

Large-scale Laboratory Electrolysis in Organic Systems. II.*

Construction and Performance of an Undivided 800 cm² Concentric Capillary Gap Cell

LARS CEDHEIM, LENNART EBERSON,** BERTIL HELGÉE, KLAS NYBERG, ROLF SERVIN and HANS STERNERUP

Division of Organic Chemistry, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

The construction of a concentric capillary gap cell of simple design is described. In principle, it consists of a graphite rod anode (surface area *ca.* 800 cm²) and a steel tube cathode arranged concentrically with a 1 mm gap between them. The electrolyte is circulated through this space *via* a reservoir and a heat exchanger.

This cell has been used for performing acetoxylation and alkoxylation reactions with different organic substrates. Currents generally fall between 20 and 50 A with applied voltages in the range 7–60 V. Due to its simplicity, the concentric capillary gap cell should be of value for trying out electroorganic reactions on an extended laboratory scale. A 3000 cm² version, permitting production volumes of the order of 1 kg/h, has been built and successfully tested.

The design of more efficient electrochemical reactors has been actively pursued in recent years.^{1–3} The capillary gap cell, in which the distance between the electrodes falls in the region of 0.1–1 mm, has proved to be especially useful for large-scale electroorganic synthesis because of the minimized energy consumption and/or the possibility of using very low concentrations of supporting electrolyte. A very ingenious design of this cell type has been developed by Beck for use on a pilot plant or industrial scale.^{4–8} It consists principally of a pile of horizontal, circular conducting discs (normally made from graphite) with a centrum hole and separated from each other by thin plastics spacers. The electrolyte solution is

pumped into the thus defined “tube” in the center of the pile and forced outward radially between the plates and recycled *via* a heat exchanger (Fig. 1a). The plates are bipolarly connected to the power source.

This design has the advantages of a high space/time yield and of permitting an easy scale-up. However, for laboratories without access to certain specialized techniques for gluing and surface treatment, the construction of such a cell presents some difficult-to-solve problems. Also, it cannot be converted into a divided cell which is a desirable feature in many cases. We have therefore developed a concentric capillary gap cell^{9–12} (Fig. 1b) for exploratory work on organic electrode processes on an extended laboratory scale, *i.e.* for currents of the order of 50 A. This cell is greatly simplified as compared to the graphite disc stack cell mentioned above, and has the additional advantage of being convertible to a divided cell. A preliminary report on its construction and use for anodic oxidations of different types was published recently,⁹ and a few other applications have appeared elsewhere.^{10–12} We now wish to describe the construction of the final version of this cell, a number of auxiliary applications, and our general experience with its operation and performance.

CELL CONSTRUCTION

The first versions of the concentric capillary gap type with anode surface areas of 360 and

* For Part I, see Ref. 9.

** To whom inquiries should be addressed.

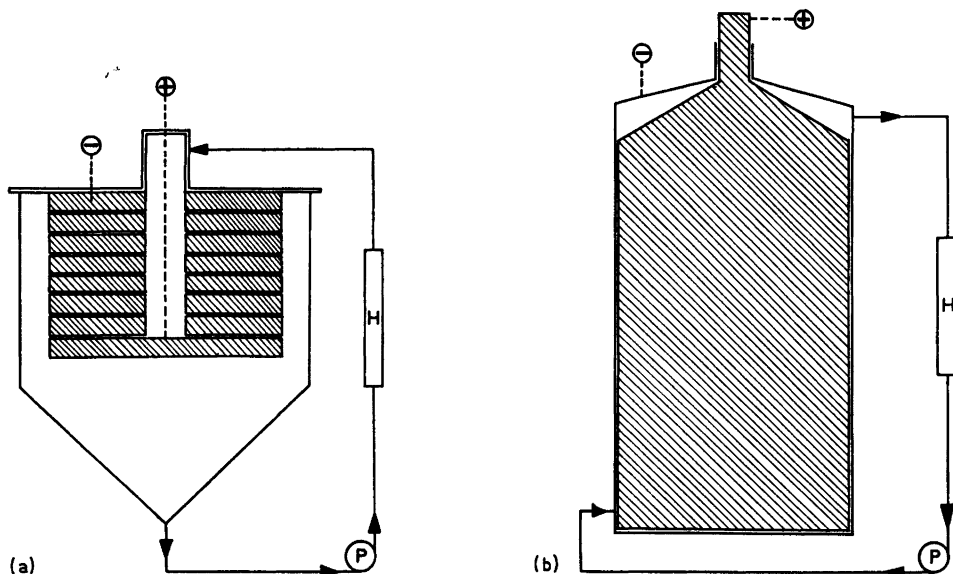


Fig. 1. Schematic representation of the arrangement of electrodes and the flow system for (a) the capillary gap disc stack cell and (b) the concentric capillary gap cell. Cross-sections (through the axis of the cells) have been drawn to illustrate the relative size of the two cell designs when the anode surface areas are identical. P = pump; H = heat exchanger.

