, it is possible to attain $A/V = 5 \text{ cm}^{-1}$. Thus, with a Pt gauze of 25 cm^2 surface area, 5 ml of the solution can be used. The thickness of the diffusion layer δ may be estimated from the equation^{5,6} valid for the rotating disc electrode

$$\delta = 1.61 \cdot D^{1/3} \nu^{1/6} \omega^{-1/2}, \quad (1)$$

where D denotes diffusion coefficient, ν kinematic viscosity, and ω angular frequency. For $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\nu = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and $\omega = 100 \text{ rad s}^{-1}$ (or approximately 950 r.p.m.) we obtain $\delta = 0.016 \text{ cm}$. With an electrode surface area 25 cm^2 , this represents a volume of 0.04 cm^3 , *i.e.* only 0.8% of the total volume 5 cm^3 . If the ratio of $A/V = 5 \text{ cm}^{-1}$ were exceeded to a large extent, a systematic error would arise, since the conditions of electrolysis would change towards thin-layer electrolysis, where the processes cannot be described by ordinary differential equations.

* Predictive coulometry makes it possible to calculate, before the electrolysis is finished, the charge necessary for complete conversion of the electroactive substance.

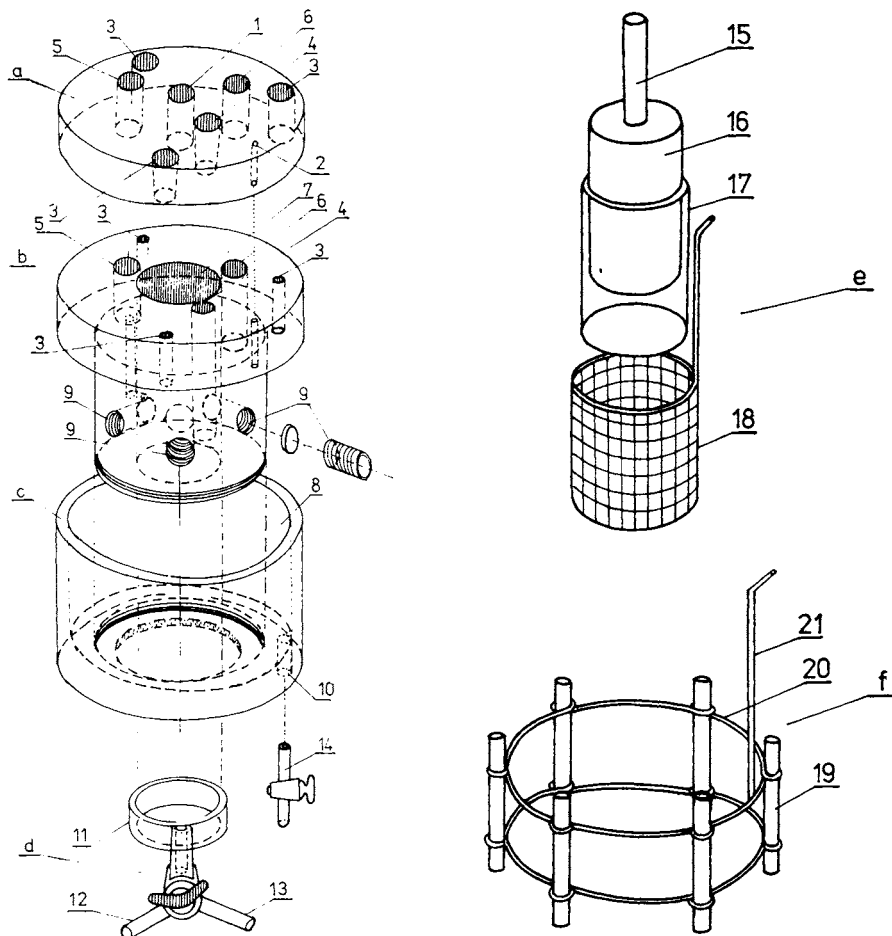


FIG. 1

New coulometric cell. a Head; b cell body; c mantle; d bottom part; e working electrode with stirrer; f auxiliary electrode. 1 hole for rotation shaft; 2 hole for auxiliary electrode lead; 3 hole for inlet of inert gas into the auxiliary electrode space; 4 hole for introducing sample (during electrolysis blinded with a Teflon cylinder); 5 space for salt bridge of reference electrode; 6 hole for inlet of inert gas above the solution level; 7 working electrode compartment; 8 auxiliary electrode compartment; 9 channels connecting the working and auxiliary electrode compartments provided with fine fritted glass discs and threaded Teflon rings; 10 outlet of electrolyte from the auxiliary electrode compartment; 11 glass or Teflon bottom of working electrode compartment; 12 inert gas inlet for bubbling the solution; 13 outlet of electrolyzed solution; 14 outlet stopcock; 15 brass shaft of the stirrer or rotating carbon electrode; 16 Teflon cylinder supporting the glass stirrer; 17 cylindrical glass stirrer; 18 Pt gauze working electrode (closely surrounding the stirrer and inserted into the working electrode compartment up to the bottom); 19 six carbon rods to be placed into the auxiliary electrode lead space so as to face the connecting channels; 20 Pt wire connecting the carbon rods; 21 Pt lead

