ELECTRO CHEMICAL ENGINEERING

The Institution of
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Pergamon
Press

ELECTROCHEMICAL ENGINEERING

A three-day symposium organised by the Department of Chemistry, University of Technology, Loughborough in association with the Society of Chemical Industry, the EFCE Working Party on Electrochemical Engineering and the Institution of Chemical Engineers and held at Loughborough University of Technology, 21 – 23 April 1986

Steering Committee

N. A. Hampson (Chairman)   Loughborough University
S. R. Ellis (Organising Secretary)   Loughborough University
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Foreword

The Conference arose as a consequence of the response to an earlier meeting held at Loughborough in 1983 when it became clear that the interest in Electrochemical Engineering was being maintained. The Conference is the result of cooperation between the Loughborough University, the Society of Chemical Industry and the Institution of Chemical Engineers with the support of the European Federation of Chemical Engineering Working Party on Electrochemical Engineering. The original Steering Committee involved in the 1983 Conference was enlarged, Dr. A.J.S. McNeil being succeeded by Dr. Steve Ellis, as the Conference Organiser.

The five "areas of interest" into which the Committee has grouped the papers were chosen with the hindsight gained in 1983. This certainly seems to have been the correct method of choice for there has been no lack of papers of high quality offered for presentation. Where possible all the authors have been accommodated, subject to a refereeing policy which conformed to the Institution of Chemical Engineers' standard. Here it is appropriate for the Committee to express thanks to these referees who have made considerable efforts, sometimes at great inconvenience, in order to execute a rapid turnround of papers.

It is hoped that these conference proceedings will be the first of many to be generated in this area of Applied Technology. The areas of interest must be expected to change, however, Electrochemical Engineering seems to be well established and can be confidently expected to continue to grow in strength.

N. A. Hampson

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ERRATA

Paper 3.   P. Brekelmans and T.Z. Fahidy
Page 24, Equation 7 should read

$$\frac{\partial \underline{w}}{\partial t} = \underline{A}_1 \frac{\partial \underline{w}}{\partial y} + \underline{A}_o \underline{w} + \underline{\phi}(\underline{w})$$

Page 25, below equation 12 should read

$$Q = \begin{pmatrix} \underline{S}_y \underline{A}_1 - \underline{S} \ \underline{A}_o & \frac{1}{2} \ \underline{S} \ \underline{A}_1 \\ \frac{1}{2} \ \underline{S} \ \underline{A}_1 & 0 \end{pmatrix}$$

Paper 6.   F. Goodridge, G.M. Mamoor and R.E. Plimley
Page 61, line 3, the first sentence should read

Two cells were used in the present work with cathodes divided into segments of dimensions 0.05 m x 0.05 m for the smaller cell and 0.05 m x 0.045 m for the larger one.

Page 69, Figure 5, the first line of the legend should read

Plot of Mass Transfer Rate Against Segment Number for Re = 8,400

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† This paper was only available as an abstract when the proceedings went to press.

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THE ICI (MOND) FM21 CELL AS A MULTI-PURPOSE ELECTROLYSER

W N Brooks*

The requirements of a "multi-purpose" cell for
electrosynthesis are discussed. It is essential that all
cell components are chemically stable to a wide range of
operating conditions and that the design of the cell allows
flexibility in the choice of electrode and separator
materials. It is shown that the ICI FM21 cell is readily
adaptable for electrosynthetic applications; the design and
construction of the cell are discussed together with an
example of its use in the synthesis of fine chemicals
intermediates.

INTRODUCTION

To preface this discussion one must first define what is meant by the
expression "multi-purpose electrolyser". One cannot expect a single
type of electrolyser to be suitable for the whole range of industrial
electrolytic processing - the requirements of a cell for aluminium
refining are clearly very different to those for chrome electroplating.
In the following discussions it is assumed that the processes are
characterised by the following:

- aqueous or other fairly high conductivity electrolytes
  ($>10^{-2}$ ohm^{-1} cm^{-1})
- reasonably high initial concentrations of substrate ($> \sim 0.1$M)
- reasonably high current density of operation (> 0.5 kA m^{-2})
- low to moderate temperature of operation (<100°C)
- reactants and products which remain in the electrolyte or gas phase
  (ie excluding metal deposition etc)
- ambient or moderately elevated (<5 bar) pressure.