580 cm², respectively, had a cylindrical graphite rod anode and a stainless steel tube cathode concentrically arranged and with provision for pumping the electrolyte through the space (1 mm wide) thus defined. The threaded end supports for the graphite anode (AUC quality from Union Carbide) were made from glassfiber-reinforced polytetrafluoroethylene (PTFE) which proved to be an expensive material and unsatisfactory from the leakage point of view. Therefore, the steel tube was provided with flanges at the ends, and the anode supports were constructed from stainless steel (Uddeholm 24L, D17730) with glassfiber-reinforced PTFE for isolation only, as depicted in Fig. 2. For leak-proof sealing, Viton® O-rings were inserted between the flanges and the end supports. These were kept together by six pairs of nuts and bolts at each end. The inlet and outlet tubes for the electrolyte solution were arranged so as to introduce the flow tangentially into the cell.¹³

The size of this version was slightly larger than that of the previous ones, the effective anode area being about 800 cm². With these dimensions the specific anode area (geometric anode area divided by cell volume) is 0.57 cm⁻¹, to be compared with values given in the literature² for the graphite disc stack cell, 1–5 cm⁻¹. In order to be able to make a realistic comparison between the two cell designs, we have built a graphite disc stack cell which is compatible with ordinary commercial laboratory glassware. It then turned out that the number

of graphite discs (size: 9 cm diameter, 1 cm thickness with a centrum hole of 2 cm diameter) could hardly exceed eight per liter of cell volume, provided the volume of the container collecting the flow from the seven capillary gaps in the stack is considered to be the cell volume. With these cell data, the specific surface area of this particular capillary gap disc stack cell is 0.42 cm⁻¹. Refinements in the design (specially designed glassware for the container collecting the flow, thinner graphite discs) might increase the value to about 1 cm⁻¹, but this would be considerably more costly and laborious. Hence the concentric cell type has distinct advantages for use on an extended laboratory scale in its simplicity and cheapness.

The flow system was identical to the one described previously⁹ and the power source was a 50A/60V controlled current instrument from Farnell Instruments, Ltd., Wetherby LS22 4DH, England. Photographs of the cell parts and the assembled system in operation have been published (Figs. 2 and 3 from Ref. 12).

CELL OPERATION

The operation of the concentric capillary gap cell is very simple. After assembling the flow system with an adjustable valve and a flask of an appropriate size as storage vessel, the electrolyte solution is introduced into the flask. With the valve almost closed the pump is started and the flow gradually adjusted until a