EXPERIMENTAL

The design of the new coulometric cell corresponds to the above conditions. Uniform potential distribution at the working electrode is ensured by two concentric cylindrical electrodes (Fig. 1). The cell is made of Teflon. The working and auxiliary electrode compartments are separated by a 2 cm thick cylindrical Teflon wall provided with six symmetrically placed openings of a diameter of 7 mm, terminated with finely porous fritted glass.

The cylindrical compartment of the working electrode has a diameter of 33 mm. The working graphite electrode is rotated by means of an equipment for a rotating electrode (constructed in the J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague) and serves at the same time as a stirrer. The electrode has a cylindrical shape, 30 mm in diameter, and occupies most of the available volume, hence a high ratio of A/V is attained. If a platinum (or gold) mesh of a cylindrical form, 32 mm in diameter, is used instead, then a cylindrical glass stirrer of 28–29 mm diameter is inserted into the available space.

The salt bridge of the reference electrode is formed by a narrow channel in the Teflon wall separating the working and auxiliary electrode compartments; it is terminated with porous graphite (5, Fig. 1).

The solution can be bubbled with inert gas through a three-way stop-cock 14, which at the same time serves as outlet of the solution. The inert gas can be allowed to stream above the solution during electrolysis through channel 6, whose outlet orifice is 5 cm above the cell bottom.

The cell is filled with the solution through a cylindrical hole of 1 cm in diameter, which is bored upright along the working electrode compartment and connected with it. During electrolysis, this hole is blinded by a special Teflon cylinder so that the working electrode space retains its simple cylindrical form and is not enlarged.

The mentioned components of the coulometric cell are placed in a hollow cylinder, which forms the inner part of the cell. This is inserted into a larger hollow cylinder forming the mantle of the cell; the space in between is the auxiliary electrode space. The auxiliary electrode is also cylindrical and is made from a platinum mesh, or else it consists of six graphite electrodes 19 placed close to the connecting openings 9 with fritted glass and connected with a platinum wire. The solution in the auxiliary electrode space is stirred by inert gas led through three symmetrically placed inlets.

The complete cell is fixed in place to a holder by means of a head which is fastened to the cell body with three stainless steel screws provided with wing nuts.

Electrolyses were carried out by using a universal electrochemical apparatus Mehrzweckpolarograph GWP 673 (ZWG Akademie der Wissenschaften, Berlin).

RESULTS AND DISCUSSION

Model coulometric experiments consisted of reduction of $K_3Fe(CN)_6$ (Fig. 2) and oxidation of $K_4Fe(CN)_6$ on graphite electrode, and oxidation of chlorpromazine⁷ (CPZ) on platinum mesh electrode (Fig. 3). The dependence of the current I on time t can be expressed as

$$I = I_0 \exp(-pt), \quad (2)$$

where I_0 denotes current at the beginning of electrolysis and p is a formal rate constant of electrolysis. With a graphite working electrode (Fig. 2), for which the ratio A/V

TABLE I

Duration of electrolysis in the new cell with a Pt or carbon working electrode compared with that in a common type cell

| $P^a, \%$ | $p \cdot t^b$ | Time of conversion in s for process | | |
|-----------|---------------|-------------------------------------------------------------------|--------------------------------------------------------------------------------------------|------------------------------------------------------------------|
| | | Oxidation of CPZ on Pt gauze ($p = 0.102 \text{ s}^{-1}$) | Red. of $\text{Fe}(\text{CN})_6^{3-}$ on C electrode ($p = 0.0255 \text{ s}^{-1}$) | Electrolysis in common cell ($p = 0.005 \text{ s}^{-1}$) |
| 99.0 | 4.605 | 45.1 | 180.6 | 921 ^c |
| 99.5 | 5.298 | 51.9 | 207.8 | 1 060 ^c |
| 99.9 | 6.908 | 67.7 | 270.9 | 1 382 ^c |

^a P denotes percent of electrolytic conversion, $P = 100 Q/Q_\infty = 100 (I_0 - I)/I_0$, where Q is the charge at time t , Q_∞ is the charge corresponding to complete conversion; ^b the dimensionless time variable is defined as $pt = -\ln(1 - P/100)$; ^c theoretical values for the rate of electrolysis normally attained, based on Eq. (2)