These figures are not absolute limitations but are simply meant to
indicate general bounds of applicability. For example if one had a
process in which the substrate concentration was only 10 mM, one would
choose a more specialised high mass-transfer (eg a packed bed) cell.

If one considers a range of electrosynthetic processes (both organic
and inorganic), as described recently for example by Jansson[1], it is
seen that many reactions of commercial importance fall within this
class. Typical examples are the syntheses of adiponitrile and

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dimethyl sebacate. Examples of "odd" reactions which require individually designed and constructed cells are electrofluorinations and the synthesis of lead alkyls.

It is now widely accepted that one of the major reasons for the slow growth in the commercial exploitation of electrosynthesis, especially for small-scale processes, has been the lack of any commercially available "general-purpose" cell in which to carry out these types of reaction. Although such cells have only recently become available many more companies have already expressed an interest in electrosynthesis in the knowledge that technology is available for scale-up. In order to compare the relative merits of different cells one must compile a list of criteria which a "multi-purpose" cell should fulfil. Such a list is proposed below:

CRITERIA FOR A MULTI-PURPOSE CELL

Like any electrolytic cell a general-purpose cell for electrosynthesis must be designed in such a way as to give good operating characteristics in terms of its basic voltage and mass transfer performance. In addition to these basic requirements, however, it must also offer sufficient flexibility to be adaptable to a wide range of operating conditions. Firstly, the components of the cell must be stable with respect to corrosion by a wide range of aqueous and non-aqueous electrolyte media:

- acids, eg H_2SO_4, HCl, organic acids
- bases, eg NaOH, KOH, amines
- oxidising agents, eg Cl_2, Br_2, $Cr(VI)$, $Ce(IV)$
- reducing agents, eg $Cr(II)$, $S_2O_4^{2-}$
- organic solvents, eg acetonitrile, DMF, DMSO, alcohols, chlorinated solvents, ethers.

These conditions must be fulfilled by all components of the cell which are in contact with the liquors, ie:

- endplates, feed-pipes, manifold pipes and ports
- spacers and liquor compartments
- gaskets
- electrodes: both substrates and electrode coatings.

Secondly, the cell must be capable of utilising a wide range of electrode materials, for example:

- titanium
- coated titanium (platinum, iridium, ruthenium dioxide etc)
- nickel
- mild steel
- stainless steels
- "speciality" alloys eg Inconels, Hastelloys etc
- lead and lead oxide
- carbons, eg graphite, glassy carbon.

Thirdly, the cell must be capable of being run in either a divided or undivided mode. In a divided mode a variety of separators must be available:

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- porous plastics, eg polyethylene, PVC, PTFE etc
- "standard" anion and cation exchange membranes
- "high performance" chemically resistant membranes, eg "Nafion"
  ("Nafion" is a registered trademark of DuPont).

Fourthly, the construction of the cell should be such that it is adaptable to a wide range of production capacities (100's of kgs to 1000's of tonnes). Scale up should be linear (ie no change in surface to volume ratios) and thus the cell should be designed along "modular" lines. Since the cell is likely to be used from pilot-scale work through to full-scale production it is important that it can be dismantled and re-assembled with the minimum of effort and equipment.

Finally, the cell may need to be run under a wide range of operating conditions:

- temperature
- current density
- liquor flow rates
- pressure.