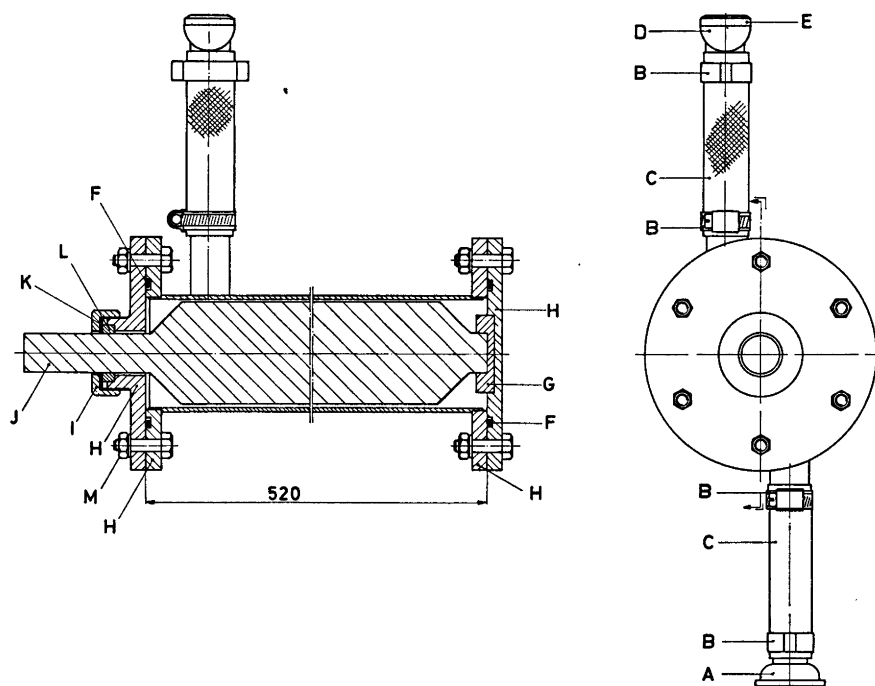


Fig. 2. Drawing of a concentric capillary gap cell with an anode area of ca. 800 cm². A, cup of a flexible joint (Rotulex® 4.692-15); B, hoseclip; C, PTFE tubing with steel wiring support (Texan® 4201-12); D, ball of a flexible joint (Rotulex® 4.691-15); E, PTFE sealing ring (Rotulex® 4.690-04); F, Viton® O-ring (65.09 × 3.53); G, glass-fiber reinforced PTFE anode support; H, stainless steel (Uddeholm 24L, D17730), flange and end support; I, polypropylene; J, graphite (AUC quality from Union Carbide) anode; K, stainless steel washer; L, sealing ring (Sovirel® 4701-26); M, M6 × 25 bolt + nut and washer.

suitable flow rate is attained (generally around 20 l/min). Since there is a tendency for sucking gas into the system if the liquid from the heat exchanger is discharged in a single vertical flow into the storage vessel, a special nozzle for breaking it up into three almost horizontal components was inserted between the heat exchanger and the storage flask. With this arrangement the pump could be run at full capacity without any problems in this respect.

When the flow rate has been adjusted properly the applied potential is gradually increased until the desired current level is reached. The flow of tap water through the condenser is then adjusted so as to maintain the electrolyte solution at a constant temperature. The condenser used as a heat exchanger had a cooling surface area of about 800 cm², which was more than adequate for removing the heat generated at the maximum effect, 3000 W.

REACTIONS

Previously run reactions in the smaller versions of the concentric capillary gap cell

include dehydrodimerizations of alkylaromatic hydrocarbons,^{9,10} acetoxylation,⁹ one case of trifluoroacetoxylation,¹⁰ and one case of additive dimerization.¹¹ Table 1 shows conditions and yields for additional reactions run in the 800 cm² cell described in this paper. As before, the supporting electrolyte concentration has been kept at a low level in most cases in order to minimize the expenditure of costly tetrabutylammonium salts. This is of course done at the sacrifice of a higher energy consumption. Together with earlier work on this cell type, our experience with the concentric capillary gap cell can be summarized as follows:

(1) In its present size and design, it is preferentially used for large-scale laboratory electrolyses at the anode, 1–5 molar runs being feasible within electrolysis periods of 1–10 h. For certain anodic reactions and most cathodic ones, a divided cell is desirable and indeed sometimes necessary; we are presently working

Table 1. Results from electrolyses in the concentric capillary gap cell.

Reaction type	Substrate (mol)	Isolated product(s)	Solvent (volume in ml)	Supporting electrolyte (conc. in M)	Current in A	Applied potential, V	Yield Material	Current
Acetoxylation	HCON(CH ₃) ₂ (5)	HCON<CH ₃ CH ₂ OAc	CH ₃ COOH (1500)	Bu ₄ NBF ₄ (0.011)	50	40–60	92	92 ^a
Acetoxylation	CH ₃ CON(CH ₃) ₂ (5)	CH ₃ CON<CH ₃ CH ₂ OAc	CH ₃ COOH (1500)	Bu ₄ NBF ₄ (0.011)	50	40–60	78	78 ^a
Acetoxylation	PhCON(CH ₃) ₂ (1.5)	PhCON<CH ₃ CH ₂ OAc	CH ₃ COOH (1000)	Bu ₄ NBF ₄ (0.008)	50	60	60	60 ^a
Acetoxylation	PhCH ₃ (3)	PhCH ₂ OAc	CH ₃ COOH (3000)	Bu ₄ NBF ₄ (0.024)	20	53–60	39	26 ^a
Acetoxylation	4- <i>t</i> -BuC ₆ H ₄ CH ₃ (2)	4- <i>t</i> -BuC ₆ H ₄ CH ₂ OAc	CH ₃ COOH (2000)	Bu ₄ NBF ₄ (0.042)	20	60	73	73 ^a
Acetoxylation	Mesitylene (1)	2,4,6-(CH ₃) ₃ C ₆ H ₂ OH ^b	CH ₃ COOH (1000)	CH ₃ COOK (0.90)	20	20	40	40 ^a
Acetoxylation	Indene (2)	<i>cis</i> - and <i>trans</i> -1,2-Indandiol diacetates + additive dimers ^d	CH ₃ COOH ^c (1200)	CH ₃ COOK (0.67)	10		39	
Methoxylation	HCON(CH ₃) ₂ (5)	HCON<CH ₃ CH ₂ OMe	CH ₃ OH (2500)	Bu ₄ NBF ₄ (0.007)	50	26	75	75
Methoxylation	Furfuryl alcohol (2.4)	2,5-Dimethoxy-2-hydroxymethyl-2,5-dihydrofuran	CH ₃ OH (1600)	NH ₄ Br (0.16)	40	7	62	71 ^{e,f}
Ethoxylation	Furan (2.8)	2,5-Diethoxy-2,5-dihydrofuran + maleic aldehyde diacetal	C ₂ H ₅ OH	NH ₄ Br	25	10	73	86 ^{e,f}