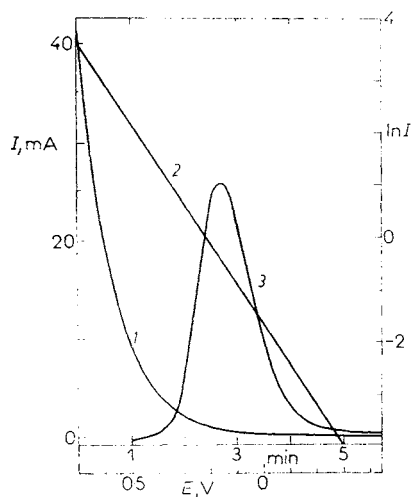


FIG. 2

Dependence of (1) I on t , (2) $\ln I$ on t , and (3) I on E for reduction of $\text{K}_3\text{Fe}(\text{CN})_6$. 15 ml of a solution of $0.001 \text{ M K}_3\text{Fe}(\text{CN})_6$ in 0.1 M HCl ; graphite electrode of 35 cm^2 effective surface area. Potential of electrolysis 0.050 V against SCE (1, 2); voltage sweep rate 0.1 V/min (3)

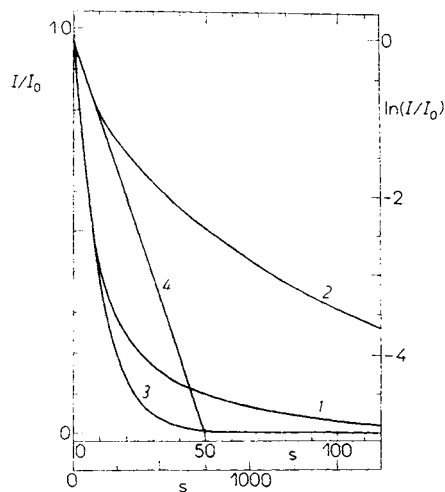


FIG. 3

Dependences of I/I_0 on t and $\ln(I/I_0)$ on t for oxidation of CPZ in 1 M HCl on a Pt electrode. 1, 3 $I/I_0 - t$ curves; 2, 4 $\ln I/I_0 - t$ curves; 1, 2 $p = 0.00642 \text{ s}^{-1}$, time scale $0-1500 \text{ s}$; 3, 4 $p = 0.102 \text{ s}^{-1}$, time scale $0-100 \text{ s}$

was less favourable, we obtained $p = 0.0255 \text{ s}^{-1}$ (and a similar value for oxidation of $\text{Fe}(\text{CN})_6^{4-}$). With a platinum mesh (Fig. 3), we obtained $p = 0.102 \text{ s}^{-1}$. These relatively high values of p imply that the electroactive species are rapidly exhausted from the solution: the calculated times of exhaustion under various conditions are given in Table I. Acceleration of the electrolysis was achieved under the conditions mentioned above; the rate of stirring was chosen so as to prevent formation of bubbles in the solution. The results are comparable with those obtained during stirring of the solution with ultrasound⁸. The most rapid electrolysis was observed⁹ in the case of oxidation of phenothiazine and its derivatives on a platinum mesh electrode in acetonitrile: 99% conversion was attained after 37 s of electrolysis ($p = 0.126 \text{ s}^{-1}$).

The importance of the rapid electrolysis can be exemplified by electrolysis of CPZ in acid medium (concentration of H^+ 1 mol/dm^3). In a coulometric experiment performed with a conventional cell and lasting 25 min, it was possible to evaluate the kinetics of disproportionation of the product of electrolysis⁷ from the $I-t$ dependence, which was different from that given by Eq. (2). The dependence of $\ln(I/I_0)$ on t , shown in Fig. 3 (curve *b*), exhibits a strong deviation from linearity; it corresponds to a change from one-electron to two-electron oxidation* and thus the total charge Q_∞ measured at the end of electrolysis is doubled. On the other hand, in rapid coulometry using the proposed cell, the $I-t$ dependence is not influenced by the chemical reaction mentioned (curves *c* and *d*), hence the total charge is not influenced either.

The reproducibility of measurements with our coulometric cell is very good; the rapid electrolysis can easily be repeated many times, which makes possible a reliable statistical treatment of the results. Thus, the new cell is suitable both for routine quantitative analysis and for studies of the mechanism of moderately rapid chemical reactions, which gives a possibility to span a gap in the rate constants values measurable by classical controlled-potential coulometry and by rapid voltammetric techniques, respectively.

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* It follows from our work^{7,10} that the experiment takes more time in the case of a disproportionation mechanism: the chemical reaction generating the electroactive substance ceases only slowly at the end of the experiment. Under the conditions of electrolysis given in the preceding work⁷ ($p = 0.00642 \text{ s}^{-1}$), 99% conversion of CPZ would be already attained after 717 s in the absence of disproportionation.

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