THE ICI(MOND DIVISION) FM21 CELL

The name "FM21" is derived from the size and mode of construction of the cell. Each electrode has a geometric area of 21 dm², the cell is Monopolar and is held together in a "Filter-Press" compression arrangement. An exploded view of the cell is shown in Figure 1. The FM21 incorporates a number of quite revolutionary design features. Firstly, there are no complex anolyte and catholyte chambers - the FM21 is simply an alternating stack of anodes, gaskets, membranes, gaskets, cathodes ... etc. The only other major components are the end-plates, copper electrical connectors and the tie-bars which compress the cell together. In all, 60 electrode pairs are typically used, giving a total electrode area of 25 m². By using this novel method of cell construction the cost of fabricating relatively complex electrolyte chambers from costly corrosion-resistant materials is avoided. Secondly, no external manifolding is used. All the internal manifolding is achieved by incorporating port devices into the electrodes and gaskets. Thirdly, the cell was designed to maximise the use of modern mass-production techniques. Although the gasket structures are of a highly sophisticated design, the unit costs of manufacture are quite modest as a result of using modern moulding techniques. Similarly, the complex "lantern-blade" electrode structures are produced using state-of-the-art metal pressing technology. In this way labour intensive and hence costly machining and finishing operations are avoided for much of the cell's fabrication.

It is because of these design features that ICI believe that the FM21 cell is so suitable as a multi-purpose electrolyser. If a cell is to have individual anolyte and catholyte compartments with external manifolding, then each of these components must be individually machined, usually at some considerable cost. Furthermore, if the cell is to be applicable to a wide range of reactions, then these components should be made of some highly resistant material; in practice this usually means expensive

fluoropolymers. The absence of these components allows the FM21 to be produced at considerably lower cost. The only components which need to be specified in such materials are the liners for the steel end plates and the gas and liquor feed and exit pipes.

A number of gaskets are available in the FM21 cell. For most applications an EPDM rubber gasket can be used; this material is stable to most acids and bases as well as oxidising agents such as chlorine and some non-aqueous solvents. For the most demanding applications PTFE-lined gaskets are available.

Electrodes

ICI has been active in the development of electrodes since the 1950's when it pioneered the development of platinised titanium anodes for the replacement of graphite in mercury cells. Since then the Company has developed a range of anodes and cathodes for chloralkali use and more recently for a wider range of electrochemical applications.

The standard electrode form for the FM21 is a lantern blade structure (see Figure 2). This structure combines the properties of good gas release and low cell voltage, due to the "zero-gap" mode of operation in which both anode and cathode touch the separator. The FM21 cell has also been used with flat sheet electrodes in which a flat sheet of metal replaces the lantern blade structure which is welded between the outer port-panels. Alternative structures such as expanded metal sheets could equally well be used as the active centre section of the electrode. A number of electrode materials are available:

- mild steel
- stainless steels
- "special" alloys, eg Incolloys, Hastelloys, Monel
- nickel
- titanium
- RuO_2-based coatings on titanium
- platinised and Pt/Ir coated titanium
- zinc
- copper
- lead and lead alloys
- aluminium
- electroplated steel (Ni, Cr, Cd, Pb etc).

Carbon electrodes have not been manufactured for the FM21 as yet, but in principle there is no reason why carbon sheets could not be mounted on a flat electrode which acts as a current carrier and mechanical support.

Separators

The FM21 is specifically designed to be used with a chloralkali membrane of the fluoropolymer "Nafion" type. ICI consequently has a great amount of expertise in this mode of operation and is in a position to advise on membrane choice and supply suitable membranes. For less chemically demanding applications a cheaper electrodialysis-type ion-exchange membrane

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could be substituted without further cell modification. Similarly one could use a porous polymer diaphragm separator. The FM21 has also been used in an undivided mode and such an application will be described in further detail below.

Conditions of Operation

In normal use as a chlorine electrolyser the FM21 operates at 85-90°C and is therefore well proven at elevated temperatures of operation. Provided that the appropriate heating or cooling arrangements are provided the cell can operate at any temperature in the range 0-100°C.