^a Run to 100 % of theoretical conversion. ^b Hydrolyzed before isolation. ^c Acetic anhydride (20 ml) added. ^d Isomers of 1,1'-diacetoxy-2,2'-bi-indane. ^e Run to 85 % of theoretical conversion. ^f Run at 4–6 °C.

on a divided version of the same size using a tubular Nafion® XR-475 membrane as cell divider and hope to be able to test it soon. The divided cell has a somewhat wider gap (ca. 3 mm), though, in order to accommodate both the catholyte and anolyte flow and the cell divider.

(2) Abrasion of the graphite anode has been almost negligible during ca. 400 h of intermittent operation using media like acetic acid, methanol, and methylene chloride at current densities of maximally 60 mA/cm².

(3) The flow rate through the cell is 330 cm³/s at a pumping rate of 20 l/min, which is equivalent to a residence time in the cell of about 0.25 s. In a typical run with a substrate concentration between 1 and 2 M, this corresponds to a very low degree of conversion per pass during most of the run, thus ensuring stable and reproducible reaction conditions.

(4) In a medium of low conductivity, such as acetic acid containing ca. 0.01 M tetrabutylammonium tetrafluoroborate, the cell resistance is of the order of 1 ohm, whereas with an electrolyte solution of relatively high conductivity, such as methanol/0.16 M ammonium bromide it is about 0.1 ohm. At the current level commonly employed, the power losses are of course relatively high in the low-conductivity media but this is compensated for by savings on supporting electrolyte, a more costly item on the laboratory scale.

(5) The construction of a scaled-up version of the concentric capillary gap cell (anode area about 3000 cm²; gap width 1 mm), permitting production volumes of the order of kg/h, presented no difficulties in principle. We have run preliminary tests on such a cell, using the acetoxylation of DMF on a 50-molar scale as a model reaction. With 0.02 M tetrabutylammonium tetrafluoroborate as supporting electrolyte, the cell could be operated at 350 A at an applied voltage of 40 V (i.e. the ohmic resistance was of the order of 0.1 ohm) at a flow rate of 60 l/min. Again, the heat evolved was easily dissipated by a heat exchanger in the flow loop.

Acknowledgements. We gratefully acknowledge generous financial support from the Swedish Natural Science Research Council and the Swedish Board for Technical Development. We also thank Messrs Braun and Petterson and

their skilful coworkers in the mechanic workshop of the Chemical Center for their valuable help with the construction of the cells.

REFERENCES

1. Danly, D. In Baizer, M. M., Ed., *Organic Electrochemistry*, Dekker, New York 1973, Chapter 28.
2. Goodridge, F. *XXIVth International Congress of Pure and Applied Chemistry, Volume 5, Applied Electrochemistry*, Butterworths, London 1974, p. 19.
3. Houghton, R. W. and Kuhn, A. T. *J. Appl. Electrochem.* **4** (1974) 173.
4. Beck, F. and Guthke, H. *Chem. Ing.-Techn.* **41** (1969) 943.
5. Beck, F. *J. Appl. Electrochem.* **2** (1972) 59.
6. Beck, F. *Angew. Chem.* **84** (1972) 798.
7. Beck, F. *Electrochim. Acta* **18** (1973) 359.
8. Beck, F. *XXIVth International Congress of Pure and Applied Chemistry, Volume 5, Applied Electrochemistry*, Butterworths, London 1974, p. 111.
9. Eberson, L., Nyberg, K. and Sternerup, H. *Chem. Scr.* **3** (1973) 12.
10. Eberson, L., Nyberg, K. and Sternerup, H. *Acta Chem. Scand.* **27** (1973) 1679.
11. Sternerup, H. *Acta Chem. Scand. B* **28** (1974) 579.
12. Eberson, L. *XXIVth International Congress of Pure and Applied Chemistry, Volume 5, Applied Electrochemistry*, Butterworths, London 1974, p. 137.
13. The cell is available for sale from this Department. For details, write to L. Eberson.

Received January 3, 1975.