The normal operating current density of the FM21 is 3-4 kA m^{-2}, but the cell can be run at current densities of up to 10 kA m^{-2}, subject to constraints imposed by the separator used, the actual chemistry involved and heat balance requirements.

Unlike many other membrane cells, the FM21 has the capability for pressure operation, up to 4 bar (gauge).

ICI are currently involved in studies of the mass transport in the FM21 under conditions of electrolyte recirculation and high flow rate. Further details of both modelling and experimental work will be published in due course. At present it is sufficient to say that experimental and pilot-scale production work have conclusively demonstrated that the mass transfer characteristics of the cell are more than adequate to cope with the conditions commonly used in electro-organic synthesis processes; this will be illustrated by way of a real example below.

Scale

As described above, the FM21 is constructed by combining the desired number of cell pairs together in a filter-press arrangement up to a maximum of ~25 m^2. Further capacity is achieved by combining cells to whatever total area is required. In this way one can undertake development work at relatively small scale, say only one to a few electrode pairs (probably following laboratory studies in small lab cells) and scale up with confidence to whatever final production capacity is required. Because the FM21 is based on a relatively small electrode size, the cell is easily dismantled and re-assembled with only a minimum of equipment. For a hypothetical process characterised by the following conditions:

- product molecular weight of 200
- 2-electron oxidation (or reduction)
- current efficiency of 80%
- current density of 1 kA m^{-2}

the capacity of a 25 m^2 FM21 unit would be 1.8 t per day. For development work the cell could be run at scales as low as 1/60th of this, ie 1.25 kg per hour.

THE USE OF THE FM21 FOR AN ORGANIC ELECTROSYNTHETIC APPLICATION

The epoxidation of 1,1-diarylalkenes

The use of electrochemical halohydrin routes for the epoxidation of alkenes is well known[2] and has been described in detail for the epoxidation of propylene[3]. The basis of the method is as follows: an undivided cell is used to oxidise halide ions (shown as bromide) at the anode and to reduce water to base and hydrogen at the cathode:

Anode $\quad$ Br$_2$+2e $\quad$ H$_2$↑+2OH⁻ $\quad$ Cathode

2Br⁻ $\quad$ 2H$_2$O+2e

⊕ $\qquad$ ⊖
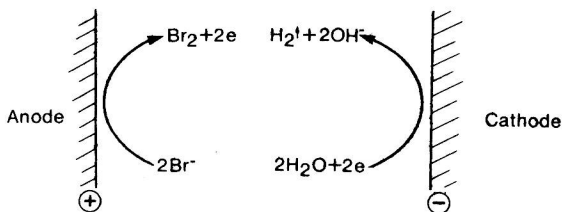
Within electrolyte:

$$Br_2 + OH^- \longrightarrow HOBr + Br^-$$

Within the cell the bromide and base react to form hypobromous acid which then reacts (in-situ) with the alkene to form the bromohydrin. This then reacts further with base to eliminate HBr with the resultant formation of the epoxide:

R$_1$, R$_2$ (alkene) +HOBr ⟶ R$_1$, R$_2$, OH, Br

R$_1$, R$_2$, OH, Br +OH⁻ ⟶ R$_1$, R$_2$, O (epoxide) + H$_2$O + Br⁻
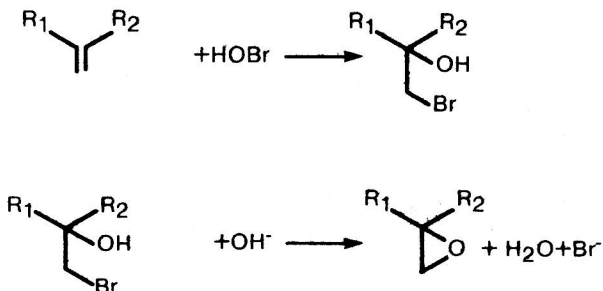
The overall electrochemical reaction is therefore simply to split water, evolving hydrogen at cathode and adding oxygen across the double bond.

During 1982 ICI identified problems in the epoxidation of
1-(2-chlorophenyl),1-(4-fluorophenyl)ethene; a product which was required
as a fine chemicals intermediate.
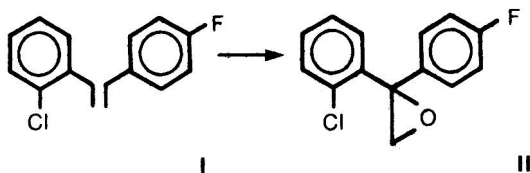
I=1-(2-chlorophenyl), 1-(4-fluorophenyl)ethene
II=1-(2-chlorophenyl), 1-(4-fluorophenyl)ethene oxide

The electrochemical epoxidation was evaluated alongside a number of
"conventional" chemical epoxidation methods. The best conventional route
developed for this particular epoxide was the reaction of the alkene with
bromine and hydrogen peroxide in DMF to give the bromohydrin, followed by
treatment with potassium carbonate to give the desired epoxide:
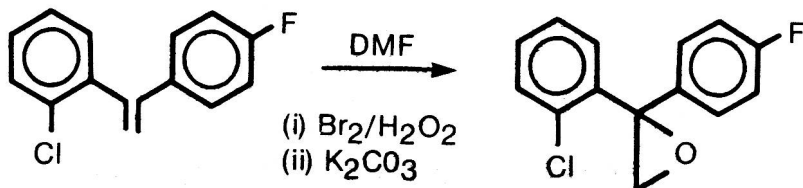
Prior to FM21-scale experiments, critical variables were studied using a
small (30 cm^2) laboratory flow cell:

- solvent
- chloride or bromide ?
- concentration of alkene
- concentration of halide
- temperature
- pH
- current density.

Ideally, one would wish to carry out the reaction in an aqueous solvent; however, the alkene of interest was virtually insoluble in water so other solvent systems had to be evaluated. The strategy adopted was to use a mixed solvent to combine reasonable alkene solubility with good conductivity. A suitable co-solvent therefore had to meet a number of criteria:

- good conductivity
- solubility of alkene, epoxide and halide salt
- water miscible
- electrochemically inert within potential range of interest
- volatile, for solvent recovery.

A number of co-solvents were evaluated: t-butanol, diglyme (diethylene glycol dimethyl ether) and DMF. Other possibilities included DMA, DMSO, acetonitrile and N-methylpyrrolidone but these were thought to be disadvantageous either in terms of their toxicity or their volatility (and hence ease of recovery). After solubility studies and preliminary electrochemical trials a mixture of 95:5 DMF/water was chosen. This allowed the process to be operated at a reasonably high alkene concentration, ~0.6 M, with an acceptable (although rather low) conductivity.

Bromide was chosen as the halide rather than chloride as the overpotential for bromide oxidation is lower than that for chloride and because it has a greater solubility in the solvent of choice. Initial experiments were undertaken with sodium bromide but this was later substituted by the ammonium salt as problems were experienced with the precipitation of insoluble sodium bicarbonate in the aqueous DMF sovent. The concentration of bromide was found to be important. If the concentration is too low then the conductivity of the electrolyte is inadequate, whereas if excessive bromide is used bromination of the alkene occurs, rather than epoxidation:
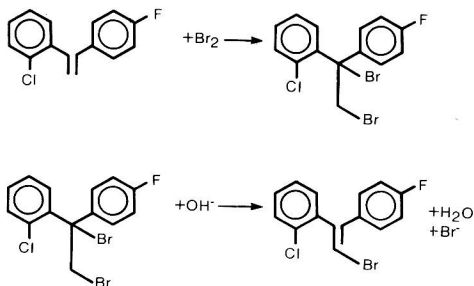
The dibromoalkane then undergoes dehydrobromination to form the bromoalkene. It was found that the optimum concentration of bromide was ~0.1 M.

Within the range 20-50°C temperature was found to have little effect on either the reaction yields or efficiencies.
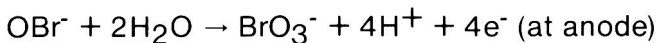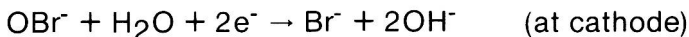
It was found that pH was a particularly important variable. If the pH was too low then the epoxide tended to rearrange to form the aldehyde:
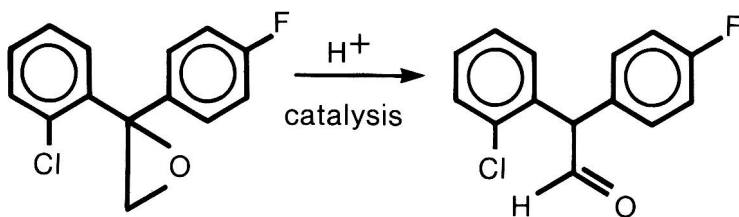
Yields of the bromoalkene by-product were also higher at low pH values, presumably due to the reduced rate of formation of hypobromous acid and hence a higher standing bromine concentration. If the pH was too high, low current efficiencies were observed. It is thought that this is due to deprotonation of the hypobromous acid (pKa in water = 8.7) to form the hypobromite anion. As this is chemically unreactive it may be reduced back to bromide at the cathode or be oxidised to bromate at the anode:

At High pH:

$$HOBr \rightarrow OBr^- + H^+ \qquad\qquad pKa(water) = 8.7$$

$$OBr^- + H_2O + 2e^- \rightarrow Br^- + 2OH^- \qquad \text{(at cathode)}$$

$$OBr^- + 2H_2O \rightarrow BrO_3^- + 4H^+ + 4e^- \text{ (at anode)}$$

In either case a reduction of current efficiency results.

For economic reasons it is desirable to operate the process at the highest current density possible. It was found that the epoxidation worked well at current densities up to 1.5 kA m^{-2} without any substantial loss in current efficiency.

Lab-scale results

The results obtained with small lab-scale flow cells were most encouraging. Because the alkene is an expensive material, itself the product of several previous synthetic stages, it was important to carry out the epoxidation reaction through to a high conversion of alkene, preferably 99%. Even at this very high conversion excellent yields (90%) of epoxide were obtained, with 4% aldehyde and 6% bromoalkene being the main identified by-products. Inevitably the high alkene conversion required resulted in a low overall current efficiency, ~25-30%, due to the high degree of electrochemical "recycling" of the HOBr at low concentration of alkene. However, since the main motivation for using the electrochemical route was to achieve high material yields, this additional energy cost was relatively insignificant. Following this success a small FM21 pilot cell was assembled for further trials.

FM21 pilot-cell results

A pilot cell was assembled using a central anode and two outer cathodes, thus giving a total electrode area of 42 dm^{-2}. The anode material chosen was titanium coated with a proprietary Mond RuO$_2$-based coating developed for the similar duty of chlorine evolution. This material was found to perform well with no visual change in electrode appearance. Initially, nickel cathodes were selected, but these were later replaced by stainless steel, due to corrosion problems. The stainless steel cathodes solved these earlier materials problems. In order to prevent electrode shorting, and to promote turbulence within the cell, the electrodes were separated by a coarse polyester gauze. Standard EPDM rubber gaskets (as used for normal chloralkali operation) were used in the aqueous DMF electrolyte without problems.

Electrolyte was recirculated through the cell at a rate of 10-20 l min^{-1} until the desired conversion of alkene had been achieved, the concentration being monitored by periodic sampling and glc analysis. The overall arrangement of the cell and other process plant items is shown in Figure 3. Typical process conditions were as follows:

- Composition: 15 litres total of 0.1 M ammonium bromide
 0.6 M alkene
 in 95:5 DMF/water
 pH adjusted 9 with .88 ammonia

- current density of 1 kA m^{-2}
- temperature of 30°C
- cell voltage = ~20 V.